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(12) **United States Patent**
Miyawaki et al.(10) **Patent No.:** **US 8,377,563 B2**
(45) **Date of Patent:** ***Feb. 19, 2013**(54) **PAPERMAKING ADDITIVE AND PAPER CONTAINING THE SAME**(75) Inventors: **Shoichi Miyawaki**, Tokyo (JP); **Shiho Katsukawa**, Tokyo (JP); **Hiroshi Abe**, Tokyo (JP); **Yuko Iijima**, Tokyo (JP); **Akira Isogai**, Tokyo (JP)(73) Assignee: **Nippon Paper Industries Co., Ltd.**, Tokyo (JP)

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427/324; 427/411(58) **Field of Classification Search** **428/532,**
428/537.5, 535; 427/324, 411

See application file for complete search history.

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(57) **ABSTRACT**

A papermaking additive comprising cellulose nanofibers whose aqueous solution at a concentration of 2% (w/v) has a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably 500 to 2000 mPa·s is used to prepare a paper having improved air resistance and smoothness. This additive is prepared by oxidizing a cellulosic material with an oxidizing agent in the presence of (1) N-oxyl compound(s) and (2) bromide, iodide or a mixture thereof to prepare oxidized cellulose, and finely grinding the oxidized cellulose in a wet condition to convert the oxidized cellulose into nanofibers.

22 Claims, 5 Drawing Sheets

Figure 1

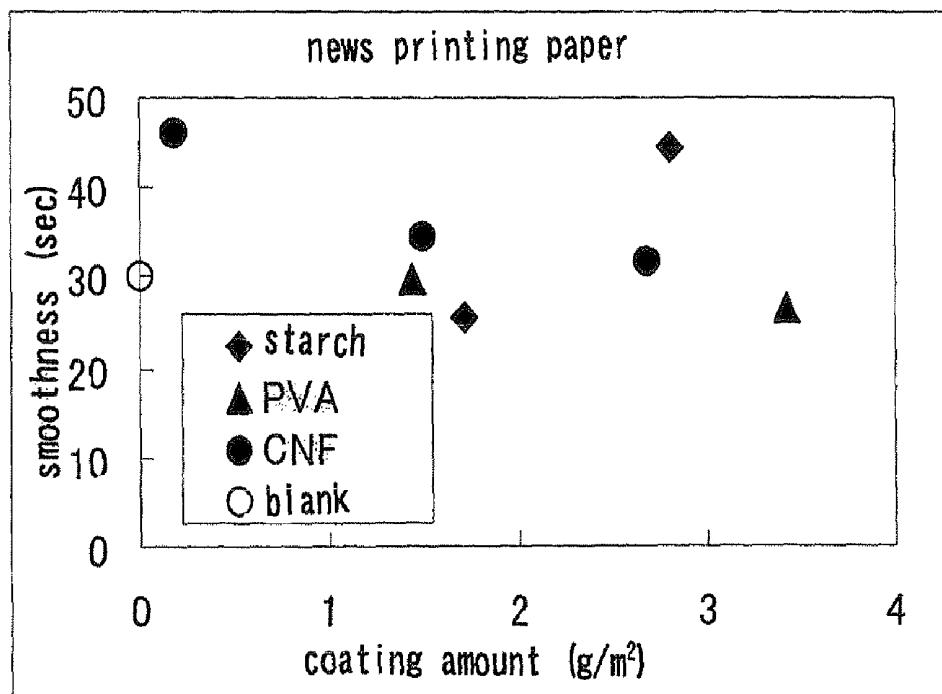


Figure 2

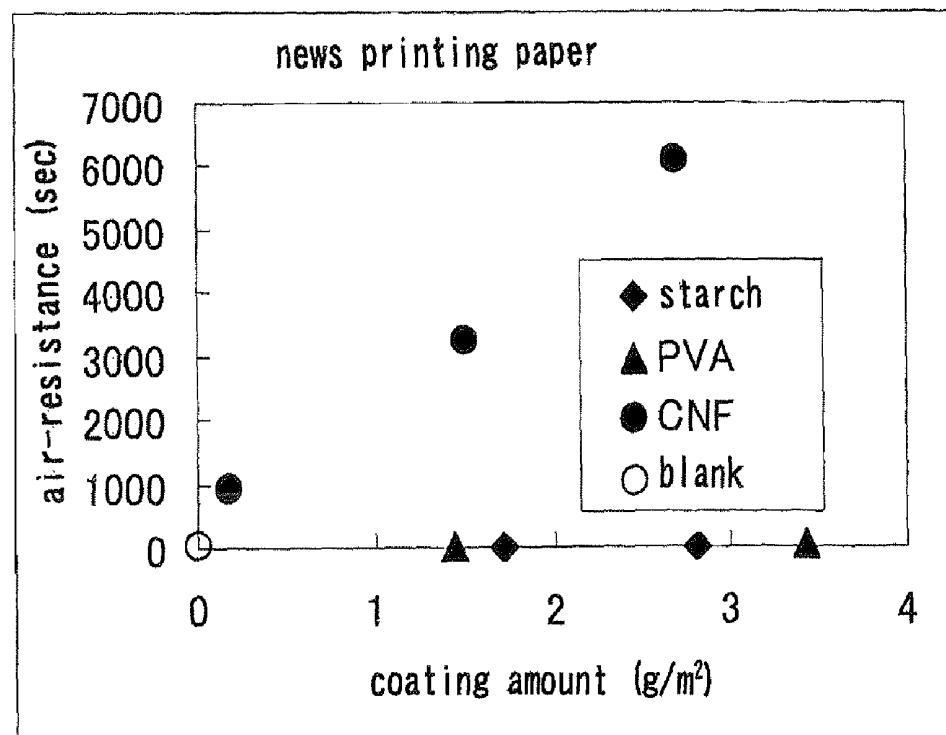


Figure 3

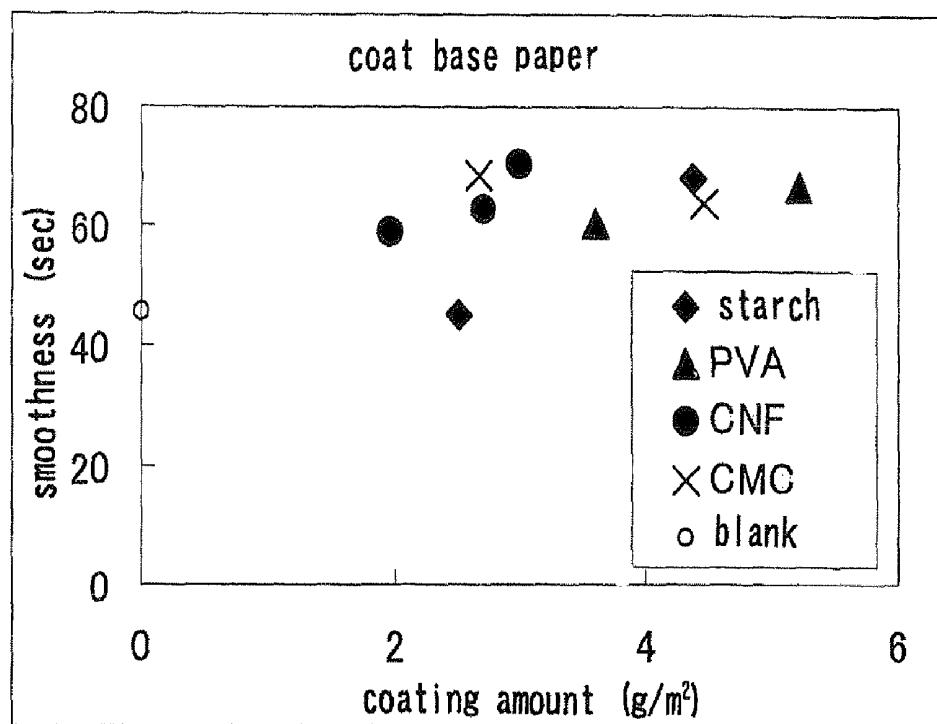


Figure 4

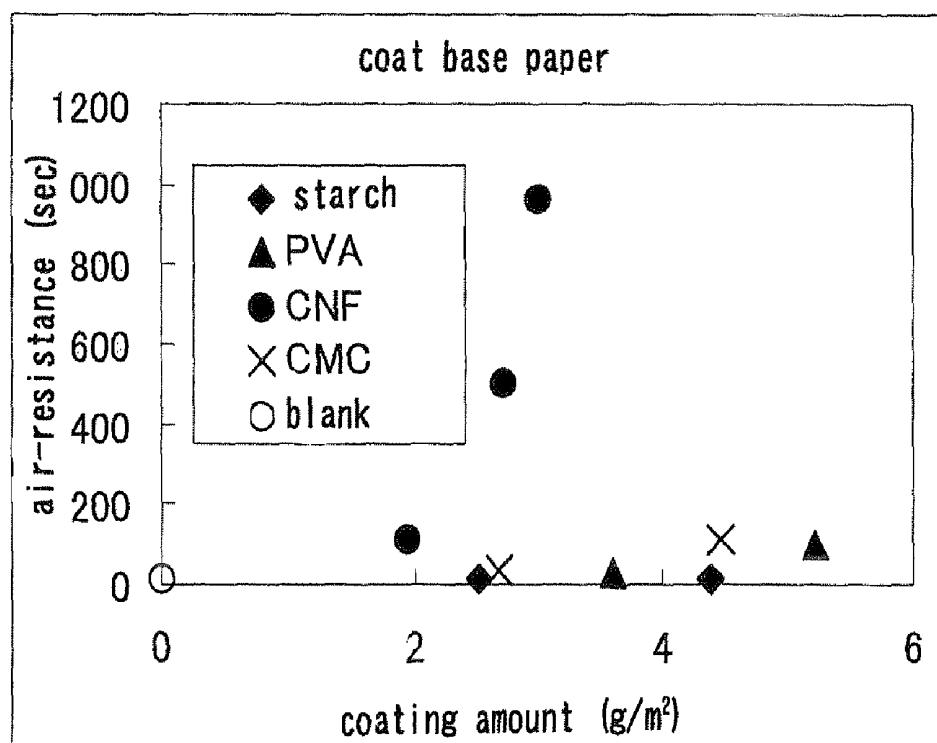


Figure 5

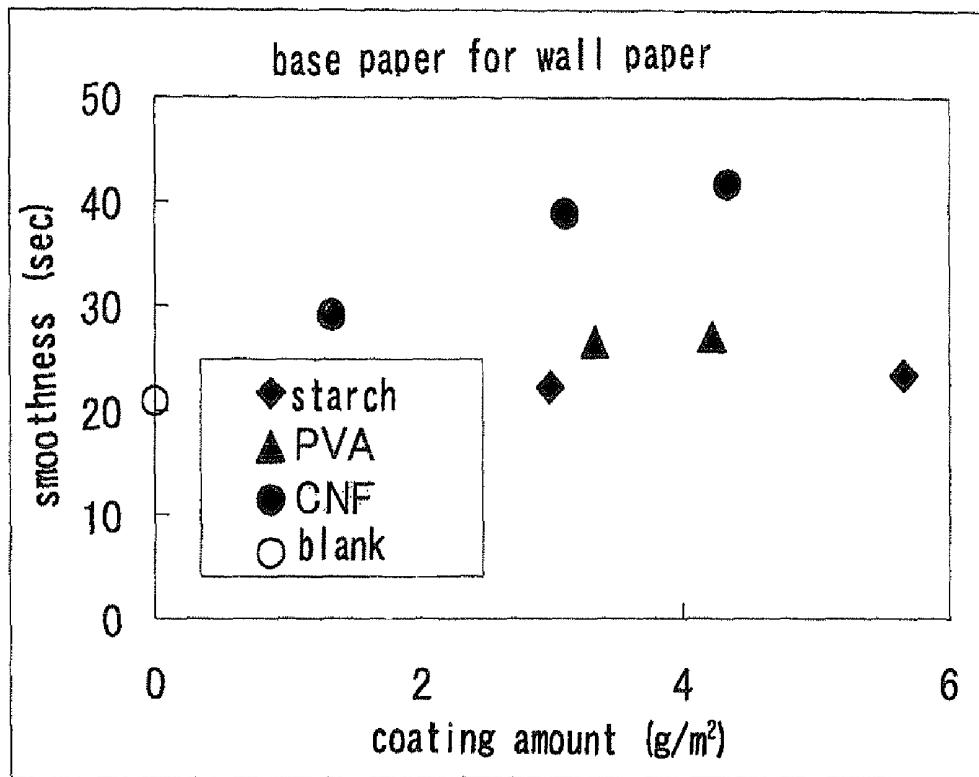


Figure 6

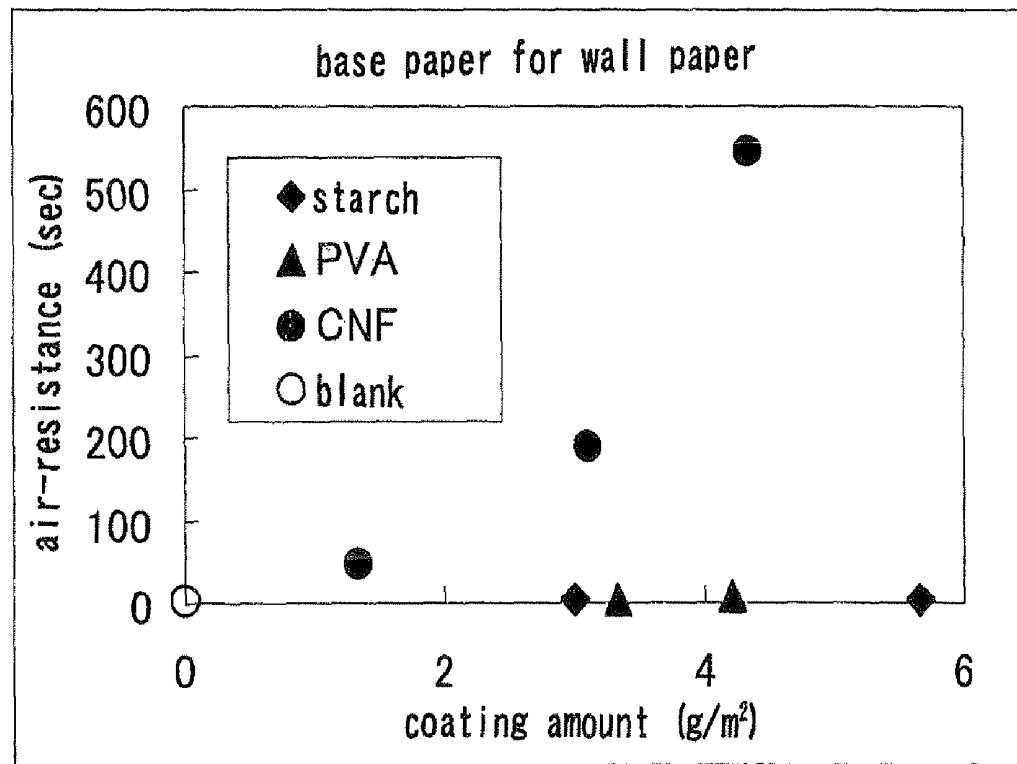


Figure 7

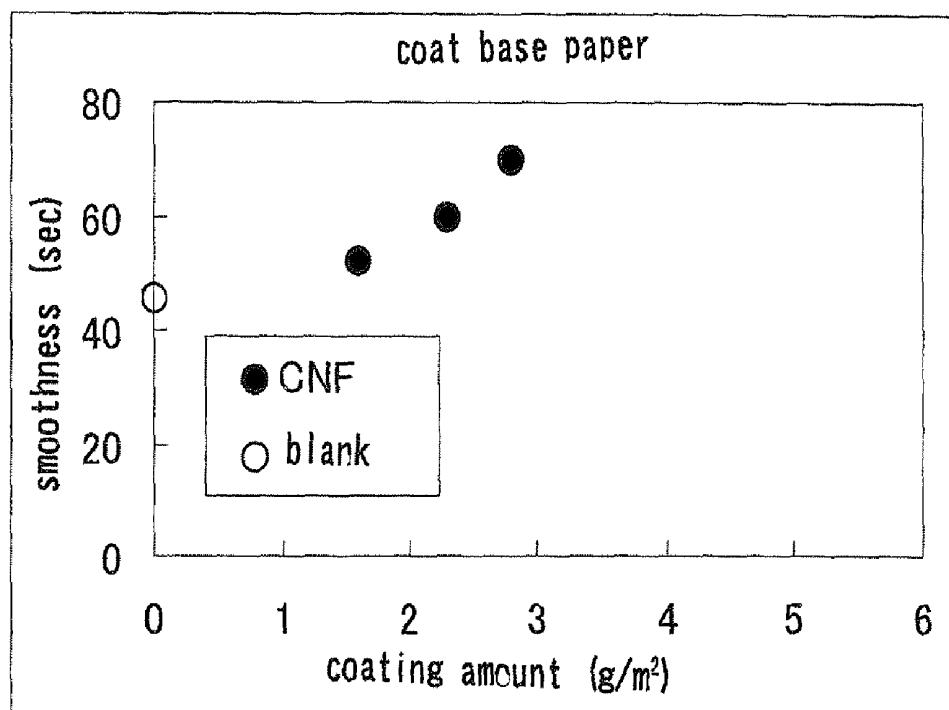


Figure 8

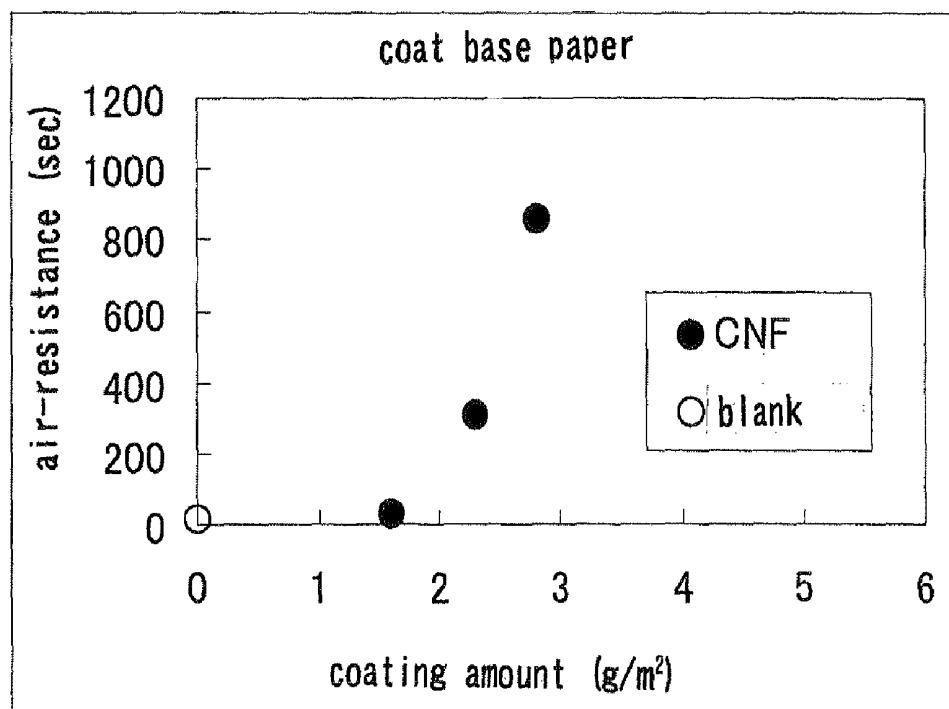


Figure 9

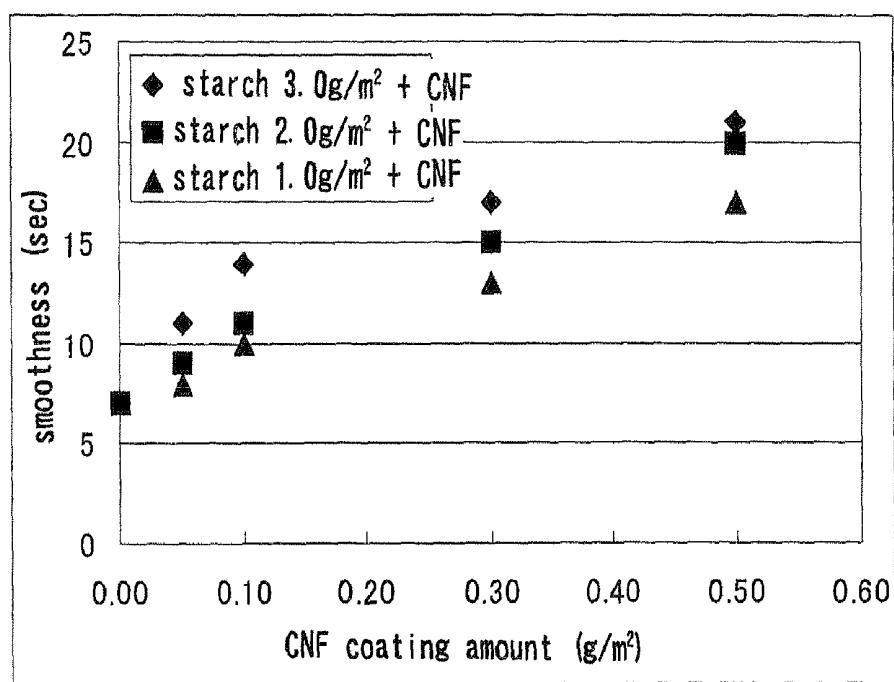
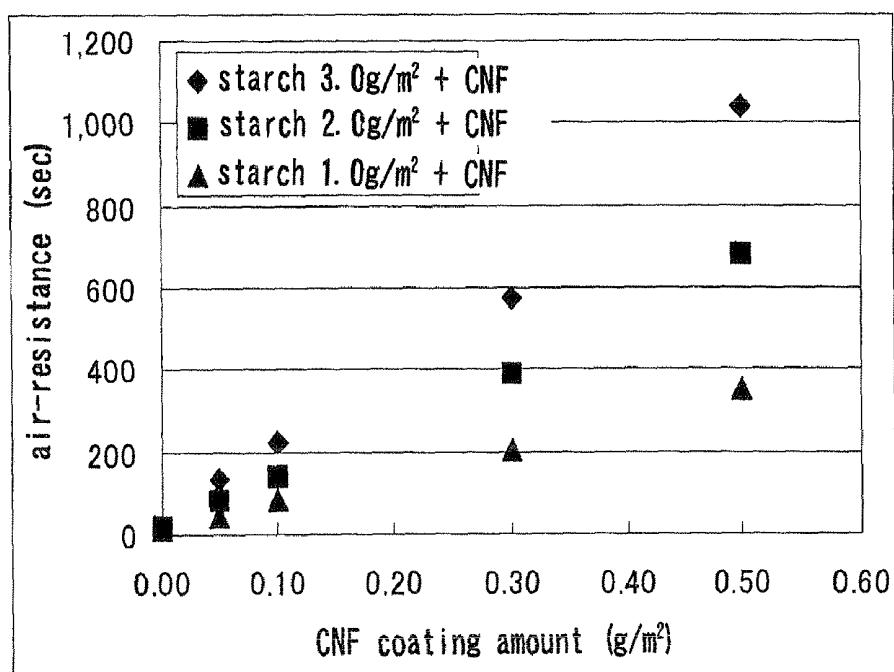


Figure 10



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**PAPERMAKING ADDITIVE AND PAPER
CONTAINING THE SAME**

This application is the U.S. national phase of International Application No. PCT/JP2009/055967, filed 25 Mar. 2009, which designated the U.S. and claims priority to Japanese Patent Application No. 2008-091333, filed 31 Mar. 2008, the entire contents of each of which are hereby incorporated by reference.

TECHNICAL FIELD

This invention relates to a papermaking additive comprising cellulose nanofibers having a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably 500 to 2000 mPa·s at a concentration of 2%; and paper containing the papermaking additive. More specifically, the invention relates to paper containing the above papermaking additive capable of improving air resistance and smoothness, the paper which is used as printing paper, news printing paper, electrophotographic transfer paper, inkjet recording paper, thermal recording paper, pressure sensitive recording paper, converting paper, paperboard, sanitary paper, or base paper for coated paper or laminated paper.

BACKGROUND ART

Paper has voids, and the voids penetrating the paper in its thickness direction, in particular, influence barrier properties against oxygen and steam, or permeability to a coating material. Patent Literature 1 discloses use of a carboxymethylcellulose sodium salt having a degree of carboxymethyl substitution of 0.25 to 0.5 and a viscosity of 5 to 300 mPa·s as an aqueous solution at a concentration of 1%, as a permeation suppressant suppressing permeation of a paint through base paper. As a method for improving the air resistance which is an indicator of voids in paper, Patent Literature 2 discloses base paper for release paper incorporating ungelatinized granular starch. Patent Literature 3 discloses an improver for paper surface quality comprising an anionic polyacrylamide resin.

Patent Document 1: JP 2004-300624 A

Patent Document 2: JP 1992-57798 B

Patent Document 3: JP 2003-49390 A

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

However, By using the above-mentioned carboxymethylcellulose, ungelatinized granular starch, and anionic polyacrylamide resin, it is difficult to form a coating film which completely fills in the voids of paper, and a paper having sufficient air resistance has not been obtained. Other methods for improving air resistance by strengthening the beating of pulp for improving bonds between fibers, or by collapsing the voids by strong calendering, increase the density of paper, and the resulting paper is difficult to be applied other than special uses.

It is an object of the present invention to provide a papermaking additive capable of improving air resistance of paper markedly, and paper containing the additive, specifically, printing paper, news printing paper, electrophotographic transfer paper, inkjet recording paper, thermal recording paper, pressure sensitive recording paper, converting paper, paperboard, or sanitary paper; and coated paper, inkjet recording paper, thermal recording paper, pressure sensitive

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recording paper, converting paper, or laminated paper which uses the paper markedly improved in air resistance as base paper.

Means for Solving the Problems

The inventors of the present invention have found that cellulose nanofiber having a suitable B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably, 500 to 2000 mPa·s at a concentration of 2% as an aqueous dispersion, and showing moderate consistency which enables the nanofibers to be applied to a base such as paper, can be obtained by oxidizing cellulosic material with the addition of an oxidizing agent in the presence of (1) N-oxyl compound(s), and (2) compound(s) selected from bromide, iodide, or mixtures thereof, and then finely grinding the oxidized cellulosic material by a wet process to defibrate the fibers in a specific manner. The inventors also have found that incorporating a papermaking additive comprising the cellulose nanofiber into paper can improve air resistance of paper, without an increase in density of paper.

Effects of the Invention

The papermaking additive containing cellulose nanofibers according to the present invention can remarkably increase air resistance of paper, as compared to starch and polyacrylamide, and using the papermaking additive of the present invention can produce a high-quality paper having high air resistance.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph showing the results of measurements of the smoothnesses of news printing papers prepared in Example 2 (CNF), Comparative Example 4 (blank), Comparative Example 5 (starch), and Comparative Example 6 (PVA).

FIG. 2 is a graph showing the results of measurements of the air resistances of the news printing papers prepared in Example 2 (CNF), Comparative Example 4 (blank), Comparative Example 5 (starch), and Comparative Example 6 (PVA).

FIG. 3 is a graph showing the results of measurements of the smoothnesses of base papers for coated paper prepared in Example 3 (CNF), Comparative Example 7 (blank), Comparative Example 8 (starch), Comparative Example 9 (PVA), and Comparative Example 10 (CMC).

FIG. 4 is a graph showing the results of measurements of the air resistances of the base papers for coated paper prepared in Example 3 (CNF), Comparative Example 7 (blank), Comparative Example 8 (starch), Comparative Example 9 (PVA), and Comparative Example 10 (CMC).

FIG. 5 is a graph showing the results of measurements of the smoothnesses of base papers for wallpaper prepared in Example 4 (CNF), Comparative Example 11 (blank), Comparative Example 12 (starch), and Comparative Example 13 (PVA).

FIG. 6 is a graph showing the results of measurements of the air resistances of the base papers for wallpaper prepared in Example 4 (CNF), Comparative Example 11 (blank), Comparative Example 12 (starch), and Comparative Example 13 (PVA).

FIG. 7 is a graph showing the results of measurement of smoothness of the base papers for coated paper prepared in Example 5 and Comparative Example 7 (blank).

FIG. 8 is a graph showing the results of measurement of air resistance of the base papers for coated paper prepared in Example 5 and Comparative Example 7 (blank).

FIG. 9 is a graph showing the results of measurement of smoothness of news printing paper prepared in Examples 9 to 12 and Comparative Example 22 (fixing the coating amount of starch at 3.0 g/m², and altering the coating amount of CNF), Examples 13 to 16 and Comparative Example 23 (fixing the coating amount of starch at 2.0 g/m², and altering the coating amount of CNF), as well as Examples 17 to 20 and Comparative Example 24 (fixing the coating amount of starch at 1.0 g/m², and altering the coating amount of CNF).

FIG. 10 is a graph showing the results of measurement of air resistance of news printing paper prepared in Examples 9 to 12 and Comparative Example 22 (fixing the coating amount of starch at 3.0 g/m², and altering the coating amount of CNF), Examples 13 to 16 and Comparative Example 23 (fixing the coating amount of starch at 2.0 g/m², and altering the coating amount of CNF), as well as Examples 17 to 20 and Comparative Example 24 (fixing the coating amount of starch at 1.0 g/m², and altering the coating amount of CNF).

DESCRIPTION OF EMBODIMENTS

(Cellulose Nanofiber)

The papermaking additive of the present invention comprises cellulose nanofibers. Cellulose nanofibers are single cellulose microfibril having a width of 2 to 5 nm and a length of 1 to 5 μm, which are obtained by defibrating fibers in cellulosic material. The present invention uses, in particular, an aqueous dispersion of cellulose nanofibers having a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably 500 to 2000 mPa·s at a concentration of 2% (w/v) (that is, 2 g of cellulose nanofiber (dry weight) is contained in 100 ml of dispersion). The papermaking additive of the present invention shows moderate consistency, and can be easily prepared to a coating material by merely adjusting its concentration to a desired level. Comparatively low value of B-type viscosity of cellulose nanofibers as a 2% (w/v) aqueous dispersion is preferred since such low-viscosity nanofibers can be easily prepared to a coating material. The viscosity is preferably about 500 to 2000 MPa·s, more preferably about 500 to 1500 MPa·s, and most preferably about 500 to 1000 MPa·s.

The B-type viscosity of the cellulose nanofiber of the present invention may be measured by a known method. For example, a viscometer, VISCOMETER TV-10, available from TOKI SANGYO Corporation can be used to measure the B-type viscosity.

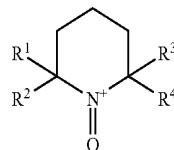
The cellulose nanofiber having a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably 500 to 2000 mPa·s as a 2% (w/v) aqueous solution, can be obtained, for example, by oxidizing a cellulosic material with the addition of an oxidizing agent in the presence of (1) N-oxyl compound(s), and (2) compound(s) selected from bromide, iodide or mixtures thereof; and then finely grinding the oxidized cellulose by a wet process to defibrate fibers in the cellulose and convert the cellulose into nanofibers.

The cellulosic material used in the present invention is not limited, and includes kraft pulp or sulfite pulp of various wood origins, powdery cellulose formed by pulverizing such pulp by a high pressure homogenizer, a mill or the like, and a microcrystalline cellulose powder formed by purifying such a material by chemical treatment such as acid hydrolysis. Among them, bleached kraft pulp, bleached sulfite pulp, powdery cellulose, and a microcrystalline cellulose powder are preferably used since comparatively low-viscosity cellulose nanofibers whose B-type viscosity is about 500 to 2000

MPa·s in an aqueous dispersion at a concentration of 2% (w/v) can be prepared effectively by using these materials. More preferably, powdery cellulose and a microcrystalline cellulose powder are used.

Powdery cellulose is a rod-like particle of microcrystalline cellulose which is obtained by removing amorphous parts from wood pulp with an acid hydrolysis treatment, and pulverizing and sieving it. In the powdery cellulose, degree of polymerization of cellulose is preferably about 100 to 500, crystallinity of powdery cellulose measured by X-ray diffraction is preferably about 70 to 90%, a mean volume diameter measured by laser diffraction is preferably not more than 100 μm, more preferably not more than 50 μm. By using powdery cellulose having a mean volume diameter of not less than 100 μm, a highly-fluid dispersion of cellulose nanofibers can be prepared. As the powdery cellulose used in the present invention, for example, a rod-like crystalline cellulose powder having a certain particle size distribution which is obtained by a method comprising subjecting a selected pulp to an acid hydrolysis treatment to obtain an undecomposed residue, and purifying, drying, pulverizing and sieving the residue, may be used, or a commercially available powdery cellulose such as KC FLOCK® available from NIPPON PAPER CHEMICALS Corporation, CEOLUS® available from ASAHI KASEI CHEMICALS Corporation, and AVICEL® available from FMC Corporation may also be used.

As the N-oxyl compound used in the present invention, any compounds which can promote desired oxidizing reaction may be used. For example, the N-oxyl compound used in the invention includes the compound represented by the following formula (1):

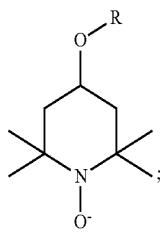


formula 1

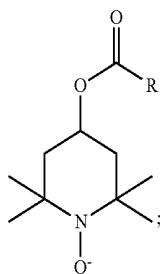
wherein R¹ to R⁴ are identical or different from each other, an alkyl group having about 1 to 4 carbon atoms.

Among the compounds represented by the formula (1), compounds which produce 2,2,6,6-tetramethyl-1-piperidin-N-oxyl radical (hereinafter referred to as TEMPO) and a 4-hydroxy-2,2,6,6-tetramethyl-1-piperidin-N-oxyl radical (hereinafter referred to as 4-hydroxy TEMPO) are preferred. In particular, derivative of 4-hydroxy TEMPO is most preferably used. As the derivatives of 4-hydroxy TEMPO, derivatives in which the hydroxyl group of 4-hydroxy TEMPO has been etherified with an alcohol containing a straight or branched carbon chain having 4 or less carbon atoms, or esterified with a carboxylic acid or a sulfonic acid, are preferably used. When etherifying 4-hydroxy TEMPO, a water-soluble derivative can be obtained by using an alcohol having 4 or less carbon atoms, regardless of the presence or absence of a saturated or unsaturated bond, and the water-soluble derivative of 4-hydroxy TEMPO can function effectively as an oxidation catalyst.

The derivatives of 4-hydroxy TEMPO include, for example, compounds represented by the following formulas 2 to 4:

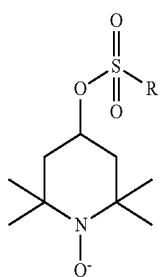


formula 2



formula 3

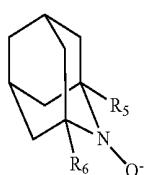
and



formula 4

wherein R is a straight or branched carbon chain having 4 or less carbon atoms.

Further, a radical of the N-oxyl compound represented by the following formula 5:



formula 5

wherein R⁵ and R⁶ are identical or different from each other, hydrogen, or a C1 to C6 straight or branched alkyl group, that is, aza-adamantane type nitroxy radical can be used preferably, since such compounds can shorten reaction time, and promote to produce a uniform cellulose nanofiber.

The amount of the N-oxyl compounds such as TEMPO and 4-hydroxy TEMPO derivatives used in the oxidation of cellulosic material is not limited, as long as it is a catalytic amount which enables the cellulosic material to be converted into nanofibers. For example, its amount is of the order of 0.01 to 10 mmols, preferably 0.01 to 1 mmol, more preferably 0.05 to 0.5 mmol, based on 1 g (absolute dry weight) of the cellulosic material.

As the bromide or iodide used in the oxidation of cellulosic material, a compound which can dissociate in water and ionize, for example, an alkali metal bromide, an alkali metal iodide or the like can be used. The amount of the bromide or iodide used can be selected within a range which can promote the oxidation reaction. For example, the amount is of the

order of 0.1 to 100 mmols, preferably 0.1 to 10 mmols, more preferably 0.5 to 5 mmols, based on 1 g (absolute dry weight) of the cellulosic material.

As the oxidizing agent used in the oxidation of cellulosic material, any oxidizing agent can be used, as long as it can proceed with the intended oxidation reaction, such as a halogen, a hypohalogenous acid, a halogenous acid, a perhalogenic acid, or a salt thereof, a halogen oxide, or a peroxide. From the viewpoint of the manufacturing cost, the preferred oxidizing agent to be used is sodium hypochlorite which is used currently most widely in industrial processes, which is inexpensive, and which imposes a minimal environmental load. The amount of the oxidizing agent used can be selected within a range which can promote the oxidation reaction. For example, the amount is of the order of 0.5 to 500 mmols, preferably 0.5 to 50 mmols, more preferably 2.5 to 25 mmols, based on 1 g (absolute dry weight) of the cellulosic material.

Oxidation of cellulosic material in the present invention is characterized that the oxidation of the cellulosic material is carried out in water with the addition of an oxidizing agent such as sodium hypochlorite in the presence of (1) N-oxyl compound(s) such as 4-hydroxy TEMPO derivative(s) and (2) compound(s) selected from the group consisting of bromide, iodide and mixtures thereof. The method has the feature that it can proceed with the oxidation reaction smoothly even under mild conditions. Thus, the reaction temperature may be room temperature of the order of 15 to 30°C. As the reaction proceeds, carboxyl groups form in the cellulose, and a decline in the pH of the reaction mixture is observed. To proceed with the oxidation reaction efficiently, it is desirable to maintain the pH of the reaction mixture at a value of 9 to 12, preferably about 10 to 11 with the addition of alkaline solution such as an aqueous solution of sodium hydroxide.

Cellulose nanofibers can be produced by finely grinding the oxidized cellulosic material which has been obtained by oxidizing cellulosic material in the presence of (1) N-oxyl compound(s) and (2) compounds selected from bromide, iodide or mixtures thereof, with the addition of an oxidizing agent, in a wet condition to defibrate it. In the wet fine grinding, mixing/stirring, emulsifying/dispersing devices, such as a high-speed shearing mixture and a high-pressure homogenizer can be used alone or in combination. In particular, an ultrahigh-pressure homogenizer which can force not less than 100 MPa, preferably not less than 120 MPa, more preferably not less than 140 MPa is preferably used in the wet fine grinding, since such a ultrahigh-pressure homogenizer can produce cellulose nanofibers having a comparatively low viscosity such as a B-type viscosity of 500 to 2000 mPa·s in an aqueous dispersion of 2% (w/v), effectively.

The cellulose nanofibers of the present invention desirably has an amount of the carboxyl groups being 0.5 mmol/g or more, preferably 0.9 mmol/g, more preferably 1.2 mmol/g, based on 1 g (absolute dry weight) of cellulose nanofibers. Such cellulose nanofibers can promote preparation of uniform dispersion. The amount of cellulose nanofibers can be measured by preparing 60 ml of slurry containing 0.5 weight % of cellulose nanofiber, adding 0.1M of hydrochloric acid to adjust the slurry's pH at 2.5, dropping 0.05N of aqueous sodium hydroxide with measuring electrical conductivity until the pH reaches 11, and determining an amount of sodium hydroxide (a) which is consumed in neutralization of weak acid when the electrical conductivity shows gentle curve, and using the following formula:

$$\text{Amount of carboxyl groups (mmol/g pulp)} = a(\text{ml}) \times 0.05 / \text{weight of oxidized pulp (g)}$$

(Paper which Contains Cellulose Nanofibers)

Incorporating the papermaking additive comprising cellulose nanofiber of the present invention into paper can improve air resistance of the paper, and can impart functions such as the suppression of permeation of a coated material, and an improvement in barrier properties. Also, when paper is coated with or impregnated with the papermaking additive of the present invention, the smoothness of the paper can be improved, thus enhancing printability. A paper prepared by coating or impregnating the papermaking additive of the cellulose nanofibers of the present invention is excellent in barrier properties and heat resistance and can be used as a packaging material.

A papermaking additive comprising the cellulose nanofibers of the present invention may be internally added or externally added to paper. However, its external addition is desirable because the external addition enables the cellulose nanofibers to be present in a larger amount in the vicinity of the paper surface and can highly improve air resistance and smoothness. In externally adding the papermaking additive, it is recommendable to coat an aqueous dispersion of the cellulose nanofibers on paper by a coating machine such as a 2-roll size press coater, a gate roll coater, a blade metering coater, or a rod metering coater, or impregnate paper with the nanofibers.

The preferred content of the papermaking additive according to the present invention is 0.1 to 10% by weight based on the dry weight of cellulose nanofibers in the dry weight of paper and, in the case of external addition, is 0.01 to 10 g/m², preferably 0.1 to 10 g/m², as the amount of coating per surface. In the case of external addition of the papermaking additive of the present invention onto a printing paper such as a news printing paper, the preferred content of the additive is 0.1 to 5 g/m² as the amount of coating per surface; in the case of external addition onto a converting paper such as base paper for wallpaper, the preferred content is 1 to 5 g/m², more preferably 2 to 5 g/m²; and in the case of external addition onto base paper for a coated paper, the preferred content is 1 to 5 g/m², more preferably 2 to 5 g/m².

Paper containing the cellulose nanofibers according to the present invention is produced by a known paper machine, and its paper making conditions are not regulated. As the paper machine, a Fourdrinier paper machine, a twin wire paper machine, or the like is used. Also, a cylinder paper machine can be used to produce multi-layer paper or a paperboard.

The paper of the present invention may be not only paper in a single layer, but also multi-layer paper in two or more layers, or a paperboard. In the multi-layer paper, the cellulose nanofibers may be contained in at least one of the layers.

The paper of the present invention uses, as a pulp component, chemical pulp (needle bleached kraft pulp (NBKP) or needle unbleached kraft pulp (NUKP), leaf bleached kraft pulp (LBKP) or leaf unbleached kraft pulp (LUKP), etc.), mechanical pulp (ground pulp (GP), thermomechanical pulp (TMP), chemithermomechanical pulp (CTMP), etc.), or recycled pulp such as deinked pulp (DIP), any of these pulps being used alone or as mixed in arbitrary proportions. During papermaking, pH may be acidic, neutral, or alkaline.

The paper of the present invention may also contain one or more filler(s). As the filler, a publicly known filler can be used, such as white carbon, talc, kaolin, clay, heavy calcium carbonate, light calcium carbonate, titanium oxide, or a synthetic resin filler. Among them, in view of protection of the environment, and improvement of preservation quality of paper, calcium carbonate is preferably used to carry out neutral papermaking, so as to make the pH of the surface of paper being 6 to 9.

Further, the paper of the present invention may, if necessary, contain aluminum sulfate, a sizing agent, a paper strength agent, a retention aid, a drainage aid, a coloring agent, a dyestuff, an anti-foaming agent, and a bulking agent.

5 (Printing Paper)

The paper of the present invention which contains cellulose nanofibers can be used as printing paper upon coating with a surface treating agent containing no pigment. Desirably, a surface treating agent consisting essentially of a water-soluble polymer, in order to improve surface strength and sizing properties. Alternatively, if a water-soluble polymer is used, the polymer may be mixed with the papermaking additive consisting of the cellulose nanofibers of the present invention, and coated therewith. When the papermaking additive is mixed with a water-soluble polymer and coated or impregnated, as compared to the case where the water-soluble polymer is used alone, a paper having high smoothness and air resistance, as well as showing high adherability of ink and low print-through in offset printing, can be obtained.

As the water-soluble polymer, a surface treating agent in common use can be used, such as starch including a starch, oxidized starch, and processed starch, carboxymethylcellulose, polyacrylamide, or polyvinyl alcohol, any of these surface treating agents being used alone or as a mixture. To the surface treating agent, in addition to the water-soluble polymer, it is possible to add a paper strength agent which can enhance water resistance and surface strength, or to externally add a sizing agent which can enhance sizing properties. If neutral papermaking is carried out, it is preferred that a cationic surface sizing agent is externally added.

35 The mixed ratio of the water-soluble polymer to the papermaking additive comprising cellulose nanofibers is not in particular limited, but it is preferred that the content of water-soluble polymer is 80 to 98 wt % and the content of the papermaking additive is 2 to 20 wt %, based on the solid content of the surface treating agent in the coating liquid. If the content of the papermaking additive is too high, viscosity of the coating liquid increases and the coating abilities of the coating decrease.

40 The surface treating agent can be coated by a coating machine, such as a 2-roll size press coater, a gate roll coater, a blade metering coater, or a rod metering coater. Of them, a film transfer type coating machine such as a gate roll coater is preferred as compared to an impregnating type coating machine such as a 2-roll size press coater, because the surface treating agent remains on the paper surface more and proves effective even in a smaller amount of coating. The preferred amount of coating with the surface treating agent is, based on 45 dry weight, 0.05 g/m² or more, but 3 g/m² or less, more preferably, 0.1 g/m² or more, but 3 g/m² or less, per surface. When the water-soluble polymer and the papermaking additive of the present invention are mixed and coated together, the preferred amount of water-soluble polymer is about 0.05 to 5 g/m² per both surfaces, and the preferred amount of cellulose nanofibers is 0.01 to 1 g/m² per both surfaces.

50 Further in the present invention, to improve the quality of print, it is possible to apply a coating layer containing pigments on the paper which has been internally or externally 55 provided with the papermaking additive of the present invention to make a printing paper. In addition, with the proviso that a desired effect is obtained, calendering may be performed. Calendering may be carried out with a commonly used linear pressure, but it is preferred that low linear pressure which can ensure smoothness of paper is used in order to increase a bulking property of the paper. A soft nip calendar is 60 preferably used.

The papermaking additive comprising cellulose nanofibers of the present invention can give a printing paper high smoothness and enhance a quality of printing.

For example, a news printing paper is a kind of printing paper, and is made from 100% recycled pulp, or a mixture of recycled pulp with a mechanical pulp prepared by grinding wood and containing little amount of needle bleached pulp. Alternatively, the news printing paper is prepared by mixing the foregoing various pulps. The news printing paper is required to be hardly cut upon high-speed rotary printing, have high smoothness in both sides, high opacity, and high printing abilities. The papermaking additive of the present invention can remarkably increase the air resistance of news printing paper, and prevent the ink from excessively penetrating into the paper to prevent decrease in density of printing. In particular, if a mixture of the papermaking additive of the present invention with a water-soluble polymer is coated on the paper, cellulose nanofibers fills depressed area of the paper, the smoothness of the paper increases, and adherability of ink on the paper also increases. Also, since the cellulose nanofibers remain on the surface of the paper, the air resistance of the paper increases and, upon printing, excess penetration of ink is prevented and properties of preventing print-through is enhanced.

The papermaking additive of the present invention can also applies to a high-quality printing paper (a wood-free paper) which is made from 100% chemical pulp prepared by subjecting wood to a chemical treatment to remove lignin and consisting of cellulose and hemi-cellulose, a medium-quality printing paper (a wood containing paper) which is made from 40 to 100% of chemical pulp. Various properties of the paper may be determined depending on its use. For example, the basis weight of news printing paper is about 30 to 60 g/m². A type of printing is not limited, and any type of printing such as offset printing, gravure printing, and anastatic printing may be used. As a type of offset printing, a heat-set type of printing which includes a step of heat drying, and a cold-set type of printing which does not include heat drying, but uses an ink which is dried by penetration of the ink, may be used.

(Electrophotographic Transfer Paper, Thermal Recording Paper, Converting Paper, Paperboard, Sanitary Paper, Inkjet Recording Paper, and the Like)

The paper of the present invention can be used not only as printing paper and news printing paper, but also as electrophotographic transfer paper, inkjet recording paper, thermal recording paper, pressure sensitive recording paper, business form, converting paper, and sanitary paper. In further detail, the converting paper may be an industrial laminates base, backing paper for wall paper, or base paper for molding purposes. The sanitary paper is, in further detail, tissue paper, toilet paper, or a paper towel. The paper of the present invention can also be used as a paperboard such as a corrugating medium.

The papermaking additive of the present invention can increase smoothness and air resistance of electrophotographic transfer paper, and thereby, transferability of toner to paper is improved and quality of printing is heightened.

The papermaking additive of the present invention can increase smoothness and air resistance of inkjet recording paper, prevent an ink from excessively penetrating, avoid breeding of ink, increase fixing of ink, and heighten density of printing.

The papermaking additive of the present invention can increase smoothness and air resistance of thermal recording paper, prevent a thermal sensitive coating from excessively penetrating into the base paper, help the coating to spread on

the surface of the paper uniformly, and increase thermal insulation properties and sensitivity of the paper.

The papermaking additive of the present invention can increase smoothness and air resistance of pressure sensitive recording paper, prevent a pressure sensitive coating from excessively penetrating into the base paper, help the coating to spread on the surface of the paper uniformly, and increase sensitivity of the paper.

The papermaking additive of the present invention can increase smoothness and air resistance of backing paper for wall paper, prevent a binder such as aquatic starch paste from excessively penetrating into the base paper, avoid fuzz of the surface of the base paper, and prevent projection of resin surface.

The papermaking additive of the present invention can increase smoothness and air resistance of sanitary paper and make the surface of paper lubricant.

The papermaking additive of the present invention can increase smoothness and air resistance of paperboard such as a corrugated paperboard, and increase the printability of the paper.

(Base Paper for Coated Paper)

Further, the paper of the present invention which contains cellulose nanofibers can be used as base paper for paper having a pigment-containing coating layer such as coated paper, inkjet recording paper, thermal recording paper, pressure sensitive recording paper, or converting paper. In further detail, the coated paper may be art paper, coat paper, light-weight coated paper, cast coated paper, or a white lined board. In further detail, the converting paper may be packaging paper, moisture-proof paper, backing paper for wall paper, base paper for a paper container, or base paper for molding purposes. In particular, paper having the papermaking additive, which comprises the cellulose nanofibers according to the present invention, externally added to paper is markedly improved in air resistance and smoothness, and when this paper is used as base paper and coated with a paint, permeation of the paint is suppressed, and a smooth coating layer is obtained. Thus, coated paper with satisfactory printability can be obtained. For example, base paper for coated paper such as wood-free paper (100% chemical pulp) and wood-containing paper (mixture of chemical pulp and mechanical pulp) may be externally applied the cellulose nanofiber of the present invention, and the resulting base paper has an improved smoothness and air resistance. In such paper, a coating color consisting of pigment such as kaolin and calcium carbonate and a binder such as starch and latex is prevented from excessively penetrating into the base paper, and thus, the coated layer has a high smoothness. Such paper has a high degree of brilliance and high printability, even when the coated amount of coating color is low.

The above paper is also preferably used as base paper for inkjet recording paper, thermal recording paper, or pressure sensitive recording paper, since such papers have a smooth inkjet recording layer, a smooth thermal recording layer, or a smooth pressure sensitive recording layer. Also, the paper of the present invention which comprises cellulose nanofibers may be used as base paper for laminated paper having one or more synthetic resin layers on one surface or both surfaces thereof.

The coated paper of the present invention is paper formed by providing base paper, which contains cellulose nanofibers, with a coating layer having a pigment and a binder. The pigment used in the coating layer is an inorganic pigment such as kaolin, clay, delaminated clay, heavy calcium carbonate, light calcium carbonate, talc, titanium dioxide, barium sulfate, calcium sulfate, zinc oxide, silicic acid, silicate, col-

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loidal silica, or satin white, or an organic pigment such as plastic pigment, which has been used so far for coated paper. Any one or more of these pigments can be selected and used, as appropriate, according to needs.

The binder used in the coating layer is any of those so far used for coated paper, including synthetic adhesives such as various copolymers, for example, a styrene-butadiene copolymer, a styrene-acrylic copolymer, an ethylene-vinyl acetate copolymer, a butadiene-methyl methacrylate copolymer, and a vinyl acetate-butyl acrylate copolymer, polyvinyl alcohol, a maleic anhydride copolymer, and an acrylic acid-methyl methacrylate copolymer; proteins such as casein, soybean protein, and synthetic protein; starches such as oxidized starch, cationic starch, urea phosphoric esterified starch, etherified starch, e.g., hydroxyethyl etherified starch, and dextrin; and cellulose derivatives such as carboxymethylcellulose, hydroxyethylcellulose, and hydroxymethylcellulose. One or more of these ordinary additives for coated paper are selected as appropriate, and put to use. Any of these additives is used in an amount of the order of 5 to 50 parts by weight with respect to 100 parts by weight of the pigment. To make surface strength more satisfactory, it is preferred to contain 10 to 25 parts by weight of a copolymer latex such as styrene-butadiene. From the point of view of flexibility, the content of starch is preferably 5 parts by weight or less.

Various auxiliaries to be compounded with ordinary pigments for coated paper, such as dispersing agents, thickening agents, water retaining agents, anti-foaming agents, water resistant additives, and coloring agents, are used appropriately according to needs.

As the coating layer provided on the base paper, a single layer or two or more layers may be provided on one surface or both surfaces of the base paper. The total amount of coating with the coating layer is preferably 5 to 30 g/m², more preferably 8 to 20 g/m², per surface. The amount of coating if an undercoating layer is provided is preferably 2 to 8 g/m².

Upon application of a coating layer consisting essentially of pigment and binder(s) on a base paper, a film transfer roll coater such as a 2-roll size press coater, a gate roll coater, a blade metering size press coater, a rod metering size press coater, or Sym-Sizer; a flooded nip/blade coater, a jet fountain/blade coater, or a short dwell time applicator; a rod metering coater using a grooved rod or a plain rod instead of a blade; or a publicly known coater such as a curtain coater or a die coater. In coating an undercoating solution, the film transfer method using a gate roll coater or the like is preferred in order to impregnate the base paper with this solution moderately.

For the purpose of, for example, improving smoothness and printing quality, it is possible to carry out the surface treatment of the coated paper obtained in the above-described manner. The method of surface treatment can be to use a publicly known surface treatment apparatus such as a super-calender using a cotton roll as an elastic roll, or a soft nip calendar using a synthetic resin roll as an elastic roll.

Actions

The reason why the papermaking additive comprising cellulose nanofibers of the present invention markedly improve smoothness and air resistance of paper remains unclear. However, it is presumed that unlike a water-soluble polymer such as starch, the cellulose nanofibers are in a fibrous form, and can exist in such a crosslinked state as to fill in the voids of pulp fibers on the surface of the paper.

EXAMPLES

The present invention will be described in more detail by the following examples, which in no way limit the present invention.

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<Preparation of Cellulose Nanofiber 1>

Powdery cellulose (manufactured by NIPPON PAPER CHEMICALS CO., LTD.; particle size 24 µm) in an amount of 15 g (absolute dry weight) was added to 500 ml of an aqueous solution having 78 mg (0.5 mmol) of TEMPO (a product of Sigma Aldrich) and 755 mg (5 mmol) of sodium bromide dissolved therein, and the mixture was stirred until the powdery cellulose was uniformly dispersed. To the reaction system, 50 ml of an aqueous solution of sodium hypochlorite (available chlorine 5%) was added, and then the mixture was adjusted to pH 10.3 using a 0.5N aqueous solution of hydrochloric acid to initiate an oxidation reaction. During the reaction, the pH within the system lowers, but a 0.5N aqueous solution of sodium hydroxide was successively added to adjust the pH to 10. After the reaction was performed for 2 hours, the oxidized powdery cellulose was separated by a centrifugal operation (6000 rpm, 30 minutes, 20° C.), and thoroughly washed with water to obtain oxidized powdery cellulose. A 2% (w/v) slurry of the oxidized powdery cellulose was treated by a mixer for 15 minutes at 12,000 rpm, and the powdery cellulose slurry was further treated 5 times under a pressure of 140 MPa by an ultrahigh pressure homogenizer, whereby a transparent gel-like dispersion was obtained.

<Preparation of Cellulose Nanofiber 2>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that the powdery cellulose slurry was treated 5 times under a pressure of 120 MPa by an ultrahigh pressure homogenizer.

<Preparation of Cellulose Nanofiber 3>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that the powdery cellulose slurry was treated 5 times under a pressure of 100 MPa by an ultrahigh pressure homogenizer.

<Preparation of Cellulose Nanofiber 4>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that, in the step of the wet process finely grinding, a rotary blade mixer (rim speed: 37 m/s, NISSEI CORPORATION, processing time: 30 minutes) was used instead of the ultrahigh pressure homogenizer.

<Preparation of Cellulose Nanofiber 5>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that 4-methoxy TEMPO was used instead of TEMPO.

<Preparation of Cellulose Nanofiber 6>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that a bleached, un-beaten sulfite pulp (manufactured by NIPPON PAPER CHEMICALS CO., LTD.) was used instead of the powdery cellulose, and the oxidized sulfite pulp slurry was treated 40 times under a pressure of 140 MPa by the ultrahigh pressure homogenizer.

<Preparation of Cellulose Nanofiber 7>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 5, with the exception that the bleached, un-beaten sulfite pulp (manufactured by NIPPON PAPER CHEMICALS CO., LTD.) was used instead of the powdery cellulose, the oxidized sulfite pulp slurry was treated by the rotary blade mixer for 5 hours.

The B-type (60 rpm, 20° C.) viscosity each of the cellulose nanofibers obtained by the foregoing preparation methods 1 to 7 was measured with the use of VISCOMETER TV-10 (TOKI SANGYO CO, LTD.), and the result is shown in Table 1.

TABLE 1

| Preparation | material | catalyst | wet process finely grinding | | cellulose nanofiber B-type viscosity (mPa · s) |
|-------------|-------------------|-----------------|---------------------------------|--------------------|--|
| | | | disperser | pressure | |
| 1 | powdery cellulose | TEMPO | ultrahigh pressure homogenizer | 140 MPa (5 times) | 890 |
| 2 | powdery cellulose | TEMPO | ultrahigh pressure homogenizer | 120 MPa (5 times) | 984 |
| 3 | powdery cellulose | TEMPO | ultrahigh pressure homogenizer | 100 MPa (5 times) | 1264 |
| 4 | powdery cellulose | TEMPO | rotary blade mixer (30 minutes) | — | 2860 |
| 5 | powdery cellulose | 4-methoxy TEMPO | ultrahigh pressure homogenizer | 140 MPa (5 times) | 850 |
| 6 | sulfite pulp | TEMPO | ultrahigh pressure homogenizer | 140 MPa (40 times) | 5568 |
| 7 | sulfite pulp | TEMPO | rotary blade mixer (5 hours) | — | 6850 |

By the preparation methods 1 to 7, cellulose nanofibers having a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s at a concentration of 2% (w/v) as an aqueous dispersion were obtained. Among them, the cellulose nanofibers obtained by the preparation methods 1 to 3, and 5 have a B-type viscosity (60 rpm, 20° C.) of 500 to 2000 mPa·s at a concentration of 2% (w/v) as an aqueous dispersion, have good flowability, and were easy to coat on a substrate such as paper. The cellulose nanofibers obtained by the preparation methods 4, 6, and 7 have a little high viscosity, and, when the nanofibers were applied on paper, penetration of the nanofibers into paper was suppressed, whereby amount of coating was decreased as compared to the case where the cellulose nanofibers obtained by the preparation methods 1 to 3, and 5, were coated on the same condition.

Next, examples of method for preparing cellulose nanofibers-containing paper by coating the cellulose nanofibers obtained by the foregoing methods on paper.

<Preparation of Wood-Free Paper Containing Cellulose Nanofibers (CNF)>

Example 1

The cellulose nanofiber dispersion obtained by the foregoing preparation method 1 was coated on wood-free paper (paper having 100% chemical pulp, manufactured by Nippon Paper Industries Co., Ltd.; basis weight 79 g/m²) by a 2-roll size press apparatus so that the amount of coating would be 1.4 g/m² on both surfaces.

Comparative Example 1

The wood-free paper used in Example 1 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 2

The wood-free paper used in Example 1 was coated with an aqueous solution of oxidized starch (commercial name:

SK200, manufactured by Nihon Cornstarch Corporation) by a 2-roll size press apparatus so that the amount of coating would be 1.4 g/m² on both surfaces.

Comparative Example 3

The wood-free paper used in Example 1 was coated with an aqueous solution of polyacrylamide (commercial name: DS4340, manufactured by SEIKO PMC CORPORATION) by a 2-roll size press apparatus so that the amount of coating would be 1.4 g/m² on both surfaces.

The thicknesses and basis weights of the papers prepared in Example 1 and Comparative Examples 1 to 3 were measured by the methods described below, and the densities were calculated based on the measured values. Further, the breaking length, Taber stiffness, whiteness, opacity, specific scattering coefficient, smoothness, and air resistance of each paper were measured by the methods described below. The results are shown in Table 2.

Thickness: Measured in accordance with JIS P8118:1998.

Basis weight: Measured in accordance with JIS P8124: 1998 (ISO 536:1995).

Density: Calculated from the measured values of the thickness and basis weight of the coated sheet.

Breaking length: Measured in accordance with JIS P8113: 1998.

Taber stiffness: Measured in accordance with JIS P8125: 1976 (ISO 2493:1992).

Whiteness: ISO whiteness was measured in accordance with JIS P8148:2001.

Opacity: Measured in accordance with JIS P8149:2000.

Specific scattering coefficient: Measured with a color-difference meter (manufactured by MURAKAMI COLOR RESEARCH LABORATORY CO., LTD.) in accordance with TAPPI T425 om-91.

Smoothness and air resistance: Measured with an Oken type smoothness/air resistance tester in accordance with Japan TAPPI Paper Pulp Testing Method No. 5-2:2000.

TABLE 2

| | density (g/cm ³) | breaking length (km) | Taber stiffness (mN) | whiteness (%) | opacity (%) | specific scattering coefficient (m ² /kg) | smooth- ness (sec.) | air resistance (sec.) |
|--------------------------|---------------------------------|----------------------------|----------------------------|------------------|----------------|---|---------------------------|-----------------------------|
| Example 1 | 0.57 | 2.97 | 0.64 | 73.5 | 95.2 | 86.1 | 43 | 49 |
| Comparative Example 1 | 0.56 | 2.55 | 0.54 | 73.2 | 95.1 | 86.2 | 27 | 6 |

TABLE 2-continued

| | density (g/cm ³) | breaking length (km) | Taber stiffness (mN) | whiteness (%) | opacity (%) | specific scattering coefficient (m ² /kg) | smooth- ness (sec.) | air resistance (sec.) |
|--------------------------|---------------------------------|----------------------------|----------------------------|------------------|----------------|---|---------------------------|-----------------------------|
| Comparative Example 2 | 0.57 | 3.01 | 0.61 | 72.9 | 95 | 83.6 | 30 | 7 |
| Comparative Example 3 | 0.57 | 3.55 | 0.67 | 72.7 | 94.9 | 82.3 | 31 | 9 |

As shown in Table 2, the paper coated with the cellulose nanofibers according to the present invention markedly improved in smoothness and air resistance as compared with the papers coated with oxidized starch or polyacrylamide.

<Preparation of News Printing Paper Containing CNF>

Example 2

News printing paper (manufactured by Nippon Paper Industries Co., Ltd.; basis weight 42 g/m², made from a little amount of mechanical pulp which contains a needle bleached pulp and a major amount of recycled pulp) was coated with the aforementioned cellulose nanofiber dispersion by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 4

The news printing paper used in Example 2 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 5

The news printing paper used in Example 2 was coated with an aqueous solution of oxidized starch (commercial name: SK200, manufactured by Nihon Cornstarch Corporation) by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 6

The news printing paper used in Example 2 was coated with an aqueous solution of polyvinyl alcohol (commercial name: PVA117, manufactured by KURARAY CO., LTD.) by a 2-roll size press apparatus, with the amount of coating being varied.

The papers prepared in Example 2 (CNF), Comparative Example 4 (blank), Comparative Example 5 (starch), and Comparative Example 6 (PVA) were measured for smoothness and air resistance. The results are shown in FIGS. 1 and 2.

<Preparation of Base Paper for Coated Paper Containing CNF>

Example 3

A coat base paper (manufactured by Nippon Paper Industries Co., Ltd.; basis weight 70 g/m², wood-containing paper made from chemical and mechanical pulps) was coated with the aforementioned cellulose nanofiber dispersion by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 7

The coat base paper used in Example 3 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 8

15 The coat base paper used in Example 3 was coated with an aqueous solution of oxidized starch (commercial name: SK200, manufactured by Nihon Cornstarch Corporation) by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 9

20 The coat base paper used in Example 3 was coated with an aqueous solution of polyvinyl alcohol (commercial name: PVA117, manufactured by KURARAY CO., LTD.) by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 10

25 The coat base paper used in Example 3 was coated with an aqueous solution of carboxymethylcellulose (commercial name: F01MC, manufactured by NIPPON PAPER CHEMICALS CO., LTD.) by a 2-roll size press apparatus, with the amount of coating being varied.

30 The papers prepared in Example 3 (CNF), Comparative Example 7 (blank), Comparative Example 8 (starch), Comparative Example 9 (PVA), and Comparative Example 10 (CMC) were measured for smoothness and air resistance. The results are shown in FIGS. 3 and 4.

<Preparation of Backing Paper for Wall Paper Containing CNF>

Example 4

45 Base paper for wall paper (manufactured by Nippon Paper Industries Co., Ltd.; basis weight 64 g/m²) was coated with the aforementioned cellulose nanofiber dispersion by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 11

50 The base paper for wall paper used in Example 4 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 12

55 The base paper for wallpaper used in Example 4 was coated with an aqueous solution of oxidized starch (commercial name: SK200, manufactured by Nihon Cornstarch Corporation) by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 13

60 The base paper for wall paper used in Example 4 was coated with an aqueous solution of polyvinyl alcohol (com-

mercial name: PVA117, manufactured by KURARAY CO., LTD.) by a 2-roll size press apparatus, with the amount of coating being varied.

The papers prepared in Example 4 (CNF), Comparative Example 11 (blank), Comparative Example 12 (starch), and Comparative Example 13 (PVA) were measured for smoothness and air resistance. The results are shown in FIGS. 5 and 6.

As shown in FIGS. 2, 4 and 6, the coating with the cellulose nanofibers of the present invention markedly improved air resistance, compared with the coating with oxidized starch, polyvinyl alcohol, or carboxymethylcellulose, regardless of the type of paper coated (news printing paper, coat base paper, base paper for wall paper). Thereby, in the case of the news printing paper, decrease in density of printing was prevented and quality of printing was improved; in the case of base paper for a coated paper, excessive penetration of a coated material was prevented and the printability was improved; and in the case of base paper for wall paper, excessive penetration of binders was prevented and workability of the wall paper was improved. Further, as shown in FIG. 5, the base paper for wall paper coated with the cellulose nanofibers of the present invention has a high smoothness, as compared with the base paper for wall paper coated with the other compounds. Thereby, fuzz of the base paper for wall paper was suppressed, and a wall paper having a smooth surface was obtained.

<Preparation of Base Paper for Coated Paper Containing CNF>

Example 5

The coat base paper used in Example 3 was with the cellulose nanofiber dispersion obtained by the foregoing preparation method 3 by a 2-roll size press apparatus, with the amount of coating being varied. The smoothness and air resistance of the resulting paper were measured, and the results are shown in FIGS. 7 and 8.

<Preparation of Thermal Recording Paper of which Base Paper Contains CNF>

Example 6

A thermal sensitive coating color having the following composition was coated on the paper obtained by Example 1 which has been coated with the cellulose nanofibers, by a Meyer bar so that the amount of coating would be 6 g/m², and then the resulting paper was dried and calendered so that the Oken type smoothness would be 500 seconds, to obtain a thermal recording paper having a thermal sensitive layer.

| Composition of the thermal sensitive layer: | |
|---|------------|
| Dispersion of color developer (dispersion A) | 36.0 parts |
| Dispersion of leuco dye (dispersion B) | 13.8 parts |
| Dispersion of sensitizer (dispersion C) | 36.0 parts |
| 10% of aqueous solution of absolutely saponified polyvinyl alcohol (commercial name: PVA117, manufactured by KURARAY CO., LTD.) | 25.0 parts |

Compositions of each of the dispersions of color developer (dispersion A), leuco dye (dispersion B), and sensitizer (dispersion C) are as follows, and the dispersions were prepared separately by wet-grinding with a sand grinder so that their average particle size would be 0.5 micron.

| Dispersion A (dispersion of color developer) | |
|--|------------|
| 4-hydroxy-4'-isopropoxy-diphenylsulfone | 6.0 parts |
| 10% of aqueous solution of polyvinyl alcohol | 18.8 parts |
| water | 11.2 parts |
| Dispersion B (dispersion of basic and colorless dye) | |
| 3-dibutylamino-6-methyl-7-anilinofluorane (ODB-2) | 3.0 parts |
| 10% of aqueous solution of polyvinyl alcohol | 6.9 parts |
| water | 3.9 parts |
| Dispersion C (dispersion of sensitizer) | |
| dibenzyl oxalate | 6.0 parts |
| 10% of aqueous solution of polyvinyl alcohol | 18.8 parts |
| water | 11.2 parts |

Comparative Example 14

A thermal recording paper was prepared in the same manner as Example 6, with the exception that the thermal sensitive coating color was coated on the paper obtained by Example 3 which has been coated with water alone.

The sensitivity of the papers prepared in Example 6 and Comparative Example 14 were measured in the manner described below. The results are shown in Table 3.

Sensitivity: Printing was performed with a TH-PMD (manufactured by OHKURA DENKI CORPORATION, a tester for thermal recording paper equipped with a thermal head manufactured by KYOCERA CORPORATION) under the applied energy of 0.41 mJ/dot. Density of printing was measured with a Macbeth densitometer (RD-914, equipped with an amber filter).

TABLE 3

| sensitivity | |
|------------------------|------|
| Example 6 | 1.39 |
| Comparative Example 14 | 1.21 |

As shown in Table 3, the thermal recording paper using base paper coated with the cellulose nanofiber of the present invention (Example 6) has an markedly improved sensitivity, as compared with the thermal recording paper using base paper coated with water. The reason for this is considered that smoothness and air resistance of the base paper coated with the cellulose nanofiber (Example 1) is much higher than the base paper coated with water (Comparative Example 1), and therefore, in the case of thermal recording paper (Example 6) which uses the base paper coated with the cellulose nanofiber, excessive penetration of the thermal sensitive coating color into the base paper is suppressed, and the thermal sensitive coating color is coated uniformly on the base paper to provide thermal insulation effect with the paper and the sensitivity is improved.

<Preparation of a Wood-Free, Off-Set Printing Paper Containing CNF>

Example 7

100 parts of leaf bleached kraft pulp (LBKP, freeness: 400 ml) was defiberized to prepare a pulp slurry. To the pulp slurry, calcium carbonate was added in an amount of 5.0% based on the absolutely dried pulp. Neutral papermaking was carried out with a twin-wire paper machine so that the basis weight would be 62 g/m² to obtain a wood free base paper. The ash content of the resulting base paper was 9.5%.

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To the base paper, a coating material containing hydroxyethylated starch and the cellulose nanofiber prepared in the preparation method 1 in an amount (solid content) shown in Table 4 was coated by a 2-roll size press apparatus so that the coating amount (solid content) of starch and the cellulose nanofiber would be 2.0 g/m² and 0.1 g/m², respectively (both surfaces), to obtain a wood-free offset printing paper.

Comparative Example 15

The base paper used in Example 7 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 16

The base paper used in Example 7 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 2.0 g/m² on both surfaces.

Comparative Example 17

The base paper used in Example 7 was coated with an aqueous solution of polyacrylamide (commercial name:

20

Adherability of ink (unevenness in printing) was evaluated by visual observation in accordance with the following basis:

◎: Highly even printing is obtained.

○: Even printing is obtained.

Δ: Printing is uneven.

X: Printing is markedly uneven.

<Test for RI Printing—Print Through>

Printing was carried out with an offset eco-ink, high viscosity AF ink manufactured by TOYO INK MFG. CO., LTD, by an RI printer (4-color printer) manufactured by ISHIKAWAJIMA INDUSTRIAL MACHINERY CO., LTD. The level of print through was evaluated by visual observation in accordance with the following basis:

◎: Penetration of ink to the back side of the printing is not observed.

○: Penetration of ink to the back side of the printing is almost not observed.

Δ: Penetration of ink to the back side of the printing is a little observed.

X: Penetration of ink to the back side of the printing is observed.

TABLE 4

| | composition of | | | | coating amount | | | | | RI printing test | |
|------------------------|------------------|-------------------|-------|-----------------|----------------------------------|----------------------|---------------------------|----------------|--------------------|---------------------------|----------------------------|
| | coating material | | | (both surfaces) | polyacryl-amide g/m ² | CNF g/m ² | density g/cm ³ | smoothness sec | air resistance sec | of ink visual observation | through visual observation |
| | starch % | polyacryl-amide % | CNF % | | | | | | | | |
| Example 7 | 9.5 | 0 | 0.5 | 10.0 | 2.0 | 0 | 0.10 | 0.604 | 22 | 92 | ◎ |
| Comparative Example 15 | 0 | 0 | 0 | 0 | 0 | 0 | 0.594 | 11 | 8 | X | X |
| Comparative Example 16 | 10.0 | 0 | 0 | 10.0 | 2.0 | 0 | 0 | 0.600 | 13 | 12 | Δ |
| Comparative Example 17 | 0 | 10.0 | 0 | 10.0 | 0 | 2.0 | 0 | 0.601 | 15 | 14 | Δ |

40

DS4340, manufactured by SEIKO PMC CORPORATION) by a 2-roll size press apparatus so that the coating amount of the polyacrylamide would be 2.0 g/m² on both surfaces.

Test

The thickness and basis weights of the papers prepared in Example 7 and Comparative Examples 15 to 17 were measured by the methods described below, and the densities were calculated based on the measured values. Further, the smoothness, air resistance, adherability of ink, and print through were measured by the methods described below. The results are shown in Table 4.

<Measurement of Basis Weight, Thickness and Density>

Basis weight: Measured in accordance with JIS P8124:1998 (ISO 536:1995).

Thickness: Measured in accordance with JIS P 8118:1998.

Density: Calculated from the measured values of the thickness and basis weight of the coated sheet.

<Measurement of Smoothness and Air Resistance>

The smoothness and air resistance were measured with an Oken type smoothness/air resistance tester in accordance with Japan TAPPI Paper Pulp Testing Method No. 5-2:2000.

<Test for RI Printing—Adherability of Ink>

Printing was carried out with an offset eco-ink, high viscosity AF ink manufactured by TOYO INK MFG. CO., LTD, by an RI printer (4-color printer) manufactured by ISHIKAWAJIMA INDUSTRIAL MACHINERY CO., LTD.

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As shown in Table 4, the paper coated with a mixture of the cellulose nanofiber of the present invention and the starch has a higher smoothness and air resistance than those of the papers coated with starch alone or polyacrylamide, and has a good adherability of ink and prevention of print through, while the density is not increased.

<Preparation of a Wood-Containing, Offset Printing Paper Containing CNF>

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Example 8

95 parts of thermomechanical pulp (TMP, freeness: 100 ml) and 5 parts of needle bleached kraft pulp (nBKP, freeness: 600 ml) were mixed and defiberized to prepare a pulp slurry.

To the pulp slurry, calcium carbonate was added in an amount of 5.0% based on the absolutely dried pulp. Neutral paper-making was carried out with a twin-wire paper machine so that the basis weight would be 53 g/m² to obtain a wood-containing base paper. The ash content of the resulting base paper was 4.4%.

To the base paper, a coating material containing hydroxyethylated starch and the cellulose nanofiber prepared in the preparation method 1 in an amount (solid content) shown in Table 5 was coated by a 2-roll size press apparatus so that the coating amount (solid content) of starch and the cellulose nanofiber would be 2.0 g/m² and 0.1 g/m², respectively (both surfaces), to obtain a wood-containing offset printing paper.

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Comparative Example 18

The base paper used in Example 8 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 19

The base paper used in Example 8 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 2.0 g/m² on both surfaces.

Comparative Example 20

The base paper used in Example 8 was coated with an aqueous solution of polyacrylamide (commercial name: DS4340, manufactured by SEIKO PMC CORPORATION) by a 2-roll size press apparatus so that the coating amount of the polyacrylamide would be 2.0 g/m² on both surfaces.

Test

The thickness and basis weights of the papers prepared in Example 8 and Comparative Examples 18 to 20 were measured by the methods described below, and the densities were calculated based on the measured values. Further, the smoothness, air resistance, adherability of ink, and print through were measured by the methods described above. The results are shown in Table 5.

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coating amount (solid content) of starch and the cellulose nanofiber would be 3.0 g/m² and 0.5 g/m², respectively (both surfaces), to obtain an off-set news printing paper.

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Example 10

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 3.0 g/m² and 0.3 g/m², respectively.

Example 11

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 3.0 g/m² and 0.1 g/m², respectively.

Example 12

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 3.0 g/m² and 0.05 g/m², respectively.

Example 13

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating

TABLE 5

| | composition of | | | | coating amount | | | | RI printing test | | |
|------------------------|------------------|--------------------------|----------|-----------------------|----------------------------|---|-------------------------|------------------------|--------------------------|---------------------------------|---|
| | coating material | | | (both surfaces) | | | | smooth- ness sec | air resistance sec | of ink visual observation | print through visual observation |
| | starch % | polyacryl- amide % | CNF % | solid content % | starch g/m ² | polyacryl- amide g/m ² | CNF g/m ² | | | | |
| Example 8 | 9.5 | 0 | 0.5 | 10.0 | 2.0 | 0 | 0.10 | 0.372 | 15 | 86 | ◎ |
| Comparative Example 18 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.366 | 7 | 5 | X |
| Comparative Example 19 | 10.0 | 0 | 0 | 10.0 | 2.0 | 0 | 0 | 0.373 | 9 | 7 | Δ |
| Comparative Example 20 | 10.0 | 10.0 | 0 | 10.0 | 2.0 | 2.0 | 0 | 0.369 | 9 | 7 | Δ |

As shown in Table 5, the paper coated with a mixture of the cellulose nanofiber of the present invention and the starch has a higher smoothness and air resistance than those of the papers coated with starch alone or polyacrylamide, and has a good adherability of ink and prevention of print through, while the density is not increased.

<Preparation of a News Printing Paper>

Example 9

80 parts of deinked pulp (DIP, freeness: 180 ml) and 15 parts of TMP (freeness: 100 ml) and 5 parts of needle bleached kraft pulp (NBKP, freeness: 600 ml) were mixed and defibrated to prepare a pulp slurry. To the pulp slurry, calcium carbonate was added in an amount of 7.5% based on the absolutely dried pulp. Neutral papermaking was carried out with a twin-wire paper machine so that the basis weight would be 42 g/m² to obtain a news printing base paper. The ash content of the resulting base paper was 12.5%.

To the base paper, a coating material containing hydroxyethylated starch and the cellulose nanofiber prepared in the preparation method 1 in an amount (solid content) shown in Table 6 was coated by a 2-roll size press apparatus so that the

amount of starch and the cellulose nanofiber was changed to 2.0 g/m² and 0.5 g/m², respectively.

Example 14

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 2.0 g/m² and 0.3 g/m², respectively.

Example 15

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 2.0 g/m² and 0.1 g/m², respectively.

Example 16

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 2.0 g/m² and 0.05 g/m², respectively.

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Example 17

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 1.0 g/m² and 0.5 g/m², respectively.

Example 18

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 1.0 g/m² and 0.3 g/m², respectively.

Example 19

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 1.0 g/m² and 0.1 g/m², respectively.

Example 20

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating

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Comparative Example 23

The base paper used in Example 9 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 2.0 g/m² on both surfaces.

Comparative Example 24

The base paper used in Example 9 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 1.0 g/m² on both surfaces.

Test

The thickness and basis weights of the papers prepared in Examples 9 to 20 and Comparative Examples 21 to 24 were measured by the methods described below, and the densities were calculated based on the measured values. Further, the smoothness, air resistance, adherability of ink, and print through were measured by the methods described above. The results are shown in Table 6, and FIGS. 9 and 10.

TABLE 6

| | composition of | | | | | | | | RI printing test | | |
|------------------------|------------------|-------|-----------------|-------------------------|----------------------|---------------------------|----------|----------------|--------------------|--------------|---------------|
| | coating material | | | coating amount | | | | smooth- | air | adherability | print |
| | solid | | (both surfaces) | | starch | CNF | density | | | | |
| | starch % | CNF % | content % | starch g/m ² | CNF g/m ² | density g/cm ³ | ness sec | resistance sec | visual observation | of ink | print through |
| Example 9 | 10.8 | 1.2 | 12.0 | 3.0 | 0.50 | 0.576 | 21 | 1038 | ◎ | ◎ | |
| Example 10 | 11.1 | 0.9 | 12.0 | 3.0 | 0.30 | 0.579 | 17 | 573 | ◎ | ◎ | |
| Example 11 | 11.5 | 0.5 | 12.0 | 3.0 | 0.10 | 0.571 | 14 | 227 | ◎ | ◎ | |
| Example 12 | 11.7 | 0.3 | 12.0 | 3.0 | 0.05 | 0.578 | 11 | 132 | ○ | ○ | |
| Example 13 | 8.8 | 1.2 | 10.0 | 2.0 | 0.50 | 0.574 | 20 | 684 | ◎ | ◎ | |
| Example 14 | 9.1 | 0.9 | 10.0 | 2.0 | 0.30 | 0.569 | 15 | 392 | ◎ | ◎ | |
| Example 15 | 9.5 | 0.5 | 10.0 | 2.0 | 0.10 | 0.575 | 11 | 141 | ◎ | ◎ | |
| Example 16 | 9.7 | 0.3 | 10.0 | 2.0 | 0.05 | 0.580 | 9 | 84 | ○ | ○ | |
| Example 17 | 5.8 | 1.2 | 7.0 | 1.0 | 0.50 | 0.577 | 17 | 348 | ◎ | ◎ | |
| Example 18 | 6.1 | 0.9 | 7.0 | 1.0 | 0.30 | 0.576 | 13 | 207 | ◎ | ◎ | |
| Example 19 | 6.5 | 0.5 | 7.0 | 1.0 | 0.10 | 0.571 | 10 | 81 | ○ | ○ | |
| Example 20 | 6.7 | 0.3 | 7.0 | 1.0 | 0.05 | 0.581 | 8 | 42 | ○ | ○ | |
| Comparative Example 21 | 0 | 0 | 0 | 0 | 0 | 0.576 | 6 | 10 | X | | X |
| Comparative Example 22 | 12.0 | 0 | 12.0 | 3.0 | 0 | 0.581 | 7 | 19 | Δ | Δ | |
| Comparative Example 23 | 10.0 | 0 | 10.0 | 2.0 | 0 | 0.577 | 7 | 17 | Δ | Δ | |
| Comparative Example 24 | 7.0 | 0 | 7.0 | 1.0 | 0 | 0.574 | 7 | 13 | Δ | X | |

amount of starch and the cellulose nanofiber was changed to 1.0 g/m² and 0.05 g/m², respectively.

Comparative Example 21

The base paper used in Example 9 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 22

The base paper used in Example 9 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 3.0 g/m² on both surfaces.

As shown in Table 6, the paper coated with a mixture of the cellulose nanofiber of the present invention and the starch has a higher smoothness and air resistance than those of the papers coated with starch alone or polyacrylamide, and has a good adherability of ink and prevention of print through, while the density is not increased.

The invention claimed is:

1. A cellulose nanofiber obtained by a method comprising the steps of:
oxidizing a cellulosic material with an oxidizing agent in the presence of:

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- (1) N-oxy compound(s), and
 (2) compound(s) selected from the group consisting of bromide, iodide and mixtures thereof to prepare an oxidized cellulose; and
 finely grinding the oxidized cellulose in a wet condition to convert the oxidized cellulose into nanofibers having an amount of carboxyl groups of 1.2 mmol or more, based on 1 g absolute dry weight of the cellulose nanofibers, and whose B-type viscosity (60 rpm, 20° C.) as an aqueous solution at a concentration of 2% (w/v) is from 500 to 10 7000 mPa·s.
2. The cellulose nanofiber according to claim 1 whose B-type viscosity (60 rpm, 20° C.) as an aqueous solution at a concentration of 2% (w/v) is from 500 to 2000 mPa·s.
3. The cellulose nanofiber according to claim 1 wherein the step of finely grinding comprises defibrating the oxidized cellulose with an ultrahigh pressure homogenizer under a pressure of not less than 100 MPa.
4. A papermaking additive comprising the cellulose nanofiber according to claim 1.
5. Paper containing the cellulose nanofiber according to claim 1.
6. Paper according to claim 5 which is used as a printing paper.
7. A thermal recording paper using the paper according to claim 5 as a base paper.
8. A coated paper using the paper according to claim 5 as a base paper.
9. The paper according to claim 5 which is used as a news printing paper.
10. The paper according to claim 5 which is used as a converting paper.
11. The paper according to claim 5 which is used as an electrophotographic transfer paper.
12. The paper according to claim 5 which is used as a paper board.
13. The paper according to claim 5 which is used as a sanitary paper.

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14. The paper according to claim 5 which is used as an inkjet recording paper.
15. The paper according to claim 5 which is used as a thermal recording paper.
16. The paper according to claim 5 which is used as a pressure sensitive recording paper.
17. An inkjet recording paper using the paper according to claim 5 as a base paper.
18. A pressure sensitive recording paper using the paper according to claim 5 as a base paper.
19. A laminated paper having one or more layers of synthetic resin on a surface or both surfaces of the paper according to claim 5 as a base paper.
20. A method for preparing cellulose nanofiber having an amount of carboxyl groups of 1.2 mmol or more, based on 1 g absolute dry weight of the cellulose nanofibers and whose B-type viscosity (60 rpm, 20° C.) as an aqueous solution at a concentration of 2% (w/v) is from 500 to 7000 mPa·s, comprising the steps of:
 oxidizing a cellulosic material with an oxidizing agent in the presence of:
 (1) N-oxy compound(s), and
 (2) compound(s) selected from the group consisting of bromide, iodide and mixtures thereof to prepare an oxidized cellulose; and
 finely grinding the oxidized cellulose in a wet condition to convert the oxidized cellulose into nanofibers.
21. The process according to claim 20 wherein the B-type viscosity (60 rpm, 20° C.) of the cellulose nanofiber as an aqueous solution at a concentration of 2% (w/v) is from 500 to 20 mPa·s.
22. The process according to claim 20 wherein the step of finely grinding comprises defibrating the oxidized cellulose with an ultrahigh pressure homogenizer under a pressure of not less than 100 MPa.

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(54) METHOD FOR PRODUCING FURNISH, FURNISH AND PAPER

VERFAHREN ZUR HERSTELLUNG EINES PAPIERSTOFFS, PAPIERSTOFF UND PAPIER
PROCÉDÉ DE PRODUCTION DE COMPOSITION DE FABRICATION, COMPOSITION DE
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DescriptionField of the Invention

- 5 [0001] The present invention relates to a method for preparing aqueous furnish to be used in paper or paper board manufacturing. The invention also relates to furnish prepared by the method according to the invention, and to paper or paper board manufactured from the furnish.

Background of the Invention

- 10 [0002] For economical reasons, the trend in paper industry is to increase the proportion of filler in paper products and thereby to reduce the use of fibres. In addition to low price and good availability, fillers also increase the printability and optical properties of paper. However, a problem related to the increasing of the filler proportion is that the filler addition leads to a deterioration in the mechanical properties of the paper product. These mechanical properties of paper depend 15 on inter-fibre bonding, and fillers inhibit partly this inter-fibre bonds formation due to their rigidity and poor capability of hydrogen bond formation. Increasing the binding between fibres and fillers is thus essential to improve the strength of filled paper. Furthermore, better affinity between the fibres and the fillers will also lead to a better retention of fillers.
- 20 [0003] The interactions between fibres and fillers have been widely studied, and many different solutions for improving the inter-fibre bonding have been presented. The loss of the paper strength has been reduced, among other things, by using thinner filler particles. Another solution to this problem is to add starch into the fibre suspension, because the adsorption of starch on fibres increases paper strength by increasing the strength of inter-fibre bonds. Although starch is very cost-effective, it cannot be used in high concentrations because of the problems of significant sticky behaviour 25 of starch on forming wire. Furthermore, the addition of fines in paper is another effective way to compensate for the strength loss which is caused by the presence of the fillers. However, added fines may induce dewatering problems.
- 30 [0004] A publication EP 1936 032 A1 discloses a method of producing a laminate paper comprising at least two layers, said method comprising (i) providing an aqueous suspension comprising cellulosic fibers (ii) adding to the suspension microfibrillar polysaccharide in an amount to yield from about 0.05 to about 50 wt percent based on the weight of the cellulosic fibers (iii) dewatering the obtained suspension and forming a first layer having a density from about 150 to about 500 kg/m³ of said laminate paper product
- 35 [0005] A publication WO 00/47628 A2 discloses a method for producing derivatized microfibrillar polysaccharide, where the electrostatic forces are provided by anionic charge or by a combination of both anionic and cationic charge, by stabilizing and/or microfibrillating a polysaccharide starting material.
- [0006] As described above, many different solutions have been presented to improve interactions between fibres and fillers in order to enhance the strength of the filled paper. However, there is still a need for a method that makes it possible to use a high content of the filler so that the strength of the final paper product will not decrease and so that the method will not cause any other unwanted effects on the manufacturing process.

Summary of the Invention

- 40 [0007] It is an aim of the present invention to provide a novel method for preparing aqueous furnish to be used in paper and paper board manufacturing in such a way that the paper product manufactured from the furnish has a high loading of filler, with good mechanical strength. The aim of the invention is also to provide a novel method for preparing a furnish in order to improve the interactions between fibres and fillers.
- 45 [0008] To achieve these aims, the method according to the invention for preparing aqueous furnish is characterized in what will be presented in the characterizing portion of claim 1.
- [0009] The invention also relates to furnish prepared by the method according to the invention, and to paper or paper board manufactured from the furnish prepared by the method according to the invention.
- 50 [0010] The invention is based on the modification of the fibre and/or filler surfaces in such a way that the fibre-filler bonding will be enhanced, because the poor capability of fillers to form bonds with fibres is greatly responsible for the low retention of fillers and for the loss of mechanical properties of filled paper. In the method according to the invention, at least the filler surface is modified by adsorption of cationic polyelectrolyte and nanofibrillated cellulose (NFC) during the furnish preparation. This modification creates a bilayer of cationic polyelectrolyte and NFC around the fillers, which improves the affinity between fillers and fibres. Also, the fibre surfaces can be treated equally by forming the bilayer of cationic polyelectrolyte and NFC around the fibres.
- 55 [0011] Filler and/or fibres are treated with cationic polyelectrolyte and nanofibrillated cellulose during the furnish preparation. The modification can be carried out in different ways. The treatment of the filler with cationic polyelectrolyte and NFC can be carried out by mixing the filler with the cationic polyelectrolyte and NFC before adding them to the fibre suspension. Alternatively, the modification of the fibre and filler surfaces can be carried out at the same time in the fibre

suspension without separate mixing steps, or the fibre surfaces can be treated with cationic polyelectrolyte and NFC before the addition of the filler to the fibre suspension. It is also possible to treat filler and fibres separately one with cationic polyelectrolyte and other with nanofibrillated cellulose. The way of the modification can be chosen according to the convenience, for example based on the existing paper mill layout.

5 [0012] One alternative way is to modify the filler surfaces by forming cationic polyelectrolyte and NFC bilayer as described above and in parallel, to modify the fibre surfaces by adsorption of cationic polyelectrolyte, because the adsorption of cationic polyelectrolyte on fibres increases the strength of inter-fibre bonds and increases the affinity of the modified filler to the cellulose fibres. Therefore, the modification of filler surface by cationic polyelectrolyte and NFC combined with the modification of fibres by cationic polyelectrolyte enhances significantly the filler-fibre bonding and thus the filler retention and the mechanical properties of the final paper product, particularly in Z-direction.

10 [0013] Any of the conventional cationic polyelectrolytes used in paper manufacturing are suitable for the method according to the invention. Preferably, cationic polyelectrolyte is cationic starch.

15 [0014] In the furnish preparation, at least a part of the filler conventionally used is replaced with the filler containing cationic starch and nanofibrillated cellulose absorbed to the surface of the filler. In addition to the modified filler, the furnish can also contain other fillers, sizing materials and additives as known by a skilled person in the art.

20 [0015] The modification of filler and/or fibre surfaces with cationic polyelectrolyte and nanofibrillated cellulose leads to increased fibre-filler bonding. This increase enhances significantly the retention of fillers and the strengthening effect of the cationic polyelectrolyte. Furthermore, when the strength of paper is increased, the nanofibrillated cellulose is beneficial in maintaining the bulk of the paper. Finally, it can also be mentioned that the strength and retention values of the paper that are achieved with the combination of cationic starch and NFC are similar to those obtained with a quantity of cationic starch not conceivable, because of stickiness problems induced by an addition of such a high amount of starch.

Description of the Drawings

25 [0016] The present invention will now be described in more detail with reference to the appended drawings, in which:

- | | |
|-------------------|--|
| Fig. 1 | shows a strategy of mixing different components which are used in the Example 1, |
| Fig. 2 | shows the amount of PCC retained in handsheets as a function of the added amount of PCC (Example 1), |
| 30 Fig. 3 | shows the tensile strength and Scott bond of handsheets as a function of filler content (Example 1), |
| Fig. 4 | shows the tensile strength of handsheets as a function of the density of handsheets (Example 1), |
| Fig. 5 | shows the tensile strength of handsheets as a function of filler content (Example 1), |
| Fig. 6 | shows the tensile strength of handsheets as a function of filler content (Example 1), |
| 35 Figs. 7a to 7g | show strategies of mixing different components which are used in Example 2, |
| Figs. 8a and 8b | show the tensile strength of the handsheets as a function of filler content (example 2), and |
| Fig. 9 | shows the tensile strength and Scott bond of the handsheets as a function of filler content (Example 2). |

Detailed Description of the Invention

40 [0017] In the method according to the invention, the filler and/or fibre surfaces are modified by adsorption of cationic polyelectrolyte and nanofibrillated cellulose (NFC) during the furnish preparation in order to improve the interaction between fibres and fillers. It has been observed that cationic polyelectrolyte and nanofibrillated cellulose can be absorbed on the surface of fillers and fibres used for paper and paper board manufacture during simple processing suitable for a paper mill process.

45 [0018] The modification of filler and/or fibre surfaces can be carried out by mixing them with cationic polyelectrolyte and nanofibrillated cellulose. Preferably, the filler and fibres are treated first with cationic polyelectrolyte and secondly with nanofibrillated cellulose by adding them to the fibre-filler suspension. Alternatively, the filler is treated with cationic polyelectrolyte and nanofibrillated cellulose before adding it to fibre suspension. Also in this case, the filler is preferably treated first with cationic polyelectrolyte and secondly with nanofibrillated cellulose by adding them to the filler suspension. The fibres can be treated with cationic polyelectrolyte before adding the modified fillers to the fibre suspension in order to increase the strength of inter-fibre bonds.

50 [0019] The term nanofibrillated cellulose refers to a collection of isolated cellulose microfibrils or microfibril bundles derived from cellulose raw material. Nanofibrillated cellulose have typically high aspect ratio: the length might exceed one micrometer while the number-average diameter is typically below 200 nm. The diameter of nanofibril bundles can also be larger but generally less than 5 µm. The smallest nanofibrils are similar to so called elementary fibrils, which are typically 2-12 nm in diameter. The dimensions of the fibrils or fibril bundles are dependent on raw material and disintegration method. The nanofibrillated cellulose may also contain some hemicelluloses; the amount is dependent

on the plant source. Mechanical disintegration of nanofibrillated cellulose from cellulose raw material, cellulose pulp, or refined pulp is carried out with suitable equipment such as a refiner, grinder, homogenizer, colloider, friction grinder, ultrasound sonicator, fluidizer such as microfluidizer, macrofluidizer, or fluidizer type homogenizer. Nanofibrillated cellulose can also be directly isolated from certain fermentation processes. The cellulose-producing micro-organism of the present invention may be of the genus *Acetobacter*, *Agrobacterium*, *Rhizobium*, *Pseudomonas* or *Alcaligenes*, preferably of the genus *Acetobacter* and more preferably of the species *Acetobacter xylinum* or *Acetobacter pasteurianus*. Nanofibrillated cellulose can also be any chemically, enzymatically or physically modified derivate of cellulose microfibrils or microfibril bundles. The chemical modification could be based for example on carboxymethylation, oxidation, esterification, or etherification reaction of cellulose molecules. Modification could also be realized by physical adsorption of anionic, cationic, or non-ionic substances or any combination of these on cellulose surface. The described modification can be carried out before, after, or during the production of microfibrillar cellulose.

[0020] Nanofibrillated cellulose can also be called nanocellulose, nanofibrillar cellulose, cellulose nanofiber, nano-scale fibrillated cellulose, microfibrillar cellulose, cellulose nanofibrils (CNF) or microfibrillated cellulose (MFC). In addition, nanofibrillated cellulose produced by certain microbes has also various synonyms, for example, bacterial cellulose, microbial cellulose (MC), biocellulose, nata de coco (NDC), or coco de nata. Nanofibrillated cellulose described in this invention is not the same material as so called cellulose whiskers, which are also known as: cellulose nanowhiskers, cellulose nanocrystals, cellulose nanorods, rod-like cellulose microcrystals or cellulose nanowires. In some cases, similar terminology is used for both materials, for example by Kuthcarlapati et al. (*Metals Materials and Processes* 20(3):307-314, 2008) where the studied material was called "cellulose nanofiber" although they clearly referred to cellulose nanowhiskers.

Typically these materials do not have amorphous segments along the fibrillar structure as nanofibrillated cellulose, which leads to more rigid structure.

[0021] The filler can be any filler used in paper manufacturing, e.g. precipitated calcium carbonate (PCC), ground calcium carbonate (GCC), kaolin, talcum or gypsum. Preferably, the filler is precipitated calcium carbonate (PCC).

[0022] In the method according to the invention, the filler is added to the furnish in an amount of 1 to 60% by the dry weight of the fibres in the furnish, preferably 20 to 40% by the dry weight of the fibres. The nanofibrillated cellulose is added in an amount of 0.01 to 20% by the dry weight of the fibres in the furnish, preferably 1 to 10%, and most preferably 1 to 3%.

[0023] Cationic polyelectrolyte can be any retention or strength polymer used in paper manufacturing, e.g. cationic starch, cationic polyacrylamide (CPAM) or polydimethylallyl ammonium chloride (PDADMAC). Also, the combinations of the different polyelectrolytes can be used. Preferably, the cationic polyelectrolyte is cationic starch (CS).

[0024] The cationic polyelectrolyte is added in an amount of 0.01 to 5% of dry weight of fibres in the furnish, preferably approximately 2 to 4%.

[0025] The furnish prepared by the method according to the invention can be used as such in paper or paper board making. However, the furnish can also contain non-treated fillers and other components, including e.g. conventional auxiliary agents and retention agents. The filler modified with cationic polyelectrolyte and nanofibrillated cellulose can be used in combination with conventional untreated fillers in filled paper grades.

[0026] The furnish prepared by the method according to the invention is used for manufacturing of a paper or paper board product. In the paper or paper board machine, the furnish is fed into a forming section and water is removed from the furnish by allowing the furnish to drain through a water permeable forming wire, and after that, the paper web thus produced is dried and finished to produce a final paper or paper board product with good mechanical strength properties and a high filler content.

[0027] The following examples were carried out to illustrate the present invention. The examples are not intended to limit the scope of the invention.

45 Example 1

[0028] This example was carried out to demonstrate that the method according to the invention clearly increases the filler retention and strength of paper sheets with a high filler content.

[0029] The materials used in this experiment were the following:

50 **Fibres**

[0030] Dried hardwood (birch) bleached chemical pulp was used in the experiments. About 360 g (o.d.) of pulp was soaked overnight in 5 l of water and beaten for 50 minutes at a consistency of 1.6% in a Valley beater (ISO 5264-1) to the Shopper-Riegler (SR) number (ISO 5267-1) of about 42. Afterwards 2 l of water was used to remove the last fibres remaining in the beater and added to the fibre suspension. This suspension was fractionated in a Bauer McNett classifier (SCAN-CM 6:05) using a 200 mesh wire to remove the fines fraction. At this point the SR number was about 18. Finally, the pulp was washed, first by acidic treatment (0.01 M hydrochloric acid) to remove metal ions and afterwards the fibres

were converted to sodium form with 1 mM of sodium bicarbonate. After these two treatments, the pulp was washed thoroughly with deionised water.

[0031] The fractioning and washing were done in order to prevent possible interference of varying fines content, pH or salts that would hamper interpretation of the results.

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Fillers

[0032] The filler was commercial scalenohedral precipitated calcium carbonate (PCC). According to the manufacturer, the average particle size of this PCC was 2.3 µm, the brightness 95% and the dry matter content was 19.9%.

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Nanofibrillated cellulose (NFC)

[0033] Nanofibrillated cellulose was obtained by high pressure homogenisation of fully bleached softwood including an enzymatic pre-treatment step. The principles of this approach have been published in Pääkkö, et al., Enzymatic hydrolysis combined with mechanical shearing and high pressure homogenization for nanoscale cellulose fibrils and strong gels, Biomacromolecules (8), pp. 1934-1941, 2007. Just before use, NFC-gel (about 1-2 % solid content) was diluted with deionised water and disintegrated with Branson Digital Sonifier (Branson Ultrasonics Corporation, Danbury, USA) with an amplitude setting of 25 % for 2 minutes.

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Cationic starch

[0034] Cationic starch (CS) with a degree of substitution of 0.035 was supplied by Ciba Specialty Chemical, Raisio, Finland. Before use, 2 g (o.d.)/l starch solution was cooked in an autoclave at 120 °C for 20 minutes.

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Water

[0035] The water used in all the experiments was deionised water.

[0036] During the preparation of pulp slurry, 1.63 g (o.d.)/l of fibres were mixed together with starch in a vessel for 15 minutes. In parallel, nanofibrillated cellulose (NFC) was mixed together with PCC for 15 minutes. Afterwards, both contents were poured into the same vessel and mixed for 15 minutes. This mixing strategy is illustrated in Figure 1.

[0037] To the preparation of the different test points (presented in Table 1), four different compositions of pulp slurry were used:

- one reference with fibre dispersion only (reference sample),
- one with fibres and cationic starch (samples CS2.5, CS5 and CS10),
- one with fibres and NFC (samples NFC25 and NFC 50), and
- one with fibres, cationic starch and NFC (samples CS2.5+NFC25 and CS2.5+NFC50).

[0038] According to the test points, three different amounts of cationic starch: 25, 50 and 100 mg/g (o.d.) of fibres and two different amounts of NFC: 25 and 50 mg/l (o.d.) were added to the suspensions. In Table 1, sample compositions CS2.5, CS5, CS10 with fibres and cationic starch comprise different amounts of cationic starch as mentioned above. Also, sample compositions NFC25 and NFC 50 with fibres and NFC comprise above mentioned amounts of NFC. Sample CS2.5+NFC25 comprises fibres, 25 mg/g CS and 25 mg/l NFC, and sample CS2.5+NFC50 comprises fibres, 25 mg/g CS and 50 mg/l NFC.

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[0039] To these four different mixtures various amount of PCC were also added. The amount of the fibres added was 1.63 g in each case.

Table 1. Summary of the experiments carried out.

50

| sample | PCC added (g/g of paper) | NFC added (mg/sheet or mg/l) | NFC (mg/g paper) | CS added (% dry fibres) | CS (mg/g paper) | Ash content(% sheet) |
|-----------|-----------------------------|------------------------------------|---------------------|----------------------------|--------------------|-------------------------|
| reference | 0 | 0 | 0 | 0 | 0 | 0 |
| | 2.00 | 0 | 0 | 0 | 0 | 25.9 |
| | 3.49 | 0 | 0 | 0 | 0 | 31.7 |
| | 5.97 | 0 | 0 | 0 | 0 | 35.9 |
| CS2.5 | 0 | 0 | 0 | 2.5 | 24 | 0 |

(continued)

| | sample | PCC added (g/g of paper) | NFC added (mg/sheet or mg/l) | NFC (mg/g paper) | CS added (% dry fibres) | CS (mg/g paper) | Ash content(% sheet) |
|----|-----------------|-----------------------------|------------------------------------|---------------------|----------------------------|--------------------|-------------------------|
| 5 | | 0.70 | 0 | 0 | 2.5 | 19 | 23.2 |
| | | 1.71 | 0 | 0 | 2.5 | 15 | 39.2 |
| | | 3.68 | 0 | 0 | 2.5 | 12 | 50.5 |
| 10 | CS5 | 0,00 | 0 | 0 | 5 | 48 | 0 |
| | | 0.58 | 0 | 0 | 5 | 32 | 32.0 |
| | | 1.39 | 0 | 0 | 5 | 23 | 52.7 |
| 15 | CS10 | 0,00 | 0 | 0 | 10 | 91 | 0 |
| | | 0.49 | 0 | 0 | 10 | 55 | 39.5 |
| | | 1.25 | 0 | 0 | 10 | 40 | 55.7 |
| 20 | NFC25 | 0 | 25 | 15 | 0 | 0 | 0 |
| | | 0.89 | 25 | 11 | 0 | 0 | 27.1 |
| | | 1.62 | 25 | 1 | 0 | 0 | 33.6 |
| | | 2.67 | 25 | 9 | 0 | 0 | 38.5 |
| 25 | NFC50 | 0 | 50 | 30 | 0 | 0 | 0 |
| | | 0.68 | 50 | 22 | 0 | 0 | 25.6 |
| | | 1.48 | 50 | 17 | 0 | 0 | 41.7 |
| | | 4.27 | 50 | 17 | 0 | 0 | 42.3 |
| 30 | CS2.5+ NFC25 | 0 | 25 | 15 | 2.5 | 24 | 0 |
| | | 0.28 | 25 | 12 | 2.5 | 20 | 17.4 |
| | | 0.87 | 25 | 8 | 2.5 | 13 | 45.5 |
| | | 1.78 | 25 | 7 | 2.5 | 11 | 53.4 |
| 35 | CS2.5+ NFC50 | 0 | 50 | 29 | 2.5 | 24 | 0 |
| | | 0.26 | 50 | 23 | 2.5 | 19 | 20.5 |
| | | 0.64 | 50 | 16 | 2.5 | 13 | 44.2 |
| | | 1.00 | 50 | 14 | 2.5 | 11 | 51.7 |

[0040] After furnish preparation, handsheets were formed. Sheets were formed in a laboratory sheet former, Lorentzen & Wettre AB, Sweden (ISO 5269-1) with a 100 mesh wire. The grammage of sheets was adjusted to about 60 g/m² by dilution of the suspension when necessary. The sheets were wet pressed under 4.2 bar for 4 minutes and dried in a frame to avoid shrinkage during drying (105 °C for 3 minutes). The samples were conditioned according to the standard SCAN_P 2:75.

[0041] All the sheet properties were measured according to SCAN or ISO standards. The grammage (ISO 536:1995 (E)), the thickness and the bulk were determined with Lorentzen & Wettre micrometer (ISO 534:2005(E)). The tensile strength, the stretch and the stiffness were determined with Alwetron TH1 (ISO 1924-2:1994(E)). The tear index was measured with Lorentzen & Wettre tearing tester (SE009 Elmendorf)(SCAN-P 11:73), and optical properties were determined by Lorentzen & WettreElrepopho. The ash content was measured according to the standard ISO 1762:2001 (E) to determine the amount of retained fillers in paper sheets.

[0042] The main objective of the above described experiments was to evaluate the effect of the modification of filler surface by NFC and CS on the fibre-filler bonding. Several strength properties as well as filler retention were measured for handsheets obtained after various treatments.

[0043] Figure 2 shows the PCC retained in handsheets as a function of the added amount of PCC. The curves illustrate results obtained from a sheet containing no additives (reference: +) and from sheets prepared either with cationic starch alone (CS2.5: Δ) or with a mixture of cationic starch and NFC (CS2.5+NFC25: ●). The PCC retained is obtained from the value of ash content at 525 °C. As shown in Figure 2, the combination of cationic starch and NFC (sample CS2.5+NFC25) allows a very great improvement of PCC retention. If we look at 0.36 g/g of paper of PCC retained (equivalent to 35% of filler content), the amount of PCC added is about 10 times less than with combination of cationic starch and NFC than with reference. The retention is also significantly higher (more than twice) than that obtained by addition of starch alone.

[0044] Figure 3 shows the tensile strength and Scott bond of handsheets as a function of filler content. The curves illustrate results obtained from sheet containing no additives (reference: +) and from sheets prepared either with cationic starch alone (CS2.5: Δ) or with a mixture of cationic starch and NFC (CS2.5+NFC25: ●). The combination of cationic starch and NFC (sample CS2.5+NFC25) leads to an increase in strength properties, particularly in Z-direction, as shown by Scott bond results.

[0045] The strength of paper is usually proportional to the sheet density. The enhancement of the strength properties also increases the density of the sheet. It would be optimal if stronger paper could be obtained without a significant increase in density. Figure 4 shows the tensile strength of handsheets as a function the density. In Figure 4, the curves also illustrate results obtained from sheet containing no additives (reference: +) and from sheets prepared either with cationic starch alone (CS2.5: Δ) or with a mixture of cationic starch and NFC (CS2.5 + NFC25: ●). From Figure 4, it can be observed that the combination of cationic starch and NFC (sample CS2.5 + NFC25) has the steepest slope. NFC is thus beneficial in maintaining the bulk.

[0046] In order to determine the influence of the NFC amount on the strength properties, the added amount of NFC was varied (see Figure 5). NFC was either mixed in the pulp together with cationic starch or added alone as such. In Figure 5, the curves illustrate results obtained from sheet containing no additives (reference: +) and from sheets prepared either with two different amounts of NFC (NFC25: Δ and dotted line, NFC50: A) or with a mixture of cationic starch and different amounts of NFC (CS2.5 +NFC25: o and dotted line, CS2.5 +NFC50: ●). When NFC is used alone, a slight improvement of tensile strength can be seen. However, the value is much lower than that obtained with the combination of cationic starch and NFC.

[0047] On the other hand, in order to compare the effect of cationic starch either alone or combined with NFC, on paper strength, three different amounts of starch were used. These results are illustrated in Figure 6. In Figure 6, the curves illustrate results obtained from sheet containing no additives (reference: +) and from sheets prepared either with three different amounts of cationic starch (CS2.5: Δ and dotted line, CS5: □ and dashed line, and CS10:○) or with a mixture of cationic starch and NFC (CS2.5 +NFC25: ●). Very high amounts of cationic starch are needed in order to obtain a similar sheet strength to using the combination of cationic starch and NFC proposed here. Thus, the combination of the cationic starch and nanofibrillated cellulose is a preferable combination for improving the tensile strength and Z-directional strength of the paper product.

Example 2

[0048] The aim of this example was to test different strategies of mixing filler and fibres with cationic starch and nanofibrillated cellulose in order to determine their influence on paper strength. Another aim was to illustrate the effect of combining NFC and cationic starch for improving the strength of filled paper in situations where fines are present.

[0049] The materials used in the experiments are the following:

Fibres

[0050] Dried hardwood (birch) bleached chemical pulp was also used in this example. About 360 g pulp was soaked overnight in 5 l of water and beaten for 50 minutes at a consistency of 1.6% in a Valley beater (ISO 5264-1) to the Shopper-Riegler (SR) number (ISO 5267-1) of about 42. Afterwards, 2 l of water was used to rinse the beater and added to the fibre suspension. Finally, the pulp was washed, first by acidic treatment (0.01 M hydrochloric acid) to remove metal ions, and afterwards, the fibres were converted to sodium form with 1 mM of sodium bicarbonate. After these two treatments, the pulp was thoroughly washed with deionized water.

[0051] The difference to the fibres used in Example 1 is that fines were not removed in this Example.

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Nanofibrillated cellulose (NFC)

[0052] Never dried hard wood was disintegrated using a Masuko supermass colloid with 200 µm gap between the stones at 3% consistency. The NFC used for paper sheets was obtained after five passes through the colloid.

[0053] The nanofibril gel was delivered at a dry content of 2%. Just before use, NFC was diluted with deionized water and dispersed with Branson Digital Sonifier (Branson Ultrasonics Corporation, Danbury, USA) with an amplitude setting of 25% for 2 minutes.

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Cationic starch

[0054] Cationic starch (CS) with a degree of substitution of 0.035 (Raisamyl 50021) was supplied by Ciba Specialty Chemical, Raisio, Finland. Before use, 2 g (o.d.)/l starch solution was cooked in an autoclave at 120°C for 20 minutes.

Fillers

[0055] Commercial scalenohedral precipitated calcium carbonate (PCC). According to the manufacturer, the average particle size of this PCC was 2.3 µm, the brightness 95% and the dry matter content 19.9%.

[0056] In this example, seven different mixing strategies were chosen in order to prepare the pulp slurry (Figs. 7a to 7g):

- Strategy 1 (Fig. 7a): Fibres were put in suspension in a vessel with deionized water. In parallel, cationic starch was diluted with deionized water in a vessel and mixed together with PCC for 15 minutes. Afterwards, these premixed suspensions were poured into a vessel and mixed for 15 minutes.
- Strategy 2 (Fig. 7b): Fibres were put in suspension in a vessel with deionized water. In parallel, cationic starch was diluted with deionized water in a vessel and mixed together with PCC for 15 minutes. Afterwards, NFC was added to this suspension and all was mixed again for 15 minutes. Finally, both contents were poured into a vessel and mixed for 15 minutes.
- Strategy 3 (Fig. 7c): Fibres were put in suspension in a vessel with deionized water. In parallel, cationic starch (CS) was diluted with deionized water in a vessel and mixed together with NFC and PCC for 15 minutes (added simultaneously into the vessel). Afterwards, both contents were poured into a vessel and mixed for 15 minutes.
- Strategy 4 (Fig. 7d): Fibres were put in suspension in a vessel with deionized water. Afterwards, PCC, cationic starch and NFC were added successively to the fibre suspension and mixed for 15 minutes.
- Strategy 5 (Fig. 7e): this strategy is similar to strategy 3, but this time the total amount of starch is divided equally between the fibre suspension vessel and the NFC and PCC one.
- Strategy 6 (Fig. 7f): Fibres were put in suspension with deionized water in a vessel and mixed together with starch for 15 minutes. In parallel, NFC was put in suspension with deionized water in a vessel and mixed together with PCC for 15 minutes. Afterwards, both contents were poured into a vessel and mixed for 15 minutes.
- Strategy 7 (Fig. 7g): Fibres were put in suspension with deionized water in a vessel and mixed together with PCC for 15 minutes. This is used as Reference sample.

[0057] To perform furnish of these seven strategies, 1.63 g/l of fibres were used. 20 or 40 mg of cationic starch per g of fibres and two different amounts of NFC: 15 and 30 mg/g of fibres were used. In all steps, the pH of the slurry was adjusted to about 9 with a sodium bicarbonate buffer solution, and the ionic strength was measured. To be able to compare results from paper testing, the furnish was further diluted with water to obtain a paper sheet grammage between 55 and 65 g/m².

[0058] After the furnish preparation, handsheets were formed from different furnishes as in the Example 1. The sheet properties were measured using the same methods as presented in Example 1.

[0059] The purpose of the two first strategies, was to determine the optimal amounts of cationic starch and NFC. Figures 8a and 8b show tensile strength of the handsheets as a function of filler content. The curves of Figure 8a illustrate results obtained from sheets prepared with two different content of cationic starch: 2% (dashed line) and 4% (continuous line). The curves of Figure 8b illustrate results obtained from sheets prepared with two different contents of cationic starch and NFC: 2% CS and 15% NFC (◊ and dotted line), 4% CS and 15% NFC (◊ and continuous line), 2% CS and 30% NFC (□ and dashed line), 4% CS and 30% NFC (□ and continuous line). The lines in these figures are only drawn to guide the eye and do not illustrate the actual trend. The increase of cationic starch content does not give significant improvement of the tensile strength. Furthermore, too high starch content may cause problems in the papermaking process, such as stickiness, the lower starch content is thus chosen for the other experiments. The same conclusion can be made for the NFC content, indeed, a higher amount of NFC does not further increase the tensile strength and the content chosen for further experiments was hence the lowest one.

[0060] The tensile strength and Scott bond obtained with the different mixing strategies are summarized in Figure 9. Figure 9 shows tensile strength and Scott bond of the handsheets as function of filler content. The curves illustrate results obtained from sheets prepared with starch alone i.e. strategy 1 (▲ and continuous line), the strategy 2 (□ and dashed line), the strategy 3 (△ and dotted line), the strategy 4 (■ and continuous line), the strategy 5 (+ and dotted line), the strategy 6 (○ and dashed line) and the reference i.e. strategy 7 (● and continuous line). The changes in tensile strength between the two filler contents are obviously not following a straight line but these lines have been drawn in order to see the trend of change more easily.

[0061] The strength properties obtained with the strategy 4 presented in Fig. 7d (mixing fibres and fillers and then adding first CS and then NFC) stands out from the other strategies by its improvement, indeed, if we compare with cationic starch alone for 30% filler content, the tensile strength is increased by 17% and the Scott bond by 26%.

[0062] Another efficient way is to treat the fillers with first CS and then NFC (forming a bilayer on the filler surface) and then to add these modified filler particles to the fibre suspension (strategy 2 presented in Fig. 7b). In this case the fibres may be unmodified or modified with CS.

[0063] Also other strategies increase the strength of the paper sheets but the most efficient way is to form a bilayer

of CS and NFC on at least the filler surface but preferably also the fibre surface.

Claims

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1. A method for preparing aqueous furnish to be used in paper or paper board manufacturing, in which method the furnish is prepared by adding at least filler to a fibre suspension, wherein the filler and/or the fibres are treated with cationic polyelectrolyte and nanofibrillated cellulose, **characterized in that** the filler and the fibres are treated first with cationic polyelectrolyte and secondly with nanofibrillated cellulose by adding them to the fibre-filler suspension.

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2. The method according to claim 1, **characterized in that** the filler content is 1 to 60% of the dry weight of the fibres in the furnish, preferably 20 to 40%.
3. The method according to any of the preceding claims, **characterized in that** the filler is precipitated calcium carbonate (PCC).
4. The method according to any of the preceding claims, **characterised in that** the nanofibrillated cellulose is added in an amount of 0.01 to 20% of the dry weight of the fibres in the furnish, preferably 1 to 10% and most preferably 1 to 3%.

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5. The method according to any of the preceding claims, **characterized in that** the cationic polyelectrolyte is added in an amount of 0.01 to 5% of the dry weight of fibres in the furnish, preferably approximately 2 to 4%.
6. The method according to any of the preceding claims, **characterized in that** the cationic polyelectrolyte is cationic starch.
7. Furnish, which is prepared by the method according to any of the preceding claims.
8. Paper or paper board manufactured from the furnish prepared by the method according to any of claims 1 to 6.

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Patentansprüche

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1. Verfahren zur Herstellung eines bei der Papier- oder Pappeherstellung zu verwendenden wässrigen Stoffeintrags, in welchem Verfahren der Stoffeintrag durch Zusetzen zumindest eines Füllstoffs zu einer Fasersuspension hergestellt wird, wobei der Füllstoff und/oder die Fasern mit kationischem Polyelektrolyt und nanofibrillierter Cellulose behandelt werden, **dadurch gekennzeichnet, dass** der Füllstoff und die Fasern zuerst mit kationischem Polyelektrolyt und zweitens mit nanofibrillierter Cellulose durch deren Zusetzen zu der Faser-Füllstoff-Suspension behandelt werden.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** der Füllstoffgehalt 1 bis 60 % des Trockengewichts der Fasern in dem Stoffeintrag, vorzugsweise 20 bis 40 %, beträgt.
3. Verfahren nach irgendeinem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** der Füllstoff ausgefällt Calciumcarbonat (PCC, precipitated calcium carbonate) ist.
4. Verfahren nach irgendeinem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** die nanofibrillierte Cellulose in einer Menge von 0,01 bis 20 % des Trockengewichts der Fasern in dem Stoffeintrag, vorzugsweise 1 bis 10 % und am meisten bevorzugt 1 bis 3 %, zugesetzt wird.
5. Verfahren nach irgendeinem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** der kationische Polyelektrolyt in einer Menge von 0,01 bis 5 % des Trockengewichts der Fasern in dem Stoffeintrag, vorzugsweise ungefähr 2 bis 4 %, zugesetzt wird.
6. Verfahren nach irgendeinem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** der kationische Polyelektrolyt kationische Stärke ist.
7. Stoffeintrag, welcher durch das Verfahren nach irgendeinem der vorangehenden Ansprüche hergestellt ist.

8. Papier oder Pappe, hergestellt aus dem durch das Verfahren nach irgendeinem der Ansprüche 1 bis 6 hergestellten Stoffeintrag.

5 **Revendications**

1. Procédé pour préparer une composition de fabrication aqueuse à utiliser dans la fabrication du papier ou du carton, procédé dans lequel on prépare la composition de fabrication en ajoutant au moins une matière de charge à une suspension fibreuse, la matière de charge et/ou les fibres étant traitée(s) avec un polyélectrolyte cationique et de la cellulose nanofibrillaire, **caractérisé en ce que** la matière de charge et les fibres sont traitées en premier lieu avec un polyélectrolyte cationique et en deuxième lieu avec de la cellulose nanofibrillaire en les ajoutant à la suspension de fibre-matière de charge.
2. Procédé selon la revendication 1, **caractérisé en ce que** la teneur en matière de charge représente de 1 à 60 % du poids à sec des fibres dans la composition de fabrication, de préférence de 20 à 40 %.
3. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la matière de charge représente du carbonate de calcium précipité (PCC, precipitated calcium carbonate).
- 20 4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la cellulose nanofibrillaire est ajoutée en une quantité de 0,01 à 20 % du poids à sec des fibres dans la composition de fabrication, de préférence de 1 à 10 % et de manière de loin préférée de 1 à 3 %.
- 25 5. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le polyélectrolyte cationique est ajouté en une quantité de 0,01 à 5 % du poids à sec des fibres dans la composition de fabrication, de préférence d'approximativement 2 à 4 %.
6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le polyélectrolyte cationique est de l'amidon cationique.
- 30 7. Composition de fabrication que l'on prépare via le procédé selon l'une quelconque des revendications précédentes.
8. Papier ou carton fabriqué à partir de la composition de fabrication préparée via le procédé selon l'une quelconque des revendications 1 à 6.

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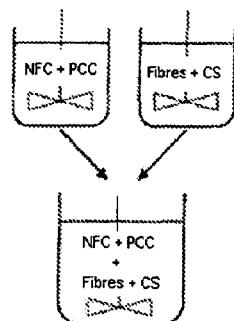


Fig. 1

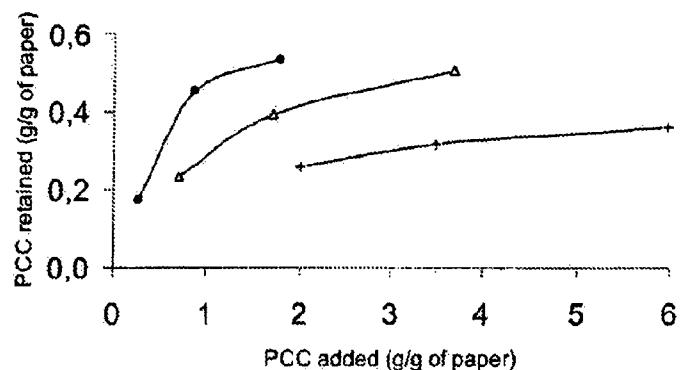


Fig. 2

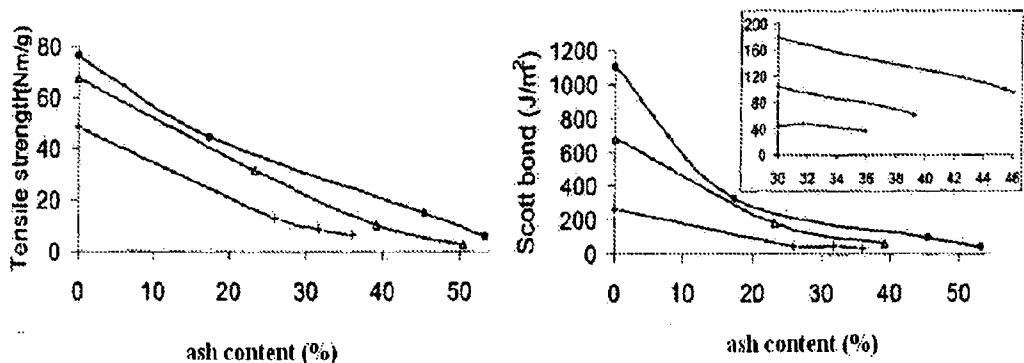


Fig. 3

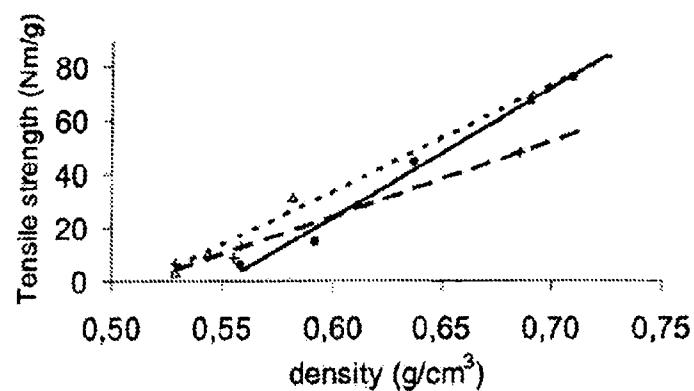


Fig. 4

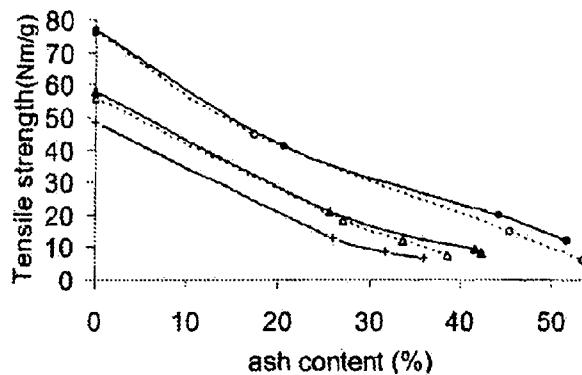


Fig. 5

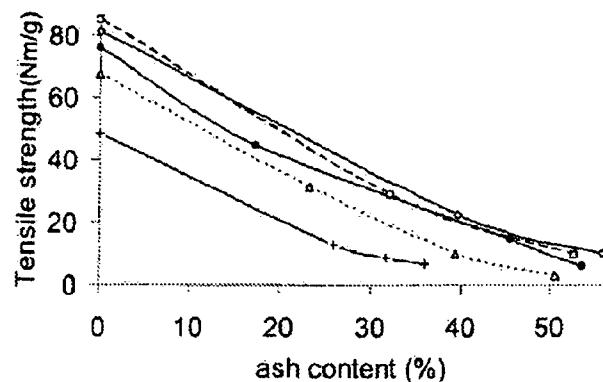
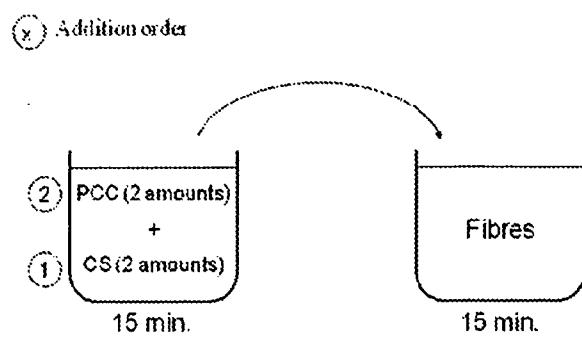
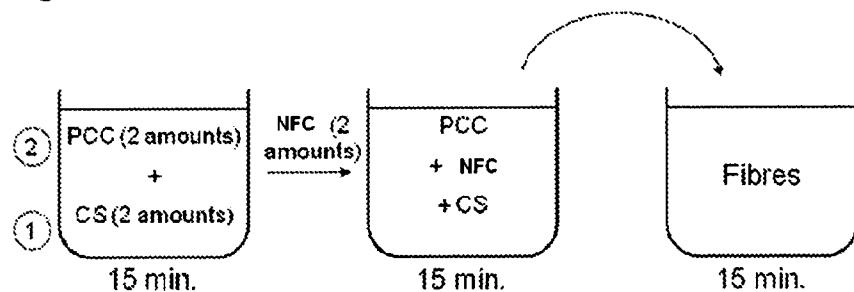
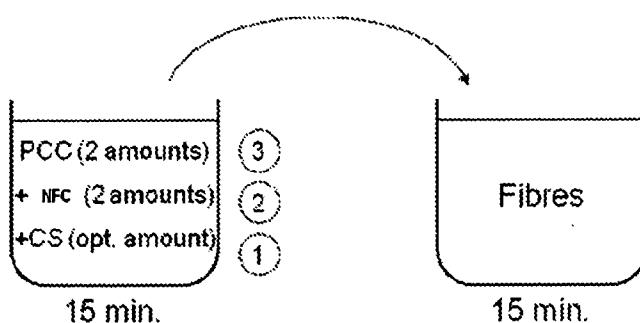
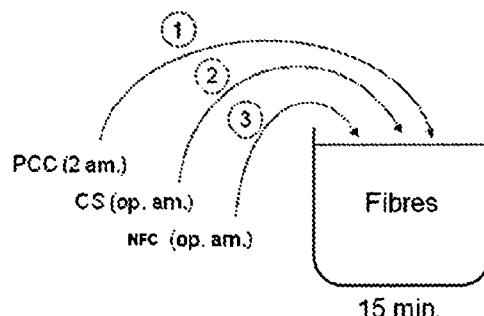


Fig. 6

**Fig. 7a****Fig. 7b****Fig. 7c****Fig. 7d**

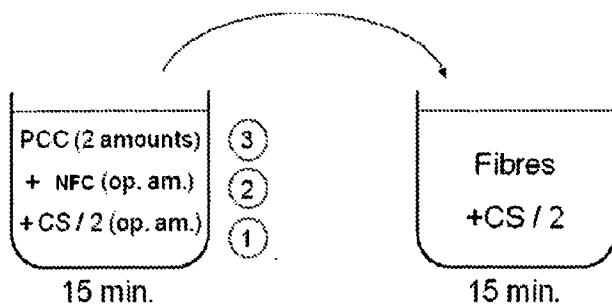


Fig. 7e

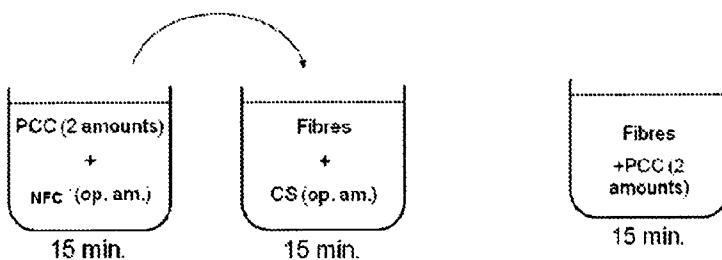


Fig. 7f

Fig. 7g

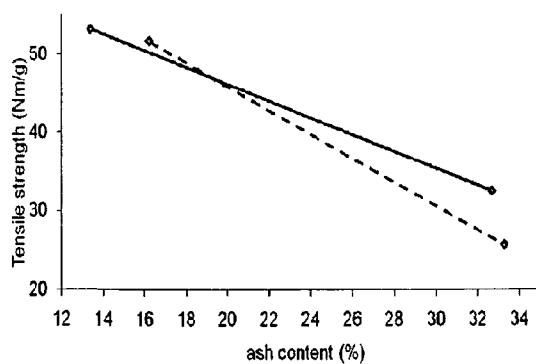


Fig. 8a

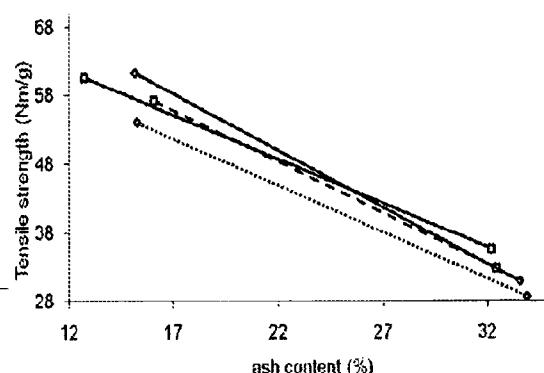


Fig. 8b

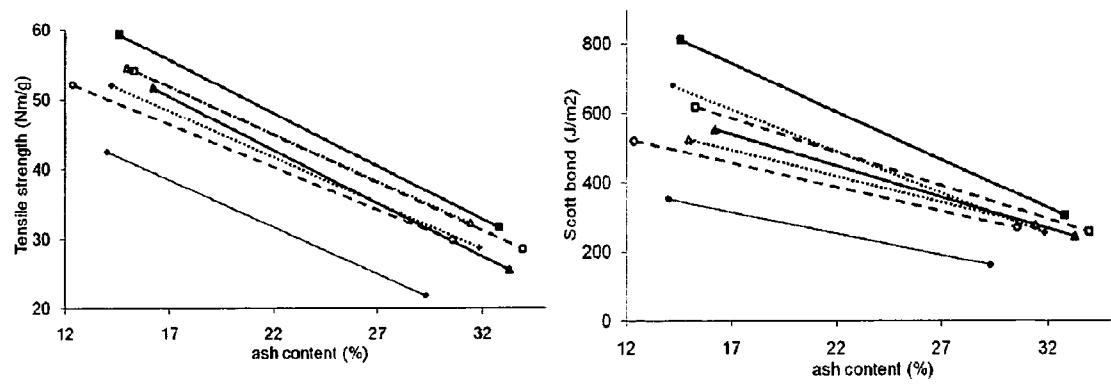


Fig. 9

REFERENCES CITED IN THE DESCRIPTION

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(54) Titre : MATIERE CELLULOSIQUE RESISTANTE AU FEU

(54) Title: FIRE-RESISTANT CELLULOSE MATERIAL

(57) Abrégé/Abstract:

A new approach for improving fire resistance of cellulosic materials is provided, especially when the cellulosic material is to be used in polymer composites. Cellulosic material is treated with an aqueous mixture of alkali metal or ammonium hydroxide and alkaline earth or aluminum metal salt simultaneously with or within a short period of time of preparing the mixture. The treated cellulosic material becomes self-extinguishing and may also have improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents and/or improved resistance to damage by ultra-violet light. The fire-resistant cellulosic material may also be treated with a layered nanoparticulate material either simultaneously with, subsequent to or prior to treatment with the aqueous mixture of alkali metal or ammonium hydroxide and alkaline earth or aluminum metal salt to impart further fire resistance to the cellulosic material. Polymer composites produced from cellulosic material treated according to the present invention have significantly improved fire resistance with small negative impact on the mechanical performance of the composite, and may have the added benefit of improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents and/or improved resistance to damage by ultra-violet light.

ABSTRACT

- A new approach for improving fire resistance of cellulosic materials is provided, especially when the cellulosic material is to be used in polymer composites. Cellulosic material is treated with an aqueous mixture of alkali metal or ammonium hydroxide and 5 alkaline earth or aluminum metal salt simultaneously with or within a short period of time of preparing the mixture. The treated cellulosic material becomes self-extinguishing and may also have improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents and/or improved resistance to damage by ultra-violet light.
- 10 The fire-resistant cellulosic material may also be treated with a layered nanoparticulate material either simultaneously with, subsequent to or prior to treatment with the aqueous mixture of alkali metal or ammonium hydroxide and alkaline earth or aluminum metal salt to impart further fire resistance to the cellulosic material. Polymer composites produced from cellulosic material treated according to the present invention have significantly 15 improved fire resistance with small negative impact on the mechanical performance of the composite, and may have the added benefit of improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents and/or improved resistance to damage by ultra-violet light.

FIRE-RESISTANT CELLULOSIC MATERIAL

Cross-reference to Related Applications

This application claims the benefit of United States Provisional patent application serial number 61/504,779 filed July 6, 2011, the entire contents of which is herein
5 incorporated by reference.

Field of the Invention

The present invention relates to a process for producing a fire-resistant cellulosic material, the fire-resistant cellulosic material produced by the process and the use of the fire-resistant cellulosic material in fire-resistant polymer composites.

10 Background of the Invention

Cellulosic materials (natural and synthetic) in different forms (fiber, film, powder, particle, pellet, chip, etc) at different sizes (nano, micro or macro) are often flammable and have low thermal resistance. They can be burned and also can spread the fire in the presence of oxygen. Thus, their use either in direct or non-direct form is limited in
15 applications requiring fire resistance. Due to their flammability, the use of cellulosic materials in polymer composites is also limited in certain applications.

Cellulosic materials are treated with different flame retardants depending on the application, for example in furniture, textiles or composites. The most commonly used flame retardants are based on halogen (e.g. WO 2004/1097088), phosphorous (e.g. US
20 3,899,483; US 6,524,653; US 4,228,202; US 5,238,464; US 2005/0215152; US 2004/0094279; WO 2002/1044470; US 6,352,786), boron (e.g. WO 2005/1042840; US 4,228,202; US 2009/0156073), ammonium (e.g. US 4,228,202; US 6,524,653; WO 2002/1044470), graphite (e.g. JP 09-031887; EP 0735187), alkaline-earth metallic compounds (e.g. US 5,434,200) or mixtures thereof. To improve fire resistance of
25 organic polymer composites, the incorporation of flame retardants based on halogen, phosphorous, metallic hydroxide (magnesium hydroxide, aluminum hydroxide, calcium hydroxide, layer double hydroxide), metallic oxide (antimony oxide, boron oxide), silicate (clay, talc), etc, in the polymer matrix has been widely used.

Among the compounds listed above, halogen based flame retardants are well
30 known to be the most efficient as they can be used at a low concentration in the final composition thus limiting their impact on other properties of the product. However, halogen compounds are considered to be harmful to the environment. Boron compounds

are supposed to be efficient, however they tend to be washed off due to their good solubility in water. Less harmful flame retardants based on phosphorous, graphite or alkaline-earth metallic compounds are much less efficient, thus a large amount of those additives must be used in the formulation. The use of flame retardant incorporated in a 5 polymer matrix alone does not satisfactorily resolve the flammability problem in cellulose-polymer composites, especially when the concentration of cellulose is quite significant in the formulation of the composite.

It is generally known that metal hydroxides, including barium hydroxide, can be used as a flame retardant for cellulosic materials (e.g. US 2009-298370; US 671,548; 10 Chen 1991; Mostashari 2008) and for polymer materials (e.g. US 7,354,958). Further, CA 2,079,302 discloses a flame retardant composition for cellulosic material comprising sodium hydroxide and a metal salt of boron among other ingredients. The metal salt of boron is defined as borax which is a sodium tetraborate. US 3,973,074 discloses a flame-proofing composition comprising potassium hydroxide and/or potassium carbonate and 15 possibly a small amount of sodium hydroxide and/or sodium carbonate and may include another potassium salt. US 5,480,587 discloses inorganic additives to impart flame resistance to polymers. The additives include hydroxides and metal salts that evolve gas. One such metal salt is barium chloride dihydrate. US 4,567,242 discloses the use of a mixture of a polycondensate of a halogenated phenol and an alkaline earth metal halide 20 in a flame retarding composition.

US 2003-0220515 discloses flame retardant compositions in which ancillary flame retardant additives may be used alone or in combination, such as metal hydroxides and metal salts, including alkaline earth metal salts. There is no disclosure of the use of an aqueous mixture of alkali metal hydroxides with alkaline earth metal salts.

25 US 4,064,317 discloses the use of "alkali compounds" for use in flame resistant plaster board. The "alkali compounds" are defined as at least one of an alkali metal hydroxide, alkali metal salt, alkaline earth metal hydroxide or alkaline earth metal salt. It is preferred to use a mixture of alkali metal salts and alkaline earth metal salts, for example a mixture of sodium and calcium formate. The combination of alkali metal 30 hydroxide and alkaline earth metal salt, especially barium salts, is not specifically disclosed.

The abstract of CN 1869154 discloses a flame retardant composition which initially involves the step of making magnesium hydroxide from the reaction of magnesium sulfate and sodium hydroxide. However, this document does not disclose

treating a cellulosic material with an aqueous reaction mixture of an alkali metal hydroxide and alkaline earth metal salt simultaneously with or shortly after mixing the alkali metal hydroxide with alkaline earth metal salt.

It is known that treatment of cellulosic materials with alkaline earth metal carbonates (e.g. barium carbonate) imparts fire resistance to the cellulosic material (e.g. Mostashari 2004-2005). Here, the alkaline earth metal carbonate is applied to the cellulosic material by first coating the cellulosic material with an alkaline earth metal chloride and then treating the so-coated material with sodium carbonate. It is also known to use both a clay and a metal hydroxide in a fire retarding composition comprising a polymer material (e.g. GB 2367064; JP 2002-180374).

There remains a need for an environmentally friendlier, effective approach to producing fire-resistant cellulosic materials.

Summary of the Invention

The present invention provides a new approach for improving fire resistance of cellulosic materials, especially when the cellulosic material is to be used in polymer composites. Cellulosic material is treated with an aqueous mixture of alkali metal or ammonium hydroxide and alkaline-earth or aluminum metal salt simultaneously with or within a short period of time of preparing the mixture. The treated cellulosic material becomes self-extinguishing and may also have improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to damage by ultra-violet light and/or reduced negative impact on fiber strength and/or modulus. The fire-resistant cellulosic material may also be treated with a layered nanoparticulate material either simultaneously with, subsequent to or prior to treatment with the aqueous mixture of alkali metal or ammonium hydroxide and alkaline-earth or aluminum metal salt to impart further fire resistance to the cellulosic material. Polymer composites produced from cellulosic material treated according to the present invention have significantly improved fire resistance with small negative impact on the mechanical performance of the composite, and may have the added benefit of one or more of improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents and improved resistance to damage by ultra-violet light.

Thus, in one aspect of the present invention there is provided a process of producing a fire-resistant cellulosic material comprising: treating a cellulosic material with

an aqueous reaction mixture of an alkali metal or ammonium hydroxide and an alkaline earth or aluminum metal salt, wherein the treating is done simultaneously with or within a short period of time of mixing the alkali metal or ammonium hydroxide and alkaline earth metal or aluminum salt; and, drying the treated cellulosic material.

- 5 In another aspect of the present invention there is provided a fire-resistant cellulosic material produced by the process of the present invention.

In yet another aspect of the present invention there is provided a polymer composite comprising a polymer matrix and the fire-resistant cellulosic material of the present invention dispersed in the polymer matrix.

- 10 Alkali metal hydroxides are the hydroxides of Group IA metallic elements and include, for example, lithium hydroxide, sodium hydroxide, potassium hydroxide and cesium hydroxide. Sodium hydroxide and potassium hydroxide are particularly preferred, especially sodium hydroxide. Ammonium hydroxide is NH₄OH. The alkali metal or ammonium hydroxide will be referred to herein as the hydroxide. The hydroxide is
15 preferably present in the aqueous reaction mixture in an amount of about 20 wt% or less, based on weight of the reaction mixture. More preferably, the amount is in a range of from about 0.1 wt% to about 10 wt%. Even more preferably, the amount is in a range of from about 0.5 wt% to about 4 wt%.

- 20 Alkaline earth metal salts or aluminum metal salts, or mixtures thereof are used in conjunction with the alkali metal salts to produce the fire-resistant cellulosic material. Alkaline earth metal salts and aluminum metal salts are ionic compounds that dissociate in an aqueous environment and comprise one or more cations and one or more counter anions. Alkaline earth metal salts are preferred. Alkaline earth metals include, for example, beryllium, magnesium, calcium, strontium and barium. Magnesium, calcium and
25 barium are particularly preferred, especially magnesium and calcium. Counter anions may be any suitable negatively charged elements or radicals or combinations thereof. Counter anions include, for example, halides (e.g. fluoride, chloride, bromide, iodide), nitrate and sulfate. Chloride and nitrate are particularly preferred. Chloride is most preferred. The alkaline earth metal or aluminum salt is preferably present in the aqueous
30 reaction mixture in an amount of about 20 wt% or less, based on weight of the reaction mixture. More preferably, the amount is in a range of from about 0.1 wt% to about 15 wt%. Even more preferably, the amount is in a range of from about 0.5 wt% to about 10 wt%.

In addition the ratio between the hydroxide and alkaline earth or aluminum metal salt can play an important role. The molar ratio between the hydroxide and the alkaline earth or aluminum metal salts is preferably in a range of from about 0.2 to about 4. More preferably, the molar ratio is in a range of from about 0.5 to about 2. The ratio between
5 the hydroxide and alkaline earth or aluminum metal salt can also be expressed on a weight basis, and is preferably in a range of from about 0.9 wt% to about 1.1 wt%.

In addition, the concentration of the product of the aqueous reaction mixture of the hydroxide and the alkaline earth or aluminum metal salt is preferably about 0.5 wt% or more, more preferably about 1.5 wt% or more, even more preferably in a range of from
10 about 1.5 wt% to about 20 wt%, yet more preferably about 1.5 wt% to about 15 wt%, based on weight of the reaction mixture.

Treating the cellulosic material with the aqueous reaction mixture is preferably done simultaneously with mixing the hydroxide and alkaline earth or aluminum metal salt. However, the reaction mixture remains effective within a short period of time of mixing.
15 The maximum desirable length of time after mixing and before treating is 1 day, preferably 5 hours or less, more preferably 5 seconds to 5 hours. More preferably, the time is in a range of from about 5 seconds to about 30 minutes, or about 5 seconds to about 10 minutes, or about 30 seconds to about 24 hours, or about 1 minute to about 5 hours.

20 The cellulosic material may be obtained from any suitable source. Cellulosic materials may be natural or synthetic, may have different forms (e.g. fiber, shives, film, powder, particle, pellet, chip, etc.) and may have different size distributions (e.g. nano, micro or macro). Some suitable sources of cellulosic include, for example, wood sources (e.g. pulp, wood flour such as sawdust, wood shavings, etc. from softwood and/or
25 hardwood, etc), agricultural sources (e.g. fruits, grain crops (e.g. triticale and flax), vegetables, cotton, hemp, grass, rice straw, etc.), synthetic sources (e.g. nanocrystalline cellulose, cellulose triacetate, cellulose propionate, cellulose acetate propionate, cellulose acetate butyrate, nitrocellulose, cellulose sulfate, methylcellulose, ethylcellulose, ethyl methyl cellulose, hydroxypropyl cellulose, hydroxyethyl methyl cellulose, hydroxypropyl
30 methyl cellulose, carboxymethyl cellulose, etc.), recycled paper and cardboard. The cellulosic material may be used alone or mixed with cellulosic materials from different sources. It is apparent to one skilled in the art that cellulosic materials from natural sources, for example wood and vegetable fibers, contain significant amount of lignin (in some case more than 30 wt%) and that such "lignocellulose materials" are encompassed
35 by the present invention. A particularly preferred form are cellulosic material is fibers. For

use in polymer composites, non-fibrous cellulosic material having an average particle size of from about 0.001-20 mm, more particularly from about 0.01-5 mm are generally suitable. Non-fibrous cellulosic material may be in the form of cellulosic nanocrystals. When the cellulosic material is fibrous, the average diameter of the fiber is preferably in a 5 range of from about 0.001 micron to 400 micron, more preferably from about 0.001 to 100 micron. Fibrous cellulosic material may be in the form of cellulosic nanofibers or nanowhiskers.

After treating with the aqueous reaction mixture, treated cellulosic material is dried to produce fire-resistant cellulosic material of the present invention. Prior to drying, the 10 treated cellulosic material may be cleaned, for example with water, if desired or required. Drying may be done by any suitable method, for example, air drying at ambient temperature and pressure, drying at elevated temperature, drying under a pressurized stream of air or other gas or a combination thereof. Specialized equipment such as fluid bed, rotary, spray and vacuum dryers may be used.

15 To further improve fire resistance of the cellulosic material, the cellulosic material may be further treated with a layered nanoparticulate material. Treating the cellulosic material with the layered nanoparticulate material may be done before, at the same time as or after treating the cellulosic material with the aqueous reaction mixture. Preferably, the cellulosic material is treated with layered nanoparticulate material after treatment with 20 the aqueous reaction mixture as this leads to a more durable fire-resistant coating. This further treatment with layered nanoparticulate material is particularly useful when the fire-resistant cellulosic material is to be used in a polymer composite as it significantly improves the fire-resistance of the composite in comparison to using fire-resistant cellulosic material that has only undergone treatment with the aqueous reaction mixture.

25 Any suitable layered nanoparticulate material may be used. Layered clays are particularly preferred. Layered clays are hydrated aluminum or aluminum-magnesium silicates comprised of multiple platelets. Layered clays may be natural, semi-synthetic or synthetic layered silicates. Suitable layered clays include, for example, bentonite, kaolinite, dickite, nacrite, staspulite, illite, halloysite, montmorillonite, sepiolite, 30 palygorskite, hectorite, fluorohectorite, nontronite, beidellite, saponite, volkonskoite, magadiite, medmontite, kenyaite, saucomite, muscovite, vermiculite, mica, fluoromica, hydromica, phegite, bramalite, celadonite, layered double hydroxides, etc., or a mixture thereof. Particularly preferred are layered double hydroxides, montmorillonite, sepiolite, palygorskite, bentonite, fluoromica or a mixture thereof. Layered double hydroxides, 35 montmorillonite or mixtures thereof are even more particularly preferred. The layered

nanoparticulate material is used in a sufficient amount to provide an improvement to the fire-resistance of the cellulosic material or composite in which the cellulosic material is used. The layered nanoparticulate material is preferably present in the aqueous mixture in an amount of about 15 wt% or less, based on weight of the mixture. More preferably, 5 the amount is in a range of from about 0.1 wt% to about 10 wt%. Even more preferably, the amount is in a range of from about 0.5 wt% to about 5 wt%.

The cellulosic material may be mixed with the aqueous mixture, and layered nanoparticulate material if desired, in any suitable way known in the art. Various systems are known in the art and include, for example, high shear mixers, in-line mixers, batch 10 mixers, colloid mills, stirrers, agitators and blending systems.

A polymer composite of the present invention comprises the fire-resistant cellulosic material dispersed in a polymer matrix. The polymer matrix may comprise one or more suitable organic or inorganic polymers, preferably one or more organic polymers. Organic polymers may be natural or synthetic and may be obtained from non-renewable 15 or renewable sources. Natural polymers include cellulose, lignin, starch, protein, etc. Polymer matrices may be classified in a number of other different ways. A suitable polymer matrix may comprise a homopolymer, a copolymer, a terpolymer, or a mixture thereof. The polymer matrix may comprise amorphous or crystalline polymers. The polymer matrix may comprise hydrophobic or hydrophilic polymers. The polymer matrix 20 may comprise linear, branched, star, cross-linked or dendritic polymers or mixtures thereof. Polymer matrices may also be conveniently classified as thermoplastic, thermoset and/or elastomeric polymers. It is clear to one skilled in the art that a given polymer matrix may be classifiable into more than one of the foregoing categories.

Thermoplastic polymers generally possess significant elasticity at room 25 temperature and become viscous liquid-like materials at a higher temperature, this change being reversible. Some thermoplastic polymers have molecular structures that make it impossible for the polymer to crystallize while other thermoplastic polymers are capable of becoming crystalline or, rather, semi-crystalline. The former are amorphous thermoplastics while the latter are crystalline thermoplastics. Some suitable 30 thermoplastic polymers include, for example, olefins (i.e., polyolefins), vinyls, styrenics, acrylonitrilics, acrylics, cellulosics, polyamides, thermoplastic polyesters, thermoplastic polycarbonates, polysulfones, polyimides, polyether/oxides, polyketones, fluoropolymers, copolymers thereof, or mixtures thereof.

Some suitable olefins (i.e., polyolefins) include, for example, polyethylenes (e.g., LDPE, HDPE, LLDPE, UHMWPE, XLPE, copolymers of ethylene with another monomer (e.g., ethylene-propylene copolymer)), polypropylene, polybutylene, polymethylpentene, or mixtures thereof. Some suitable vinylics include, for example, polyvinylchloride, 5 chlorinated polyvinylchloride, vinyl chloride-based copolymers, polyvinylidenechloride, polyvinylacetate, polyvinylalcohol, polyvinyl aldehydics (e.g., polyvinylacetal), polyvinylalkylethers, polyvinylpyrrolidone, polyvinylcarbazole, polyvinylpyridine, or mixtures thereof. Some suitable styrenics include, for example, polystyrene, 10 polyparamethylstyrene, polyalphamethylstyrene, high impact polystyrene, styrene-based copolymers, or mixtures thereof. Some suitable acrylonitrilics include, for example, polyacrylonitrile, polymethylacrylonitrile, acrylonitrile-based copolymers, or mixtures thereof. Some suitable acrylics include, for example, polyacrylicacid, polymethacrylicacid, polymethacrylate, polyethylacrylate, polybutylacrylate, polymethylmethacrylate, polyethylmethacrylate, cyanoacrylate resins, 15 hydroxymethylmethacrylate, polacrylamide, or mixtures thereof. Some suitable cellulosics include, for example, cellulose, cellulose esters, cellulose acetates, mixed cellulosic organic esters, cellulose ethers, methylcellulose, ethylcellulose, carboxymethylcellulose, hydroxyethylcellulose, or mixtures thereof. Some suitable polyamides include, for example, aliphatic polyamides (i.e., nylons), aromatic polyamides, 20 transparent polyamides, or mixtures thereof. Some suitable thermoplastic polyesters/polycarbonates are, for example, polyalkylene terephthalates (e.g., polyethylene terephthalate, polybutylene terephthalate), polycyclohexanedimethanol terephthalates, polyarylesters (e.g., polyarylates), polycaprolactones, polyactides, polyhydroxyalkanoates (e.g. polyhydroxybutanoate), polycarbonate, or mixtures thereof. 25 Some suitable polysulfones include, for example, diphenylsulfone, polybisphenolsulfone, polyethersulfone, polyphenylethersulfones, or mixtures thereof. Some suitable polyimides include, for example, polyamideimide, polyetherimide, or mixtures thereof. Some suitable polyether/oxides include, for example, polymethyleneoxides, polyethyleneoxide, polypropyleneoxide, polyphenyleneoxides, or mixtures thereof. Some 30 suitable polyketones include, for example, polyetheretherketone-1. Some suitable fluoropolymers include, for example, polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylfluoride, polyvinylidenefluoride, polyperfluoroalkoxy, polyhexafluoropropylene, polyhexafluoroisobutylene, fluoroplastic copolymers, or mixtures thereof.

Thermoset polymers (thermoset resins) generally arise from a complex 35 combination of polymerization and cross-linking reactions, which convert low- or relatively low-molecular weight molecules into three-dimensional networks. The reaction is

irreversible and the resulting polymeric species is generally hard. The polymerization and cross-linking reactions may be temperature-activated, catalyst-activated or mixing-activated. Some suitable thermosets include, for example, phenolic systems, formaldehyde systems, furan systems, allyl systems, alkyd systems, unsaturated polyester systems, vinylester systems, epoxy systems, urethane/urea systems, isocyanurate systems or mixtures thereof.

Some suitable phenolic systems include, for example, phenol-formaldehyde resins, phenol acetaldehyde resins, alkylphenol-formaldehyde resins, lignin formaldehyde resins or mixtures thereof. Some suitable formaldehyde systems include, for example, 10 urea-formaldehyde resins, melamine-formaldehyde resins, phenol-formaldehyde resins, or mixtures thereof. Some suitable furan systems include, for example, furan resins, furfural resins, furfuryl alcohol resins, or mixtures thereof. Some suitable allyl systems include, for example, diallyl phthalate, diallyl isophthalate, diethyleneglycol bis(allyl carbonate), or mixtures thereof. Some suitable alkyd systems include, for example, the 15 reaction product of ethylene glycol, glycerol and phthalic acid with fatty acids. Some suitable unsaturated polyester systems include, for example, one component which is a polyester product of a reaction between a difunctional acid or anhydride (e.g., maleic acid, maleic anhydride, phthalic anhydride, terephthalic acid) with a difunctional alcohol (e.g., ethylene glycol, propylene glycol, glycerol), and, a second component which is a 20 monomer capable of polymerizing and reacting with unsaturations in the polyester component (e.g., styrene, alphamethylstyrene, methylmethacrylate, diallylphthalate). Some suitable vinylester systems include, for example, the reaction of diglycidyl ether of bisphenol A with methacrylic acid. Some suitable epoxy systems include, for example, the reaction between epichlorohydrin and a multifunctional acid, amine or alcohol. Some 25 suitable urethane/urea systems include, for example, the reaction product of a liquid or solid isocyanate (e.g., 2,4-toluenediisocyanate, 2,6-toluenediisocyanate, methylene diisocyanate monomer or oligmer of different molecular weight) with a polyol (e.g., polyethylene ether glycol, polypropylene ether glycol).

Elastomeric polymers (elastomers) can generally be defined as materials capable 30 of large elastic deformations and are often referred to as rubbers. Elastomers may be classified as vulcanizable elastomers, reactive system elastomers and thermoplastic elastomers. Some suitable elastomers include, for example, polyisoprene, polybutadiene, polychloroprene, polyisobutylene, styrene-butadiene rubber, acrylonitrile-butadiene rubber, ethylene-propylene rubber, ethylene-propylene-diene rubber, 35 chlorinated polyethylene, chlorosulfonated polyethylene, ethylene-vinylacetate copolymer,

ethylene-acrylate copolymer, fluoroelastomers (e.g., polyvinylidene fluoride, polychlorotrifluoroethylene), silicone polymers (e.g., polydimethylsiloxane), acrylic rubber, epichlorohydrin rubber, polysulfide rubbers, propyleneoxide rubbers, polynorbornene, polyorganophosphazenes, olefinic thermoplastic rubbers, styrenic thermoplastic rubbers, 5 urethane thermoplastic rubbers, etherester thermoplastic rubbers, etheramide thermoplastic rubbers, copolymers of an elastomer, or mixtures thereof.

Particularly preferred polymer matrices include, for example, homopolymers and copolymers of PP, PE, PET, PBT, PHA, PHB, PLA, PA, PS, PVC, PVF, PVA, PVAc, polybutadiene, polychloroprene, polyisobutylene, styrene-butadiene rubber, acrylonitrile-10 butadiene rubber, ethylene-propylene rubber, ethylene-propylene-diene rubber, chlorinated polyethylene, chlorosulfonated polyethylene, ethylene-vinylacetate copolymer, ethylene-acrylate copolymer, phenolformaldehyde, ligninformaldehyde, ureformaldehyde, melamine formaldehyde, epoxide, unsaturated polyester, vinylester, PU, polyisocyanurate, lignin, starch or mixtures thereof.

15 For thermoplastics, the number average molecular weight (M_n) of the polymer matrix may vary considerably depending on the specific type of polymer and the use to which the polymer composite is to be put. Preferably, the number average molecular weight is greater than about 500. Polymer matrices having a number average molecular weight of from about 1,300 to about 15,000,000 are suitable for a number of applications. 20 In one embodiment, the number average molecular weight may be from about 1,500 to about 2,000,000. In another embodiment, the number average molecular weight may be from about 1,500 to about 500,000.

25 Compatibility of the fire-resistant cellulosic material with the polymer matrix in a composite may be improved by treating the fire-resistant cellulosic material with a surfactant. The surfactant may improve compatibility through primary or secondary interactions between the fire-resistant cellulosic material and the polymer matrix. Where a layered nanoparticulate material is also employed, the fire-resistant cellulosic material may be treated with the surfactant before or after, preferably after, treatment with the layered nanoparticulate material. Suitable surfactants for a given case will depend on the 30 nature of the polymer matrix and the nature of the layered nanoparticulate material, if any, and are within the abilities of one skilled in the art to determine for any particular combination.

Surfactants generally comprise a functional group and a hydrocarbon chain. The functional group may be provided in the form of a positively charged ion (e.g. ammonium

or phosphonium ions) or a negatively charged ion (e.g. carboxylate, sulfonate or phenolate) depending on the charge availability on the surface. The hydrocarbon chain preferably comprises 1 or more carbon atoms, more preferably from 6 to 20,000 carbon atoms, even more preferably from 10 to 40 carbon atoms. Hydrocarbon chains may be
5 linear, branched or cyclic and may be substituted or unsubstituted. The surfactant may comprise one or more functional groups. The one or more functional groups interact with the clay surface and the polymer matrix and/or compatibilizer.

Some suitable surfactants include, for example, amines (e.g. dimethyldioctadecyl ammonium (DMDODA) salts, octadecyl amine (ODA) or its salts, trimethyloctadecyl ammonium salts, trimethylhexadecyl ammonium salts, dimethylhexadecyl amine or its salts, hexadecyl amine or its salts, dimethylbenzyloctadecyl ammonium salts, methyloctadecyldihydroxyethyl ammonium salts, methylamine or its salts, dimethylbenzyl amine or its salts, tribenzyl amine or its salts, glycine or its salts), di- and poly-functional amines (e.g. diethylenetriamine or its salts, ethylenediamine or its salts, Jeffamine™ T-
10 403 or its salts, Jeffamine™ D-2000 or its salts), alkanolamines (e.g. ethanolamine or its salts, triethanolamine or its salts), acids or carboxylates (e.g. lauric acid, palmitic acid, stearic acid, stearate, oleic acid, oleate, linoleic acid, linoleate, ricinoleic acid) or mixtures thereof.
15

Polymer composites may also include other suitable additives normally used in polymers. Such additives may be employed in conventional amounts and may be added directly to the process during formation of the polymer composite. Illustrative of such additives known in the art are processing aid agents, colorants, pigments, carbon black, fibers (glass fibers, carbon fibers, aramid fibers), fillers, impact modifiers, antioxidants, stabilizers, flame retardants, reheat aids, crystallization aids, acetaldehyde reducing
20 compounds, recycling release aids, oxygen scavengers, anti-UV agents, plasticizers, flexibilizers, nucleating agents, foaming agents, mold release agents, and the like, or their combinations.
25

The amounts of polymer matrix, fire-resistant cellulosic material and additives present in the polymer composite will depend on the particular use to which the polymer composite is put and the particular polymer matrix. The polymer matrix may be present in an amount from about 0.1 to about 99.9 weight percent based on the total weight of the polymer composite, or from about 20 to about 99 weight percent, or from about 40 to about 98 weight percent. The fire-resistant cellulosic material may be present in an amount from about 0.1 to about 99.9 weight percent based on the total weight of the
30

polymer composite, or from about 1 to about 80 weight percent, or from about 10 to about 60 weight percent.

Standard polymer processing techniques may be used to prepare the polymer composites of the present invention. Such techniques are generally known in the art
5 (Charrier 1991; Manas-Zloczower 1994; Rauwendaal 1998). Standard composite forming techniques may be used to fabricate products from the polymer composites of the present invention. For example, melt spinning, casting, vacuum molding, sheet molding, injection molding and extruding, melt blowing, spun bonding, blow molding, overmolding, compression molding, resin transfer molding (RTM), L-DFT, spraying, gel spinning,
10 thermo-forming, roll-forming and co- or multilayer extrusion may all be used.

Advantageously, the process of the present invention is less harmful to the environment due to the absence of halogen compounds, organic solvents and toxic chemicals while the cellulosic materials treated according to the present invention pose less health risk to animals and human than boron and phosphorous compounds. Self-
15 extinguishing cellulosic materials can be produced in accordance with the present invention using less harmful chemicals at significantly reduced concentrations. In addition, while the process involves the use of an aqueous mixture comprising a hydroxide and an alkaline earth or aluminum metal salt, and optionally a layered nanoparticulate material, fire resistance of the treated cellulosic material is not unduly
20 compromised even after washing the fire-resistant cellulosic material several times with water, which is a significant advantage compared to other traditional water soluble flame retardants based on boron or phosphorous compounds. In addition, fire-resistant cellulosic material according to the present invention and their polymer composites may also have improved mechanical properties, improved thermal stability, improved
25 interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents (e.g. bacteria, mold, fungi, termites and other insects) and/or improved resistance to damage by ultra-violet light. Overall, the present invention provides several improvements to fire-resistant cellulosic materials and their polymer composites, which have not been realized before.

30 Commercial applications for the present invention are extensive, including applications in the textile (e.g. cloth, tapis, matte), transportation, aerospace, marine, construction, household and agriculture industries. Fire-resistant cellulosic materials of the present invention may be used with commercially available polymer materials and existing conventional equipment, thereby reducing capital investment and investment risk

involved with the production of polymer composites. This opens new opportunities for cellulose composites in more demanding fields such as the aerospace industry.

Further features of the invention will be described or will become apparent in the course of the following detailed description.

5 Brief Description of the Drawings

In order that the invention may be more clearly understood, embodiments thereof will now be described in detail by way of example, with reference to the accompanying drawings, in which:

Fig. 1A depicts a graph comparing flexural modulus (GPa) of laminates prepared
10 by compression of various polypropylene (PP)-flax fiber composites; and,

Fig. 1B depicts a graph comparing flexural strength (MPa) of laminates prepared by compression of various polypropylene (PP)-flax fiber composites.

Description of Preferred Embodiments

Without being held to any particular mode of action, there may be one or more possible explanations for the efficacy of the present invention. It is currently believed that alkalinity of the aqueous reaction mixture causes the surface of the cellulosic material to swell and possibly generate anionic groups in the cellulosic material, possibly due to the reaction of the hydroxide with -CH₂OH groups of glucose and fructose units in the cellulose polymer. Alkaline earth metal or aluminum cations can then more easily penetrate the surface as the surface is swollen by alkalinity and the cations possibly form ionic bonds or otherwise interact with anions created by the hydroxide or with hydroxyl groups available on the fiber surface. Subsequent drying or heating then shrinks the surface of the cellulosic material further immobilizing the alkaline earth or aluminum metal on the cellulosic material. In this manner, a durable coating of alkaline earth or aluminum metal is formed on the cellulosic material giving rise to a self-extinguishing cellulosic material in which the coating is not easily washed off. In contrast, simply treating the cellulosic material with an alkaline earth metal salt or even an alkaline earth metal hydroxide that was pre-prepared does not lead to satisfactory self-extinguishing properties and the coating of alkaline earth metal is easily washed off eliminating what little effect the coating did have. Where a layered nanoparticulate material is employed, the layered nanoparticulate material may be attached chemically to the cellulosic material by ionic bonds (for example when montmorillonite (MMT) is used) or by strong van der

Waals interactions including hydrogen bonds (for example when a layered double hydroxide (LDH) is used). Layered double hydroxides are particularly preferred since they provide greater surface coverage. When a surfactant is used to improve compatibility of the fire-resistant cellulosic material with a polymer matrix, the surfactant can bind to the 5 surface of the layered nanoparticulate material.

Example 1: Materials

Table 1 provides a description of chemicals and Table 2 provides a description of the fibers used in the following examples.

10

Table 1 – Description of Chemicals

| Chemicals | Company | Purification |
|--|-----------------------------|--|
| CaCl ₂ .2H ₂ O | Fisher | - |
| Ca(NO ₃) ₂ .4H ₂ O | Aldrich | ≥ 99% |
| Ca(OH) ₂ | Aldrich | ≥ 96% |
| MgCl ₂ | Sigma Life Science | - |
| MgSO ₄ | Sigma-Aldrich | ≥ 99.5% |
| Mg(NO ₃) ₂ .6H ₂ O | Fluka | ≥ 99% |
| Mg(OH) ₂ | Alfa Aesar | 95-100.5% |
| NaOH | Aldrich | ≥ 98% |
| KOH | Sigma-Aldrich | ≥ 90% |
| Al(OH) ₃ | Aldrich | Reagent grade, Al ₂ O ₃ : 50-57% |
| AlCl ₃ | Sigma-Aldrich | 98% |
| NH ₄ OH | Sigma-Aldrich | ACS reagent, NH ₃ : 28-30% |
| BaCl ₂ | Fisher | Lab grade |
| BaCl ₂ .2H ₂ O | JTBaker Chemical | 100.5% |
| Ba(OH) ₂ | Aldrich | ~95% |
| Clay MMT | Southern Clay Products, Inc | Montmorillonite Cloisite Na™ clay (CEC: 92 meq/100 g) |
| Clay LDH | AkzoNobel | Layered Double Hydroxides (LDH)-anionic clay |

Table 2 – Description of Cellulosic Fibers

| Sample | Fiber | Weight (g/m ²) |
|--------|---|-------------------------------|
| C1 | Belgium flax fabric C 20M-2/2 twill from Moss Composites received in 2008. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 149 |
| C2 | Belgium flax fabric C 20M-2/2 twill from Moss Composites received in 2010. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 149 |
| C3 | Belgium flax fabric C10M-8H satin from Moss Composites received in 2010. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 258 |
| C4 | France unidirectional flax fiber Mutistrat MRCL1-180/17 UD 45° from Conseil Recherche Supstrats Textiles (CRST) received in 2010. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 180 |
| C5 | France bi-directional flax fiber Mutistrat MRL2-250/12 bi biais 2x45° from Conseil Recherche Supstrats Textiles (CRST) received in 2009. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 250 |
| C6 | Canada woven flax fabric from JBMatin received in 2010. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 240 |
| C7 | Hemp mat 1 supplied by CIC. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 350 |
| C8 | Hemp mat 2 supplied by CIC. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 500 |
| C9 | Paper 1CHR from Whatman received in 2008. | 85 |
| C10 | Cotton pad from Govmark for UL94 test received in 2009. | 210 |
| C11 | Belgium flax fabric C 007M twill from Moss Composites received in 2012. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 180 |

Example 2: General Procedure for Treatment of Fibers

Solution preparation:

In a single component solution, only one chemical is dissolved in demineralized water. For example, A2% means 2wt% of this chemical A in demineralized water.

5 In a single component suspension, only one mineral (e.g. clay) is dispersed in demineralized water. For example, X2% means 2wt% of mineral X in demineralized water.

In a bi-component solution or a bi-component suspension, separate solutions or suspensions of each of the two chemicals were prepared in an equal amount of
10 demineralized water and then they were mixed together. If both of the solutions could produce hydroxide product, the ratio of the amount of the chemicals in the first and the second solutions was calculated based on the assumption that the reaction between the chemicals in the first and the second solutions was quantitative to form the hydroxide without excess amount of any chemical left over. For example, (A+B)2% means 2wt% of
15 the hydroxide product produced by the reaction between A and B assuming that the reaction was quantitative without having any excess amount of A or B in the product. If the two systems could not produce hydroxide product the concentrations of the chemical in the first and the second solutions or suspensions were equal.

Treatment processes:

20 In one-step treatment processes (P1), about 10 g of cellulosic fiber was soaked in about 60 ml of a single component solution or a single component suspension or a bi-component solution for a period of time. The fibers were then dried in air for 6 hours and then in an oven at 120°C for 2 hours prior to testing.

25 Two types of two-step treatment processes (P2-1 and P2-2) were used. In P2-1, 10 g of cellulosic fiber was soaked in about 60 ml of a single component solution or a single component suspension or a bi-component solution or a bi-component suspension for 5 to 300 seconds. The fibers were then removed from the treating medium and allowed to dry in air for 6 hours, and then dried in an oven at 120°C for 2 hours. The dried fibers were then soaked in about 60 ml of another single component solution or a single
30 component suspension or a bi-component solution or a bi-component suspension for 5 to 300 seconds. Finally the fibers were dried in air for 6 hours and then in an oven at 120°C

for 2 hours prior to testing. The concentrations of the first and the second solutions or suspensions were equal.

In P2-2, 10 g of cellulosic fiber was soaked in about 30 ml of a single component solution or a single component suspension or a bi-component solution or a bi-component suspension for 5 to 300 seconds. Then, about 30 ml of another single component solution or a single component suspension or a bi-component solution or a bi-component suspension was added into the system and mixed. The fibers were soaked for 5 to 300 seconds then removed them from the treating medium. Finally the fibers were dried in air for 6 hours, and then in an oven at 120°C for 2 hours prior to testing.

10 *Example 3: General Procedure for Preparation of Fiber/Polymer Composite Plaques*

For fiber/phenolic resin composites, fibers were dried in an oven at 120°C for about 2 hours to remove humidity before use. Phenolic resin was then wetted on the fibers and dried in an oven to remove solvent from the resin and to let the resin transfer to stage B before compression. Wabash PC 100-2418-2TM compression was used to fabricate the composites under 100 psi pressure at 150°C. The amounts of polymer and fiber in the final product were about 60 wt% and 40 wt%, respectively. The thickness of the composite plaque was about 3 mm.

For fiber/polypropylene composites, fibers were dried in an oven at 120°C for about 2 hours to remove humidity before use. Laminate composites were prepared with Basell Profax 1274 PCD by compression molding with Wabash PC 100-2418-2TM under 100 psi pressure at 190°C. The amounts of polymer and fiber used were about 60 wt% and 40 wt%, respectively. The thickness of the composite plaque was about 3 mm.

For fiber/epoxy composites, fibers were dried in an oven at 120°C for about 2 hours to remove humidity before use. Laminate composites were prepared with Shell Epon 828 by compression molding with Wabash PC 100-2418-2TM under 100 psi pressure at 80°C. The amounts of polymer and fiber used were about 60 wt% and 40 wt%, respectively. The thickness of the composite plaque was about 3 mm.

For fiber/unsaturated polyester (UPE) composites, fibers were dried in an oven at 120°C for about 2 hours to remove humidity before use. Laminate composites with Progress RL 2710 resin were prepared by compression molding with Wabash PC 100-2418-2TM under 100 psi pressure at 50°C. The amounts of polymer and fiber used were about 70 wt% and 30 wt%, respectively. The thickness of the composite plaque was about 3 mm. The UPE resin contains 20 wt% alumina trihydrate Hubert SB332.

Example 4: General Procedure for Burning Tests

A Govmark UL94 and vertical chamber were used to conduct burning tests. For each example, results are provided using numbers and the terms "NB" and "G". The term "NB" means "no burning" and is an indication that there was no flame and no glow after removing the flame. "NB" represents excellent fire resistance as the sample did not continue to burn appreciably after the external flame source was removed, thus the sample was self-extinguishing. The term "NB/B" means that some fiber did not burn and that some fiber did burn. The term "G" means "glow" and is an indication that the sample continued to glow after removal of the flame. The numbers are the time in seconds that the sample continued to glow after removal of the flame.

UL94 Horizontal Burning Test (HB):

For fiber samples, five specimens having width x length (WxL) of 0.5x6.0 inch (12.7x152.4 mm) were cut from bulk fiber. Specimens were held at one end in a horizontal position and tilted at 45° with marks at 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 inch from the free end. A flame was applied to the free end of the specimen for 30 seconds or until the flame front reached the 1 inch mark. If combustion continued, the duration was timed between each 0.5 inch mark. A thin metallic wire was inserted to support the specimen.

For polypropylene, epoxy and unsaturated polyester (UPE) composite samples, five specimens having width x length (WxL) of 0.5x6.0 inch (12.7x152.4 mm) were cut from the 3 mm thick composite plaque prepared as described in Example 3. Specimens were held at one end in a horizontal position and tilted at 45° with marks at 1, 2.0, 3.0, 4.0, 5.0 inch from the free end. A flame was applied to the free end of the specimen for 30 seconds or until the flame front reached the 1 inch mark. If combustion continued, the duration was timed between each 1.0 inch mark.

UL94 Vertical Burning Test (VB):

For phenol formaldehyde composite samples, five specimens having width x length (WxL) of 0.5x6.0 inch (12.7x152.4 mm) were cut from the 3 mm thick composite plaque prepared as described in Example 3. Specimens were held at one end in the vertical position. The flame was applied for ten seconds and then removed until flaming stopped, at which time the flame was reapplied for another ten seconds and then removed. The combustion time and burning length were recorded.

Vertical Burning Test (VC-2):

For phenol formaldehyde composite samples, three specimens having width x length (WxL) of 3x12 inch (76.2x304.8 mm) were cut from the 3 mm thick composite plaque prepared as described in Example 3. Specimens were held at one end in the vertical position. The flame was applied for sixty seconds and then removed until flaming stopped. The combustion time and burning length was recorded. If the specimen has burning length and burning time less than 8 inch and 15 seconds, respectively, it is considered to be passed the standard (self-extinguished).

Example 5: General Procedure for Mechanical Tests**10 Fibers:**

Tensile tests on fibers were conducted on a tow (strand) disassembled from the fabric. The tows in the longitudinal direction in the fabric were separated from the ones in the orthogonal direction. Tests were carried out for both series separately. The tensile properties of the fiber tow were determined at room temperature and 50% relative humidity on an Instron 5548 micro-tester machine, with crosshead distance of 50 mm and speeds of 120 mm/min. The maximum load at break was recorded for each specimen. A minimum 10 specimens were tested for each type of sample.

Composites:

The tensile properties of the composites were determined at room temperature and 50% relative humidity on an Instron 5500R machine, with crosshead speeds of 5 mm/min according to ASTM 3039-00. A minimum 5 specimens were tested for each type of sample.

Example 6: Fibers Treated with Single Component Solutions - Comparative

Belgium flax fiber samples C1 as described in Table 2 were treated with different single component solutions as indicated in Table 3 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 3. It is evident from Table 3 that all of the C1 fibers treated with various single component systems are not self-extinguishing, although these treatments slowed down flame propagation.

30 Belgium flax fiber samples C2 as described in Table 2 were treated with different single component systems as indicated in Table 4 for 120 s using the process P1.

Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 4. It is evident from Table 4 that all of the fibers treated with a single component system, including a barium hydroxide system (C1-6/P1), are not self-extinguishing. Fibers treated with NaOH or KOH did not continue to burn but did continue to glow. Fibers treated with NaOH and then washed with water did continue to burn, demonstrating that any fire resistant effect afforded by an alkali metal hydroxide alone is easily removed if the fibers get wet.

Collectively, Tables 3 and 4 demonstrate that single component systems of metal hydroxides, metal salts or clays do not impart self-extinguishing properties on fibers treated with the systems.

Table 3 - C1 Fibers Treated with Single Component Solutions

| Sample | Description | Burning Length (inches) | | | | | | |
|---------|--|-------------------------|-----|-----|-----|-----|-----|-----|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 |
| | | Burning Time (seconds) | | | | | | |
| C1 | Untreated C1 | 3 | 7 | 10 | 14 | 17 | 21 | 25 |
| C1-1/P1 | C1+clay MMT2%/P1 | 5 | 9 | 14 | 18 | 22 | 26 | 31 |
| C1-2/P1 | C1+clay MMT4%/P1 | 5 | 9 | 14 | 18 | 22 | 27 | 31 |
| C1-3/P1 | C1+clay LDH2%/P1 | 5 | 9 | 14 | 20 | 25 | 30 | 34 |
| C1-4/P1 | C1+clay LDH4%/P1 | 6 | 13 | 19 | 25 | 30 | 38 | 44 |
| C1-5/P1 | C1+(BaCl ₂)2%/P1 | 4 | 7 | 11 | 15 | 18 | 22 | 26 |
| C1-6/P1 | C1+(Ba(OH) ₂)2% | 5 | 8 | 14 | 18 | 23 | 27 | 32 |
| C1-7/P1 | C1+(BaCl ₂)2% then washed with water | 4 | 7 | 10 | 14 | 17 | 21 | 25 |
| C1-8/P1 | C1+(Ba(OH) ₂)2% then washed with water | 5 | 8 | 14 | 18 | 22 | 26 | 31 |

Table 4 - C2 Fibers Treated with Single Component Solutions

| Sample | Description | Burning Length (inches) | | | | | | | | |
|--------------------------------|------------------------------------|-------------------------|-----|-----|------|------|------|------|------|-------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| Average Burning Time (seconds) | | | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-1/P1 | C2+(Ba(OH) ₂)2% | 3.2 | 6.1 | 8.9 | 11.9 | 15 | 17.6 | 20.4 | 23.3 | 26.5 |
| C2-2/P1 | C2+(BaCl ₂)2% | 2.3 | 5.0 | 7.1 | 9.1 | 11.0 | 13.3 | 15.3 | 17.5 | 19.8 |
| C2-3/P1 | C2+(BaCl ₂)2% twice | 4.0 | 7.3 | 9.8 | 12.6 | 14.7 | 17.8 | 20.1 | 22.4 | 25.2 |
| C2-4/P1 | C2+(MgNO ₃)2% | 2.3 | 4.8 | 7.1 | 9.4 | 11.4 | 14.0 | 16.0 | 18.1 | 20.3 |
| C2-5/P1 | C2+(MgCl ₂)2% | 3.7 | 6.1 | 8.8 | 11.7 | 15.3 | 18.2 | 21.7 | 24.6 | 27 |
| C2-6/P1 | C2+(MgSO ₄)2% | 2.6 | 5.2 | 7.3 | 9.5 | 11.5 | 14.0 | 16.2 | 18.1 | 19.5 |
| C2-7/P1 | C2+(Mg(OH) ₂)2% | 3.0 | 6.2 | 8.2 | 10.1 | 12.1 | 14.6 | 16.4 | 18.8 | 20.6 |
| C2-8/P1 | C2+(Ca(NO ₃)2% | 2.6 | 4.8 | 7.0 | 8.7 | 10.9 | 12.6 | 14.6 | 16.3 | 18.1 |
| C2-9/P1 | C2+(CaCl ₂)2% | 2.8 | 5.1 | 7.5 | 9.5 | 11.6 | 14.3 | 16.6 | 19.0 | 21.0 |
| C2-10/P1 | C2+(KOH)2% | G | G | G | G | G | G | G | G | G-250 |
| C2-11/P1 | C2+(NaOH)2% | G | G | G | G | G | G | G | G | G-250 |
| C2-12/P1 | C2+(NaOH)2% twice | G | G | G | G | G | G | G | G | G-280 |
| C2-13/P1 | C2+(NaOH)2% then washed with water | 2.8 | 5.5 | 7.7 | 10.0 | 12.5 | 14.5 | 17.0 | 19.7 | 22.0 |
| C2-14/P1 | C2+(AlCl ₃)2% | 3.6 | 6.5 | 9.2 | 12.3 | 15.4 | 18.4 | 21.3 | 24.8 | 27.8 |
| C2-15/P1 | C2+(Al(OH) ₃)2% | 2.8 | 5.3 | 7.8 | 10.2 | 11.8 | 14.7 | 16.6 | 18.6 | 20.9 |

*Example 7: Fibers Treated with Bi-component Solutions**C1 Fibers Treated with Barium-containing Bi-component Systems:*

5 Belgium flax fiber samples C1 as described in Table 2 were treated with different barium-containing bi-component systems as indicated in Table 5 for 120 s using the processes P1 and P2-1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 5. It is evident from Table 5 that all of the C1 fibers treated with bi-component systems involving the mixture of barium chloride and sodium hydroxide are self-extinguishing. Fibers treated with barium chloride alone then with clay or barium hydroxide alone then with clay are not self-extinguishing. Thus, single component systems are not self-extinguishing, even with the subsequent addition of clay. A mixture of both the alkaline metal salt and the alkali metal hydroxide is needed to make the fibers self-extinguishing. It is further clear that washing the fibers after treatment with a bi-component system does not remove the self-extinguishing properties imparted by the

10

15

treatment. Further, the order in which clay is introduced into the bi-component does not affect the self-extinguishing properties of the fibers after treatment.

Table 5 - C1 Fibers Treated with Barium-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | |
|------------|---|-------------------------|-----|-----|-----|-----|-----|-----|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 |
| | | Burning Time (seconds) | | | | | | |
| C1 | Untreated C1 | 3 | 7 | 10 | 14 | 17 | 21 | 25 |
| C1-9/P2-1 | C1+(BaCl ₂)2% then +clay MMT2% | 4 | 8 | 13 | 17 | 21 | 26 | 31 |
| C1-10/P2-1 | C1+(Ba(OH) ₂)2% then +clay LDH2% | 5 | 11 | 15 | 20 | 25 | 30 | 35 |
| C1-11/P1 | C1+(BaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB |
| C1-12/P1 | C1+(BaCl ₂ +NaOH)2% then washed with water | NB | NB | NB | NB | NB | NB | NB |
| C1-13/P2-1 | C1+(BaCl ₂ +NaOH)2% then +clay MMT2% | NB | NB | NB | NB | NB | NB | NB |
| C1-14/P2-1 | C1+(BaCl ₂ +NaOH)2% then +clay LDH2% | NB | NB | NB | NB | NB | NB | NB |
| C1-15/P2-1 | C1+clay MMT2% then +(BaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB |
| C1-16/P2-1 | C1+clay LDH2% then +(BaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB |

5 C2 Fibers Treated with a Barium-containing Bi-component System:

Nine different specimens of Belgium flax fiber samples C2 as described in Table 2 were treated with one barium-containing bi-component systems as indicated in Table 6 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 6. It is evident from Table 6 that fiber quality is not always consistent even in the same batch, and that fire resistance behavior of fibers treated with a bi-component system (BaCl₂+NaOH)2% can vary from specimen to specimen. Some specimens are self-extinguishing while others are not, although they were all treated at the same time.

Table 6 - C2 Fibers Treated with a Barium-containing Bi-component System

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|---|-------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-16/P1 | C2+(BaCl ₂ +NaOH)2% specimen 1 | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| | C2+(BaCl ₂ +NaOH)2% specimen 2 | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| | C2+(BaCl ₂ +NaOH)2% specimen 3 | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| | C2+(BaCl ₂ +NaOH)2% specimen 4 | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| | C2+(BaCl ₂ +NaOH)2% specimen 5 | 5.0 | 8.5 | 11.0 | 13.5 | 16.5 | 19.5 | 22.0 | 26.0 | 31.0 |
| | C2+(BaCl ₂ +NaOH)2% specimen 6 | 4.5 | 10.5 | 14.5 | 18.5 | 21.5 | 27.5 | 31.5 | 35.5 | 39.5 |
| | C2+(BaCl ₂ +NaOH)2% specimen 7 | 4.0 | 8.5 | 11.5 | 14.5 | 18.5 | 22.5 | 26.5 | 30.0 | 34.0 |
| | C2+(BaCl ₂ +NaOH)2% specimen 8 | 4.5 | 8.5 | 11.0 | 14.0 | 17.5 | 21.0 | 24.5 | 27.0 | 31.5 |
| | C2+(BaCl ₂ +NaOH)2% specimen 9 | 5.0 | 8.5 | 11.5 | 14.5 | 18.5 | 21.0 | 24.5 | 28.5 | 32 |

C2 Fibers Treated with a Calcium-containing Bi-component System at Different Treatment Periods:

- 5 Belgium flax fiber samples C2 as described in Table 2 were treated with calcium-containing bi-component systems as indicated in Table 7 for different treatment periods from 5-300 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 7. It is evident from Table 7 that fibers treated with bi-component system
10 (CaCl₂+NaOH)2% at different treatment periods (5-300 s) are all self-extinguishing. Further, the (CaCl₂+NaOH)2% system appears to have greater tolerance to cellulosic fiber quality than the (BaCl₂+NaOH)2% system (compare Table 6 to Table 7).

Table 7 - C2 Fibers Treated with a Calcium-containing Bi-component System at Different Treatment Periods

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|---|-------------------------|-----|-----|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-17/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 5s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-18/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 10s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-19/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 30s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-20/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 60s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-21/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 120s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-22/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 180s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-23/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 300s | NB | NB | NB | NB | NB | NB | NB | NB | NB |

C2 Fibers Treated with a Calcium-containing Bi-component System at Different

5 *Concentrations:*

Belgium flax fiber samples C2 as described in Table 2 were treated with one calcium-containing bi-component systems at different concentrations from 1 wt% to 3 wt% of the hydroxide product of the alkaline metal salt and alkali metal hydroxide as indicated in Table 8 for 120 s using the process P1. Burning tests were conducted in 10 accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 8. It is evident from Table 8 that to obtain self-extinguishing fibers treated with the bi-component system (CaCl₂+NaOH) for 120s using the process P1, the minimum concentration must be 1.5%.

Table 8 - C2 Fibers Treated with a Calcium-containing Bi-component System at Different Concentrations

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|----------------------------------|-------------------------|-----|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-24/P1 | C2+(CaCl ₂ +NaOH)1% | 4.0 | 7.6 | 11.5 | 13.9 | 17.0 | 20.0 | 23.2 | 25.7 | 28.4 |
| C2-25/P1 | C2+(CaCl ₂ +NaOH)1.5% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-21/P1 | C2+(CaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-26/P1 | C2+(CaCl ₂ +NaOH)3% | NB | NB | NB | NB | NB | NB | NB | NB | NB |

C2 Fibers Treated with Magnesium-containing Bi-component Systems at Different

5 *Concentrations:*

Belgium flax fiber samples C2 as described in Table 2 were treated with magnesium sulfate-containing bi-component systems at 1 wt% and 2 wt% of the hydroxide product of the alkaline metal salt and alkali metal hydroxide as indicated in Table 9 for 120 s using the process P1. Burning tests were conducted in accordance with 10 the general procedure described in Example 4 and the results from the burning tests are also shown in Table 9.

Table 9 - Fibers Treated with a Magnesium Sulfate-containing Bi-component System at Different Concentrations

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|------------------------------------|-------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-27/P1 | C2+ (MgSO ₄ +NaOH)1% | 4.4 | 8.3 | 11.6 | 14.6 | 18.3 | 21.8 | 25.6 | 28.7 | 32.3 |
| C2-28/P1 | C2+ (MgSO ₄ +NaOH)2% | 5.1 | 10.6 | 14.6 | 19.5 | 24.7 | 29.5 | 33.7 | 38.7 | 43.4 |

15 Belgium flax fiber samples C2 as described in Table 2 were treated with magnesium chloride-containing bi-component systems at 1 wt% and 2 wt% of the hydroxide product of the alkaline metal salt and alkali metal hydroxide as indicated in Table 10 for 120 s using the process P1. Burning tests were conducted in accordance

with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 10.

Table 10 - Fibers Treated with a Magnesium Chloride-containing Bi-component System at Different Concentrations

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|------------------------------------|-------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-29/P1 | C2+ (MgCl ₂ +NaOH)1% | 5.1 | 11.0 | 15.2 | 19.3 | 24.0 | 30.4 | 34.7 | 39.9 | 47.0 |
| C2-30/P1 | C2+ (MgCl ₂ +NaOH)2% | 7.0 | 14.0 | NB |

5

It is evident from Table 9 that all fibers treated with the (MgSO₄+NaOH) system burned at a slower rate than the untreated one but they are not self-extinguishing. From Table 10, it is evident that fibers are self-extinguishing after treatment with the bi-component system (MgCl₂+NaOH) for 120s using the process P1 at 2.0% solution, but 10 not for the 1.0% solution. Thus, (MgCl₂+NaOH) is more effective than the (MgSO₄+NaOH). Therefore, sulfate is not as good a counter anion in the alkaline metal salt as chloride.

C2 Fibers Treated with NaOH and CaCl₂ or NaOH and Clay

Belgium flax fiber samples C2 as described in Table 2 were treated sequentially 15 with calcium chloride and sodium hydroxide in different orders as indicated in Table 11 for 120 s using the process P2-2. Likewise, C2 fibers were treated with sodium hydroxide and then clay as indicated in Table 11 for 120 s using the process P2-2. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 11. It is evident from Table 11 20 that fibers treated first with NaOH and then with CaCl₂ are self-extinguishing, but this is not the case for the reverse order although the burning time is slower when compared to untreated fiber. Further, fibers treated with a 2.0% solution of NaOH and then a 2.0% suspension of MMT clay are not self-extinguishing but the burning time is slower when compared to untreated fiber.

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Table 11 - Fibers Treated with NaOH and CaCl₂ or NaOH and Clay

| Sample | Description | Burning Length (inches) | | | | | | | | |
|------------|--|-------------------------|-----|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-31/P2-2 | (C2+NaOH) then add CaCl ₂ | G 125 | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-32/P2-2 | (C2+CaCl ₂) then add NaOH | 4.4 | 8.4 | 12.6 | 15.2 | 17.8 | 20.6 | 22.6 | 25.0 | 28.0 |
| C2-33/P2-2 | C2+(NaOH)2% then add clay MMT2% | 4.1 | 7.6 | 10.6 | 13.5 | 16.6 | 19.9 | 22.9 | 25.7 | 29.0 |

C2 Fibers Treated with Different Aluminum-containing Bi-component Systems

Belgium flax fiber samples C2 as described in Table 2 were treated with aluminum chloride-containing bi-component systems at different concentrations (0.75-2 wt%) of the hydroxide product of the aluminum salt and hydroxide as indicated in Table 12 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 12. It is evident from Table 12 that aluminum chloride together with ammonium hydroxide at a concentration of 0.75% or more resulted in fibers that were self-extinguishing, but this is not the case with aluminum chloride with sodium hydroxide, although the rate of burning was slowed relative to untreated fibers.

Table 12 - Fibers Treated with Aluminum-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|---|-------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-34/P1 | C2+ (AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-35/P1 | C2+ (AlCl ₃ +NH ₄ OH)1.5% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-36/P1 | C2+ (AlCl ₃ +NH ₄ OH)1.0% | G | NB |
| C2-37/P1 | C2+ (AlCl ₃ +NH ₄ OH)0.75% | G 7.9 | NB |
| C2-38/P1 | C2+ (AlCl ₃ +NaOH)0.5% | 3.2 | 6.7 | 11.1 | NB/B | NB/B | NB/B | NB/B | NB/B | NB/B |
| C2-39/P1 | C2+ (AlCl ₃ +NaOH)2% | 6.7 | 12.9 | 16.9 | 20.4 | 24.6 | 28.7 | 32.7 | 36.4 | 40.0 |

C2 Fibers Treated with Bi-component Systems Containing Different Magnesium and Calcium Salts

Belgium flax fiber samples C2 as described in Table 2 were treated with bi-component systems containing different magnesium and calcium salts at 2 wt% of the hydroxide product of the alkaline earth metal salt and hydroxide as indicated in Table 13 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 13. It is evident from Table 13 that fibers treated with $(\text{MgCl}_2+\text{NaOH})2\%$ and with $(\text{CaCl}_2+\text{NaOH})2\%$ are self-extinguishing. Fibers treated with $(\text{Mg}(\text{NO}_3)_2+\text{NaOH})2\%$ and with $(\text{Ca}(\text{NO}_3)_2+\text{NaOH})2\%$ did not burn but continued to glow. Fibers treated with $(\text{MgSO}_4+\text{NaOH})2\%$ continued to burn, but at a slower rate than untreated fibers. The efficiency of the $(\text{MgCl}_2+\text{NaOH})2\%$ system is greater than the $(\text{Mg}(\text{NO}_3)_2+\text{NaOH})2\%$ system, which is greater than the $(\text{MgSO}_4+\text{NaOH})2\%$ system. This is also similar for the calcium-containing systems where the efficiency of the $(\text{CaCl}_2+\text{NaOH})2\%$ system is greater than the $(\text{Ca}(\text{NO}_3)_2+\text{NaOH})2\%$ system. Thus, chloride is the most preferred counter anion for the alkaline earth metal cation.

Table 13 - Fibers Treated with Mg- and Ca-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|--|-------------------------|------|------|------|------|------|------|------|------------------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-30/P1 | C2+ $(\text{MgCl}_2+\text{NaOH})2\%$ | 7.0 | 14.0 | NB |
| C2-40/P1 | C2+ $(\text{Mg}(\text{NO}_3)_2+\text{NaOH})2\%$ | G | G | G | G | G | G | G | G | G 180- 260 |
| C2-28/P1 | C2+ $(\text{MgSO}_4+\text{NaOH})2\%$ | 5.1 | 10.6 | 14.6 | 19.5 | 24.7 | 29.5 | 33.7 | 38.7 | 43.4 |
| C2-21/P1 | C2+ $(\text{CaCl}_2+\text{NaOH})2\%$ | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-41/P1 | C2+ $(\text{Ca}(\text{NO}_3)_2+\text{NaOH})2\%$ | G | G | G | G | G | G | G | G | G 50- 300 |

Different Fibers Treated with a Calcium-containing Bi-component Systems

Various fiber samples C2, C3, C4 and C7 as described in Table 2 were treated with a calcium-containing bi-component systems as indicated in Table 14 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure 5 described in Example 4 and the results from the burning tests are also shown in Table 14. It is evident from Table 14 that all of the fibers were self-extinguishing after treatment with the (CaCl₂+NaOH)2% system.

Table 14 - Different Fibers Treated with a Calcium-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|--------------------------------|--|------------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-21/P1 | C2+(CaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C3 | Untreated C3 | 4.6 | 8.5 | 12.0 | 15.5 | 19.0 | 22.9 | 26.6 | 30.2 | 34.1 |
| C3-1/P1 | C3+(CaCl ₂ +NaOH)2% | G 20-85 | G 20-85 | NB |
| C4 | Untreated C4 | Burned fast and whole sample was fired | | | | | | | | 12 |
| C4-1/P1 | C4+(CaCl ₂ +NaOH)2% | NB-G 10-15 | NB | NB | NB | NB | NB | NB | NB | NB |
| C7 | Untreated C7 | 2.9 | 5.7 | 8.0 | 10.0 | 12.4 | 14.8 | 17.2 | 19.6 | 22.6 |
| C7-1/P1 | C7+(CaCl ₂ +NaOH)2% | G 25-80 | NB | NB | NB | NB | NB | NB | NB | NB |

10 *Different Fibers Treated with a Magnesium-containing Bi-component Systems*

Various fiber samples C2, C3, C4, C6 and C7 as described in Table 2 were treated with a magnesium-containing bi-component systems as indicated in Table 15 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown 15 in Table 15. It is evident from Table 15 that all of the fibers were self-extinguishing after treatment with the (MgCl₂+NaOH)2% system. Taken together, Tables 14 and 15 show that the treatments are useful across a range of cellulosic materials.

Table 15 - Different Fibers Treated with a Magnesium-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|------------------------------------|--------------------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-30/P1 | C2+ (MgCl ₂ +NaOH)2% | 7.0 | 14.0 | NB |
| C3 | Untreated C3 | 4.6 | 8.5 | 12.0 | 15.5 | 19.0 | 22.9 | 26.6 | 30.2 | 34.1 |
| C3-2/P1 | C3+ (MgCl ₂ +NaOH)2% | G 80-110 | NB |
| C4 | Untreated C4 | Burn fast and whole sample was fired | | | | | | | | 12 |
| C4-2/P1 | C4+ (MgCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C6 | Untreated C6 | 2.6 | 4.8 | 6.7 | 8.4 | 10.3 | 12.0 | 13.9 | 15.6 | 18.0 |
| C6-2/P1 | C6+ (MgCl ₂ +NaOH)2% | G 35-215 | NB |
| C7 | Untreated C7 | 2.9 | 5.7 | 8.0 | 10.0 | 12.4 | 14.8 | 17.2 | 19.6 | 22.6 |
| C7-2/P1 | C7+ (MgCl ₂ +NaOH)2% | G 20-70 | NB |

Different Fibers Treated with an Aluminum-containing Bi-component Systems

Various fiber samples C2-C11 as described in Table 2 were treated with an aluminum-containing bi-component systems as indicated in Table 16 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 16. It is evident from Table 16 that all of the fibers were self-extinguishing after treatment with the (AlCl₃+NH₄OH)2% system. Taken together, Tables 14, 15 and 16 show that the treatments are useful across a range of cellulose materials.

Table 16 - Different Fibers Treated with an Aluminum-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|---|--------------------------------------|-----|------|------|------|------|------|------|-------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-34/P1 | C2+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C3 | Untreated C3 | 4.6 | 8.5 | 12.0 | 15.5 | 19.0 | 22.9 | 26.6 | 30.2 | 34.1 |
| C3-3/P1 | C3+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C4 | Untreated C4 | Burn fast and whole sample was fired | | | | | | | | 12 |
| C4-3/P1 | C4+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C5 | Untreated C5 | Whole sample was fired | | | | | | | | 40 |
| C5-3/P1 | C5+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C6 | Untreated C6 | 2.6 | 4.8 | 6.7 | 8.4 | 10.3 | 12.0 | 13.9 | 15.6 | 18.0 |
| C6-3/P1 | C6+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C7 | Untreated C7 | 2.9 | 5.7 | 8.0 | 10.0 | 12.4 | 14.8 | 17.2 | 19.6 | 22.6 |
| C7-3/P1 | C7+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C8 | Untreated C8 | Burn fast and whole sample was fired | | | | | | | | 10-15 |
| C8-3/P1 | C8+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C9 | Untreated C9 | 1.9 | 3.7 | 5.4 | 6.8 | 8.5 | 10.2 | 11.8 | 13.0 | 14.2 |
| C9-3/P1 | C9+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C10 | Untreated C10 | Burn fast and whole sample was fired | | | | | | | | 7.6 |
| C10-3/P1 | C10+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C11 | Untreated C11 | 4.5 | 9.7 | 15.3 | 20.7 | 26.3 | 31.8 | 38.2 | 43.3 | 48.7 |
| C11-3/P1 | C11+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |

Example 8: Tensile Properties of Fiber Tows

Tensile properties of untreated Belgium flax fiber samples C2 as described in
5 Table 2 and of various treated C2 fiber samples were measured in accordance with the procedure described in Example 5. Table 16 lists the fiber tows that were tested as well

as their tensile properties. The tows in the longitudinal direction in the fabric are denoted as parallel, whereas the ones in the orthogonal direction are denoted as perpendicular.

It is evident from Table 17 that the tensile properties did not change much for most of the systems indicating that treatment did not generally have a detrimental effect 5 on tensile properties. However, for fibers treated with alkali metal hydroxide alone (e.g. (KOH)2% and (NaOH)2%) or treated with aluminum-containing salt (e.g. (AlCl₃+NH₄OH)2%), there is a significant loss in tensile properties. It is clear, therefore, that cellulosic materials treated with both alkaline earth metal salt and alkali metal hydroxide are advantageously very fire retardant, often self-extinguishing, while retaining 10 good tensile properties, in contrast to fibers treated only with alkali metal hydroxide or treated with another metal salt. Drying at lower temperature of 100°C could help to maintain the tensile properties of the fiber treated with (AlCl₃+NH₄OH)2%).

Table 17 – Tensile Strength of Tows of Treated C2 Fibers

| Fiber | Description | Tensile Properties | |
|--------------------------|---|--------------------|---------------|
| | | Parallel | Perpendicular |
| C2 | Untreated C2 | 20.4 ± 3.3 | 23.8 ± 4.1 |
| C2-1/P1 | C2+(Ba(OH) ₂)2% | 21.7 ± 3.2 | 24.1 ± 4.4 |
| C2-2/P1 | C2+(BaCl ₂)2% | 21.1 ± 3.1 | 25.1 ± 2.9 |
| C2-7/P1 | C2+Mg((OH) ₂)2% | 19.2 ± 3.4 | 23.6 ± 2.7 |
| C2-10/P1 | C2+(KOH)2% | 15.8 ± 2.1 | 20.2 ± 2.9 |
| C2-11/P1 | C2+(NaOH)2% | 15.8 ± 1.4 | 19.0 ± 2.6 |
| C2-13/P1 | C2+(NaOH)2% then washed with water | 13.2 ± 1.9 | 18.4 ± 4.8 |
| C2-15/P1 | C2+(Al(OH) ₃)2% | 22.8 ± 1.8 | 23.6 ± 2.7 |
| C2-21/P1 | C2+(CaCl ₂ +NaOH)2% | 19.5 ± 3.4 | 24.9 ± 3.1 |
| C2-28/P1 | C2+(MgSO ₄ +NaOH)2% | 23.0 ± 3.6 | 25.8 ± 3.3 |
| C2-30/P1 | C2+(MgCl ₂ +NaOH)2% | 21.3 ± 3.2 | 23.7 ± 3.2 |
| C2-31/P2-2 | (C2+NaOH) then add CaCl ₂ | 23.0 ± 2.6 | 27.4 ± 3.9 |
| C2-32/P2-2 | (C2+CaCl ₂) then add NaOH | 22.4 ± 3.2 | 24.2 ± 3.4 |
| C2-34/P1 | C2+(AlCl ₃ +NH ₄ OH)2% | 16.9 ± 1.6 | 16.0 ± 1.5 |
| C2-34/P1 dry at 100°C | C2+(AlCl ₃ +NH ₄ OH)2% dried at 100°C | 24.1 ± 0.6 | 24.1 ± 5.9 |
| C2-40/P1 | C2+(Mg(NO ₃) ₂ +NaOH)2% | 23.8 ± 3.5 | 25.5 ± 4.7 |
| C2-41/P1 | C2+(Ca(NO ₃) ₂ +NaOH)2% | 24.4 ± 3.8 | 24.8 ± 3.9 |

*Example 9: Properties of Fire-resistant Flax Fiber/Polymer Composites**Phenol formaldehyde (PF)/flax fiber composites*

Phenol formaldehyde/flax fiber composites were prepared as indicated in Table 18 in accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 60% and 40% by weight, respectively. UL94 vertical burning tests were conducted in accordance with the procedure described in Example 4, and the results are shown in Table 18. Sample PF-C1 is a comparative example of a PF composite containing untreated flax fiber. PF-C1-1/P1 and PF-C1-3/P1 are comparative examples of PF composites containing flax fibers treated two different clays. PF-C1-11/P1 is an example of a PF composite of the present invention containing flax fibers treated with a bi-component barium-containing system. PF-C1-13/P2-1 is an example of a PF composite of the present invention containing flax fibers treated with a bi-component barium-containing system and then clay.

In this example, burning time is the time it takes for the sample to self-extinguish after the external flame is removed. Thus, a shorter burning time is indicative of a more fire resistant sample. Phenol formaldehyde is a phenolic thermoset resin which itself has considerable resistance to fire. Because of the fire resistance of phenol formaldehyde, it is the flax fiber that primarily burns during the burning test. As is evident from Table 18, fire-resistant flax fibers of the present invention provide a tremendously significant greater resistance to burning in the phenol formaldehyde matrix than untreated flax fibers or flax fibers treated just with clays. The fire-resistance effect is particularly pronounced when the flax fibers are treated with both an aqueous mixture of BaCl₂ and NaOH and an aqueous suspension of clay (PF-C1-13/P2-1).

Table 18 - Phenol Formaldehyde/Flax Fiber Composites

| Sample | Composition | Burn Time (s) 5 inch length |
|---------------|--|--------------------------------|
| PF-C1 | Phenol formaldehyde matrix Flax fabric C1 (untreated) | 118 |
| PF-C1-1/P1 | Phenol formaldehyde matrix Flax fabric C1-1/P1 (C1+clay MMT2%) | 119 |
| PF-C1-3/P1 | Phenol formaldehyde matrix Flax fabric C1-3/P1 (C1+clay LDH2%) | 101 |
| PF-C1-11/P1 | Phenol formaldehyde matrix Flax fabric C1-11/P1 (C1+(BaCl ₂ +NaOH)2%) | 74 |
| PF-C1-13/P2-1 | Phenol formaldehyde matrix Flax fabric C1-13/P2-1 (C1+(BaCl ₂ +NaOH)2%+clay MMT2%) | 10 |

Mechanical properties of the phenol formaldehyde/flax fiber composite samples are shown in Table 19. It is evident from Table 19 that PF composites containing fibers treated in accordance with the present invention have good mechanical properties. However, due to impregnation difficulties during the preparation of the composites, it is 5 difficult to draw completely accurate conclusions about the mechanical properties of the samples listed in Table 19. Once the impregnation difficulties are resolved, the mechanical properties of composites containing fire-resistant fibers of the present invention are expected to improve.

Table 19 –Mechanical Properties of Phenol Formaldehyde/Flax Fiber Composites

| Sample | Young Modulus (GPa) | Tensile Strength (MPa) | Strain at max load (%) | Energy to break point (J) | Density (g/cm ³) |
|---------------|---------------------|------------------------|------------------------|---------------------------|------------------------------|
| PF-C1 | 9.20 (0.38) | 95.66 (10.59) | 2.90 (0.70) | 6.63 (2.17) | 1.563 (0.022) |
| PF-C1-1/P1 | 7.89 (0.27) | 70.81 (1.57) | 4.03 (0.23) | 8.45 (0.69) | 1.494 (0.005) |
| PF-C1-3/P1 | 10.46 (0.28) | 87.71 (4.64) | 1.88 (0.35) | 4.15 (1.08) | 1.442 (0.002) |
| PF-C1-11/P1 | 9.20 (1.98) | 77.36 (5.09) | 2.15 (0.52) | 4.33 (1.05) | 1.387 (0.001) |
| PF-C1-13/P2-1 | 6.25 (0.66) | 66.67 (1.42) | 3.22 (0.29) | 5.67 (0.64) | 1.473 (0.010) |

10

Phenol formaldehyde/flax fiber composites were prepared another time as indicated in Table 20 in accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 60% and 40% by weight, respectively. Vertical VC-2 burning tests were conducted in accordance with the procedure described in 15 Example 4, and the results are shown in Table 20. Sample PF-C2 is a comparative example of a PF composite containing untreated flax fiber. PF-C2-34/P2-2% and PF-C2-34/P2-23% are examples of PF composites of the present invention containing flax fibers treated with a bi-component aluminum-containing system at 2 and 3%.

In this example, burning time is the time it takes for the sample to self-extinguish 20 after the external flame is removed. Thus, a shorter burning time is indicative of a more fire resistant sample. Phenol formaldehyde is a phenolic thermoset resin which itself has considerable resistance to fire. Because of the fire resistance of phenol formaldehyde, it is the flax fiber that primarily burns during the burning test. As is evident from Table 20, fire-resistant flax fibers of the present invention provide a tremendously significant greater 25 resistance to burning in the phenol formaldehyde matrix than untreated flax fibers that allows the obtained composites with the treated flax fibers to be classified as self-extinguished.

Table 20 - Phenol Formaldehyde/Flax Fiber Composites

| Sample | Composition | Max flame time (s) | Max burn length (inches) | Glow | Pass VC-2 test |
|-----------------|---|--------------------|--------------------------|------|----------------|
| PF-C2 | Phenol formaldehyde matrix Flax fabric C2 (untreated) | 35.8 ± 8.2 | 1.3 ± 0.1 | No | No |
| PF- C2-34/P1-2% | Phenol formaldehyde matrix Flax fabric C2-34/P1-2% (C2+(AlCl ₃ +NH ₄ OH)2%) | 7. 5± 5.6 | 0.5 ± 0.1 | No | Yes |
| PF- C2-34/P1-3% | Phenol formaldehyde matrix Flax fabric C2-34/P1-3% (C2+(AlCl ₃ +NH ₄ OH)3%) | 2.1 ± 2.4 | 0.2 ± 0.1 | No | Yes |

Mechanical properties of the phenol formaldehyde/flax fiber composite samples are shown in Table 21. It is evident from Table 21 that PF composites containing fibers
5 treated with a bi-component aluminum-containing system at 2% in accordance with the present invention have comparable flexural properties with the reference. However, due to impregnation difficulties during the preparation of the composite containing fibers treated with a bi-component aluminum-containing system at 3%, the flexural strength of this sample reduced.

10 Table 21 -Mechanical Properties of Phenol Formaldehyde/Flax Fiber Composites

| Sample | Composition | Flexural strength (MPa) | Flexural modulus (GPa) |
|-----------------|---|-------------------------|------------------------|
| PF-C2 | Phenol formaldehyde matrix Flax fabric C2 (untreated) | 129.8 ± 8.2 | 10.2 ± 0.3 |
| PF- C2-34/P1-2% | Phenol formaldehyde matrix Flax fabric C2-34/P1-2% (C2+(AlCl ₃ +NH ₄ OH)2%) | 118.1± 4.2 | 10.1 ± 0.8 |
| PF- C2-34/P1-3% | Phenol formaldehyde matrix Flax fabric C2-34/P1-3% (C2+(AlCl ₃ +NH ₄ OH)3%) | 65.9 ± 2.6 | 9.5 ± 0.3 |

Polypropylene (PP)/flax fiber composites

Polypropylene/flax fiber composites were prepared as indicated in Table 22 in
15 accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 60% and 40% by weight, respectively. Sample PP-C1 is a comparative example of a PP composite containing untreated flax fiber. PP-C1-3/P1 is a comparative example of PP composite containing flax fibers treated only with LDH clay. PP-C1-6/P1 is a comparative example of a PP composite containing flax fibers treated only with Ba(OH)₂. PP-C1-10/P2-1 is a comparative example of a PP composite containing flax fibers treated with Ba(OH)₂ and then LDH clay. PP-C1-11/P1 is an example of a PP composite of the present invention containing flax fibers treated with a bi-component barium-containing system. PP-C1-13/P2-1 is an example of a PP

composite of the present invention containing flax fibers treated with a bi-component barium-containing system and then MMT clay. PP-C1-14/P2-1 is an example of a PP composite of the present invention containing flax fibers treated with a bi-component barium-containing system and then LDH clay. Horizontal burning tests were conducted in 5 accordance with the procedure described in Example 4, and the results are shown in Table 23. Burning time represents the amount of time it took for the sample to burn the stated length. Thus, a longer time to burn a given length is an indication of better fire resistance. It is evident from Table 23 that the fire-resistant flax fibers of the present invention have less effect on the fire resistance of a polypropylene composite as 10 compared to a phenol formaldehyde composite (see Table 18). This is likely due to the fact that polypropylene itself is highly flammable, thus the matrix burns in any event. However, the inclusion of clay in the polypropylene/flax fiber composite of the present invention does offer a marked improvement over composites having fire-resistant flax fibers of the present invention but not including clay, and over composites having clay 15 and regular flax fibers.

Table 22 - Composition of Polypropylene/Flax Fiber Composites

| Sample | Composition |
|---------------|--|
| PP-C1 | Polypropylene matrix Flax fabric C1 (untreated) |
| PP-C1-3/P1 | Polypropylene matrix Flax fabric C1-3/P1 (C1+clay LDH2%) |
| PP-C1-6/P1 | Polypropylene matrix Flax fabric C1-6/P1 (C1+Ba(OH) ₂ 2%) |
| PP-C1-10/P2-1 | Polypropylene matrix Flax fabric C1-10/P2-1 (C1+Ba(OH) ₂ 2%+clayLDH2%) |
| PP-C1-11/P1 | Polypropylene matrix Flax fabric C1-11/P1 (C1+(BaCl ₂ +NaOH)2%) |
| PP-C1-13/P2-1 | Polypropylene matrix Flax fabric C1-13/P2-1 (C1+(BaCl ₂ +NaOH)2%+clay MMT2%) |
| PP-C1-14/P2-1 | Polypropylene matrix Flax fabric C1-13/P2-1 (C1+(BaCl ₂ +NaOH)2%+clay LDH2%) |

Table 23 - Burning Tests on Polypropylene/Flax Fiber Composites

| Sample | Burning length (inches) | | | | | |
|---------------|-------------------------|-----|-----|-----|-----|-----|
| | 0.0 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| | Burning Time (seconds) | | | | | |
| PP-C1 | 0 | 103 | 186 | 263 | 344 | 382 |
| PP-C1-3/P1 | 0 | 112 | 190 | 270 | 351 | 399 |
| PP-C1-6/P1 | 0 | 117 | 186 | 255 | 332 | 370 |
| PP-C1-10/P2-1 | 0 | 108 | 174 | 246 | 322 | 365 |
| PP-C1-11/P1 | 0 | 103 | 182 | 268 | 351 | 369 |
| PP-C1-13/P2-1 | 0 | 125 | 201 | 276 | 352 | 386 |
| PP-C1-14/P2-1 | 0 | 147 | 230 | 313 | 409 | 446 |

Mechanical properties of the polypropylene/flax fiber composite samples are shown in Fig. 1A (flexural modulus) and Fig. 1B (flexural strength). It is evident from Fig.

5 1A and Fig. 1B that polypropylene composites containing flax fibers treated in accordance with the present invention have significantly better flexural modulus than the comparative samples, while maintaining a flexural strength that is at least as good as the comparative samples.

Epoxy/flax fiber composites

10 Epoxy/flax fiber composites were prepared as indicated in Table 24 in accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 60% and 40% by weight, respectively. Sample Epo-C2 is a comparative example of an epoxy composite containing untreated flax fiber. Epo-C2-34/P1 is a comparative example of epoxy composite containing flax fibers treated only with a bi-component aluminum-containing system at 2%. Epo-C2-34-Clay/P2 is a comparative example of epoxy composite containing flax fibers treated only with a bi-component aluminum-containing system at 2% and then MMT clay. Horizontal burning tests were conducted in accordance with the procedure described in Example 4, and the results are shown in Table 25. Burning time represents the amount of time it took for the sample to burn the stated length. Thus, a longer time to burn a given length is an indication of better fire resistance. It is evident from Table 25 that the fire-resistant flax fibers of the present invention have stopped the composites from burning. Mechanical properties of the epoxy/flax fiber composite samples are shown in Table 26. It is evident from Table 26 that epoxy composites containing flax fibers treated in accordance with the present invention have very slightly reduction in tensile strength and modulus than the

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comparative samples, while improving the energy to break which represents the composite toughness.

Table 24 - Composition of Epoxy/Flax Fiber Composites

| Sample | Composition |
|-------------------|--|
| Epo-C2 | Epoxy matrix Flax fabric C2 (untreated) |
| Epo-C2-34/P1 | Epoxy matrix Flax fabric C2-34/P1 (C2+(AlCl ₃ +NH ₄ OH)2%) |
| Epo-C2-34-Clay/P2 | Epoxy matrix Flax fabric C2-34/P1 (C2+(AlCl ₃ +NH ₄ OH)2%+clay MMT2%) |

5

Table 25 - Burning Tests on Epoxy/Flax Fiber Composites

| Sample | Burning length (inches) | | | | | |
|-------------------|-------------------------|-----|-----|-----|-----|-----|
| | 0.0 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| | Burning Time (seconds) | | | | | |
| Epo-C2 | 0 | 111 | - | - | 425 | 542 |
| Epo-C2-34/P1 | 0 | NB | NB | NB | NB | NB |
| Epo-C2-34-Clay/P2 | 0 | NB | NB | NB | NB | NB |

Table 26 - Mechanical Properties of Epoxy/Flax Fiber Composites

| Sample | Tensile stress (MPa) | Tensile modulus (GPa) | Energy to break (J) |
|-------------------|----------------------|-----------------------|---------------------|
| EPO-C2 | 117.7 ± 4.0 | 9.8±0.6 | 33.7±2.0 |
| Epo-C2-34/P1 | 106.4 ± 1.0 | 7.2±0.3 | 36.7±2.6 |
| Epo-C2-34-Clay/P2 | 103.7 ± 4.2 | 8.4±0.2 | 36.7±2.6 |

Unsaturated polyester/flax fiber composites

10 UPE/flax fiber composites were prepared as indicated in Table 27 in accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 70% and 30% by weight, respectively. Sample UPE-C2 is a comparative example of an epoxy composite containing untreated flax fiber. UPE-C2-34/P1 is a comparative example of epoxy composite containing flax fibers treated only with a bi-component aluminum-containing system at 2%. Horizontal burning tests were conducted in accordance with the procedure described in Example 4, and the results are shown in Table 28. Burning time represents the amount of time it took for the sample to burn the

15

stated length. Thus, a longer time to burn a given length is an indication of better fire resistance. It is evident from Table 28 that the fire-resistant flax fibers of the present invention have stopped the composites from burning.

Table 27 - Composition of UPE/Flax Fiber Composites

| Sample | Composition |
|--------------|---|
| UPE-C2 | UPE matrix Flax fabric C2 (untreated) |
| UPE-C2-34/P1 | UPE matrix Flax fabric C2-34/P1 (C2+(AlCl ₃ +NH ₄ OH)2%) |

5

Table 28 - Burning Tests on UPE/Flax Fiber Composites

| Sample | Burning length (inches) | | | | | |
|--------------|-------------------------|-----|-----|-----|-----|-----|
| | 0.0 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| | Burning Time (seconds) | | | | | |
| UPE-C2 | 0 | 114 | - | - | 421 | 522 |
| UPE-C2-34/P1 | 0 | NB | NB | NB | NB | NB |

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Other advantages that are inherent to the structure are obvious to one skilled in the art. The embodiments are described herein illustratively and are not meant to limit
20 the scope of the invention as claimed. Variations of the foregoing embodiments will be evident to a person of ordinary skill and are intended by the inventor to be encompassed by the following claims.

Claims:

1. A process of producing a fire-resistant cellulosic material comprising: treating a cellulosic material with an aqueous reaction mixture of an alkali metal or ammonium hydroxide and an alkaline earth or aluminum metal salt, wherein the treating is done

5 simultaneously with or within a short period of time of mixing the alkali metal or ammonium hydroxide and alkaline earth or aluminum metal salt; and, drying the treated cellulosic material.

2. The process according to claim 1, wherein the alkaline earth or aluminum metal salt comprises alkaline earth metal salt.

10 3. The process according to claim 2, wherein the alkaline earth metal salt comprises magnesium or calcium.

4. The process according to any one of claims 2 to 3, wherein the alkaline earth metal salt is a chloride, a fluoride, a bromide, an iodide or a nitrate.

15 5. The process according to claim 2, wherein the alkaline earth metal salt is calcium or magnesium chloride.

6. The process according to claim 1, wherein the alkaline earth or aluminum metal salt comprises aluminum chloride.

7. The process according to any one of claims 1 to 6, wherein the hydroxide is an alkali metal hydroxide.

20 8. The process according to any one of claims 1 to 6, wherein the hydroxide is NaOH.

9. The process according to any one of claims 1 to 6, wherein the hydroxide is NH₄OH.

25 10. The process according to claim 1, wherein the hydroxide is NH₄OH and the metal salt is AlCl₃.

11. The process according to any one of claims 1 to 10, wherein the aqueous reaction mixture utilizes 0.5-10 wt% of the alkaline earth or aluminum metal salt and 0.5-4 wt% of the alkali metal or ammonium hydroxide, and wherein a product of the reaction of the alkaline earth or aluminum metal salt and the alkali metal or ammonium hydroxide is present in an amount of 0.5 wt% or more.

12. The process according to any one of claims 1 to 11, wherein the short period of time is 1 day or less.

13. The process according to any one of claims 1 to 11, wherein the short period of time is 5 seconds to 5 hours.

5 14. The process according to any one of claims 1 to 11, wherein the short period of time is 5 seconds to 30 minutes.

15. The process according to any one of claims 1 to 11, wherein the short period of time is 5 seconds to 10 minutes.

10 16. The process according to any one of claims 1 to 11, wherein the short period of time is from 1 minute to 5 hours.

17. The process according to any one of claims 1 to 16, wherein the cellulosic material is fibrous.

15 18. The process according to any one of claims 1 to 17, wherein the cellulosic material comprises material from wood sources, agricultural sources, synthetic sources, recycled paper or recycled cardboard.

19. The process according to any one of claims 1 to 18, wherein the cellulosic material is further treated with a layered nanoparticulate material before, at the same time or after treating with the aqueous reaction mixture.

20. The process according to claim 19, wherein treating with the layered nanoparticulate material is done after treating with the aqueous reaction mixture.

21. The process according to any one of claims 19 to 20, wherein the layered nanoparticulate material comprises a layered clay.

25 22. The process according to any one of claims 19 to 20, wherein the layered nanoparticulate material comprises a layered double hydroxide, montmorillonite, sepiolite, palygorskite, bentonite, fluoromica or a mixture thereof.

23. The process according to any one of claims 19 to 20, wherein the layered nanoparticulate material comprises a layered double hydroxide, montmorillonite or a mixture thereof.

24. A fire-resistant cellulosic material produced by the process as defined in any one of claims 1 to 23.

25. The fire-resistant cellulosic material according to claim 24 which is self-extinguishing.

5 26. A polymer composite comprising a polymer matrix and the fire-resistant cellulosic material as defined in claim 24 or 25 dispersed in the polymer matrix.

27. The polymer composite according to claim 26, wherein the polymer matrix comprises an organic polymer.

10 28. The polymer composite according to claim 26, wherein the polymer matrix comprises a thermoset resin.

29. The polymer composite according to claim 26, wherein the polymer matrix comprises a polyolefin or a phenolic resin.

30. The polymer composite according to claim 26, wherein the polymer matrix comprises a polypropylene or a phenol formaldehyde.

15 31. The polymer composite according to claim 26, wherein the polymer matrix comprises an unsaturated polyester or an epoxy polymer.

32. The polymer composite according to any one of claims 26 to 31 further comprising a surfactant for improving compatibility of the fire-resistant cellulosic material with the polymer matrix.

20 33. The polymer composite according to claim 32, wherein the surfactant comprises an amine, a di-functional amine, a poly-functional amine, an alkanolamine, an acid, a carboxylate or any mixture thereof.

34. The polymer composite according to any one of claims 26 to 32, wherein the polymer matrix is present in an amount from about 0.1 to about 99.9 weight percent based on total weight of the polymer composite.

25 35. The polymer composite according to any one of claims 26 to 32, wherein the polymer matrix is present in an amount from about 40 to about 98 weight percent based on total weight of the polymer composite.

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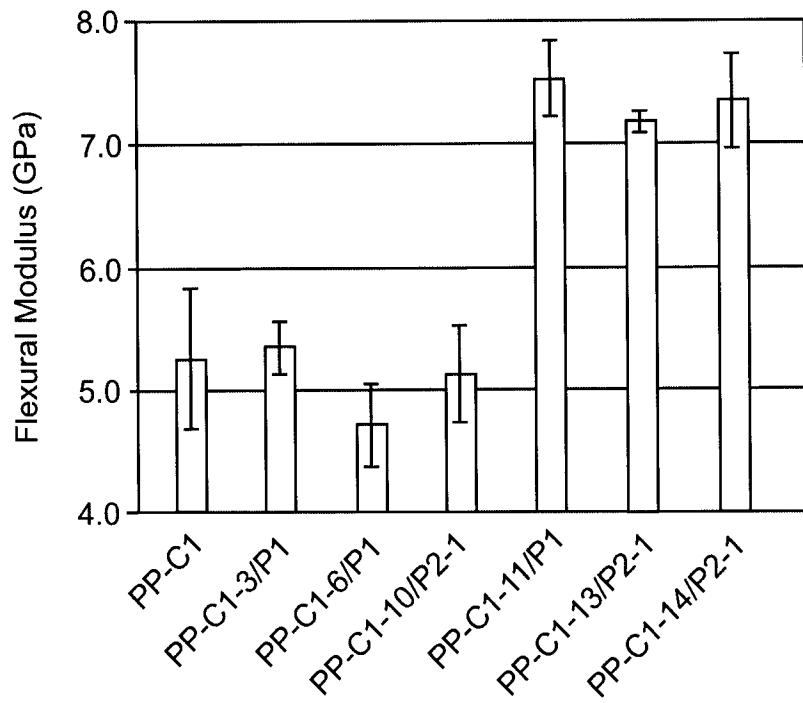


Fig. 1A

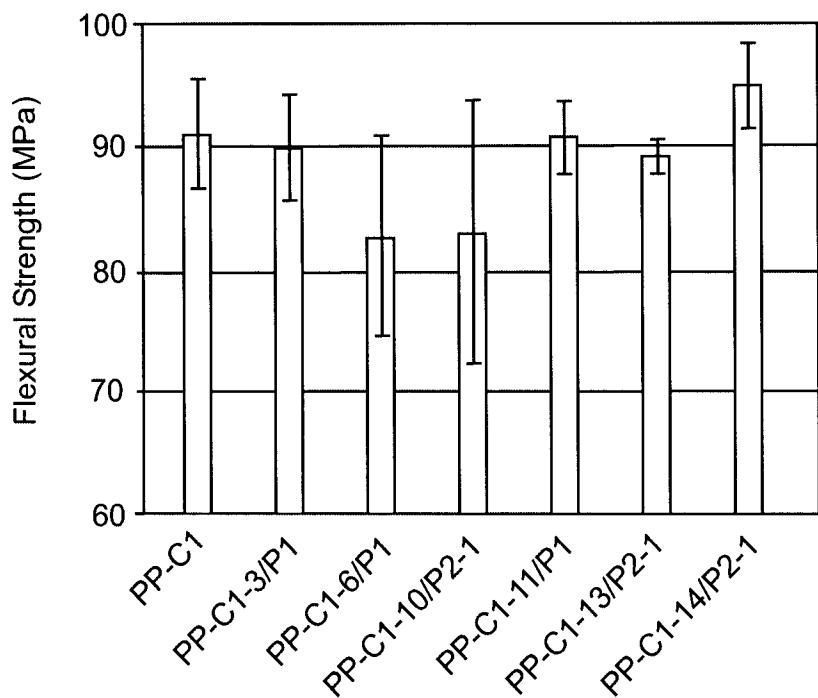


Fig. 1B



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(19) United States

(12) Patent Application Publication

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(43) Pub. Date: May 23, 2013

(54) FABRICATION AND APPLICATION OF POLYMER-GRAFHTIC MATERIAL NANOCOMPOSITES AND HYBRIDE MATERIALS

(76) Inventors: Pasi Moilanen, Jyvaskyla (FI); Jorma A. Virtanen, Las Vegas, NV (US)

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(86) PCT No.: PCT/FI10/00077

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(2), (4) Date: Jun. 22, 2012

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H01G 9/00 (2006.01)

(52) U.S. Cl.

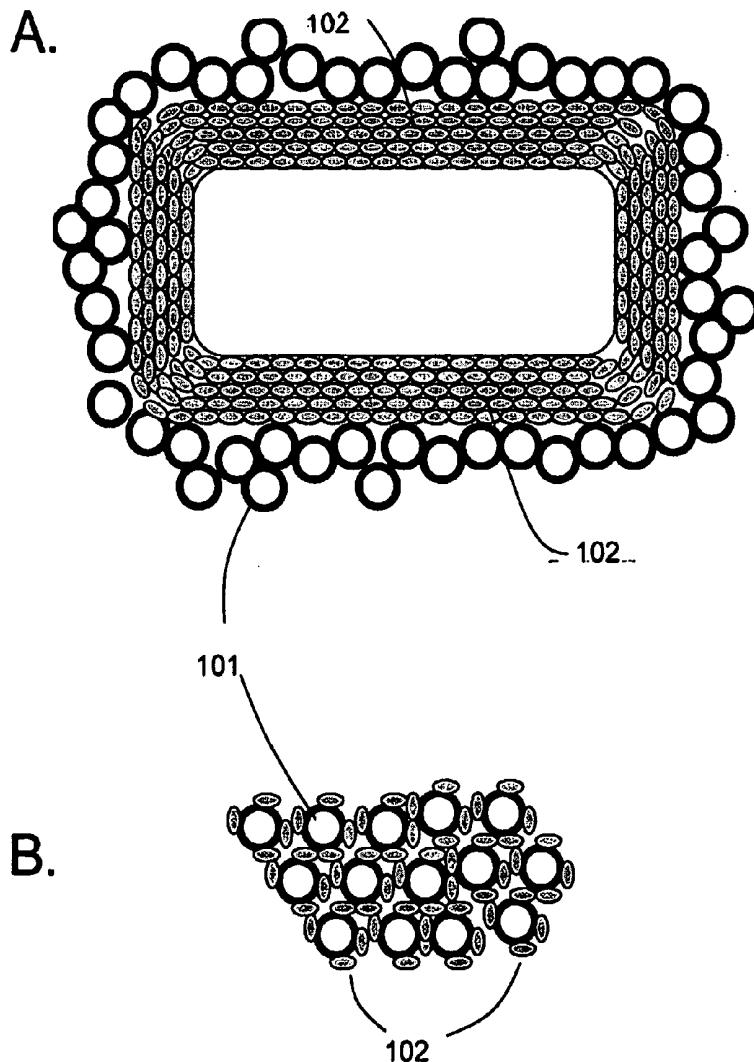
CPC H01G 9/042 (2013.01); H01G 9/155

(2013.01)

USPC 428/532; 252/509; 252/62.51R; 361/502

(57) ABSTRACT

The present invention describes a nanocomposite and hybride material of functionalized carbon nanotubes and cellulose and associated methods for the fabrication of that nanocomposite or hybride material containing electromagnetically active nanoparticles. The fabrication is fast, environmentally friendly, and economical. These nanocomposites are strong and electrically conducting, and have many materials and electronic applications.



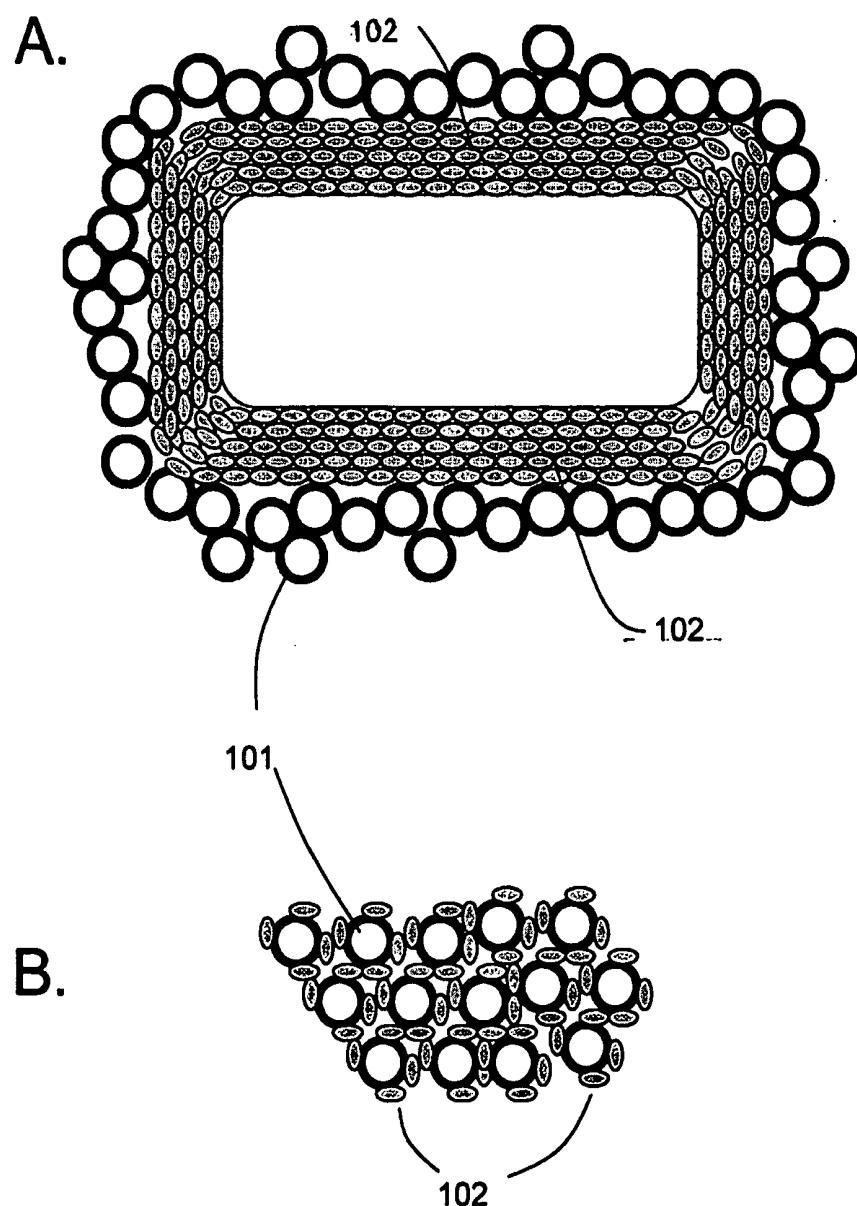


Fig.1

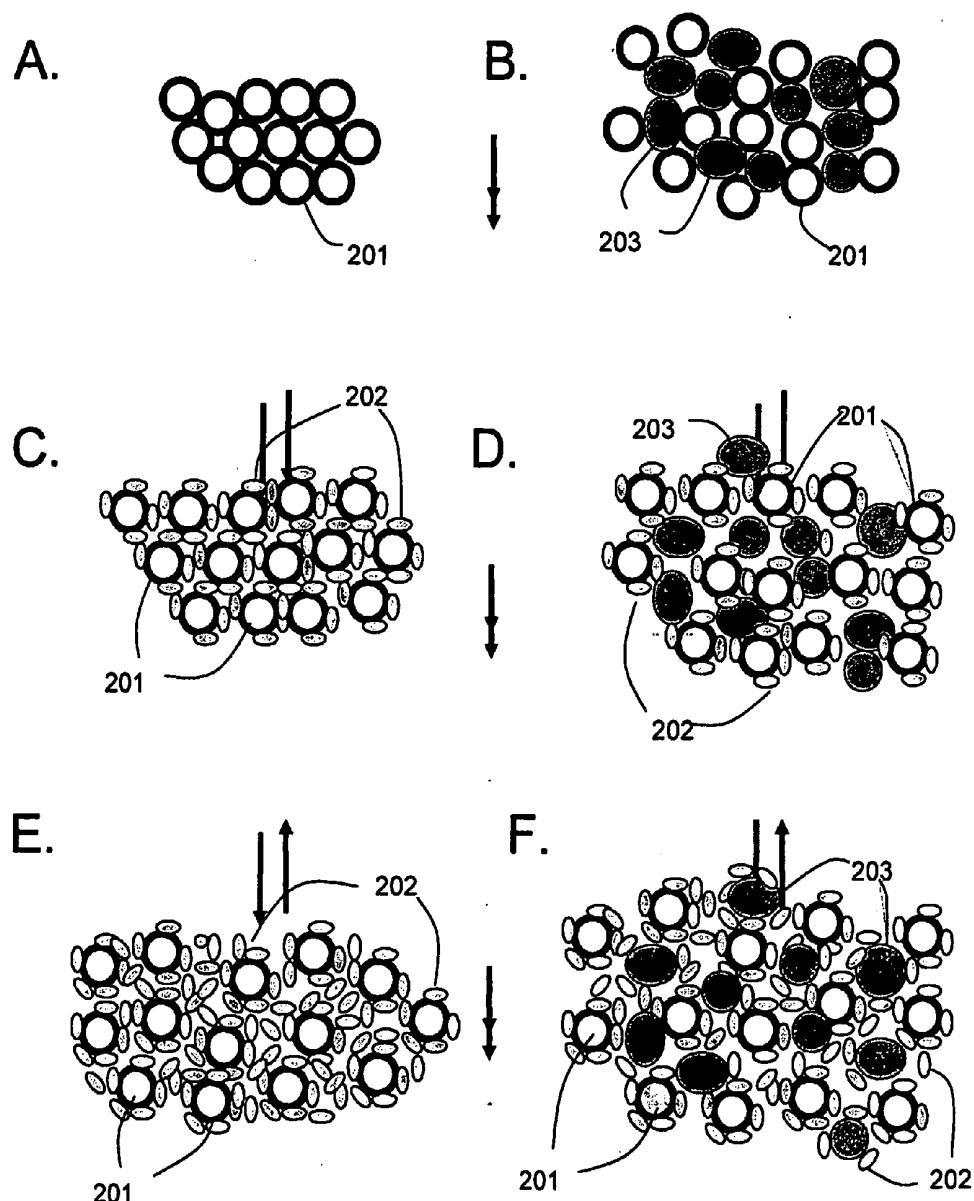


Fig.2

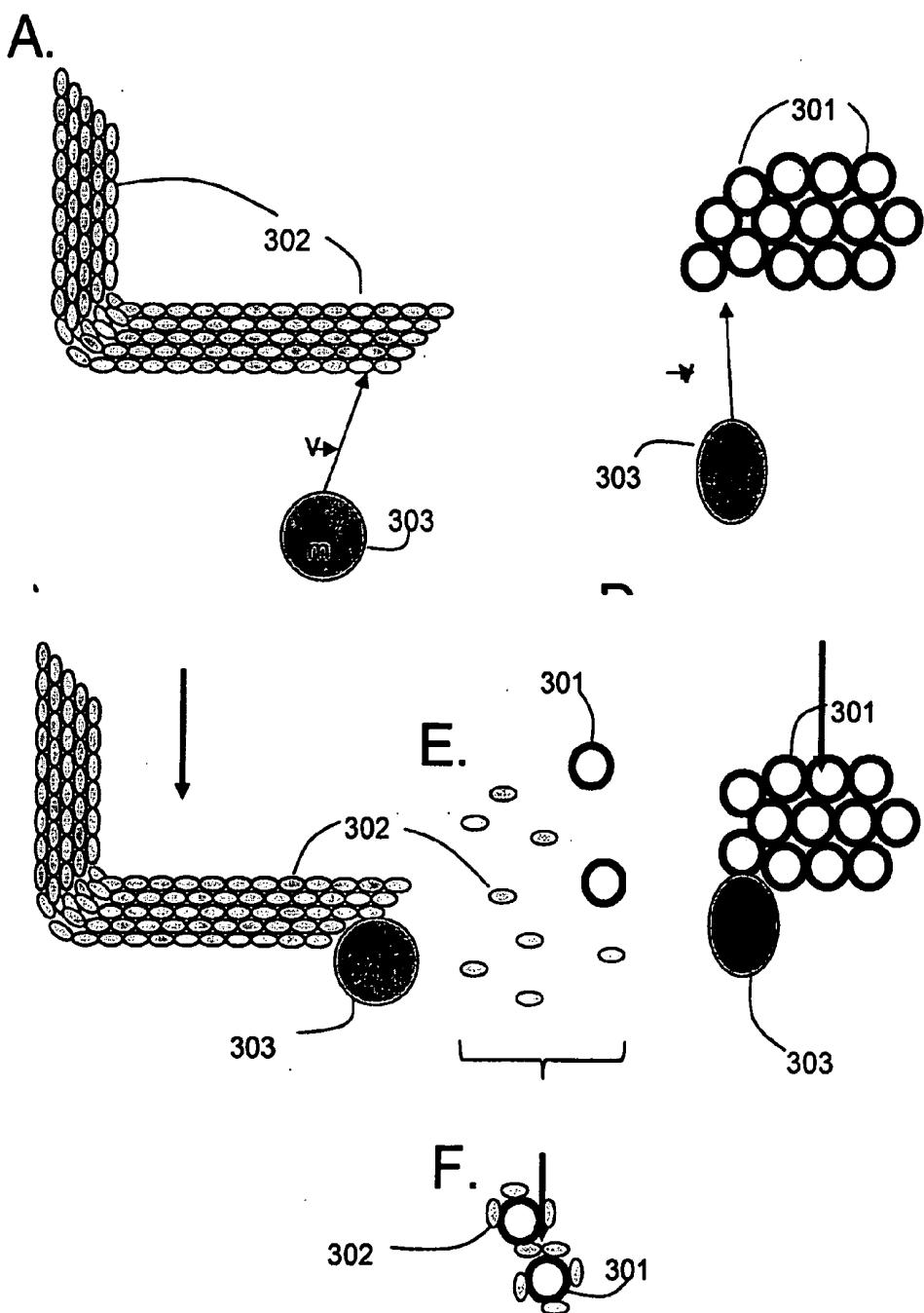


Fig.3

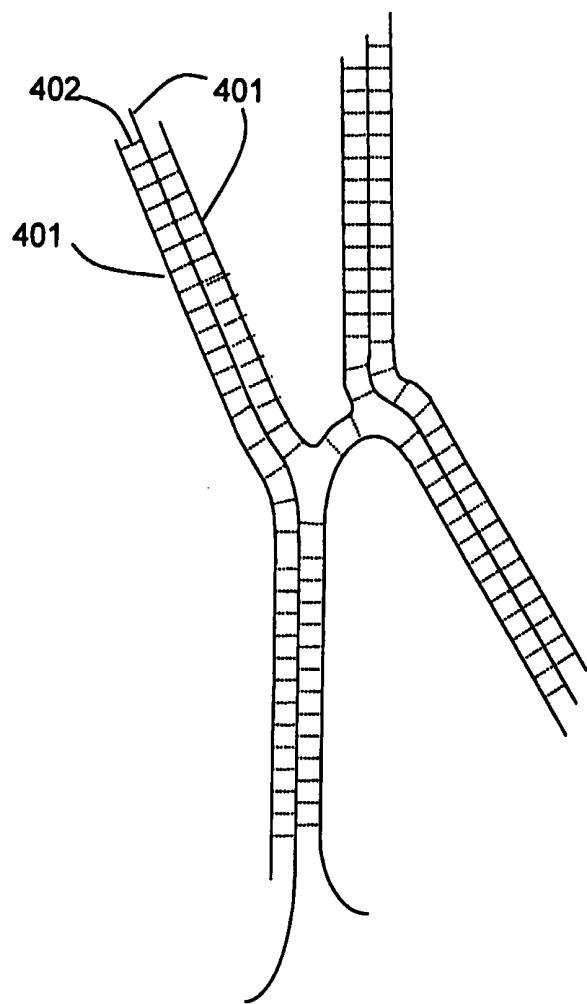


Fig.4

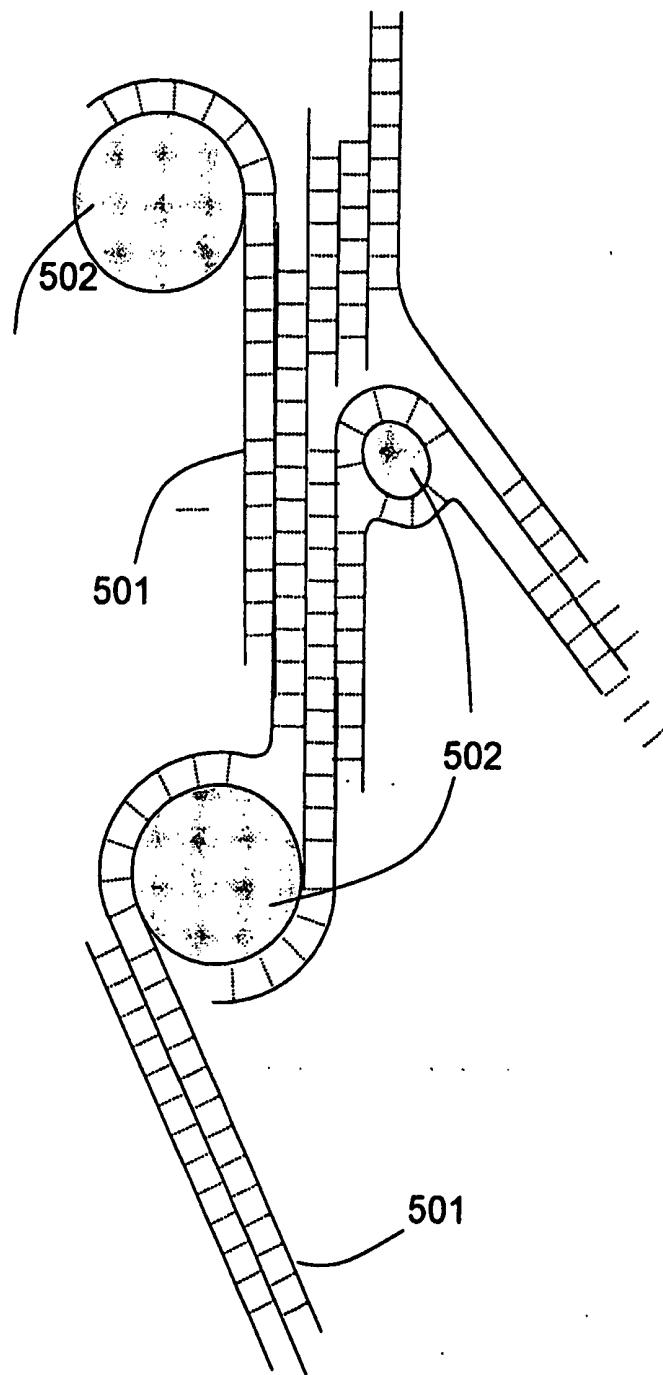


Fig.5

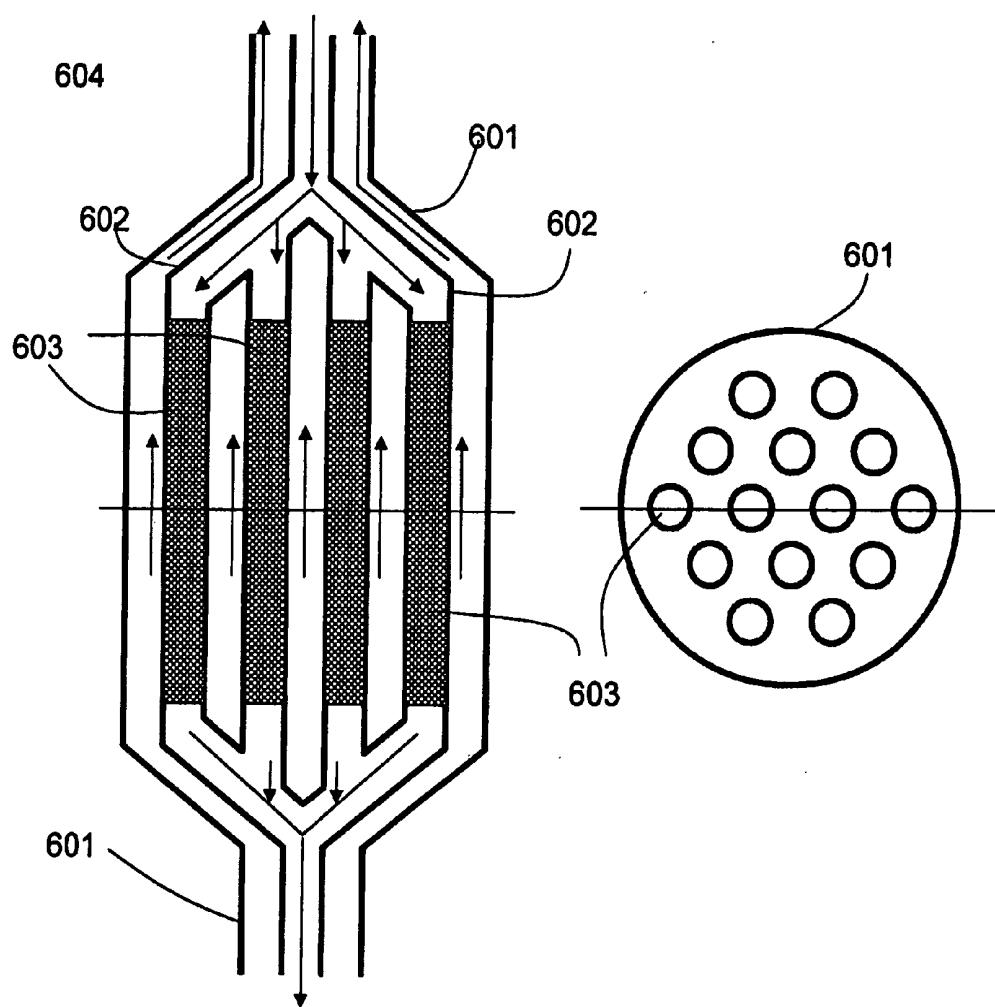


Fig.6

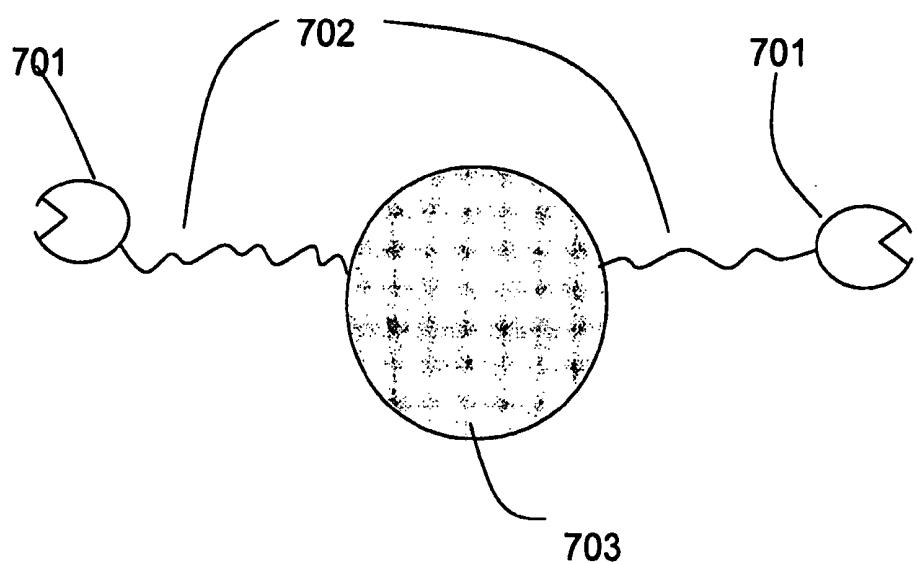


Fig.7

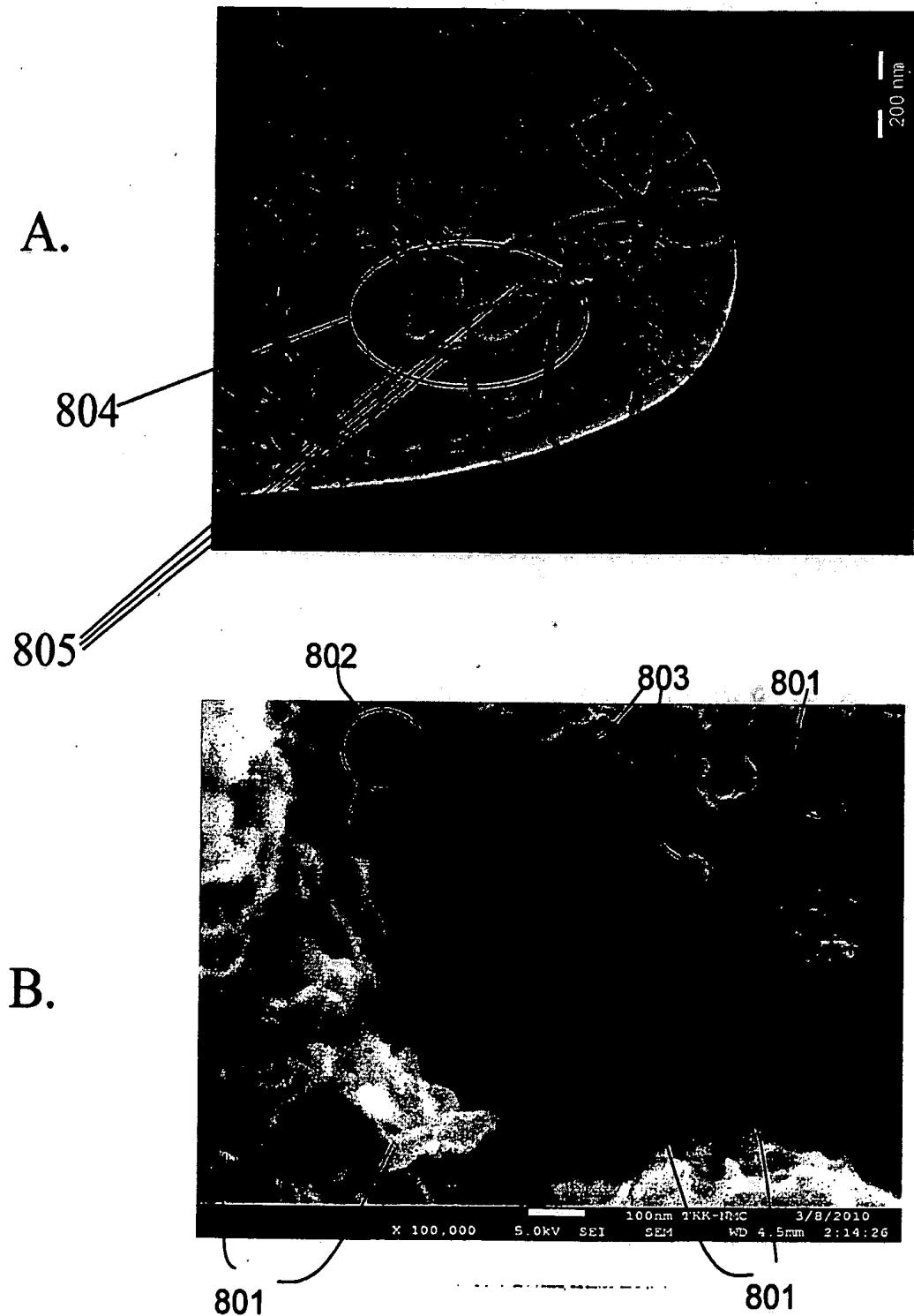


Fig.8

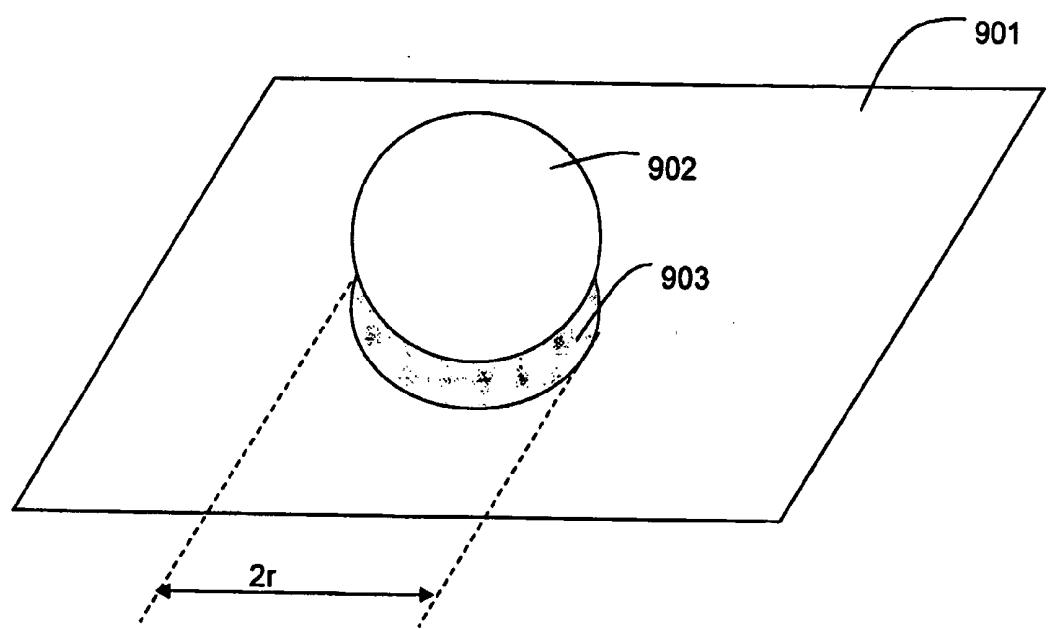


Fig.9

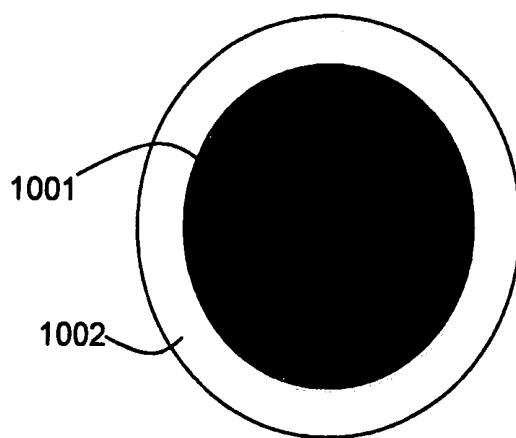


Fig.10

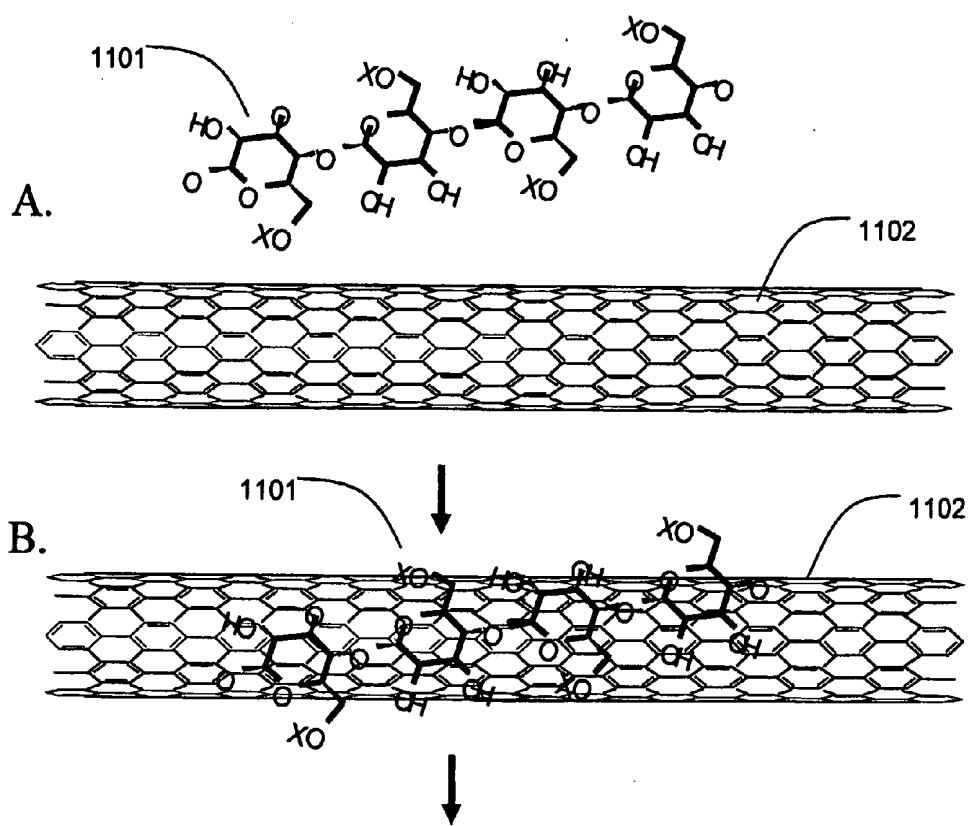


Fig.11

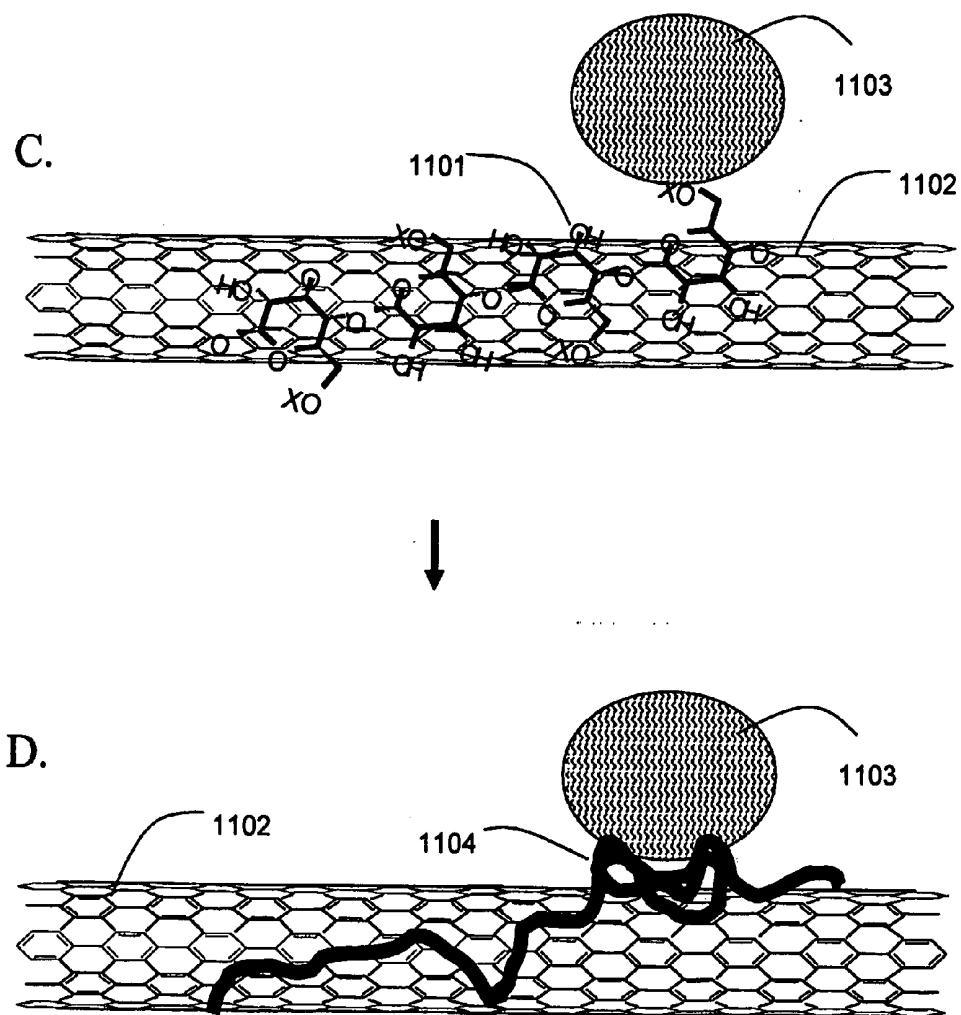


Fig.11

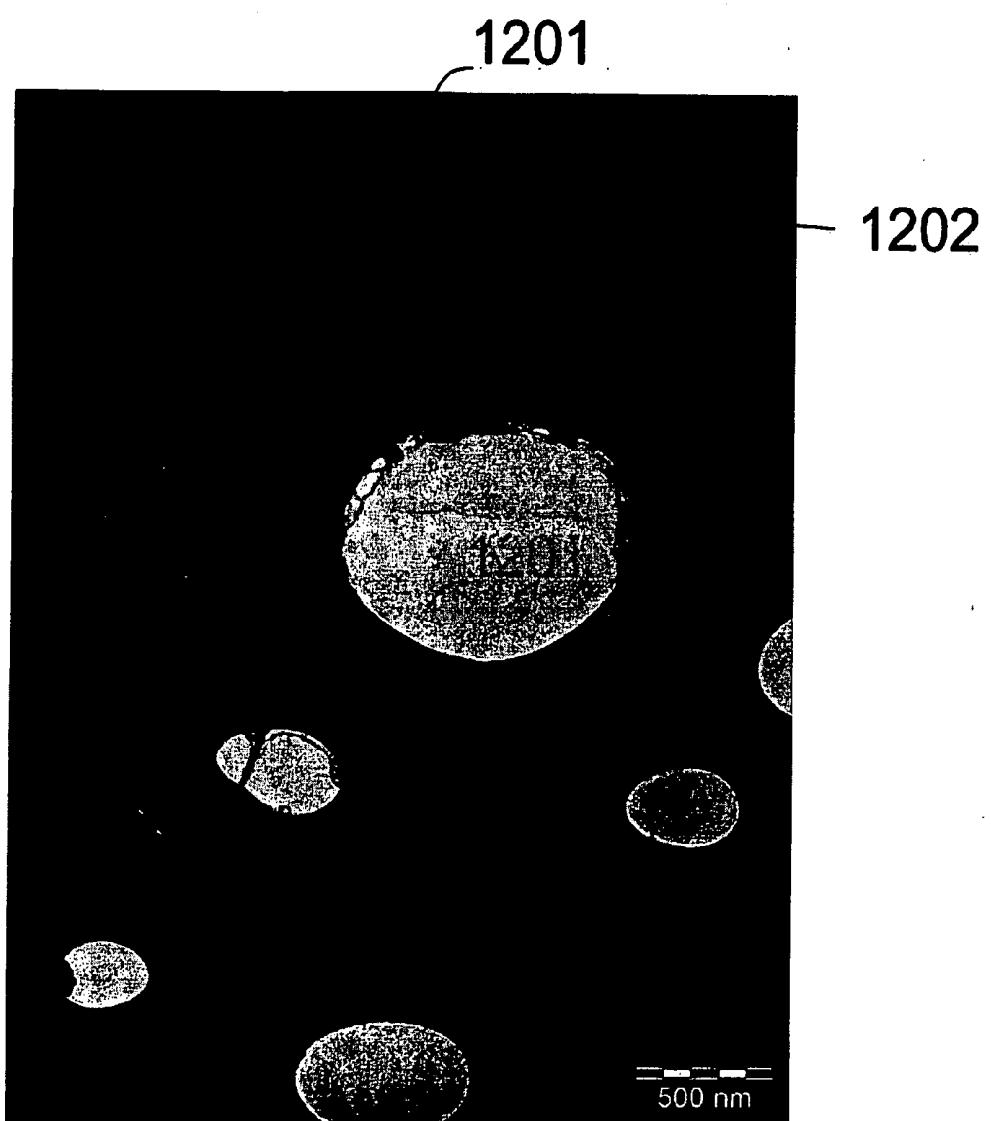


Fig.12

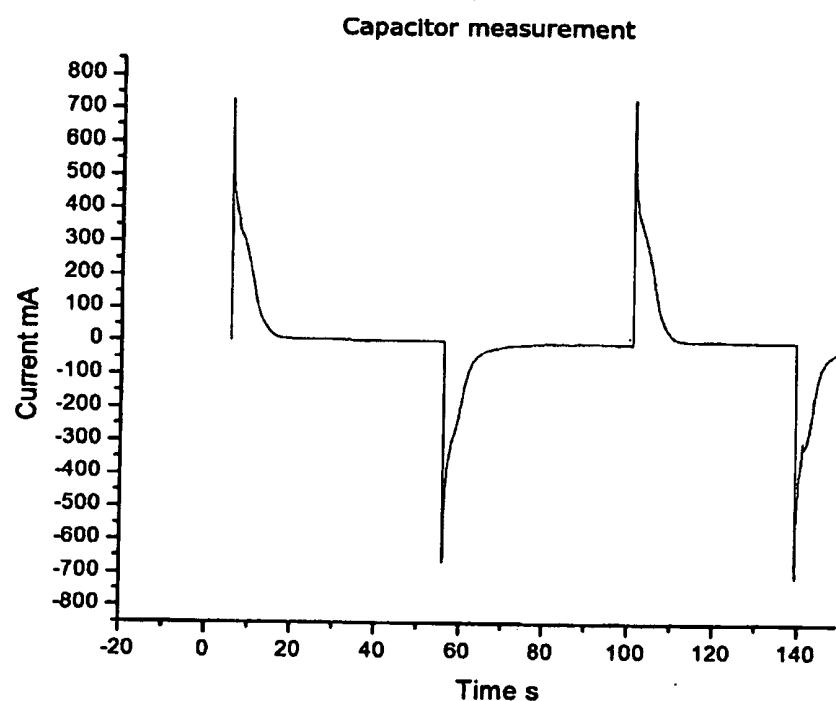


Fig.13

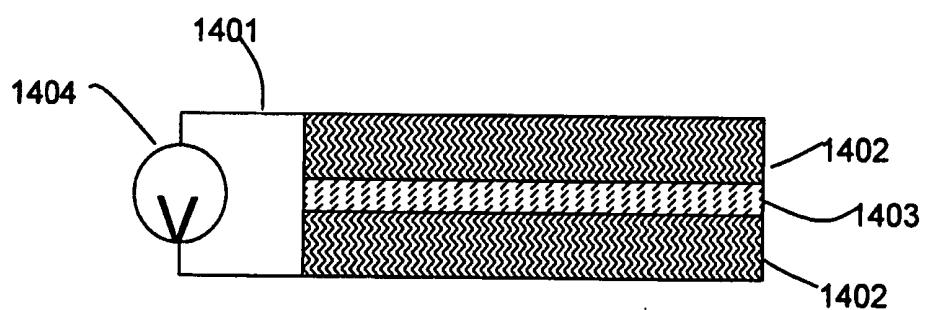


Fig.14

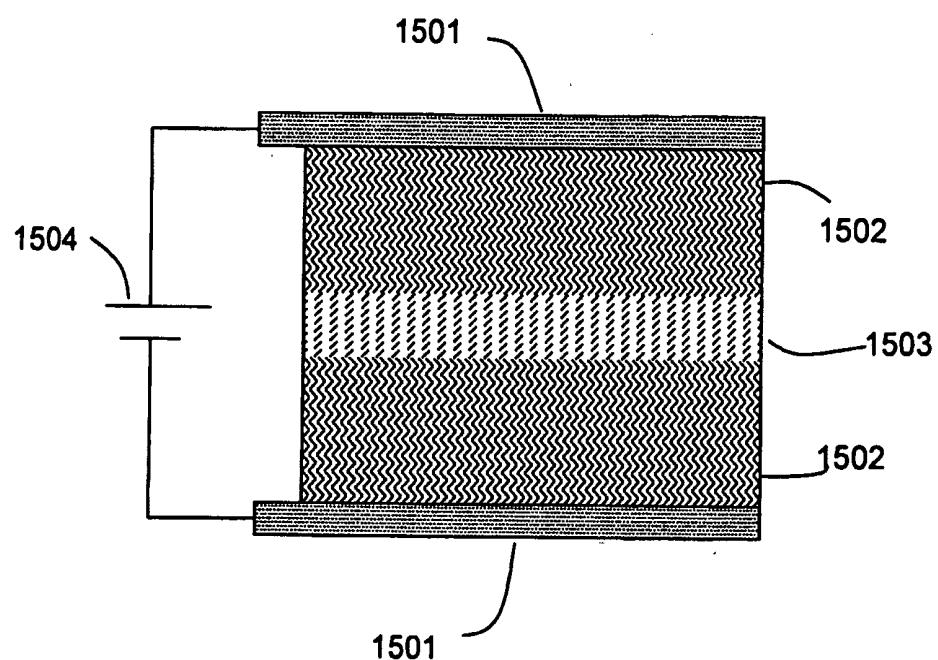


Fig.15

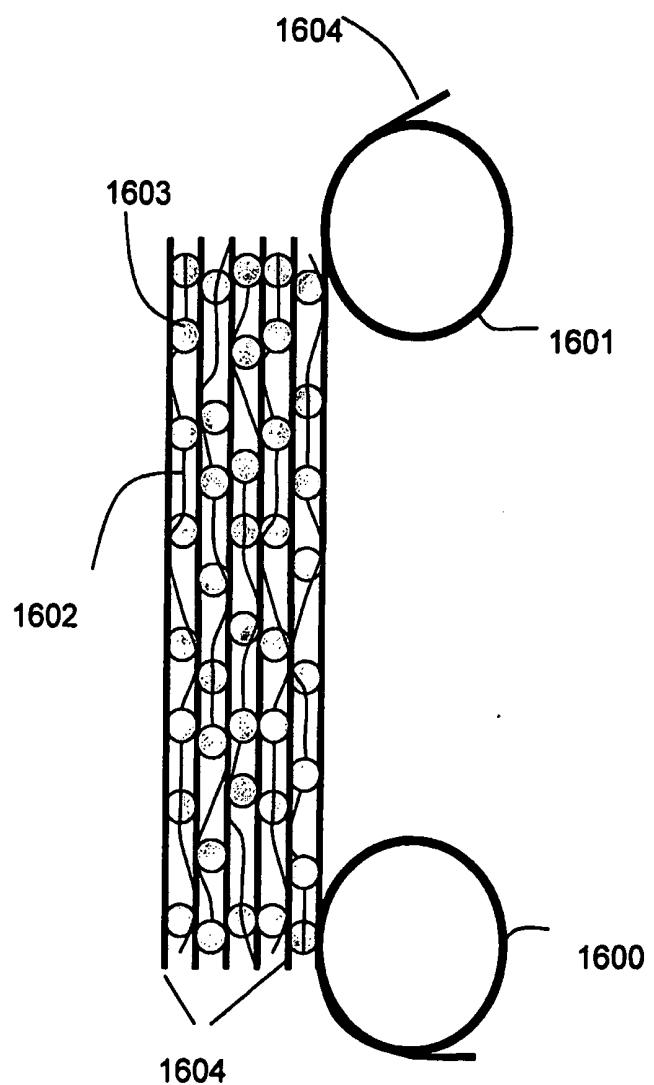


Fig. 16

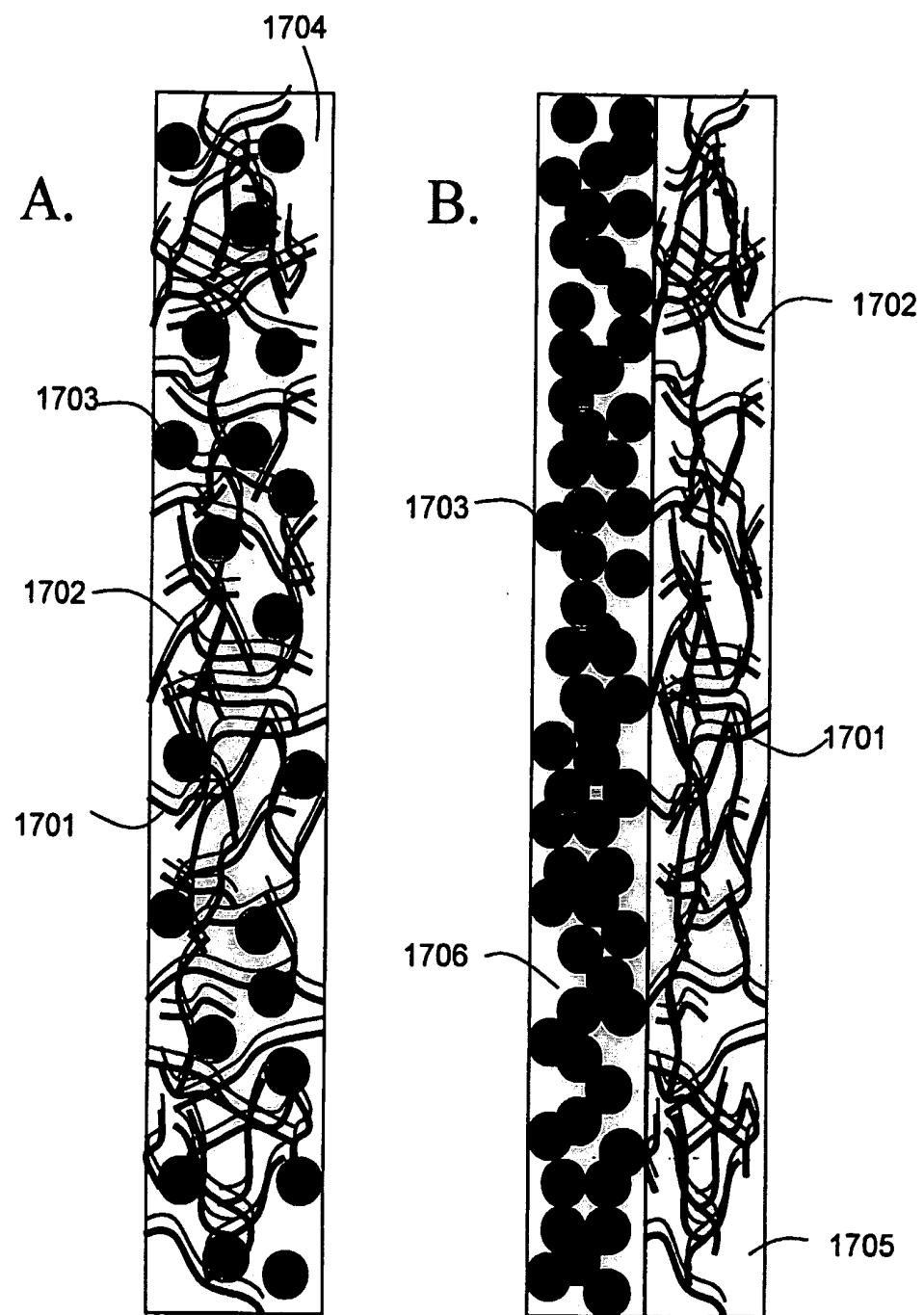


Fig.17

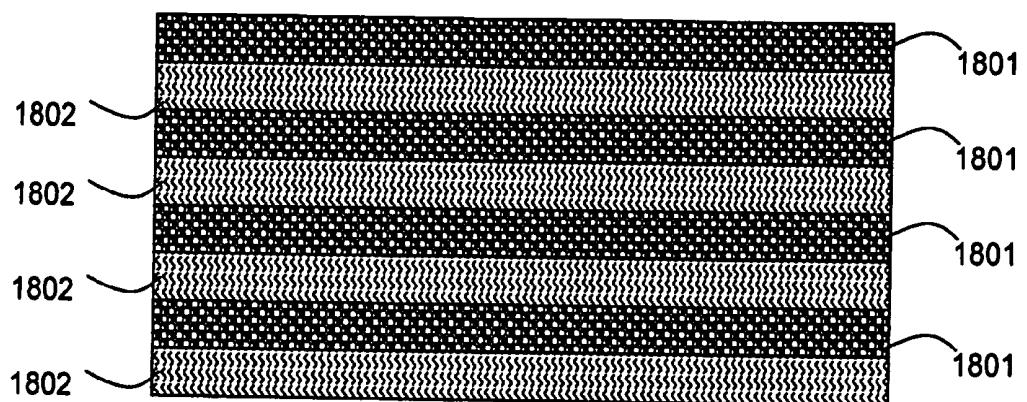


Fig.18

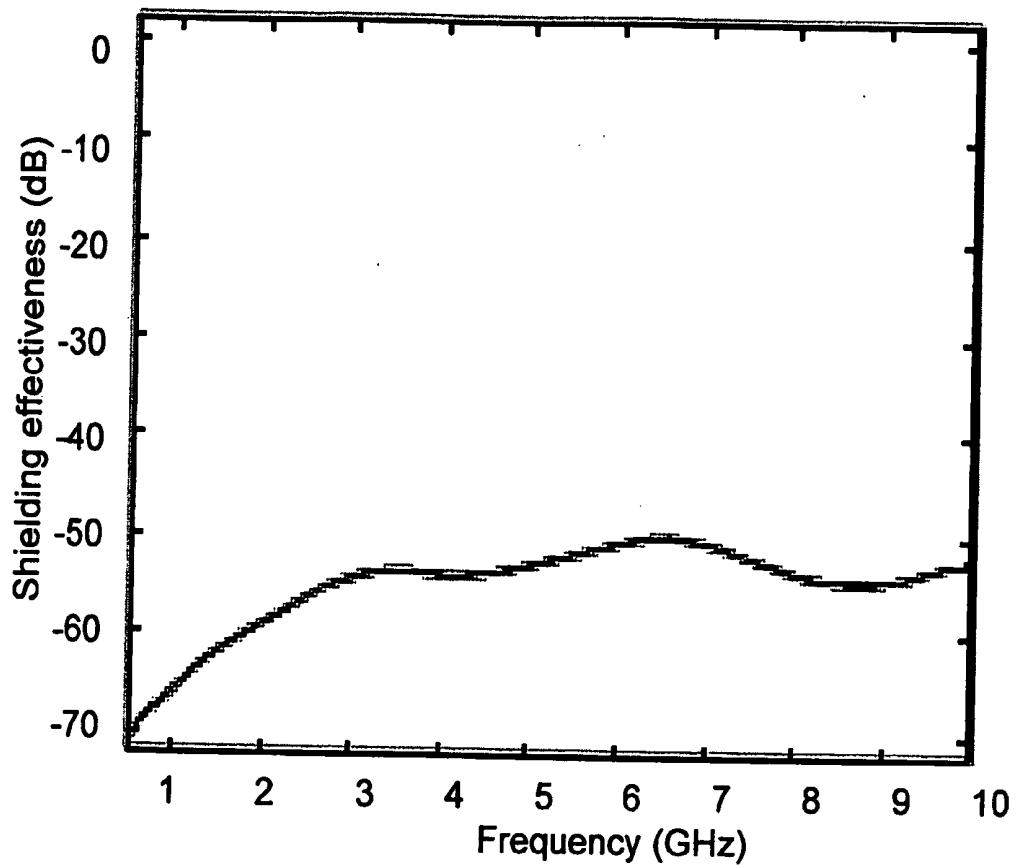
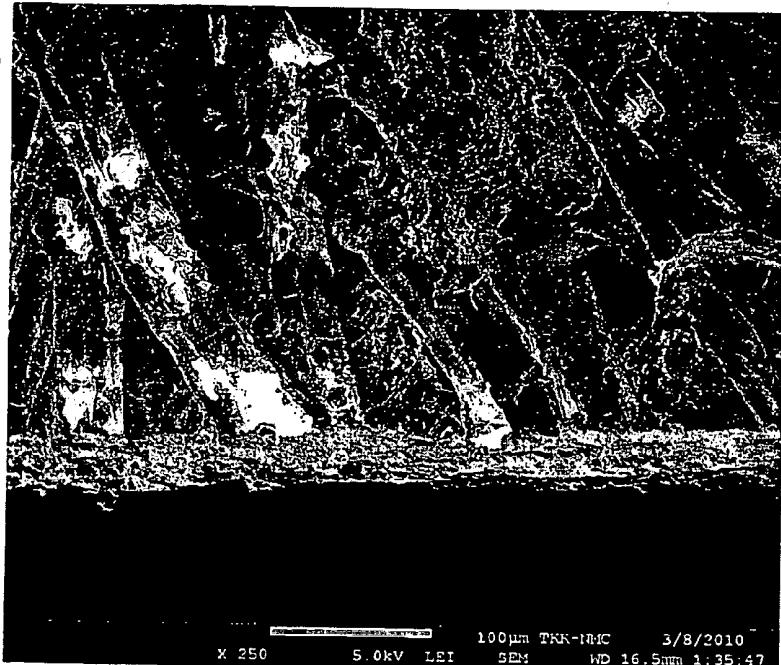


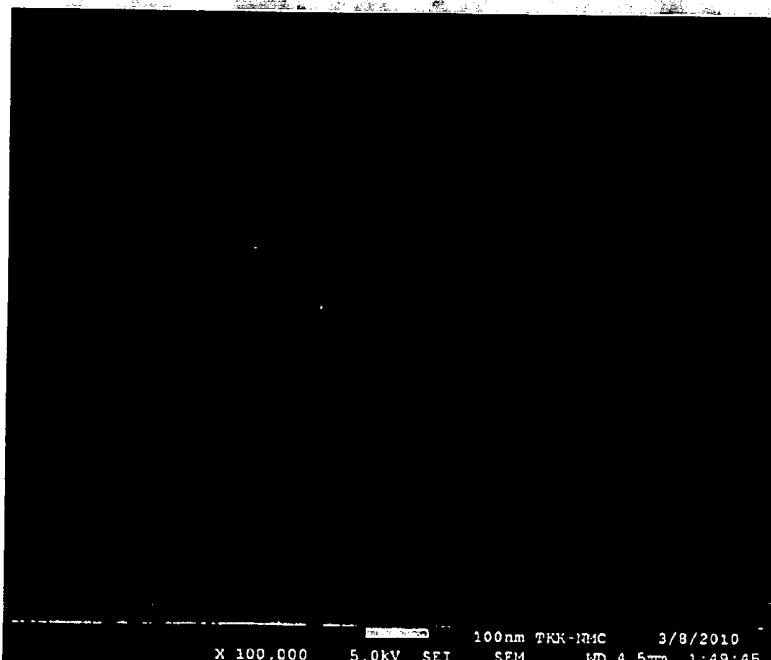
Fig.19

A.



100μm TKK-NMC 3/8/2010
X 250 5.0kV LEI SEM WD 16.5mm 1:35:47

B.



100nm TKK-NMC 3/8/2010
X 100,000 5.0kV SET SEM WD 4.5mm 1:49:45

Fig.20

FABRICATION AND APPLICATION OF POLYMER-GRAFHTIC MATERIAL NANOCOMPOSITES AND HYBRIDE MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from Finnish Application Serial No. 20090495, filed Dec. 22, 2009, and Finnish Application Serial No. 20100143, filed Apr. 9, 2010, and
Finnish Application Serial No. 20106077, filed Oct. 18, 2010, and
U.S. Provisional application Ser. No. _____, filed January 2010, titled Fabrication and Application of Functionalized cellulose-carbon nanotube nanocomposite and Hybride Materials

BACKGROUND

[0002] 1. Field of Invention

[0003] This invention relates to the fabrication of nanocomposites from two or more materials that have low solubility in a liquid milieu and large scale structures of these materials. More specifically fabrication of nano-composites or hybride materials of polymer and graphitic material using nanoparticles as dispersion facilitators is described. In addition, the present invention involves the electromagnetic utilization graphitic material-polymer nanocomposites for supercapacitors and electromagnetic shielding.

[0004] 2. Prior Art and Overall Description

[0005] Fabrication of nanocomposites of two or more materials is not straightforward. Often these materials do not have a common solvent. Even, when both or all materials have a common solvent, their deposition will most probably result into a random structure, in which both components can be clustered as well as mixed in a nanoscale. The present invention solves this problem using carbon nanotubes and cellulose as examples. Efficient dispersion of graphitic materials, such as carbon nanotubes (CNTs) and graphite into polymers continues to be problematic. Graphitic materials tend to aggregate, especially, if their concentration exceeds 10% in the medium. Aggregation prevents the full utilization of the graphitic material. For example, a capacitance of supercapacitor depends on the available surface area of the graphitic material. Aggregate has much less available surface area than individually separated graphitic particles have combined surface area. Electromagnetic interference (EMI) protection efficiency is hampered by clustering. Material strength is much better served by individually dispersed graphitic particles than by clusters.

[0006] This invention provides very efficient dispersion methods and materials that are often accompanied by functionalization of graphitic particles. Currently preferred embodiments are almost exclusively related to the fabrication of CNT-cellulose nanocomposite, i.e., graphitic material consists of CNTs, and polymer is cellulose or modified cellulose. Although scanning electron microscope (SEM), and transmission electron microscope (TEM) images prove good dispersion, more importantly, capacitances of supercapacitors, EMI shielding efficacy, and material strength are practically important implications of the efficacy of the dispersion method. Carbon nanotubes (CNTs) can be single walled (SWNT), double walled (DWNT) or multiwalled (MWNT).

They can have diameters that range from subnanometer to over 100 nm. Also CNTs have a multitude of chiralities. Thus, there are hundreds of different kind of CNTs. Some CNTs are metallic conductors and some are semiconducting. Many CNTs are better electrical conductors than silver at room temperature. All CNTs are very strong, and the tensile strength of the CNTs is tens of times better than that of steel.

[0007] CNTs can be functionalized by several methods. One commonly used method is oxidation with the mixture of sulfuric and nitric acids to form carboxylic groups (R. E. Smalley, et al., Method for forming an array of single-wall carbon nanotubes and compositions thereof, US2002/0159943 A1). Many moieties can be attached with carboxylic groups. In another method radicals are generated from diazonium salts, and these radicals react with the CNTs (J. M. Tour, et al., Process for functionalizing carbon nanotubes under solvent-free conditions, Int. Appl. WO 2004/007364). In a co-owned method (J. Virtanen et al. PCT/FI2005/000437) CNTs are cut, and the nascent dangling bonds react with a reagent that is present. These are just some examples that are well known in-the-art. Functionalized CNTs are not really CNTs anymore. They will also be called hybride nanotubes (HNTs) in this context. The term HNT-cellulose material will be used all hybride materials of the present invention.

[0008] CNTs and cellulose are sparingly soluble into all solvents. Due to large particle size they form suspensions rather than solutions, although terms solubility, solution and solubilization will be used here frequently as well as more accurate term dispersion.

[0009] CNTs can be solubilized into water using detergents, and into organic solvents as such or using compounds, such as pyrene, that increase the solubility of the CNTs. Detergents may hamper the good properties of CNT-cellulose materials.

[0010] Cellulose and its derivatives can be used to disperse CNTs, and cellulose-CNT composites have been used as supercapacitors, and EMI protection cellulose is renewable material, and its annual production in the nature might be more than the production of any other natural or man-made polymer. In wood cellulose is intertwined with lignin that is an aromatic polyether. Pure cellulose fibers are few micrometers long, and they have a rectangular cross-section. The cellulose fibers are hollow. Cellulose fibers bind with each other by hydrogen bonds. Because of the large number of hydrogen bonds the interaction is strong. However, water is able to break at least partially the hydrogen bonding network between fibers, and wet paper is very weak.

[0011] When nanoparticles or fibers are mixed, composite is formed. If the mixing is efficient, so that the components are mixed also in nanoscale, a nanocomposite will be formed. Fabrication of nanocomposites is not trivial, because often each component tends to separate into clusters that do not contain or contain very little of the other component(s). When the nanocomponents are chemically bound, the material is classified as a hybride material. The main focus of this invention is the fabrication and applications of HNT-cellulose nanocomposites and hybride materials.

[0012] It is possible to fabricate cellulose nanofibers that have diameters between 5-100 nm. They are still several micrometers long, and are called microfibrillated cellulose (M. Ankerfors, et al., A manufacturing method for microfibrillated cellulose, 6th International Paper and Coating Chemistry Symposium, 2006).

[0013] It is possible to fabricate even smaller bundles of cellulose. Cellulose fragment gel is made of cellulose by cutting the long cellulose molecules shorter and disintegrating the original cellulose fibers into amorphous structures.

[0014] One currently preferred method is acid hydrolysis of δ -cellulose in order to produce microcrystalline cellulose that has polymerization degree between 200 and 1000 α -glucose units, preferably between 300 and 500.

[0015] Another currently preferred cutting method is enzymatic. Cellulose fragment gel forms very strong nanocomposite with CNTs and HNTs. We have found that in the presence of CNTs and nanoparticles, individual molecular fragments of chemically, enzymatically, or biologically fragmented cellulose will be separated and reassembled around CNTs and nanoparticles. This form of fragmented cellulose is currently favored for the dispersion of CNTs. This kind of product is different from other known forms of cellulose composites, and is cellulose-nanoparticle gel, and is called Celose. Cellulose fragments form an amorphous continuum, and the material is mechanically very strong cellulose fragment-nanoparticle gel is essential for the present invention, and separates it from the prior art that utilizes various forms of cellulose. Carboxymethyl cellulose alone or mixed with cellulose gives good results, but we found that cellulose fragment gel is clearly better. In cellulose fiber hundreds of cellulose molecules are bound together. If cellulose fibers are used as carrier material for CNTs, only the surface of the fibers will be utilized, and the CNT/cellulose mass ratio is small. Despite of small CNT/cellulose ratio the CNTs are not well separated in two directions, although they are excessively separated in third direction (FIG. 1). The situation will be improved, if microfibrillated or nanocellulose will be used. Even nanocellulose has tens of (cut) cellulose molecules in one nanofiber. In cellulose fragment gel molecules are equally separated in all directions, and separation can adjusted at molecular accuracy by choosing the desired CNT/cellulose ratio. Cellulose fragments interact individually with CNTs by wrapping around the CNTs. Thus, the CNT/cellulose ratio will be maximized. Although nano-, and microparticles are useful for the dispersion they are not mandatory, especially for the short chained cellulose fragments, such as some forms of microcrystalline cellulose. Organic ionic solvents are good solvents for both cellulose and CNTs. Their high price is a serious drawback for several practical applications. Also during various deposition processes some CNTs and cellulose molecules form homoaggregates. The same problem is encountered with many other methods, in which cellulose is solubilized. When molecular components are well solvated, their mutual interaction in solution is suppressed. While solubilized cellulose is not properly wrapping CNTs, and deposition results at least into partial phase separation. When the deposition is induced by an outside effect, the product tends to be under kinetic control. In the method of present invention two water insoluble solids, fragmented cellulose and CNTs, are mixed in water using uneven distribution of kinetic energy that is able to separate cellulose fragments as well as CNTs from their own fibers and clusters. Cellulose molecular fragments will wrap around individual CNTs under thermodynamic control. Advantageously, nano- or microparticles will be used to enhance the effect of the kinetic energy. The resulting CNT-cellulose nanocomposite is stable enough so that the components do not separate under the conditions that are used in this invention.

[0016] The situation with various forms of cellulose is somewhat analogous to various forms of iron, such as chemically pure iron, cast iron, steel, stainless steel, and acid resistant steel. There are several subspecies of each of these. They have different mechanical properties, malleability, molding properties, chemical resistance, electrical conductivity, and magnetic properties. In some applications it might be possible to choose between two or more kinds of iron. However, in many applications only one kind of iron may be used. Similarly, we have found that out of several kinds of cellulose and its derivatives, cellulose nanoparticle gel (Celose) is best for the electrical applications of this invention, although some other forms of cellulose can be used with partial success.

[0017] In a co-owned patent application is described the fabrication of CNT-cellulose nanocomposite that contains also electrically conducting nanoparticles (J. A. Virtanen and P. Moilanen, WO/2008/034939). Combination of CNTs and electrically conducting nanoparticles is not enough. For several applications, including supercapacitors and EMI protection, there must be a good electrical contact between CNTs and nanoparticles. Mixing of the components even at nanoscale does not guarantee always the good electrical contact.

[0018] The composites of the present invention are also based on CNT-cellulose nanocomposite that contains electrically conducting nanoparticles. In the present invention the methods and compositions will be provided that ensure good electrical contact between CNTs and electrically conducting nanoparticles. Thus, the full utility of electrically conducting nanoparticles is obtained.

[0019] This nanocomposite may contain also paramagnetic particles, such as magnetite particles, or these particles may be advantageously in an adjacent layer. Thus, the macrostructure will contain both electrically and magnetically active particles providing superior protection against electromagnetic interference (EMI protection).

[0020] Magnetic particles can be made from iron, nickel, or cobalt, for example. Paramagnetic particles are typically ferrites. Magnetite is one specific example.

[0021] One major class of supercapacitors utilizes carbon nanoparticles (CNPs). Because CNPs have poor electrical conductance, only thin layers can be used. Similarly one class of EMI protecting materials is based on CNPs. CNPs give a random structure that can not be the best possible structure. More control of the structure is obtained, if CNTs or graphene will be used. However, so far the results have been disappointing mainly because CNTs and graphene tend to aggregate.

[0022] Prior art, all of which are given here as reference in their entirety:

[0023] M. Ankerfors, et al., US Patent Application 20090221812

[0024] Method for the Manufacture of Microfibrillated cellulose

cellulose was enzymatically (endoglucanase) cut, refined, and homogenized with high pressure fluidizer/homogenizer. The resulting product is micro- (or nano) fibrous cellulose that is different from the product of the present invention. Although the methods resemble each other, the different product can be explained by the presence of CNTs and/or nanoparticles in the methods of the present invention. CNTs and nanoparticles bind individual cellulose molecules and prevent their recombination into fibers after they have been separated even temporarily.

[0025] J. Engelhardt, et. al., WO 2009/021687 A1

Nanoparticles of amorphous cellulose

[0026] Fabrication of amorphous cellulose nanoparticles is described by a method that resembles that of Ankerfors et al. except that chemical cleaving of cellulose is used instead of enzymatic cleaving. However, the method of Engelhardt et al. provides amorphous nanoparticles instead of nano- or microfibers. One reason is shearing and ultrasonic vibration of fragmented cellulose. In the present invention the formation of cellulose particles, even nanoparticles, is undesirable. The formation of cellulose particles is avoided, because cellulose molecules wrap around of CNTs and nanoparticles.

[0027] H. Tennent, et al., US Application 856657

[0028] Graphitic nanofibers in electrochemical capacitors.

[0029] The capacitor in which nanofibers are coated with a thin coating layer of carbonaceous polymer. Polymer can be cellulosic polymer. However, no example is given.

[0030] C. Niu, et al., Appl. Phys. Lett. 70 (1997) 1480

[0031] CNT electrodes for high power electrochemical capacitors

[0032] P. Glatkowski, et al., U.S. Pat. No. 6,265,466

[0033] EMI shielding composite containing CNTs and polymer is described. Disclosure and examples limit the concentration of CNTs to 15%. Higher concentration require new methods, such as described in the present invention that allows any concentration between 0 and 100%. Glatkowski et al. require also orientation of CNTs by a shearing force. The present invention provides so good dispersion that enough CNTs will be oriented into every direction for EMI protection.

[0034] W. Li, H. Pröbstle, and J. Fricke, J. Non-Crystalline Solids 325 (2003) 1.

carbon aerogel supercapacitor is described.

[0035] C. H. Cooper et al., US Patent Application 20050272856 Jul. 7, 2004

[0036] CNT containing materials and articles containing such materials for altering electromagnetic radiation,

[0037] Claims are limited for the case, in which the length of CNTs is more than half the wavelength. In the present invention this requirement is not necessary. As a matter of fact the CNTs that are one hundredth of this limit work well, when the present method is used. This will make the materials of the present invention much more economical.

[0038] P. J. Glatkowski, et al., U.S. Pat. No. 7,118,693 Oct. 10, 2006

[0039] Conformal coatings comprising CNTs.

[0040] CNT diameter is claimed to be smaller than 3.5 nm that essentially requires that the CNTs are SWNTs. Very low loadings were used that are far lower than optimal concentration. One reason that can be the inefficient dispersion of CNTs over 1% and difficult dispersion over 10%. cellulose is mentioned as a possible polymer, but is not described in Experimental section. Sonication of CNTs into toluene solution, and mixing this solution with epoxy, polyurethane, acrylic, or silicone coatings was described by Glatkowski et al. cellulose was not an example. Repeating the method of Glatkowski et al. for cellulose was performed by the inventors of this invention. CNTs were dispersed either into water or 2-propanol in the absence or presence of cellulose. One typical example is in FIG. 20. The results were very different from those of the present invention. In FIG. 20 cellulose fibers are virtually intact (FIG. 20 A), and CNTs are lying on the surface of

cellulose fibers (FIG. 20 B, schematics in FIG. 1A). Thus, the EMI shielding efficacy obtained by Glatkowski et al. is limited by dispersion method.

[0041] P. J. Glatkowski, et al., U.S. Pat. No. 7,118,693

[0042] Conformal EMI shielding coating is described. CNTs have outer diameter 3.5 nm or less, while in the present invention the diameter is 3.5 nm or more. Glatkowski et al. require also insulating layer. While one embodiment of the present invention also contains CNT-polymer layer and an insulating layer that layer contains magnetically active particles. A three layer structure of the present invention has an insulating layer sandwiched between two CNT-polymer layers, and destructive interference of electromagnetic radiation is created between two CNT-polymer layers. This is totally new effect that is not described by Glatkowski et al.

[0043] C. Du and N. Pan, nanotechnology 17 (2006)5314

[0044] Electrophoretic deposition of carbon nanotubes on electrodes is described.

[0045] C.-C. Hu, et al., J. Phys. Chem. Solids 68 (2007) 2353.

[0046] Modification of MWNTs for electric double-layer capacitors.

[0047] S. Yoshimitsu, U.S. Pat. No. 7,382,601 Jun. 3, 2008

[0048] Electric double layer capacitor and method of manufacturing same.

[0049] Incorporating fullerene into CNT electrodes by microwave radiation is described.

[0050] J. S. Douglas, US Patent Application 20080044651

[0051] A coating or ink comprising CNTs is described. Dispersion may also contain nanoparticles and polymers including cellulose. cellulose is only mentioned by name without further definition or enabling embodiments. Also surface roughness is required to be about 100 nm or less. This is almost impossible to achieve with a mixture CNTs and cellulose, because both are fibrous solids.

[0052] W. Lu and H. Kent Douglas, US Patent Application 20080192407

[0053] Ultracapacitors with carbon nanomaterials and ionic liquids.

[0054] Ionic liquids are used as electrolytes. Polymers are carrier materials so that the supercapacitor is largely solid. Inorganic material is used to prevent crystallization of polymeric material.

[0055] P. M. Ajayan, et al., US Patent Application 20080212261

[0056] Energy storage devices and composite articles associated with the same.

[0057] Method claims of Ajayan et al. require polymer is dissolved into a liquid. That is in sharp contrast of the present invention, in which the polymer is advantageously poorly soluble into the liquid. Importantly, no kinetic energy input is mentioned in disclosure or in any embodiments.

[0058] US Patent Application 20080254362

[0059] Nano-Composite structures, methods of making, and use thereof.

[0060] Nanocomposite containing CNTs and semiconducting or metallic nanoparticles is described. Also polymeric binder may be included. Apparently no polymers are defined in the disclosure, and no examples of their use is given. However, several specific polymers are claimed, but cellulose is not included.

- [0061] U.S. Pat. No. 7,553,341 Jun. 30, 2009
- [0062] High power density supercapacitors with carbon nanotube electrodes.
- [0063] Electrophoretic deposition of CNTs.
- [0064] J. S. Glatkowski, et al., US Patent Application 20090131554
- [0065] EMI shielding CNT-polymer composite is provided. In strong contrast with present invention the composite has low or essentially no bulk conductivity. Glatkowski et al. realized that entanglement of CNTs is essential for good EMI protection. Entanglement is difficult to obtain with high loadings. This problem has been solved in the present invention, and high concentrations of CNTs can be used, and CNT-polymer nanocomposite has also good bulk conductivity.
- [0066] K.-L. Jiang and S.-S. Fan, US Patent Application 20090168302
- [0067] Electrochemical capacitor with CNTs.
- [0068] Use of cellulose in porous middle membrane is mentioned. However, Membrane is not integrated with CNT layers.
- [0069] J.-H. Kwon, et al, U.S. Pat. No. 7,588,700
- [0070] Specific EMI shielding material comprising epoxy or polyimide resin and CNTs that contain both C=O and N—H functionalities. Composition may further comprise metal particles.
- [0071] A. G. Rinzler, et al., U.S. Pat. No. 7,704,479
- [0072] Highly accessible, nanotube electrodes for large surface area contact applications. Fabrication of porous CNT-membrane is described. Sacrificial nano- or microparticles are used. These particles will be removed after the fabrication of a film. Dispersion method is not specified, but the requirement is that CNTs and particles do not flocculate from suspension. This is in sharp contrast to the present invention, in which the CNT-polymer-nanoparticle nanocomposite flocculates advantageously from suspension. Also in the present invention nano- or microparticles will be used to focus kinetic energy, and they must have density that is advantageously twice that of the solvent. Rinzler et al. use nano-, and microparticles only as spacers, and the density is not important, unlike in the present invention.

FIGURE CAPTIONS

- [0073] FIG. 1. Schematic cross-section of A. CNT-cellulose composite, in which CNTs have been deposited onto a cellulose fiber surface, B. CNT-cellulose nanocomposite, in which components are mixed at molecular scale.
- [0074] FIG. 2. Schematic depiction of fabrication (F to A) of nanocomposite of this invention, and final control of the composition (reverse direction, i.e., A to F, but not necessarily in alphabetical order).
- [0075] FIG. 3. Schematic depiction of kinetic energy focusing at molecular level by using nanoparticles.
- [0076] FIG. 4. Schematics of binding of cellulose fragments via hydrogen bonded segments. Each fragment can change direction suddenly, and bind with several different other cellulose fragments.
- [0077] FIG. 5. Schematics of a structure of cellulose fragment-nanoparticle nanocomposite or gel.
- [0078] FIG. 6. Schematics of one embodiment of a countercurrent flow reactor that can be used to fabricate CNT-cellulose fragment gel of this invention.
- [0079] FIG. 7. Schematics of a micro- or nanoparticle that is at least partially coated with enzymes.
- [0080] FIG. 8. TEM image (A), scale bar is 200 nm and SEM (B) image of amorphous CNT-cellulose-nanoparticle nanocomposite of this invention, 100 000 fold magnification.
- [0081] FIG. 9. Schematic demonstration of the increase of the area achieved by coating a flat surface by spherical particles.
- [0082] FIG. 10. Schematic depiction of a particle 1001 that is coated with a layer 1002.
- [0083] FIG. 11. Schematic depiction of one embodiment of the nanocomposite fabrication method. A. Functionalized cellulose 1101 and carbon nanotube 1102, B. Combination of CNT and functionalized cellulose. C. Precursor nanoparticle 1103 is attached with functionalized cellulose. D. Amorphous carbon 1104 is formed from functionalized cellulose 1101 after pyrolysis, and precursor nanoparticle is enlarged and attached with CNT 1102.
- [0084] FIG. 12. TEM micrograph of MWNT-cellulose-CMC-Prussian Blue nanocomposite. Prussian blue nanoparticle 1201, carbon nanotube 1202
- [0085] FIG. 13. Graph of charging cycles of a supercapacitor that was made of MWNT-cellulose-CMC-Prussian Blue gel.
- [0086] FIG. 14. Schematics of one embodiment of the present invention. Two layers of CNT-molecular cellulose-nanoparticle nanocomposite 1402 of the invention are separated by an ion permeable membrane 1403. The electric wires 1401 are connected directly with nanocomposite layers 1402, and no separate electrodes will be needed.
- [0087] FIG. 15. Schematics of another embodiment of the present invention, in which CNT-molecular cellulose-nanoparticle layers 1502 have been integrated into one continuous layer via a center layer that consists of molecular cellulose that may contain nanoparticles, but no CNTs.
- [0088] FIG. 16. Schematics of a cross-section of two CNTs 1600 and 1601 that are connected electronically by a graphite sheet 1604, that is stacked by several graphite sheets 1604. Intercalated between graphite sheets are nanoparticles 1603 and molecular cellulose fragment 1602.
- [0089] FIG. 17. Schematic structure of A., Single layer composite containing both electric 1701 and magnetic particles 1703 in the same layer, B., Double layer structure, in which the electric 1701 and magnetic particles 1703 are in different layers.
- [0090] FIG. 18. Schematic depiction of multilayer alternating structure.
- [0091] FIG. 19. Graph of EMI shielding efficiency of DWNT-fragmented cellulose paper vs. frequency.
- [0092] FIG. 20. SEM images of CNT-cellulose fiber composite A. 250 \times magnification, and B. 100 000 magnification of the area, in which CNTs are visible. Schematic FIG. 1 A is drawn on the basis of this SEM image. This figure is provided as a reference, and does not represent the present invention.

DEFINITIONS

- [0093] Cellulose fiber is a hollow fiber consisting thousands of cellulose molecules.
- [0094] Nanocellulose is a nanofiber consisting of tens of cellulose molecules, diameter is about 5 nm.
- [0095] Cellulose molecule is less than 1 nm thick, and several micrometers long.
- [0096] In common language cellulose refers often to a pulp consisting of cellulose fibers. In this disclosure cellulose means individual cellulose molecules.

[0097] Cellulose fragment has between 200 and 4000 glucose units.

[0098] Amorphous cellulose does not have crystalline or even fibrous structure, and no long range order. Few molecules can run parallel a short distance (FIG. 4).

[0099] Cellulose gel is amorphous cellulose that contains solvent.

[0100] Cellulosic material is any polymer or oligomer fabricated from cellulose.

[0101] Nanoparticle has a diameter between 10 and 100 nm.

[0102] Graphitic material consists almost entirely of sp^2 hybridized carbon atoms arranged into hexagonal network. Some heteroatoms may be especially at the edges. Examples are graphite, graphene, carbon nanotubes, and nanohorns.

[0103] Material is slightly soluble, if the solubility is less than 0.5% (w/w) as molecules.

[0104] Material is sparingly soluble, if the solubility is less than 0.05% (w/w) as molecules.

Acronyms:

[0105] CAP is cellulose acetate propionate

CMC is carboxymethyl cellulose

CNP is carbon nanoparticle

CNT is carbon nanotube

EMI is electromagnetic interference

ESD is electrostatic dissipation

HNT is Hybride nanotube, HNT will include CNTs unless otherwise specified.

SUMMARY OF THE PRESENT INVENTION

[0106] The present invention provides methods for the fabrication of nanocomposites and hybride materials from two materials in a liquid into which both materials are slightly or sparingly soluble.

[0107] The present invention provides methods and compositions for the efficient, fast, and economical fabrication of polymer-graphitic material nanocomposites using nanoparticles for the facilitation of dispersion especially, if both materials are sparingly soluble.

[0108] In the currently preferred method polymer is cellulose or modified cellulose, and graphitic material consists of CNTs or functionalized CNTs, and CNT/cellulose ratio is more than 1:10.

[0109] In another currently preferred embodiment CNTs, chemically or enzymatically cut cellulose, and nanoparticles, such as calcium carbonate nanoparticles, will be first mechanically mixed, and then hydrodynamically mixed so that the amount of CNTs and cellulose is about equal, and the amount of nanoparticles is more than the combined amount of CNTs and cellulose. Depending on actual components and applications the relative amounts can be varied considerably.

[0110] Still another embodiment allows to increase the concentration of CNTs by the partial or total removal of some nanoparticles, such as calcium carbonate nanoparticles, by acid treatment, and partial or total removal of cellulose by pyrolysis that generates only volatile components. CNT concentration can be increased up to 100%, but in order to avoid reaggregation CNT concentration will be preferably under 75%.

[0111] In one aspect of the present invention the materials of the present invention can be advantageously used in supercapacitors, for EMI protection, and dispersion of graphitic materials into other polymers.

[0112] In one embodiment that is especially useful for EMI protection the material may contain magnetic or paramagnetic nanoparticles.

[0113] In another embodiment of the present invention the material that is useful for supercapacitors, contains electrically active nanoparticles, such as magnetite, Prussian blue, cobalt oxide, lead(II,II,IV)oxide, carbon nanoparticles, ruthenium oxide, titanium oxide, tin oxide, or manganum oxide.

[0114] In one advantageous embodiment of the present invention cellulose derivatives, such as cellulose fragment gel, cellulose acetate, nitrate, methyl cellulose, carboxymethyl cellulose, or ethyleneoxide cellulose are mixed or reacted with HNTs. In one currently preferred embodiment the cellulose derivative is cellulose acetate propionate that can be melted without decomposition, and the HNTs can be mixed with the melted cellulose derivative without using any solvents. Magnetic or paramagnetic nanoparticles can be deposited or mixed with these composites.

[0115] It is a further aspect of the present invention to improve the mechanical properties by chemical cross-linking cellulose or functionalized cellulose with HNTs and/or HNTs with each other, and magnetic nanoparticles. Cross-linked material is hybride material.

[0116] In one embodiment the HNT-cellulose fragment gel that is used in supercapacitors is also mechanically strong so that is also a structural component in various devices and vehicles, while the main purpose is storing electricity. Mechanical strength can be further increased by carbon fibers that will also have dual function, because they are able to distribute electric current evenly into a supercapacitor.

[0117] In another aspect of the present invention, a supercapacitor is electrically connected with two or three electrical potential sources. The first potential source is used to charge the supercapacitor. The second potential source forms a closed circuit with the first electrode of the supercapacitor. Optionally, the third potential source forms a closed circuit with the second electrode of the supercapacitor. This kind of supercapacitor may be flat, cylindrical, or some other form, and can be used to conduct electricity longitudinally.

[0118] In still another aspect of the present invention a layered structure is formed from HNT-cellulose nanocomposite and a dielectric material. If dielectric material contains paramagnetic material, a dual layer structure is useful. If no paramagnetic particles are included, a triple layer structure, in which dielectric layer is sandwiched between two HNT-cellulose nanocomposite layers is useful. This kind of layered structure can be used advantageously for the protection against electromagnetic interference (EMI).

[0119] In one advantageous embodiment HNT-cellulose nanocomposite is embedded inside a thermoplastic or thermoset resin, combining good material properties and EMI protection, and possibly also electrical storage.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0120] Fabrication of Graphitic Material-Polymer Nanocomposite The present invention provides graphitic material-polymer nanocomposites, in which individual molecules of graphitic material will not be clustered. Thus, a full utility of

graphitic material for many applications will be obtained. In most currently preferred embodiments graphitic material consists of CNTs, and polymer is cellulose or modified cellulose.

[0121] The essence of one embodiment of the present invention is a material, in which graphitic material **101** (CNTs in FIG. 1) is wrapped in molecular polymer **102** so that the surface of the graphitic material is maximally exposed at molecular level, i.e., it is not covered by another graphitic molecule, except at small areas that provide bulk conductivity. In these examples polymer is cellulose or fragmented cellulose. Cellulose provides a porous and hydrophilic structure, in which several types nanoparticles can be incorporated. Also ions can move easily in a porous and hydrophilic milieu. The distance of graphitic material particles can be adjusted very accurately by the mass ratio of graphitic material and fragmented cellulose provided that fragmented cellulose is not clustered (FIG. 1 B.). This is achieved by cutting cellulose fibers chemically, biochemically, biologically, and/or physically. Advantageously, dispersion is done in the presence of nano- or microparticles, such as alumina, silica, calcium carbonate, calcium sulfate, calcium phosphate, iron phosphate, iron oxide (ferrite), tin oxide, titanium oxide, or zinc oxide. These particles amplify the dispersion of graphitic material and cellulose, and act as spacers that prevent their recombination into homoclusters. Some of these nanoparticles are electromagnetically useful in applications. Fabrication is depicted in FIG. 2, in which cross-sections of the components are shown for simplicity. CNTs are examples of graphitic material, and the cross-section of a CNT is a circle **201**. FIG. 2 A depicts a bundle of CNTs. Nanoparticles **203** are added from left to right (FIG. 2 A to B, C to D, and E to F). Molecular cellulose is added downward (FIG. 2 A to C, B to D, C to E, and D to F). In the fabrication methods of this invention all these components are present at the same time, because positive cooperative effect. nanoparticles **203** would not mix very well with CNTs **201**. However, their high relative density promotes detachment of molecular cellulose **202** from cellulose fibers, and cellulose encapsulates both CNTs and nanoparticles.

[0122] Dispersion and the resulting interaction of two insoluble solids, graphitic material and cellulose, is achieved in this invention by using unevenly distributed kinetic energy. Many forms of mechanical or hydrodynamic mixing can be used, including blade mills, ball mills, millstones, blasting with ceramic or polymeric particles, powerful liquid jets, and ultrasonic vibration. In one currently favored method the cellulosic material is mixed with graphitic material, alumina nanoparticles, and enzyme, such as endocellulobiose, or chemicals, such as sodium hypochlorite, in water and milled with very fast blades. The mixture is further subjected into ultrasonic vibration. Nano- and microparticles have much higher density than the solvent, cellulose, or CNTs. They will greatly amplify the mixing effect, and will make the large scale fabrication of CNT-cellulose nanocomposite economical and practical. nano- and microparticles can be considered as kinetic energy concentrators that can focus the kinetic energy to individual molecules, CNTs (FIG. 3 B), and cellulose fragments (FIG. 3 A, cellulose fiber has already been cut mechanically). Kinetic energy is required for the separation of individual cellulose molecular fragments and CNTs (FIG. 3 E) or other graphitic particles. Because they are sparsely soluble into water, or other solvents that can be used in this context, they will recombine very fast, and under these con-

ditions they combine often to form CNT-cellulose nanocomposite (FIG. 3 F), in which cellulose fragment molecules are helically wrapped around CNTs. Cellulose is not only amorphous, but is molecular form, i.e., divided into smallest possible units that are molecules. Cellulose fragment molecules are not easily detached any more from the CNTs. This method works really well, when cellulose is partially cut. Intact cellulose is very difficult to separate as individual molecules. Although detergents will be avoided, but not totally forbidden in conjunction of the present invention, some other soluble agents that will help partial dissolution of the starting materials may be used. Examples are polyvinyl alcohol, polyallyl amine, CMC, scarbonch, and hemicellulose. SEM image (FIG. 8 B) proves that cellulose does not form fibers or crystallites in this material. Most of material surface is structureless and resembles the circled area **802**. This image is taken from a hole, in which several features can be seen. CNTs are in this image similar to sparsely deposited CNTs (not shown), expect that they are coated by a thin layer of molecular cellulose. Thicker layer will appear white. Some nanoparticles (calcium carbonate) **803** are also visible. The material is amorphous, and is very different from microfibrillated cellulose or nanocellulose. TEM image (FIG. 8 A) is taken from same sample. The coating layer of cellulose is very readily visible in circled area **804**. Cellulose can be seen as uneven shape around very well visible edges of MWCNT's **805**. Microcrystalline cellulose can also be advantageously used as a starting material. Microcrystalline cellulose is obtained from β -cellulose by acid hydrolysis. Kinetic energy is directly proportional to the mass m and second power of the velocity of the particle **303** (FIG. 3 A). Nanoparticles follow the liquid flow very closely. If the kinetic energy of a nanoparticle is compared with a equal volume element of a liquid, that nanoparticle can have several times bigger kinetic energy, if the density of the nanoparticle is much higher than that of liquid. Nanoparticle **303** will hit only one or few molecules, and the kinetic energy of the nanoparticles is transferred to few molecules (FIG. 3 E), while surrounding molecules experience much smaller impact from liquid. This mechanism works really well only, if the density of nano- or microparticles is considerably higher than that of the solvent. Advantageously the density of particles is at least twice the density of the solvent. This will lead to an efficient separation of molecules from a cluster or bulk material. Nanoparticles **303** will also be incorporated into the nanocomposite.

[0123] Some nanoparticles that are used during the fabrication of CNT-cellulose nanocomposite can be easily removed. For example, calcium carbonate can be removed by acid. Calcium chloride is soluble in water and is largely or totally removed during filtration, and washing. Alumina and silica can be removed with sodium hydroxide. Because cellulose can be partially or totally removed by pyrolysis, the CNT content of the final product can be deliberately adjusted anywhere between 0-100%. This is one further aspect of the present invention. Using excess of inert solid material for the dispersion of the CNTs or other graphitic materials, gives a better dispersion (FIG. 2 F). When the excess of intervening solid is removed, CNTs will still stay separated, provided that too much of cellulose **202** and/or solid nano- or microparticles **203** will not be removed (FIG. 2 B or C). Instead of totally removing nanoparticles **203** their size can be reduced. Because nanoparticles will be incorporated into the nanocomposite, and they will be consumed, their amount is advantageously quite large, typically over 50% of the total mass.

This is not mandatory, and the amount can be much smaller. Large amount of nanoparticles, such as calcium carbonate, is not problematic, because many of them are inexpensive, and can easily be removed by acid or base. Acid is consumed in the process of removing calcium carbonate, and the end product will be neutral. Soluble products can be filtered away. Moreover, dielectric nanoparticles act as spacers between CNTs like cellulose does.

[0124] When powerful solvents, such as ionic liquids, are used to solubilize CNTs and cellulose, they do not really separate CNTs completely, or CNTs will cluster with each other, when the ionic liquid is removed. Although cellulose will often be amorphous, when deposited from solution, it is still strongly clustered. Solubilized cellulose will wrap around CNTs only partially. This kind of method is under kinetic control, unlike the method of the present invention that is thermodynamically controlled. In kinetic control large molecules, CNTs and cellulose molecules, cluster with the molecules that happen to be closest, when deposited by lower temperature of addition of poor solvent. Partial reassociation of CNTs can not be prevented under kinetic control. Thermodynamic control gives good quality CNT-polymer nanocomposite as is evidenced by the present invention. If cellulose wrapped CNTs are thermodynamically stable, as experimental results of this invention demonstrate, virtually all CNTs will be wrapped inside cellulose. They can still have contact points that provide bulk electrical conductance.

[0125] One currently favored embodiment of the present invention provides electrically well conducting CNT or HNT network that is coated with electrically conducting nanoparticles so that there is a good electrical contact between HNTs and nanoparticles. Currently most advantageous particles are CNPs. Some other possibilities, cuprous iodide, cobalt oxide and Prussian blue. Graphite is one special type of CNP. Graphite is exfoliated graphite that has very good electrical conductivity, and surface area per gram is 2600 m²/g, if both sides of the sheet are included. CNPs can be made in several methods. One currently preferred method is to cutting HNTs very short, and then oxidizing them in nitric acid-sulfuric acid mixture even shorter. Some of them will exfoliate so that they are intermediates of HNTs and graphene.

[0126] In supercapacitors the role of nanoparticles is straightforward. The purpose is to increase the surface area that can be charged electrically. If the particle is spherical, it has the surface area that is four times larger than it covers on the HNT (FIG. 5). In addition many nanoparticles are porous, and the effective area is many times larger. Graphene is flat and can connect two or more HNTs. Contact area between graphene and CNTs is relatively large, while contact between two cylindrical CNTs is point-like and very small.

[0127] For EMI protection the role of the electromagnetically active nanoparticles is less obvious. The EMI protection can be obtained by two different mechanisms, reflection or absorption. Metals reflect electromagnetic fields. HNTs behave somewhat similarly. However, absorption is preferred. HNTs will be excited to higher energy levels by electromagnetic waves transiently, but they will relax by emitting electromagnetic waves. Part of the electromagnetic energy will be reflected back. When HNTs are coated with nanoparticles that are able to absorb the excitation energy from the HNTs, there will be minimal reflection. Nanoparticles act as sinks for the electromagnetic energy. This is the ideal situation, because it is desirable to minimize electromagnetic background from all electrical devices. Reflectors, such as

metals and pure CNTs do not achieve this goal, they only redirect the electromagnetic energy.

[0128] In order to obtain the full merit of these nanoparticles, a good electrical contact between HNTs and nanoparticles is necessary. This can be obtained by various means. When CNPs are used, they are well dispersed with CNTs using a dispersing agent. Cellulose fragment gel and carboxymethyl cellulose (CMC, X=CH₂COOH in FIG. 11) are currently preferred. Also cellulose succinate, maleate, and other dicarboxylic acid esters are applicable. One glucose unit may contain 1-3 acidic or other substituents. One currently preferred method for the creating a good electrical contact is pyrolysis of CMC or another cellulose derivative (FIG. 11). Cellulose and its derivatives 1101 start to decompose at temperatures above about 260° C. Cellulose will decompose mainly into volatile small molecules. Although the chemical structure of the decomposition products of cellulose derivatives are not currently known, the electrical contact between HNTs 1102 and precursor nanoparticles 1103 will be improved. Precursor nanoparticle can be nanoparticle, such as carbon including graphite, titanium dioxide, lead dioxide, lead(II,II,IV)oxide, iron phosphate, tin dioxide, magnesium dioxide, cadmium sulfide. It can be a single ion, for example, copper(II), iron(II), iron(III), or lanthanum that serves as a nucleus for the growing nanoparticle. These are nonlimiting examples. The term precursor nanoparticle is used, because the particle can be so small that it is not a nanoparticle in the strict sense of definition. During pyrolysis the precursor nanoparticle will be partially or totally coated with amorphous carbon. The chemical composition and structure of the pyrolysis product may depend strongly on the temperature of pyrolysis. We suppose that at higher temperatures, about 800° C., the product will resemble amorphous carbon 1104, and call the pyrolysis product amorphous carbon even, if the pyrolysis temperature is lower than 800° C. (FIG. 11). The result will also depend on heating method to some extent. Joule heating is fairly even. IR- or microwave heating may heat some components, CNTs and CNPs, very strongly, while having virtually no direct effect on cellulose or modified cellulose itself. However, the junction of CNT and CNP will be strongly heated, and vicinal cellulose will be pyrolyzed to provide a seal for the junction. We consider this process to be analogous to soldering. Instead of tin the soldering is performed by a decomposition product of CMC or some other functionalized cellulose. Before the pyrolysis, the CMC molecules can be connected with metal ions, such as copper, zinc, aluminum, or alike. Presence of metal ions will create cavities during pyrolysis. Acid treatment will form hydrogen bonds between CMC molecules. Additional advantage of the pyrolysis is that most of the cellulose backbone will decompose into small molecules that evaporate. Still the porosity is largely retained. Thus, the final weight of the product is reduced considerably, while quality is improved.

[0129] Another method for the connecting HNTs and electrically conducting nanoparticles, is to deposit nanoparticles directly on the surface of the HNTs. Especially, if the HNTs are dispersed using CMC, many metal ions bind with CMC that is tightly bound with HNT, and the nanoparticles can be fabricated directly onto the surface of HNTs. Currently cuprous iodide, magnetite, Prussian blue, tin oxide, and cobalt oxide nanoparticles are favored. For EMI protection also magnetite nanoparticles are advantageous. In these cases the precursor nanoparticle can be a single metal ion that is

attached with functionalized cellulose or HNT. The nanoparticle will grow around this ion, when more reagents will be added.

[0130] Currently cellulose and its derivatives are used advantageously to disperse HNTs and in some cases also electromagnetically active nanoparticles. cellulose provides also porosity that is useful especially for supercapacitors.

[0131] Still another mixing method is provided by shear force that can be especially strong in a high pressure dispersion apparatus, which is commercially available, for example DeBEE 2000 Pilot Homogenizer. The pressure gradients in these devices can be hundreds of bars.

[0132] Mechanical mixing is ineffective at very short distances because the molecules move together about the same speed, although counterstroke mixer alleviates partly this problem. The ultrasonic vibration agitates molecules and particles by accelerating them back and forth in a rapid succession. Thus, the diffusion gradients of the reagents are diminished. This greatly increases the rate of the diffusion dependent collision and binding of particles.

[0133] The power of one sonotrode can be between 0.1 and 50 kW, most advantageously between 1 and 20 kW. When multiple sonotrodes are used, the power may vary with time so that interference pattern will change all the time. Thus, the whole reaction mixture can be more evenly agitated. Ultrasonic processes can be easily scaled up and optimized (Hielscher T., Ultrasonic production of nano-size dispersions and emulsions, ENS'05, Paris, France, 14-16 Dec. 2005).

[0134] Cellulose xanthate is used industrially for the fabrication of cellulose fibers. Cellulose acetate, pthalate, acrylate, and nitrate are also much better soluble into organic solvents than cellulose. Sulfonation, carboxylation, amination, and many other functionalizations increase the solubility of the CNTs into water several orders of magnitude. All these and other functionalized cellulose derivatives and CNTs can be used as additives in the context of the present invention. Often the primary hydroxyl group is easiest to functionalize (X in FIG. 11), although other hydroxyl groups can also be functionalized.

Currently Preferred Embodiment for the Fabrication of Modified Cellulose Fragment-Nanoparticle Gel

[0135] The starting material for the method of this invention can be cellulose that is made from wood, grass, or any other plant material. Also bacterial cellulose, such as produced by *Acetobacter xylinum*, can be used. Because of low cost, one preferred starting material is the finely divided suspension that is not retained in paper during the fabrication of paper that also contains nanoparticles. Microcrystalline cellulose is another preferred starting material, because of consistent good quality.

[0136] Cellulose molecules consists of about 5 000 β -glucose moieties. Vicinal cellulose molecules are strongly hydrogen bonded, and separation of individual cellulose molecules is nearly impossible. Hydrolysis of β -glucoside bonds produces fragments that are easier to separate. Fragments should be long enough so that they are still interesting for the materials applications, i.e., they should form strong hydrogen bonded network and be slightly or sparingly soluble into water. Hydrolysis can be performed by chemical means, for example, catalyzed by acids, such as sulfuric or hydrochloric acids, or enzymatically. Also certain molecules or ions, including boric acid, aluminum, iron, zinc, magnesium, and calcium ions, will catalyze the hydrolysis. Cellulose is also

thermally unstable above 260° C. Superheated steam above 260° C. will be able to cut cellulose molecules.

[0137] Separation of the cellulose fibers and cellulose fragments (fragmented cellulose) is essential for the fast reaction. Otherwise the product will inhibit the further reaction. Boric acid under basic conditions will assist the transfer of cellulose fragment. Chaotropic agents will also break hydrogen bonds that keep cellulose molecules and fibers together. One of the most powerful chaotropic agent is guanidinium isothiocyanate. Ultrasonic vibration is one currently preferred method for the detachment of fragments from cellulose fibers. Temperature has also a significant effect on the breaking of hydrogen bonds.

[0138] Reactions rely on diffusion on a molecular scale. Mechanical mixing is ineffective at very short distances because the molecules move together about the same speed. The ultrasonic vibration agitates molecules and particles by accelerating them back and forth in a rapid succession. Thus, the diffusion gradients of the reagents are diminished. This greatly increases the rate of the diffusion dependent reactions. The separation of large molecules and nanoparticles benefits even more from the ultrasonic agitation. For example, diffusion of an enzyme is relatively slow, but ultrasonic vibration promotes the movement of an enzyme to and from the surface of a cellulose fiber. The cellulose fragment that is partly or totally detached from the cellulose fiber will have different acceleration in the same oscillating medium than the remaining aggregate. Thus, they are pulled apart. If the process relies on the diffusion alone, it would take much longer time. One aspect of the present invention is to use enzymes 701 that are conjugated with spacers, such as PEG, with nanoparticles 703 (FIG. 7). Conjugation of enzymes with nanoparticles is well known in the art. These kind of particles act simultaneously mechanically and biochemically.

[0139] Also purely chemical reaction, such as acid hydrolysis, can be accelerated by nanoparticles that loosen the structure of a cellulose fiber. This will further promote the chemical reaction and separation of components. Nanoparticles must be tolerant against the chemical milieu of the process. For example, hydroxyapatite nanoparticles tolerate basic conditions, and silica particles are resistant to acidic conditions. Earth alkali sulfates are suitable in the presence of sulfuric acid, because the excess of the sulfate ions prevents the dissolution of these particles. Some carbonates, such as calcium or barium carbonates, may be used especially, if the solution contains soluble carbonate, such as sodium carbonate.

[0140] Removal of the reaction product is not enough, if the product can diffuse back onto the cellulose fibers. Nanoparticles can assist the removal by bonding the cellulose fragments. Also CNTs will be coated by cellulose fragments. Binding of cellulose fragments by particles is advantageous for the hydrolysis of cellulose, but also fragments can be further hydrolyzed. In order to prevent further fragmentation of primary cellulose fragments flow through reactor is currently preferred (FIG. 6).

[0141] In the simplest form the flow reactor has outer and inner tube. A part of the inner tube is tubular grid that has mesh size between 200 and 2000. A thick slurry of cellulose starting material that contains catalytic agent, such as acid, enzyme, or microbe, and nanoparticles flows downward. Water that might contain nanoparticles or CNTs flows upward in the outer tube. The content is agitated, preferably by ultrasonic vibration. Cellulose fragments will be trans-

ferred from inner tube into the outer tube. Catalytic agent may be bound onto a solid substrate so that it is retained inside the inner tube. For example, an enzyme may be bound by a spacer onto a relatively large particle, or ion exchange resin may be used to carry protons or catalytic metal ions. In order to facilitate the transfer the product through the grid, the pressure between the two tubes may oscillate so that there is back and forth flow between the inner and outer tube. Oscillation can be accomplished by coordination of pumps or valves that are part of the system. In an alternative embodiment cellulose and CNTs are mixed mechanically, and the mixture is suspended into water, and flows in the inner tubular grid. It is obvious that the role of inner and outer tube may be reversed, and also any combination of flow directions will be applicable.

[0142] Flow reactor that has more throughput is depicted in FIG. 6. It has 14 tubular grids. The starting material is pumped into one tube that is divided into 14 tubes, and after passing the grids inside the reaction chamber these tubes are connected into one tube again.

[0143] Although the continuous reactor (FIG. 6) is currently preferred, it is obvious that the ultrasonic method of this invention is applicable also in bath type reactors. The ultrasonic vibration is more efficient at higher pressures. The pressure can be increased in continuous reactors by hydrostatic pressure. About 10 m high column of water based liquid in a tube or pipe corresponds to one bar (megapascal) of pressure. The pressure can be between 1 and 50 bar and most advantageously between 2 and 5 bars. Excessively long tubular reactor can be avoided, if the reactor is closed and pumps are used.

[0144] The ultrasonic vibrator generates heat, and the temperature can actually increase slightly in the reactor. External or internal heating is also possible in the reactor. The heating can be accomplished by the methods that are well known in the art. Also electromagnetic radiation can be used, especially IR-, or microwave radiation. The wavelength is preferably chosen so that cellulose, nanoparticles, or CNTs absorb it effectively. This radiation may be advantageously directed into the reaction chamber.

[0145] The reactor may contain a mechanical mixer. The mixer may have blades, propellor, or screw. The motor is advantageously outside the reactor and on the top, and the shaft comes into the reactor. Mechanical mixing can be used with or without ultrasonic vibration.

[0146] While cellulose molecules are strongly hydrogen bonded within one cellulose fiber, the interaction of molecules between two fibers is much weaker, i.e., the structure is granular. On the contrary, when solid material is reconstructed from individual cellulose fragment molecules, they can form continuous 3D network, in which vicinal molecules will be strongly hydrogen bonded, and essentially a continuous, isotropic material will be formed. Although some molecules bind parallel with each other, no significant fibrous structure is formed. The material is amorphous gel-like. This is clear distinction with nano-, and microfibrillated cellulose, and, of course, with cellulose itself. Very strong paper, boards, and other pieces that have more complicated shapes can be produced from cellulose fragment gel. Nanoclay, and other micro- or nanoparticles, including but not limited to silica, alumina, magnetite, titanium dioxide or silicate, cadmium sulfide, Prussian blue, CNTs, carbon, and graphite, can be mixed with fragmented cellulose mass advantageously during fragmentation. Mixing of particles and cellulose frag-

ments can also be done before the fabrication solid objects. These particles can give desired additional properties, such as increased modulus, color, magnetic or electric properties. The product is Celose™ in all cases. If it contains CNTs, for example, it can be specified as CNT-Celose™.

[0147] If only ESD is required, mixing of 0.1-2% of CNTs will be sufficient. Good EMI protection is obtained if the material contains about 10-40% of CNTs. Because CNTs reflect microwave radiation, addition of carbon nanoparticles is advantageous so that the microwave radiation is mostly absorbed. Magnetic protection will require 1-20% of ferrite particles. Ferrite particle can be quite large, up to 50 µm, and they may be coated with silica or alumina layer. Material that is used for heating elements should have specific resistance around 1 Ωcm, which is obtained, when the CNT content is 10-30%. Supercapacitors are advantageously made of CNT-cellulose nanocomposite that contains 20-70% of CNTs. Conducting ink for printable electronics should contain 20-70% of CNTs. Product that contains 70% of CNTs and 30% cellulose (molecular fragments) is still paper-like and can be easily handled and formatted into various shapes. However, the good properties of CNT-cellulose nanocomposite do not increase linearly with CNT content. Instead it seems that capacitance and EMI protection reach optimum around 50% of CNTs.

[0148] While fragmented cellulose is advantageous for the dispersion of nanoparticles and CNTs, part of it or all of it can be removed after dispersion process. For example, the weight of supercapacitors should be minimized, and cellulose or cellulose fragments do not have active role in the electric storage function. The excess cellulose can be removed by further fragmentation so that the fragments become soluble, and can be washed away, or are transformed into carbon that is actually active in the supercapacitor (FIG. 2 F to D, or E to C). In the extreme case the thermal fragmentation can go so far that fragments will evaporate. Enzymatic fragmentation is very gentle, and will retain the overall structure of the CNT network so that the collapse is avoided. The voids that will be created by enzymatic treatment can be filled with nanoparticles that can be deposited using soluble components, or with the premade nanoparticles. These nanoparticles should be electrically active in supercapacitor function. Nonlimiting examples include iron phosphate, magnetite, Prussian Blue, cadmium sulfide, lanthanum fluoride, cobalt oxide, tin oxide, titanium oxide, or lithium titanate. Cobalt oxide is very convenient, because it can be electrochemically deposited that guarantees that the deposition happens on the surface of CNTs.

[0149] Paper or formatted pieces can be compressed under pressure, between 2 and 100 bar, in order to make pieces thinner and harder. Heating will further assist compactification.

Functionalization

[0150] In some cases the starting material may be functionalized, for example, it can be carboxymethyl cellulose, acetyl cellulose, nitrocellulose, glycidyl cellulose, hydroxyethyl cellulose, or PEG-cellulose. Degree of functionalization is especially important for the microbial or enzymatic hydrolysis. High degree of functionalization may prevent hydrolysis. On the other hand optimal functionalization will allow limited hydrolysis so that long fragments will be obtained that are resistant to further hydrolysis.

[0151] Cellulose fragment can be functionalized by any method known in-the-art after they have been fabricated. Because they are more easily detached from other fragments than cellulose molecules from cellulose fibers, functionalization of fragments is often relatively straightforward. Especially the interaction with solid particles, such as nanoparticles and CNTs is fast and might require minimal amount of solvent, such as water.

[0152] Cellulose fragment can bind nanoparticles with covalent, ion, coordination, or hydrogen bond (FIG. 5). Hydroxyl groups bind with many metal ions with coordination bonds. Nonlimiting examples are aluminum, magnesium, calcium, and titanium ions. Large number of bonds makes the interaction very strong. This has important implications for the fabrication of high modulus materials. Silica and alumina form hydrogen bonds with cellulose fragments. Carboxymethyl functionalized cellulose fragments will form ion bonds with metal ions, and metal ion containing particles. Strong bond is formed with aluminum, copper, zinc, and tin ions. These are nonlimiting examples. Covalent bonds require a chemical coupling reaction, for example, amide bond formation between amino functionalized CNT and carboxymethyl functionalized cellulose fragment using carbodiimide as a coupling reagent. Glycidyl cellulose fragments will bind spontaneously with amino groups.

Supercapacitors

[0153] The capacitance is

$$C = \frac{Q}{V} = \frac{A\epsilon}{d} \quad (1)$$

where Q is the charge, V is the potential, $\epsilon = \epsilon_0 \epsilon_r$, in which ϵ_0 is the permittivity of empty space and ϵ_r of the medium and d is the thickness of the electric double layer, which is about 0.3 nm almost independently of the materials involved. Dielectric constant (permittivity) of solution is dictated by the solvent that is water or some other polar solvent in electrolyte capacitors. In the table 1 are some solvents and their dielectric constants.

TABLE 1

| Permittivities of some solvents that can be used in supercapacitors of the present invention. | |
|---|--------------|
| Liquid | Permittivity |
| Methanol | 33 |
| Acetonitrile | 36 |
| Glycerol | 47 |
| Water | 80 |
| Ethylene carbonate | 90 |
| Formamide | 111 |
| N-methylacetamide | 179 |
| N-methylformamide | 189 |

[0154] Electrolytes dissolve also better into the solvents that have high permittivity. Solvents should be electrochemically as inert as possible. Water is perhaps most reactive solvent that is listed in Table 1. In organic solvents tetramethyl-lammonium tetrafluoroborate or an ionic liquid can be used as an electrolyte.

[0155] The electrically conducting surface area is linearly correlated with the capacitance. One way to further increase

the active surface area is to adsorb or couple conducting particles 902 with the HNTs 901 (FIG. 9). Spherical particle has a fourfold area compared to the area 903 that it covers. Moreover, most of the covered area is still active. In the ideal case the active area can be increased fivefold. This increase is independent of the radius of the particles. Thus, it is advantageous to use as small nanoparticles as possible, because overall mass and volume will increase minimally. Porosity or roughness of the particle 902 will increase the area even more.

[0156] The conductivity of the nanoparticles is not of prime concern. Because cellulose-HNT network conducts electricity well, the nanoparticles that are in contact with HNTs will be charged even, if they are poor electrical conductors. Nanoparticles should be resistant to corrosion under electrical potential. nanoparticle 1001 may be coated with a thin layer 1002 that is chemically and physically very stable (FIG. 10). Example is coating of magnetite, or Prussian Blue particle with iron phosphate, plumbate, or silicate, or cobalt oxide with cobalt phosphate. Coating may be dielectric, if it is very thin, almost atomic layer, but will still increase stability. Thin phosphate coating may be done by dipping CNT-cellulose-nanoparticle nanocomposite into dilute phosphoric acid or sodium phosphate solution.

[0157] In addition of the surface area the capacitance depends on the ratio ϵ/d . Because in water the distance of ions from the surface of HNTs is about 0.3 nm, this ratio is about 267 ($=80/0.3$). If HNTs are coated with a 3 nm layer that has $\epsilon_r > 800$, the capacitance will increase. One such material is barium titanate that has $\epsilon_r \approx 10,000$. The capacitance will increase 12-fold in ideal case. Because of defects in the coating, the increase in the capacitance will be less, for example, 4-fold. HNTs are now coated with electrically insulating layer, and potential of the HNTs can be increased many fold, up to 3-fold, without electrolysis of water. Total charge will be 12-fold as compared the same system without any coating of HNTs. Power density in this example will be 36-fold (3×12). In general the energy of a capacitor is:

$$W = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} CV^2$$

[0158] Because continuous coating with a highly polarizable dielectric can increase both capacitance (C) and potential (V), the increase in the stored energy can be very large.

[0159] The present invention provides one additional advantage over conventional supercapacitors. Traditionally only a thin layer of active material, such as carbon black is compressed onto an electrode, such as aluminum foil. Because HNT network is fairly well conducting, much thicker electroactive layers can be used. This is especially true, when the contact between HNTs has been improved, for example, by partial graphene connectors (FIG. 16).

[0160] CNT-cellulose-nanoparticle layers can be dried so that they are easy to handle. Thickness of the layers can be between 1 μm and 1 cm, advantageously between 0.1 mm and 1 mm. Pulp-like mass can be deposited directly onto a grid that can be made, for example, of copper. Grid can be coated with a thin layer of gold or platinum. This process resembles the conventional papermaking. In this case the composite layer and grid will not be separated. Alternatively the grid can be made of plastic. Then the grid is separated and replaced with a copper grid. The latter method is preferred, because the holes in the grid can be much bigger, i.e., the mesh number

can be smaller. Currently, the mesh number about four is preferred. Layers will be stacked and the grids will be electrically connected with each other within a stack. The stack will be connected also with one electrode. Two stacks will be placed into a container so that they will be separated with a semipermeable membrane. When copper grid is used, the liquid is preferably an organic solvent. Grid can also be made of some other material, such as aluminum, stainless steel, chromium, copper, silver, or graphite. It can be also coated so that it is not corroded on water. Coating material can be, for example, gold, platinum, polyaniline, polythiophene, or silver or HNT containing epoxy. There is virtually no size limit for this kind of supercapacitor. Instead of stacking of layers, the HNT-cellulose nanoparticle composite can be rolled with the grid into a cylinder. Other constructions are equally possible.

[0161] In many applications it is preferable to have a capacitor that is essentially one piece (FIG. 15). This can be accomplished, if the semipermeable membrane 1503 is made of cellulose, or modified cellulose. Very wide range of cellulose derivatives may be used. First, paper of CNT-cellulose fragment gel is fabricated, but dried only partially. On top of this CNT containing paper 1502 is fabricated a layer of non-conducting paper 1503, and the two-layer paper will be partially dried. CNT-cellulose fragment gel is added on top of the non-conducting paper so that a seamless structure (FIG. 15) will be obtained.

[0162] Especially, when supercapacitor is one piece, it is desirable that the electrolyte is solid. Electrolyte can be ionic liquid, such as methyl ethyl imidazole tetrafluoroborate, absorbed into polymer that can be cellulose or some other polymer. Electrolyte can be also be any commonly used salt in polyethylene glycol (PEG) or poly(ethylene carbonate). These kinds of supercapacitors can be printed, and in any case they require minimal casing.

[0163] In another analogous embodiment a three-layered hard board will be fabricated, two CNT-cellulose fragment gel layers on both sides and cellulose or modified cellulose layer in the middle. Hard boards are manufactured by compressing pulp between one grid and plate or two grids using high pressure, between 2 and 40 bar. Aluminum foils or other similar electrodes will optionally be glued on both sides so that electrical contact is created. Electrodes may be in several layers inside the hard board. If water is used as a solvent for electrolyte, then graphite electrodes, such as graphite fiber, will be preferred.

[0164] An alternative embodiment does not have semipermeable membrane, but instead ion selective membrane. The ion selective membrane will allow noncompatible electrolytes in anodic and cathodic compartments. Examples are sodium sulfate or potassium phosphate in anodic compartment, and magnesium or calcium chloride in cathodic compartment. If semipermeable membrane is used in these cases, a precipitate would be formed and the supercapacitor would be clogged.

[0165] Still another advantage of the ion selective membrane is that electrochemically active ions or particles can be more advantageously used. For example, magnetite, lead(II, II, IV)oxide, Prussian blue, or cuprous iodide can all be oxidized and reduced. Nickel and cobalt analogues of magnetite and Prussian blue can be equally well be used. Prussian Blue contains both ferro (ironII) and ferri (ironIII) ions, and can be oxidized or reduced. Some metal ions can be both oxidized and reduced. These include Cr³⁺, and Mn⁴⁺. In general, par-

ticles that can be oxidized or reduced are applicable within the scope of this invention. These particles add both capacitance and pseudocapacitance that is electrochemical process. Using these kind of particles will increase the capacitance more than Eq. 1 implies, because of the space charge also volume of the particle is important.

[0166] The electrochemical products would gradually diffuse through a semipermeable membrane and the supercapacitor would be discharged. The ion selective membrane retains the electroactive species in their compartments. In addition to the actual capacitance, these electroactive species contribute to so called pseudocapacitance that is very efficient way to increase the apparent capacitance. While conventional capacitance relays on the surface charge, the pseudocapacitance utilizes space charge, i.e., particles are charged also inside. Because this process requires only movement of electrons inside the particles, and particles are not consumed, unlike the electrodes in batteries, the lifetime of the supercapacitor can still be very long. In other words, there is no material removal and consequent reassembly of electrodes as is the case in batteries. In FIG. 12 is a TEM image of CNT-cellulose-Prussian Blue material. The sample was dispersed into water by ultrasonic vibration. TEM grid was dipped into a very dilute dispersion. TEM grid had holes that appear as light large oval shapes in FIG. 12. CNTs 1202 and Prussian Blue nanoparticles 1201 are clearly visible. While most nanoparticles are attached with CNTs, the ultrasonic vibration separated some nanoparticles from CNTs.

[0167] Ion selective membranes can be made of many materials including ion exchange plastics, glass, ceramics, such as zeolites. Superionic conductors are one currently one preferred class of materials for ion selective membranes. Polyethylene glycol is sodium and lithium ion conductor. Many ion selective membranes have ion exchange properties, and in addition well defined very small pore size. Zeolites are a prime example of such materials.

[0168] Graphene is one currently preferred nanomaterial for the increasing the surface area, and connecting HNTs 1600 and 1601 electrically FIG. 16. Cellulose 1602 will also separate graphite sheets 1604 from each other so that flat sheets do not collapse back together. Another method to prevent collapse of graphite sheets is to coat them with nanoparticles 1603, such as silica, alumina, carbon, gold, silver, chromium, cadmium sulfide, tin oxide, magnetite, Prussian blue, lithium titanate, lanthanide fluoride, or iron phosphate that will act as spacers. Advantageously, these nanoparticles are also electrically conducting so that their surface will contribute also to supercapacitor function. If they are electrochemically active they act as pseudocapacitors.

Continuous Coating of CNTs

[0169] Eq. 1 implies that increase of the dielectric constant will increase the capacitance linearly. Dielectric constant can be increased by proper choice of solvent, and also by some high dielectric constant coating. While the choice of a solvent is well known in-the-art, the coating is a subject of the present invention.

[0170] In one currently preferred embodiment CNTs are first suspended into water using either CMC, or cellulose fragment gel. Water is replaced by 2-propanol. A mixture of barium i-propoxide and titanium i-propoxide in 2-propanol is added. When potassium hydroxide water solution is added barium titanate is formed. Polarity may be affected by applying electrical potential during the deposition. Preprepared

barium titanate nanoparticles may be added before the deposition of barium titanate from alcoholates so that these barium titanate nanoparticles will be glued by in situ deposited barium titanate with CNTs. Chemical vapor deposition (CVD) or atomic layer deposition (ALD) provide good quality layers. Especially ALD allows atomic precision in growing of the coating layer. These methods are well known in the art.

[0171] Although the distance of ions from CNT (d in Eq. 1) will increase, the dielectric constant will increase much more, and capacitance will be much bigger, for instance 10 times bigger. The increased surface charge density will increase conductivity. Thus, during charging the conductivity should increase, and no additional electrodes will be needed. In supercapacitors the density of electrons (in cathode) or holes (in anode) increases and electric wire having supercapacitor structure can be fabricated. Conductivity can increase substantially, if the temperature is lowered so that electrons form Cooper pairs.

EMI Protection

[0172] Structures that provide electromagnetic shield can be made from CNT-cellulose-MP materials. The electromagnetic noise will penetrate poorly through most CNT-cellulose-MP materials.

[0173] HNT-cellulose-nanoparticle material may additionally contain magnetic or paramagnetic particles for ideal EMI protection. Paramagnetic particles are advantageously ferrite particles, for example magnetite particles. Particle size can be between 5 nm and 50 μm . Particle concentration should be advantageously such that percolation threshold will be exceeded. Magnetic particles and paramagnetic particles are simply called magnetic particles in this disclosure, and denoted as MP.

[0174] CNT(1701)-cellulose (1702) composite and magnetic particles (1703) can be in the same layer 1704 (FIG. 17 A), or in separate layers 1705 and 1706 (FIG. 17 B). MPs are advantageously coated with silica or aluminum oxide layer (See FIG. 10). This is accomplished by dipping into tetraethyl silicate or aluminum isopropoxide solution, for example in 2-propanol.

[0175] Currently dual layer structure is preferred for EMI protection, mainly because the density of electrically and magnetically active particles can be higher than in one layer containing both. It must be noted that dual layer structure can contain layers, which contain both CNTs and magnetic particles. In this case one layer contains more CNTs and the other more magnetic particles.

[0176] Triple layer structure is even more efficient than single layer or dual layer. In this structure electrically conducting layers are outside, and magnetically active particles or even an inert layer is in the middle. Triple layer is several orders more effective even, if the total amount of active materials is the same as in the single layer structure. The efficacy is partially due to multiple reflections between layers so that interference destroys most of the incoming electromagnetic radiation. Another reason for the increased efficacy is that the node of the radiation can not be coincident with both layers simultaneously.

[0177] When paramagnetic particles are deposited on solid surface, for example, by spraying, a magnetic field be applied. The first magnetic field is advantageously parallel with the surface. Another layer may be deposited so that the second magnetic field is still parallel with the surface, but perpen-

dicular to the direction of the first magnetic field. If multiple layers (FIG. 18) will be deposited the magnetic field direction can be different every time. Single layer structures can be fabricated so that MPs are mixed simultaneously with cellulose and CNTs, or they are added afterwards. They can be added as premade particles, or synthesized in situ. In dual layer structures the MP layer can be fabricated with known methods. Also then cellulose and functionalized cellulose can be used as binding agents.

[0178] In most applications the EMI protective paper will be impregnated with plastic, such as polypropylene, polyacrylate, or polycarbonate or resin, such as epoxy or polyurethane. Plastic prevents the release of CNTs in consumer products. It also helps the attachment of shield into an electronic device by hot pressing, gluing or by some other commonly used dealing method.

[0179] Applications are plentiful, including all electronics, including computers, mobile devices, wireless link stations, electric motors, and electrical wires.

Further Processing

[0180] Paper and paper-like products can be fabricated with the same methods that conventional paper is fabricated. CNT-molecular cellulose-nanoparticle nanocomposite is a gel in water, and retains water very well. Water must largely be removed during the fabrication of paper. Coagulants, such as copolymer of acrylic amide and acrylic acid or other well known coagulants, can be used. These materials can also be used instead of cellulose to wrap graphitic materials according to this invention. We have found that freezing of the gel before paper fabrication will decrease the filtration time considerably. Thus, the fabrication of paper either in sheet format or roll format can be done by conventional methods. Supercapacitors and EMI protection materials can be layered structures. These can also be made by modified methods, in which the first layer is filtered so that most of the water is removed, and on top of the first layer is added a second layer, and so on. Various layers form one continuous paper-like structure, in which the layers are firmly connected with each other.

[0181] Especially a three-layer structure can be formed by coating a premade paper or plastic on both sides with a CNT-molecular cellulose-nanoparticle nanocomposite gel or ink. All kinds of surfaces and shapes can be coated with wet material. After drying the surface is partially or totally covered with cellulose-HNT material.

[0182] The materials of the present invention can be mixed with other composite or hybride materials. These include thermoplastics, resins, ceramic, and even metals.

[0183] HNT-cellulose and HNT-cellulose-MP materials can be mixed with melted thermoplastics or with monomers that will be polymerized after the mixing, cellulose, HNTs, or both can be functionalized so that they will bind chemically with the matrix. For instance, cellulose acrylate may be mixed with the acrylate monomer. HNTs may be added into this mixture, and the mixture is polymerized. In this case there is no need for prefabrication of HNT-cellulose nanocomposite. Also HNTs may be functionalized with acrylates in this specific example. Similarly, cellulose-HNT can be incorporated in polycarbonate, silicone, nylon, Kevlar, polystyrene, polyethylene, polypropylene, and polyvinylchloride.

[0184] Carboxymethyl cellulose (CMC) is currently preferred with MPs. Carboxylates bind strongly with MPs, and

will disperse them. Additional ferro, ferri, copper, tin, aluminum, or several other salts will cross-link CMC, and create strong structure.

[0185] In one currently preferred method a concentrated mixture of the HNTs and cellulose acetate propionate (CAP) is fabricated first, and this mixture is then mixed with a thermoplastic. The advantage of this process is that CAP can be melted without decomposition, and no solvent is required in the fabrication process. Once HNTs are dispersed into the CAP, they can be easily mixed with the thermoplastic. The HNT-CAP and thermoplastic can be mixed as powders and heated so that both of them will be melted. The good mechanical mixing is sufficient for the dispersion of HNT-CAP into the thermoplastic, although optionally ultrasonic vibration may be used.

[0186] CAP may be partially hydrolyzed with a base, so that some or all of the hydroxyl groups of cellulose are released. The purpose of this hydrolysis is to make the composite more polar or hydrophilic, and also more porous. This can be important in some applications, such as capacitors, in which ions must be able to move.

[0187] If covalent coupling with the matrix is not essential, the mixing of the cellulose-HNT with a polymer melt is preferred over copolymerization. In several cases mixing is easier, if proper cellulose derivative is used. Often cellulose acetate is preferred. For polystyrene, cellulose benzoate is adequate, while for polypropylene cellulose butyrate or palmitate is a better fit.

[0188] Thermoset plastics and resins are typically fabricated from two components, which are mixed shortly before the use. Cellulose, HNTs and MPs can be mixed with one of these components or both. For example, cellulose glycidyl ether-HNT nanocomposite may be mixed with bisphenol A bisglycidyl ether. When this epoxy is mixed with a hardener before the use, HNT-cellulose nanocomposite is chemically coupled with the epoxy matrix via cellulose. Coupling may be assisted by addition of alumina nanoparticles into HNT-cellulose-nanoparticle nanocomposite. Other alternative is to soak nanocomposite into aluminum i-propoxide solution in i-propanol. Aluminum ion will catalyze the reaction between hydroxyl groups and epoxy groups leading into a covalent linkage between epoxy matrix and cellulose and similarly between epoxy matrix and HNTs. If HNTs are functionalized with epoxy groups, also HNTs and cellulose will be chemically coupled. Similarly, HNT-cellulose may be mixed with urethanes. The hydroxyl groups of cellulose react with isocyanate groups, and cellulose serves as a hardener. Other resins include phenol-formaldehyde, in which can represent phenol-formaldehyde resin. HNT-cellulose-nanoparticle paper can be used to reinforce plastics and resins similarly as glass or carbon fiber. Because CNT or HNT content can be very high the effect will be significant.

[0189] Many ceramics can be fabricated by mixing the components first in water. Also water-alcohol mixtures can be used. These are suitable for the mixing of cellulose and CNTs.

[0190] Thus, all components can be mixed simultaneously. For example, compounds like calcium hydroxide, aluminum hydroxide, copper chloride, and iron chloride can be mixed with cellulose-NT slurry, and sodium hydroxide can be added, when applicable. The mixture is heated at about 110° C., dried, and calcinated at relatively low temperature of about 250° C. under nitrogen. If silicic acid is added, glass-

like product will be obtained. If pyrolysis of cellulose backbone is desired, the temperature can be much higher, up to 800° C.

[0191] Sol-gel method is amenable for the fabrication of HNT-cellulose nanocomposites. This method is closely related to the fabrication of ceramics. In the sol-gel method the solvent is preferably alcohol, and additional gel forming component, such as tetraethyl silicate, is part of the mixture. When small amount of water is added, tetraethyl silicate is hydrolyzed, and silica gel is formed. Silicon atom may be connected with one or two alkyl or aryl groups like methyl, or phenyl groups, which may also have functional groups, such as hydroxyl, amino, or carboxylic groups. Metal alcoholates are hydrolyzed by water into metal hydroxides, which often transform into corresponding oxides either spontaneously, or after heating. In order to neutralize the hydroxide ions, the water may contain acid, such as hydrochloric, hydrobromic, nitric, perchloric, sulfuric, formic, trifluoroacetic, or an easily hydrolysable ester like methyl formate. If the water phase contains anions, such as halogenides, sulfide, selenide, telluride, carbonate, sulfate, phosphate, arsenide, and oxalate a corresponding salt is formed. The solution may contain several different alcoholates, and tetramethoxy or tetraethoxy silicate. Either composite nanoparticle, or metal silicate nanoparticles are formed in this case. Typical metal alcoholates or related compounds include barium(II)isopropoxide, zinc(II)methoxy ethoxide, aluminum(III)isopropoxide, iron (III)isopropoxide, nickel(II)methoxy-ethoxide, holmium(III) iso-propoxide, yttrium(III)iso-propoxide, europium(III)-D-3-trifluoro-acetylcamphorate, tin(IV)iso-propoxide, titanium (IV)isopropoxide, titanium(IV)iso-butoxide, tungsten(V) ethoxide, tungsten(VI)isopropoxide, bismuth(III)methoxy-2-methyl-2-propoxide, hafnium(IV)tert-butoxide, hafnium tri-isopropoxy tetramethylheptane-dionate, zirconium(IV) tert-butoxide, niobium(V)iso-propoxide, vanadium(V)tri-isopropoxide oxide, aluminium cobalt isopropoxide, lead(II) titanium(IV)isopropoxide, lead zirconium ethylhexano-isopropoxide, and SrTa₂(OEt)₁₀(dmae)₂. Almost any ceramic nanocomposite can be prepared using alcoholates. Examples are lead zirconium titanate, barium titanate, and strontium bismuth thallium oxide containing nanocomposites, which are piezo electric materials, and yttrium barium copper oxide that is a high temperature superconducting material. Barium titanate has very high dielectric constant, and is useful in supercapacitors. Barium and strontium titanates are examples of ferroelectric materials. Another example is potassium tantalum niobate.

[0192] Silylamides are another class of soluble metal compounds that are hydrolyzed by water. These include tris[N,N-bis(trimethylsilyl)amide]-cerium(III), and analogous compounds of erbium(III), europium(III), gadolinium(III), holmium(III), lanthanum(III), lutetium(III), neodium(III), praseodymium(III), samarium(III), scandium(III), terbium (III), thulium(III), ytterbium(III), and yttrium(III). These metal cations are lanthanides, and form fluorescent nanocomposites. Some other metals can be coprecipitated in order to change absorption or emission properties, or simply to reduce the cost.

[0193] Cellulose-HNT aerogels are made from the compounds mentioned above by replacing alcohol with supercritical carbon dioxide, and slowly evaporating carbon dioxide.

[0194] Thermal instability of cellulose prevents the incorporation of HNT-cellulose into any metal that has melting

point above 260° C. However, there are other methods that are applicable. These include compression of nano- or micropowders, electrochemical deposition of metals, and flash cooling of evaporated metals so that amorphous metals are formed around HNT-cellulose at a low temperature. Again, if pyrolysis is desired, it can be performed before mixing the HNT-amorphous carbon-nanoparticle nanocomposite with metal. Then the temperature limit can be much higher, up to 800° C. The pyrolysis can also be combined with mixing the cellulose-HNT-nanoparticle-nanocomposite with hot metal.

EXPERIMENTAL DETAILS

[0195] While this invention has been described in detail with reference to certain examples and illustrations of the invention, it should be appreciated that the present invention is not limited to the precise examples. Rather, in view of the present disclosure, many modifications and variations would present themselves to those skilled in the art without departing from the scope and spirit of this invention. The examples provided are set forth to aid in an understanding of the invention but are not intended to, and should not be construed to limit in any way the present invention.

[0196] In all examples starting materials, and the produced nanocomposites are slightly or sparingly soluble in the solvent that is used.

Example 1

[0197] One gram of CNTs, and two gram of cellulose, two grams of calcium carbonate nanoparticles were suspended into 100 ml of 0.2% CMC solution in water by using 400 W ultrasonic vibration 1 h. Similarly, one gram of CNPs were dissolved into 100 ml of 0.2% of CMC solution. These two dispersions were mixed, and the mixture was further sonicated 1 h. The mixture was made slightly acidic by 2 M hydrochloric acid. Paper sheet was fabricated by conventional paper making process, so that the thickness of the paper was about 150 µm after compression. Paper was heated between a stainless steel grid and a glass plate 2 h at 280° C. The weight loss was 36%. The specific resistance of the paper was 0.6 Ωcm, and specific capacitance 212 F/g.

[0198] When the heating was done in a microwave oven the specific capacitance was 112 F/g.

Example 2

[0199] One gram of enzymatically fragmented cellulose, and one gram of calcium carbonate nanoparticles were suspended into 50 ml of 2-propanol, and 500 mg of HNTs were added. The mixture was sonicated 60 minutes with tip sonicator, power 400 W. Paper was prepared by conventional methods. After drying the paper was dipped into 0.5 M CuCl₂ solution. After drying the paper was dipped into 0.5 M KI solution, and immediately into methanol in order to remove iodine. This paper had specific capacitance 260 F/g.

Example 3

[0200] Two grams of cellulose fragment gel, two grams of calcium carbonate, and one gram of CNTs were suspended into 50 ml of water using ultrasonic vibration (500 W, one hour). The mixture was filtered. A specific capacitance of this material was 90 F/g.

Example 4

[0201] Two grams of microcrystalline cellulose, two grams calcium carbonate nanoparticles and one gram of CNTs and hundred milligrams of amorphous carbon nanoparticles were suspended into 50 ml of water using ultrasonic vibration (500 W, one hour). The mixture was filtered. A specific capacitance of this material was 97 F/g. When the microcrystalline cellulose was partially pyrolyzed at 300° C., the specific capacitance increased to 115 F/g.

Example 5

[0202] Instead of pyrolysis of cellulose, calcium carbonate was removed by addition of 2 M HCl on the paper that was prepared by filtration. Paper was washed neutral by water. Into the paper was added 0.5 M CuCl₂ solution and 0.5 M KI solution. The mixture was filtered and washed with methanol. The specific capacitance of this material was 265 F/g.

Example 6

[0203] Two grams of cellulose fragment gel and one gram of CNTs and hundred milligrams of amorphous carbon nanoparticles and hundred milligrams of graphene were suspended into 50 ml of water using ultrasonic vibration (500 W, one hour). The mixture was filtered. A specific capacitance of this material was 272 F/g.

Example 7

[0204] 3 g of mechanically and enzymatically processed molecular cellulose that is coordinated with 3 g calcium of carbonate nanoparticles is first dispersed into 200 ml of water. Carbon nanotubes are treated with HCl in order to make the dispersion process easier. The treatment removes unwanted residues from the manufacturing process. First 100 grams of carbon nanotubes are put in a closed container. Then 300 ml of HCl is added on top of the carbon nanotubes. The container is then shaken and let stand for 2 hours. After this the carbon nanotubes are washed with distilled water until their pH is neutral. Washed tubes are dried in oven at 120 degrees of Celsius for over night. After drying they are mechanically ground using planetary mill.

[0205] 200 ml of the molecular cellulose pulp and calcium carbonate dispersion is mixed with 1.3 grams of dry carbon nanotubes in a beaker. The mixture has now 30% weight/weight carbon nanotubes. The mixture is stirred shortly with spoon and then the mixture is treated with tip ultra-sonicator. Sonication time is 10 minutes at power of 750 watts. The dispersion is treated with HCl to remove inorganic salts. HCl is added until calcium carbonate is solubilized, and no carbon dioxide evolution is observed. After this the mass is washed with distilled water until the filtrate is neutral.

[0206] Desired amount of pulp is filtered through metal mesh or plastic netting sieve. Quite often 80 g/m² square weight is preferred. Two pieces of filter paper are put on top of filtered paper. Paper is then pressed with heavy rolling pin until it is detached from the mesh. The sample paper is now put between four filter papers and further pressed with hydraulic press while heating at 90° C. After this sample is dried in paper dryer for 2 hrs. EMI shielding efficacy of the paper was 25-30 dB.

Example 8

[0207] Procedure of example 7 was repeated expect that double walled carbon nanotubes were used instead of MWNTs. EMI shielding efficacy was measured by self constructed ASTM coaxial EMI SE tester and Anritsu 37369D VNA. Results are displayed in FIG. 19.

Example 9

[0208] Carbon nanotubes (1 g Baytubes, Bayer, Germany), 1 g microcrystalline cellulose, 0.2 g cellulose, 1 g of calcium carbonate, and carboxymethyl cellulose (0.2 g) were dispersed into 100 ml of water using ultrasonic vibration. Onto this solution was added ferric chloride and sodium sulfite solution. After careful mixing, ammonia solution was added. The CNT-cellulose-magnetite nanocomposite was separated with a permanent magnet. Soluble salts were removed by washing with water, and finally with alcohol. The alcohol suspension was mixed with reactive diluent. The nanocomposite was mixed with diglycidylether of bisphenol A (100 g). Tall oil based hardener (30 g, Arizona Chemicals Inc.) was added, and mixed well. After curing the epoxy resin was electrically conductive ($25 \Omega\text{m}$) and paramagnetic.

Example 10

[0209] One gram of HCl treated carbon nanotubes and 1 gram of microcrystalline cellulose is first ground dry in mortar. Then 200 ml of purified water is added and sample is sonicated with 750 W sonicator 30 minutes. From this sample 20 ml is taken to be mixed with 400 mg of fibrous cellulose.

[0210] This fibrous cellulose is first prepared as following. Starting point is as received cellulose sheet from the pulp factory. The cellulose is shredded dry into even sized small pieces and put in beaker with 200 ml of water. First the pulp is vigorously mixed with magnet stirrer for 12 hrs and then sonicated while mixed at 750 W for 30 minutes.

[0211] A mixture of carbon nanotubes, microcrystalline cellulose and fibrous cellulose is sonicated at 750 W power for 30 minutes. Paper sheets are then prepared. Resistance of 80 g/m^2 paper is less than 10 ohms with two point measurement and less than 1 ohm with 4 point measurement. Shielding efficiency of such paper was 25 dB at 10 GHz.

[0212] Additional modifications and advantages will readily occur to those skilled in the art. Therefore the invention in its broader aspects is not limited to the specific details, and representative materials and devices shown and described. Accordingly, various modifications may be made without departing from the spirit and scope of the general inventive concept as described in the disclosure and defined by the claims and their equivalents.

1. A method for the fabrication of nanocomposite from the first material and the second material, known for the use of liquid medium, into which both the first material and the second material are slightly or sparingly soluble, and using soluble material, such as hemicellulose to assist dissolution of the first material and the second material and use of power source to provide kinetic energy for the partial or total separation of molecular components from the first material and the second material so that the said nanocomposite will be formed and deposited, while the said kinetic energy is provided into the mixture.

2. A method of claim 1 for the fabrication of a nanocomposite, known for the use of first nano-, or microparticles in order to distribute kinetic energy unevenly at molecular scale

for the separation of molecular components from the said first material and the said second material so that the said molecular components will form the said nanocomposite.

3. A method of claim 1, in which the said first material is a graphitic material.

4. A method of claim 1, in which the said second material is a cellulosic material, or polyacrylate derivative.

5. A method of claim 3, in which the said graphitic material consists of carbon nanotubes or functionalized carbon nanotubes

6. A method of claim 5, in which the said carbon nanotubes consists more than 90% of double walled carbon nanotubes or functionalized double walled carbon nanotubes

7. A method of claim 3, in which the said graphitic material consists of graphite or graphene or combination of carbon nanotubes and graphene.

8. A method of claim 4, in which the said cellulosic material consists of cellulose, or biochemically, biologically, or chemically modified cellulose.

9.-13. (canceled)

14. A method of claim 2, in which the said first nano- or microparticles are alumina, silica, calcium carbonate, calcium sulfate, barium sulfate, barium oxalate, strontium sulfate, barium or strontium titanate, titanium oxide, tin oxide, lead oxide, iron oxide, iron phosphate, nickel, cobalt, silver, or gold particles.

15.-16. (canceled)

17. A method of claim 1, in which the said kinetic energy is produced mechanically, or hydrodynamically.

18. A method of claim 17, in which the said hydrodynamic kinetic energy is in the form of high pressure liquid jets, or ultrasonic vibration.

19. A method of claim 1, in which the second nanoparticles, that are electromagnetically active, are included in the fabrication of nanocomposite or hybride material.

20. A method of claim 2, in which the second nanoparticles, that are electromagnetically active, are included in the fabrication of nanocomposite or hybride material.

21. A method of claim 20, in which the said second nanoparticle is cuprous iodide, Prussian blue, magnetite, iron phosphate, cobalt oxide, manganese oxide, tin oxide, zinc oxide, titanium oxide, barium titanate, or strontium titanate.

22. A method of claim 20, in which the said second nanoparticle is covered with a thin layer of metal phosphate, sulfate, or silicate.

23.-24. (canceled)

25. A material that is fabricated by the method of claim 3.

26. A material that is fabricated by the method of claim 4.

27. A material that is fabricated by the method of claim 5.

28. A material that is fabricated by the method of claim 6.

29. A material that is fabricated by the method of claim 7.

30. A material that is fabricated by the method of claim 8.

31. A material that is fabricated by the method of claim 20.

32. A material that is fabricated by the method of claim 21.

33. A material that is fabricated by the method of claim 22.

34. (canceled)

35. A hybride material that is fabricated from the material of claim 2 by chemical cross-linking.

36. (canceled)

37. A hybride material that is fabricated from the material of claim 30 by chemical cross-linking.

38.-39. (canceled)

40. Use of the material of the claim 25 in a supercapacitor.

41. Use of the material of the claim 26 in a supercapacitor.

- 42.** Use of the material of the claim **27** in a supercapacitor.
43. Use of the material of the claim **28** in a supercapacitor.
44. Use of the material of the claim **29** in a supercapacitor.
45. Use of the material of the claim **30** in a supercapacitor.
46. Use of the material of the claim **31** in a supercapacitor.
47. Use of the material of the claim **32** in a supercapacitor.
48. Use of the material of the claim **33** in a supercapacitor.
49.-50. (canceled)
51. Use of the material of claim **25** for the protection against electromagnetic interference.
52. Use of the material of claim **26** for the protection against electromagnetic interference.
53. Use of the material of claim **27** for the protection against electromagnetic interference.
54. Use of the material of claim **28** for the protection against electromagnetic interference.
55. Use of the material of claim **29** for the protection against electromagnetic interference.
56. Use of the material of claim **30** for the protection against electromagnetic interference.
- 57.** Use of the material of claim **31** for the protection against electromagnetic interference.
58. Use of the material of claim **32** for the protection against electromagnetic interference.
59. Use of the material of claim **33** for the protection against electromagnetic interference.
60. A layered structure containing at least two layers known for the first layer that is made of the material of claim **29**, and the second layer contains magnetically active particles.
61. A layered structure containing at least three layers known for the first layer that is made of the material of claim **29**, and the second dielectric layer between the first and third layer, and the third layer that is made of the material of claim **29**.
62. (canceled)
63. A supercapacitor that is electrically connected with two potential sources.

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(54) Title: NANOCRYSTALLINE CELLULOSE (NCC) IN TAPE JOINT COMPOUND (JC)

(57) Abstract: A joint compound with improved crack resistance is formed by combining water, a filler such as calcium carbonate, a latex emulsion binder, a thickening system such as methyl hydroxyethyl cellulose, and nanocrystalline cellulose. The nanocrystalline cellulose is provided in an amount effective to reduce the crack formation during drying.

NANOCRYSTALLINE CELLULOSE (NCC) IN TAPE JOINT COMPOUND (JC)

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit under 35 U.S.C. 119 (e) of U.S. Provisional Patent Application Serial No. 61/602,671, filed February 24, 2012, the entire content of which is hereby expressly incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Disclosed and Claimed Inventive Concepts

[0002] The presently disclosed and claimed inventive concept(s) relates generally to a joint compound that can totally eliminate cracking in various thicknesses of the joint compound and thick coatings. Specifically, the joint compound comprises nanocrystalline cellulose, water, a filler, a binder and a thickener.

2. Background and Applicable Aspects of the Presently Disclosed and Claimed Inventive Concept(s)

[0003] Wallboard is generally installed in large panels, which are nailed, screwed, or glued to the studding of walls of buildings. The joints where sections of the wallboard are butted together are covered with a joint compound and then a fiberglass or paper reinforcing tape is embedded within the joint compound and then permitted to dry. When the joint compound is dry, a second application of the joint compound is applied over the joint and is permitted to dry. A coating of the joint compound is also applied to cover nail heads or screws or any cracks in the wall board and let dry. After the joint compound dries, the joint and covering of the nails or screws are lightly sanded and the wall is then finished with decorating material such as paint.

[0004] Typically, tape joint compositions, which are normally referred to as joint compounds, contain a binder, a thickener system, a filler, water, a biocide, clay and mica. This joint composition is a ready-mix, drying type composition that is normally sold in five-gallon cans or corrugated boxes. The water and filler are the ingredients that comprise the largest weight percentage in the joint composition. Joint compounds are either regular weight compounds that are the traditional type or lightweight compounds.

[0005] Optimally, a joint compound will not alter its dimensions as it dries. However, when a relatively thick coating of the joint compound is applied to a surface, it can crack as it dries. The thicker the coating is the more likely the cracking and the more severe the

cracking. This requires additional applications to fill in the voids in the cracks, increasing the cost of finishing a wall surface.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. 1 is a photograph showing a thick coating of dried joint compound which does not include nanocrystalline cellulose.

[0007] FIG. 2 is a photograph showing a thick coating of dried joint compound which includes nanocrystalline cellulose.

[0008] FIG. 3 is a photograph of the compound shown in FIG. 1 without nanocrystalline cellulose.

[0009] FIG. 4 is a photograph of the compound shown in FIG. 2 with nanocrystalline cellulose.

DETAILED DESCRIPTION

[0010] Before explaining at least one embodiment of the inventive concept(s) in detail by way of exemplary drawings, experimentation, results, and laboratory procedures, it is to be understood that the inventive concept(s) is not limited in its application to the details of construction and the arrangement of the components set forth in the following description or illustrated in the drawings, experimentation and/or results. The inventive concept(s) is capable of other embodiments or of being practiced or carried out in various ways. As such, the language used herein is intended to be given the broadest possible scope and meaning; and the embodiments are meant to be exemplary - not exhaustive. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

[0011] Unless otherwise defined herein, scientific and technical terms used in connection with the presently disclosed and claimed inventive concept(s) shall have the meanings that are commonly understood by those of ordinary skill in the art. Further, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular. Generally, nomenclatures utilized in connection with, and techniques of chemistry described herein are those well known and commonly used in the art. Reactions and purification techniques are performed according to manufacturer's specifications or as commonly accomplished in the art or as described herein. The nomenclatures utilized in connection with, and the laboratory procedures and techniques of, analytical chemistry, synthetic organic chemistry, and medicinal and pharmaceutical chemistry described herein are those well known and commonly used in the art. Standard techniques are used for

chemical syntheses, chemical analysis, pharmaceutical preparation, formulation, and delivery, and treatment of patients.

[0012] All patents, published patent applications, and non-patent publications mentioned in the specification are indicative of the level of skill of those skilled in the art to which this presently disclosed and claimed inventive concept(s) pertains. All patents, published patent applications, and non-patent publications referenced in any portion of this application are herein expressly incorporated by reference in their entirety to the same extent as if each individual patent or publication was specifically and individually indicated to be incorporated by reference.

[0013] All of the compositions and/or methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the inventive concept(s) as defined by the appended claims.

[0014] As utilized in accordance with the present disclosure, the following terms, unless otherwise indicated, shall be understood to have the following meanings:

[0015] The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims and/or the specification may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.” The use of the term “or” in the claims is used to mean “and/or” unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and “and/or.” Throughout this application, the term “about” is used to indicate that a value includes the inherent variation of error for the device, the method being employed to determine the value, and/or the variation that exists among the study subjects. The use of the term “at least one” will be understood to include one as well as any quantity more than one, including but not limited to, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 100, etc. The term “at least one” may extend up to 100 or 1000 or more, depending on the term to which it is attached; in addition, the quantities of 100/1000 are not to be considered limiting, as higher limits may also produce satisfactory results. In addition, the use of the term “at least one of X, Y and Z” will be understood to include X alone, Y alone, and Z alone, as well as any combination of X, Y and Z.

[0016] As used in this specification and claim(s), the words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as

"have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0017] The term "or combinations thereof" as used herein refers to all permutations and combinations of the listed items preceding the term. For example, "A, B, C, or combinations thereof" is intended to include at least one of: A, B, C, AB, AC, BC, or ABC, and if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB.

Continuing with this example, expressly included are combinations that contain repeats of one or more item or term, such as BB, AAA, MB, BBC, AAABCCCC, CBBAAA, CABABB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context.

[0018] In accordance with the presently disclosed and claimed inventive concept(s), a joint compound comprises nanocrystalline cellulose, a binder, a thickener, a filler, water, a biocide and clay. Additional components that are commonly used in joint compounds are perlite, mica, preservatives, wetting agents, defoamers, and plasticizers. With the exception of perlite and mica, these additional components are normally used in minor amounts generally ranging from about 0.05 to about 1.0% by weight based on the total dry weight of the compound.

[0019] Nanocrystalline cellulose is a crystalline portion of cellulose which can be formed by acid hydrolysis of cellulose combined with mechanical treatment. These nanometer size cellulose particles are crystalline in nature, insoluble in water, stable, chemically inactive and physiologically inert with attractive binding properties.

[0020] Cellulose is one of the most abundant biopolymers on earth, occurring in wood, cotton, hemp and other plant-based material and serving as the dominant reinforcing phase in plant structures. Cellulose can also be synthesized by algae, tunicates, and some bacteria. It is a homopolymer of glucose repeating units which are connected by 1-4 β -glycosidic linkages. The 1-4 β -linkages form cellulose in linear chains, which interact strongly with each other through hydrogen bonds. Because of their regular structure and strong hydrogen bonds, cellulose polymers are highly crystalline and aggregate to form substructures and microfibrils. Microfibrils, in turn aggregate to form cellulosic fibers.

[0021] Purified cellulose from wood or agricultural biomass can be extensively disintegrated or produced by bacterial processes. If the cellulosic material is composed of nanosized fibers, and the properties of the material are determined by its nanofiber structure, these polymers are described as nanocelluloses or nanocrystalline cellulose. The terms are used interchangeably herein.

[0022] In general, nanocelluloses are rod shaped fibrils with a length/diameter ratio of approximately 20 to 200. In one non-limiting embodiment, the nanocelluloses have a diameter less than about 60 nm. In another non-limiting embodiment, the nanocelluloses have a diameter between about 4 nm to about 15 nm, and a length of about 150 nm to about 350 nm. The size and shape of the crystals vary with their origins. For example, but not by way of limitation, nanocrystalline cellulose from wood can be about 3 to about 5 nm in width and about 20 to about 200 nm in length. Other nanocrystalline cellulose obtained from other sources such as cotton may have slightly different dimensions.

[0023] The nanocrystalline cellulose has high stiffness, large specific surface area, high aspect ratio, low density and reactive surfaces that can facilitate chemical grafting and modification. At the same time, the material is inert to many organic and inorganic substances.

[0024] The production of nanocrystalline cellulose by fibrillation of cellulose fibers into nano-scale elements requires intensive mechanical treatment. However, depending upon the raw material and the degree of processing, chemical treatments may be applied prior to mechanical fibrillation. Generally preparation of nanocrystalline cellulose can be described by two methods, acid hydrolysis and mechanical defibrillation. In the first method, nanocellulose can be prepared from the chemical pulp of wood or agricultural fiber mainly by acid hydrolysis to remove the amorphous regions, which then produce nano-size fibrils. The hydrolysis conditions are known to affect the properties of the resulting nanocrystals. Different acids also affect the suspension properties. Nanocrystal size, dimensions, and shape can also be determined to a certain extent by the nature of the cellulose source.

[0025] The acid hydrolysis can be conducted using a strong acid under strictly controlled conditions of temperature, agitation and time. The nature of the acid and the acid-to-cellulosic ratio are also important parameters that affect the preparation of nanocellulose. Examples of the acids can include, but are not limited to, sulfuric acid, hydrochloric acid, phosphoric acid and hydrobromic acid. The hydrolysis temperature can range from room temperature up to about 70 °C and the corresponding hydrolysis time can be varied from about 30 minutes to about 12 hours depending on the temperatures. Immediately following hydrolysis, suspension can be diluted to stop the reaction.

[0026] In one non-limiting embodiment, the suspension can be diluted from about five-fold to about ten-fold to stop the reaction. Then the suspension can be centrifuged, washed once with water and re-centrifuged and washed again. This process can be repeated for about four to five times to reduce the acid content. Regenerated cellulose dialysis tubes or Spectrum Spectra/Pro regenerated cellulose dialysis membrane having a molecular cutoff of about 12,000-14,000 can be used to dialyze the suspension against distilled water for

several days until the water pH reach a constant value, for example but not by way of limitation, a pH value of about 7.0.

[0027] To further disperse and reduce the size of the cellulose crystals, the suspensions of cellulose crystals can be processed by either sonicating or passing through a high shear micro fluidizer. This kind of prepared material is referred to as nanocellulose, nanocrystalline cellulose (NCC), cellulose nanocrystals, cellulose nanofibres or cellulose whiskers.

[0028] The second method is primarily a physical treatment. Bundles of microfibrils called cellulose microfibril or microfibrillated cellulose with diameters from tens of nanometers (nm) to micrometers (μm) are generated by using high pressure homogenizing and grinding treatments. A novel process using high-intensity ultrasonication has also been used to isolate fibrils from natural cellulose fibers. High intensity ultrasound can produce very strong mechanical oscillating power, so the separation of cellulose fibrils from biomass is possible by the action of hydrodynamic forces of ultrasound. This method can produce a microfibrillated cellulose with a diameter with a diameter less than about 60 nm. In one non-limiting embodiment, a microfibrillated cellulose between about 4 nm to about 15 nm, and a length less than 1000 nm. The microfibrillated cellulose can optionally further undergo chemical, enzymatic and/or mechanical treatment. Both methods for preparing nanocrystalline cellulose are described in U.S. Patent No. 8,105,430, the entire disclosure of which is hereby incorporated by reference.

[0029] Generally, about 0.05% to about 0.5% by weight of nanocrystalline cellulose can be used. In one non-limiting embodiment, about 0.05 to about 0.15% by weight can be incorporated into the joint compound.

[0030] The binder is typically a latex emulsion, for example, but not by way of limitation, polyvinyl alcohol, ethylene vinyl acetate latex, or poly(vinyl acetate) latex. The binder is a coalescent agent that upon drying of the compound forms a thin matrix to hold the compound. In other words, the binder is the matrix that holds the other components in their proper places so as to form the desired product. Hence, the binder is an essential ingredient in the joint compound. Other materials that can be used as binder can include, but are not limited to, starch, casein, polyacrylamide, and copolymers of acrylamide and acrylic acid. In general, the binder ranges from a lower limit of about 1% to an upper limit of about 3%, by weight based on the total weight of the compound. In one non-limiting embodiment, the upper limit can be about 2.5 weight % by weight, based on the total weight of the compound.

[0031] The thickener of the presently disclosed and claimed inventive concept(s) can be, for example, but by no way of limitation, ethylhydroxyethyl cellulose (EHEC), hydroxyethyl cellulose (HEC), hydrophobically modified hydroxyethyl cellulose,

hydroxypropyl methylcellulose (HPMC), methylhydroxyethyl cellulose (MHEC), carboxymethyl cellulose (CMC), hydroxypropyl guar, and underivatized guar.

[0032] The amount of the thickener in the joint compound can have a lower limit of about 0.01 weight % based on the total dry weight of the joint compound (excluding the water present in the joint compound). In one non-limiting embodiment, the lower limit can be about 0.3 weight % based on the total dry weight of the joint compound. The upper limit of the thickener system can be about 0.6 weight%. In one non-limiting embodiment, the upper limit can be about 0.5 weight %.

[0033] Fillers are an important component in joint compounds. They serve the purpose of adding body to the joint compound, making the compound economical, and controlling the pH of the compound. Conventional fillers that can be used either alone or in combination in the presently disclosed and inventive concept(s) can include, but are not limited to, calcium carbonate, calcium sulfate dihydrate (gypsum), and dolomitic limestone. Calcium sulfate hemihydrate (plaster of Paris) may be used as a minor component in the presence of other fillers in order to better control open time and cracking and other joint compound properties.

[0034] In one non-limiting embodiment, the filler can be finely ground calcium carbonate. The filler can be a dry powder, which usually comprises at least about 45 weight % based on the weight of the joint compound. In one non-limiting embodiment, the filler comprises at least 50 weight %, based on the weight of the joint compound. Generally, the filter can fall within the range of about 45 to an upper limit of about 65% by weight. In order to achieve the desired pH of the compound of 8 to 10, the filler is the principal alkaline ingredient and therefore, is the main ingredient that controls the pH. If necessary, a pH modifier may be also added to increase the alkalinity of the compound.

[0035] Water can be added to the dry ingredients of the joint compound to provide the viscosity of the joint compound composition generally in the range of from about 300 to about 700 Brabender units.

[0036] Biocides increase the shelf life of the joint compound and prevent the composition from spoiling. In other words, biocides prevent microorganisms, such as mold, bacteria, and fungi, from growing in the compound and also on the walls of the building structure in which it is used. Examples of two efficient industry-accepted biocides can be Mergal® 174, 2[(hydroxymethyl)amino]ethanol, a broad spectrum biocide, manufactured by Troy Chemical Corp; and Proxel™ GXL product, 1,2-benzisothiazolin-3-one, an all purpose biocide, manufactured by Arch Chemicals, Inc.

[0037] Other biocides can include, but are not limited to, copper oxine, zinc stearate, calcium borate, zinc borate, barium borate, zinc omadine, zinc omadine/zinc oxide mix, 2,5-dimethyl-1, 3, 5-thiadiazinane-2-thione (Thione), 2-n-octyl-4-isothiazolin-3-one (octhilinone),

5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, hexahydro-1,3,5-triethyl-2-triazine, 5-bromo-5-nitro-1,3-dioxane, 2-(hydroxymethyl)amino-ethanol, 2-(hydroxymethyl)amino-2-methylpropanol, α -benzoyl- α -chloroformaldoxime, benzylbromoacetate, p-chloro-m-xylenol, bis-(2-hydroxy-5-chlorophenyl)sulfide, p-tolydiiodomethylsulfone, 3-iodo-2-propynylbutylcarbamate, bis-(2-hydroxy-5-chlorophenyl)methylene, dipropylamine ether, dodecylamine, and 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride.

[0038] The biocide should generally be present in the amount ranging from a lower limit of about 0.05 to an upper limit of about 1.0% by weight based on the total weight of the compound.

[0039] In accordance with the presently disclosed and claimed inventive concept(s), suitable clays for use in a joint compound can be any of the natural earthy, fine-grained, largely crystalline substances of hydrous aluminum silicates usually containing alkalis, alkaline earth, and iron that make up the group of clay materials. Included in this group can be, but are not limited to, sepiolite, montmorillonite, bentonite, illite, kaolin, and attapulgite. In one non-limiting embodiment, the clay is attapulgite. Attapulgite can typically be used at levels ranging from about 1.5 to about 3.5% of the total weight of the joint compound.

[0040] If a lightweight drying type joint compound having improved crack resistance is desired, the lightweight property can be provided by incorporating specially treated expanded perlite into the formulation. It is well known in the art that the expanded perlite should have a particle size that can pass through a 100-mesh screen, if it is to be incorporated into a joint compound. The expanded perlite can be a very lightweight material which can contain many fine cracks and fissures which may be penetrated by water and could thereby destroy its ability to render the joint compound lightweight. As a result, the expanded perlite is often treated to render it water-insensitive. The preferred method is to treat the expanded perlite with a silicone compound but other materials may be used to render it water-insensitive. The specially treated expanded perlite is commercially available from suppliers such as Silbriko Corporation. If non-treated perlite is used, care is taken to prevent undue water absorption during manufacture and over the expected shelf life of the joint compound. The lightweight examples illustrated herein were prepared using Silbriko's SiiCell® 3534 product, a surface treated perlite that is commonly used in the industry. The perlite can be used in amounts having an upper limit of about 8.5 weight percent. In one non-limiting embodiment, the upper limit can be 6.0 weight percent.

[0041] Depending on local preferences, other ingredients may be used in the joint compound formulations. These can include, but are not limited to, air entraining agents,

surfactants, humectants, pH buffering salts, defoamers, and mixtures thereof.

[0042] Normally, joint compounds can be prepared by combining all of the wet ingredients and mixing for one minute to homogenize. A blend of all the solids is then added to the mixing bowl, with continuing mixing. The entire mass is blended for a total of up to about 20 minutes. Different manufacturers may modify this procedure. In general, the higher the concentration of clay, the greater the required mixing time. Hence, the use of the reduced levels of clay described herein may in many cases permit the reduction of said mix time, with increase in total plant output.

[0043] The following examples illustrate the presently disclosed and claimed inventive concept(s), parts and percentages being by weight, unless otherwise indicated. Each example is provided by way of explanation of the presently disclosed and claimed inventive concept(s), not limitation of the presently disclosed and claimed inventive concept(s). In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the presently disclosed and claimed inventive concept(s) without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the presently disclosed and claimed inventive concept(s) covers such modifications and variations as come within the scope of the appended claims and their equivalents.

EXAMPLES

Preparation of Nanocrystalline Cellulose

[0044] Nanocrystalline cellulose (NCC) was prepared using the procedure similar to D. G. Gray et al, Langmuir, V.12, p. 2076-2082 (1996), which is incorporated herein by reference in its entirety. The details of the procedure are given below.

[0045] Prior to acid hydrolysis, the pulp was fluffed using a grinder. The fluffed pulp was hydrolysed in about 65% of sulfuric acid at about 45 °C for about 2 hrs. The solid content of the reaction was about 10%. First, the fluffed pulp was added into acid in a water bath with mechanical mixing and allowed to hydrolyze. After hydrolysis, the cellulose suspension was diluted with deionized (DI) water (~10 times volumes of the acid solution) and centrifuged twice to remove the acid. 2% sodium carbonate solution was then added to neutralize the residue acid. The suspension was dialyzed with DI water to remove the salt. The purified suspension was dried to determine the yield.

Evaluations

[0046] In order to evaluate the initial crack formation of the joint compound of the presently disclosed and claimed inventive concept(s), the following joint compound formulation was prepared:

Water—31.5 weight percent
30 micron CaCO₃—60.9 weight percent
Attapulgite clay—2 weight percent
Mica—3 weight percent
PVA latex (55%)—2 weight percent
MHEC—0.4 weight percent

[0047] This is a standard joint compound formulation. A formulation utilizing the presently disclosed and claimed inventive concept(s) was prepared using the same components listed above. However, the percentage of MHEC was reduced to 0.3 weight percent and 0.1 weight percent of nanocrystalline cellulose was added.

[0048] Quarter-inch thick layers of each of the above joint compounds were applied to a surface at a thickness of 1/4 inch, and allowed to dry. The images of the dried joint compound layers are shown in Figs. 1 and 2. Fig. 1 shows the joint compound with 0.4% MHEC, the joint compound shown in Fig. 2 has 0.3% MHEC and 0.1% NCC. The crack formation in Fig. 1, without the nanocrystalline cellulose, is significantly larger and more developed than that with the nanocrystalline cellulose in Fig. 2.

[0049] To further test this, the same compounds were tested at varying thicknesses from 1/32 of an inch up to 1/4 of an inch. The disk on the lower right of Figs. 3 and 4, being 1/32, with the disk on the upper left being 1/4 inch. The thickness of the two disks at the bottom of each column varied from the thickness of the two disks at the top of each column by 1/32 of an inch. The sample with 0.4% MHEC, Fig. 3, shows a significant crack at 1/8 of an inch, whereas, the sample with the 0.1% NCC, Fig. 4, shows crack formation at about 5/32 of an inch and significantly less crack formation.

[0050] This evidence demonstrates that by including a small percentage of nanocrystalline cellulose into joint compound formulations, crack formation can be significantly reduced. At the same time, this permits reduction in the amount of thickener added to the composition.

[0051] It is, of course, not possible to describe every conceivable combination of the components or methodologies for purpose of describing the disclosed information, but one of ordinary skill in the art can recognize that many further combinations and permutations of the disclosed information are possible. Accordingly, the disclosed information is intended to embrace all such alternations, modifications and variations that fall within the spirit and scope of the appended claims.

WHAT IS CLAIMED IS:

1. A joint compound comprising nanocrystalline cellulose, water, a filler, a binder and a thickener, wherein the amount of the nanocrystalline cellulose is effective to improve crack resistance of the joint compound upon drying.
2. The joint compound of claim 1, wherein the nanocrystalline cellulose is present in an amount of from about 0.05 to about 0.5 percent by weight based on the total weight of the compound.
3. The joint compound of claim 1, wherein the filler is selected from the group consisting of calcium carbonate, calcium sulfate dihydrate, limestone, calcium sulfate hemihydrate, and combinations thereof.
4. The joint compound of claim 3, wherein the filler comprises calcium carbonate.
5. The joint compound of claim 4, wherein the filler is present in an amount of from about 45 to about 65 percent by weight based on the total weight of the compound.
6. The joint compound of claim 1, wherein the binder is selected from the group consisting of polyvinyl alcohol, ethylene vinyl acetate latex, poly(vinyl acetate) latex, starch, casein, polyacrylamide, copolymers of acrylamide and acrylic acid, and combinations thereof.
7. The joint compound of claim 6, wherein the binder is present in an amount of from about 1 to about 2.5 percent by weight based on the total weight of the compound.
8. The joint compound of claim 1, wherein the thickener is selected from the group consisting of carboxymethyl cellulose, ethylhydroxyethyl cellulose, hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, hydroxypropylmethyl cellulose, methylhydroxyethyl cellulose, methylcarboxycellulose, hydroxypropyl guar, underivatized guar, and combinations thereof.
9. The joint compound of claim 8, wherein the thicker is present in an amount of from about 0.3 to about 0.5 percent by weight based on the total weight of the compound.
10. The joint compound of claim 8, wherein the thickener is methylhydroxyethyl cellulose.

11. The joint compound of claim 1 further comprising perlite.
12. The joint compound of claim 1 further comprising a biocide.
13. The joint compound of claim 12, wherein the biocide is present in an amount ranging from about 0.05 to about 1.0% by weight based on the total weight of the compound.
14. The joint compound of claim 1 further comprising about 1.5 to about 3.5 percent by weight of clay based on the total weight of the compound.
15. The joint compound of claimn14, wherein the clay comprises attapulgite clay.
16. The joint compound of claim 1 further comprising mica.
17. The joint compound of claim 1, wherein the nanocrystalline cellulose is present in an amount of about 0.05 to about 0.1 % by weight and the thicker is present in an amount of from about 0.3 to 0.5% by weight based on the total weight of the compound.

Enhanced crack formation in 14 inch
JC control (No NCC added)
0.4% MHEC

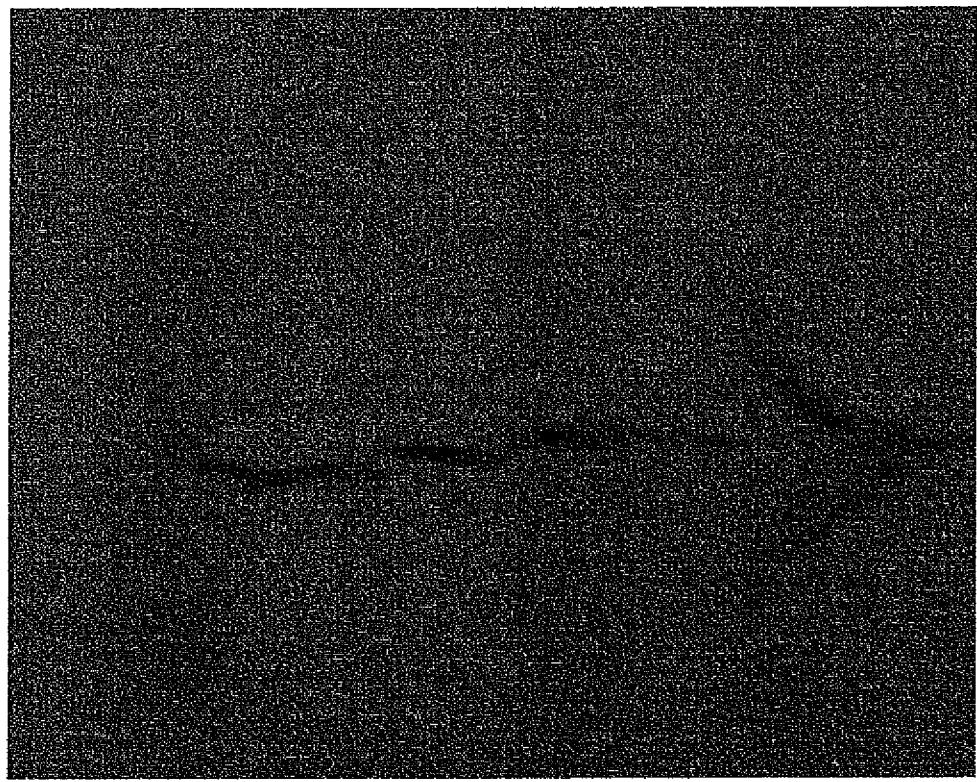


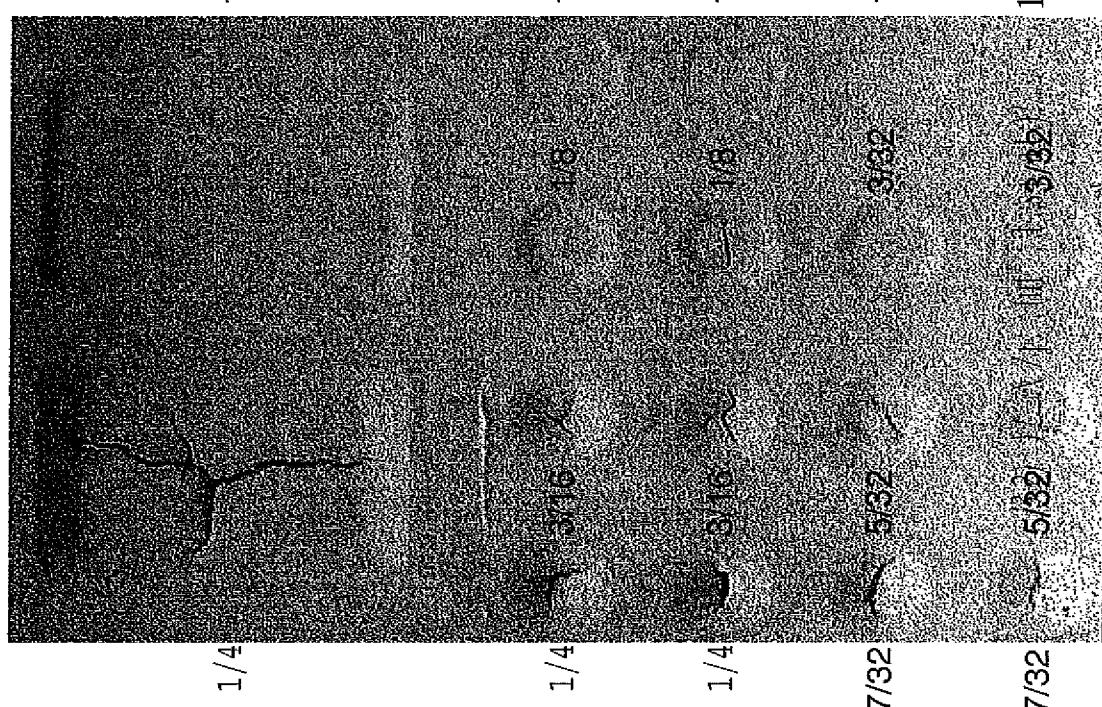
FIG. 1

Suppressed crack formation with
added NCC
0.3% MHEC + 0.1% NCC



FIG. 2

0.4% MHEC



0.3% MHEC + 0.1% NCC

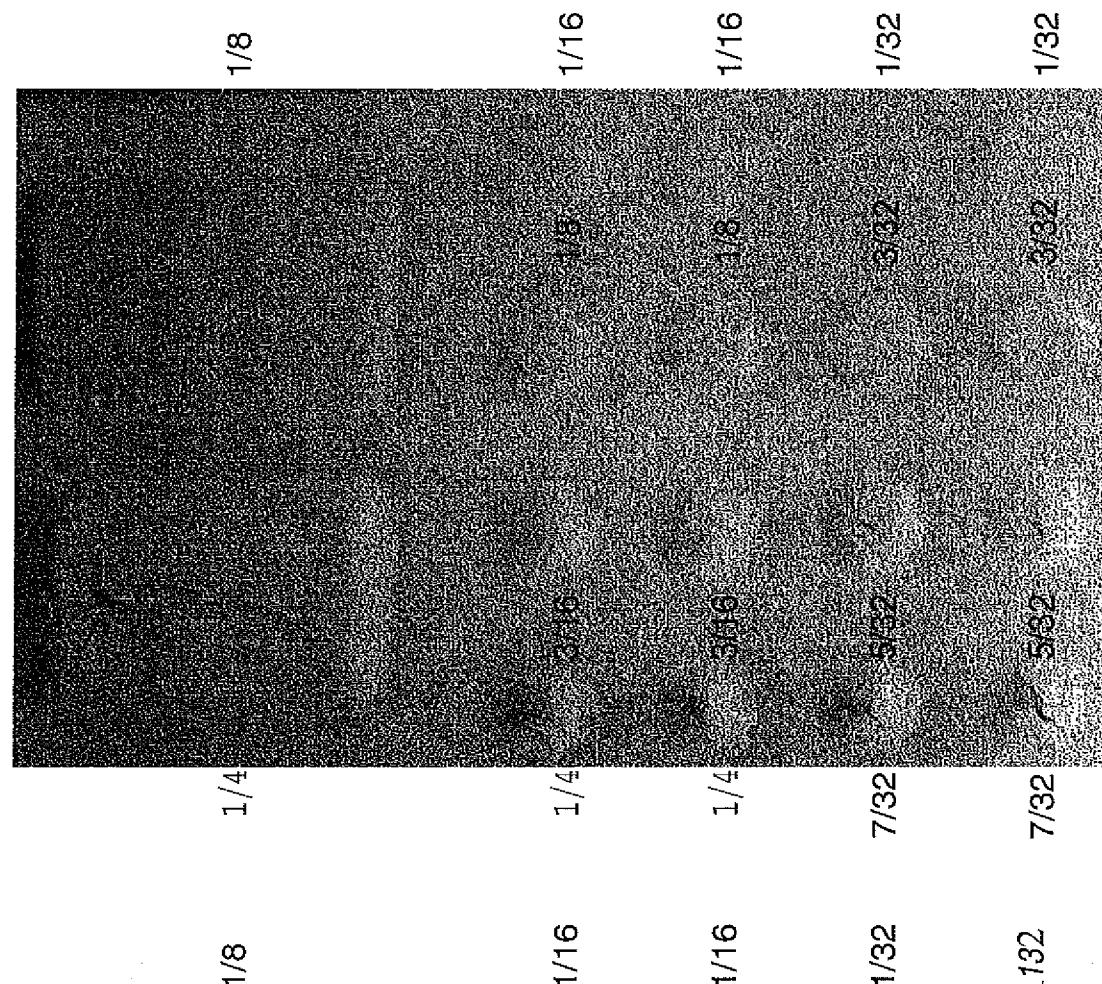


FIG. 3

FIG. 4

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/026640

| | | | | |
|-------------------------------------|-----------|-----------|-----------|-----------|
| A. CLASSIFICATION OF SUBJECT MATTER | | | | |
| INV. C04B26/04 | C04B26/06 | C04B26/28 | C04B26/02 | C04B28/14 |
| ADD. | | | | |

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-------------------------|
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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| Date of the actual completion of the international search | Date of mailing of the international search report |
| 29 July 2013 | 06/08/2013 |
| Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3046 | Authorized officer Gattinger, Irene |

INTERNATIONAL SEARCH REPORT

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| International application No PCT/US2013/026640 |
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INTERNATIONAL SEARCH REPORT

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International application No

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| Patent document cited in search report | | Publication date | | Patent family member(s) | | Publication date |
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US007867358B2

(12) **United States Patent**
Medoff(10) **Patent No.:** US 7,867,358 B2
(45) **Date of Patent:** Jan. 11, 2011(54) **PAPER PRODUCTS AND METHODS AND SYSTEMS FOR MANUFACTURING SUCH PRODUCTS**7,026,635 B2 4/2006 Rangwalla et al.
7,267,744 B2 9/2007 Graveson et al.
2006/0169427 A1 8/2006 Cartier(75) Inventor: **Marshall Medoff**, Brookline, MA (US)(73) Assignee: **Xyleco, Inc.**, Woburn, MA (US)

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(21) Appl. No.: **12/417,707**(22) Filed: **Apr. 3, 2009**

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(65) **Prior Publication Data**

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Related U.S. Application Data

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(60) Provisional application No. 61/049,391, filed on Apr. 30, 2008.

Primary Examiner—Eric Hug*Assistant Examiner*—Jacob Thomas Minskey(74) *Attorney, Agent, or Firm*—Celia H. Leber(51) **Int. Cl.****D21C 5/00** (2006.01)(52) **U.S. Cl.** **162/50**; 162/9; 162/158;
162/192(58) **Field of Classification Search** 162/50,
162/9, 158, 192

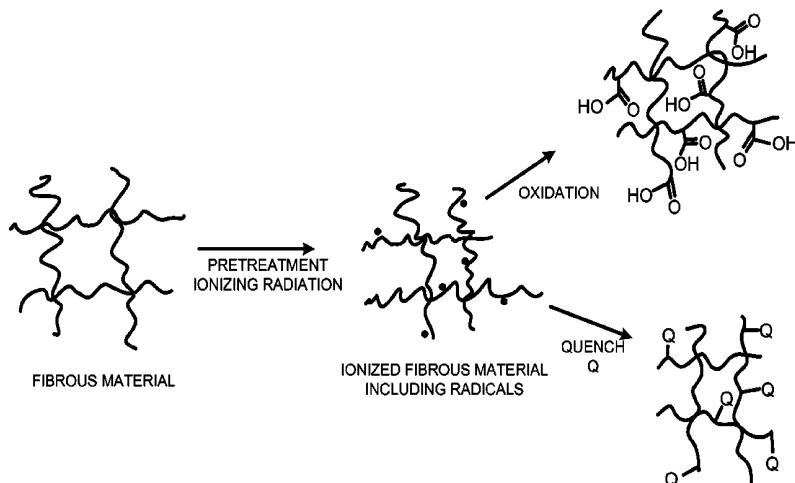
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Methods of producing cellulosic or lignocellulosic materials for use in papermaking include treating a cellulosic or lignocellulosic dry feedstock having a first average molecular weight with ionizing radiation, and controlling the dose of ionizing radiation such that the average molecular weight of the feedstock is reduced to a predetermined level. A method of producing an irradiated paper product includes treating a paper product including a first carbohydrate-containing material having a first molecular weight with ionizing radiation, and controlling the dose of ionizing radiation so as to provide an irradiated paper product with a second carbohydrate-containing material having a second molecular weight higher than the first molecular weight. Pulp and paper products are produced.

7 Claims, 15 Drawing Sheets

US 7,867,358 B2

Page 2

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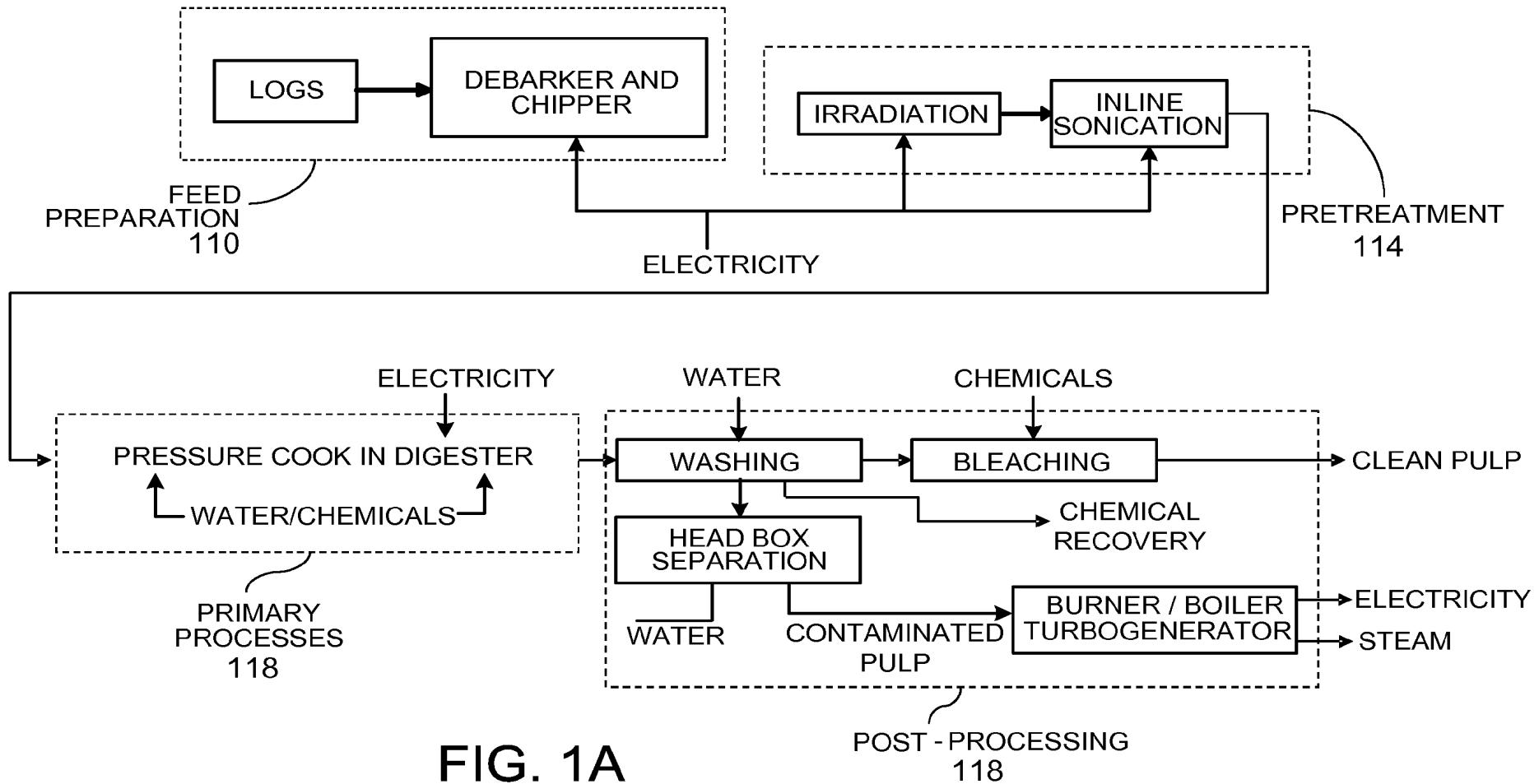
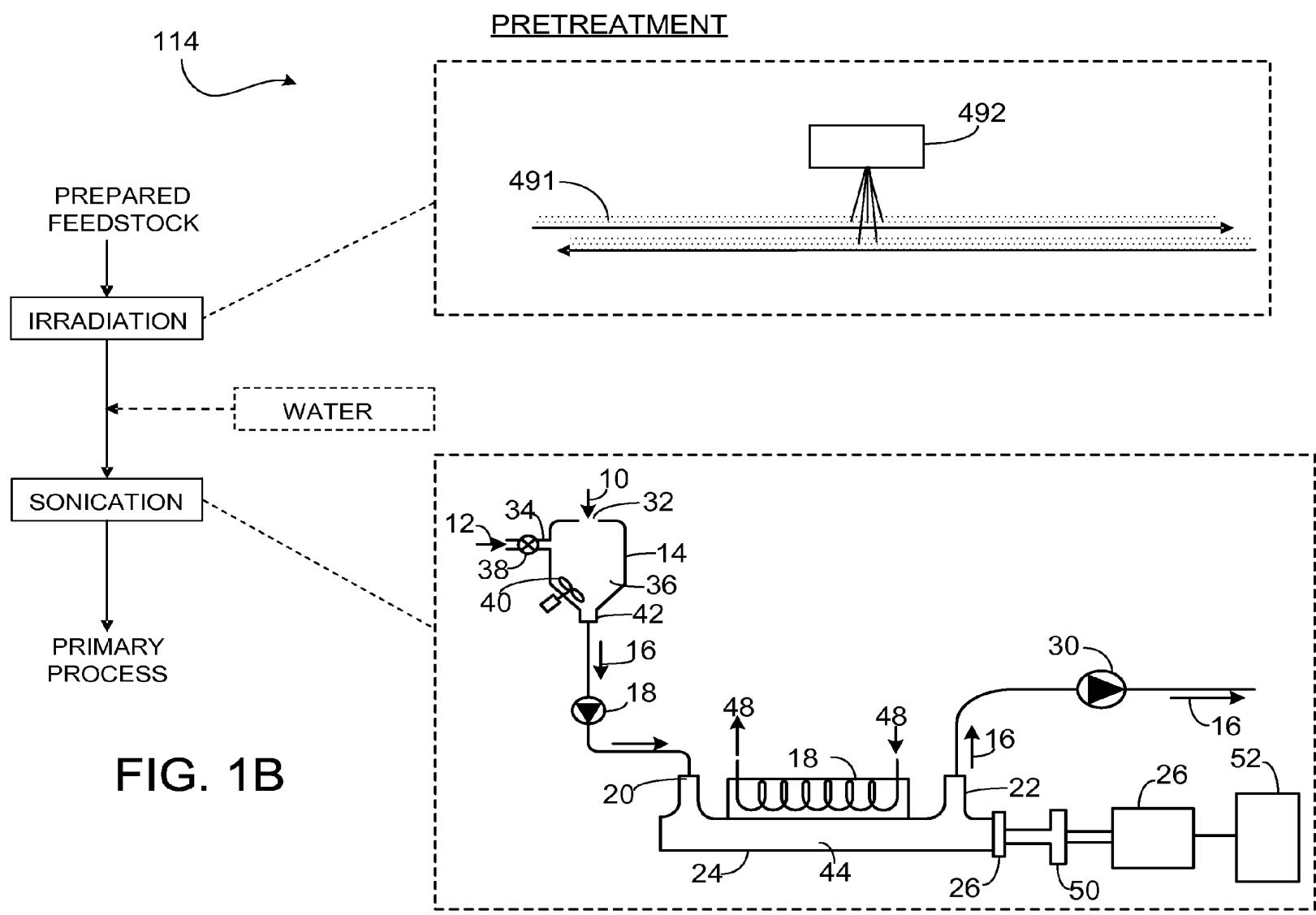


FIG. 1A



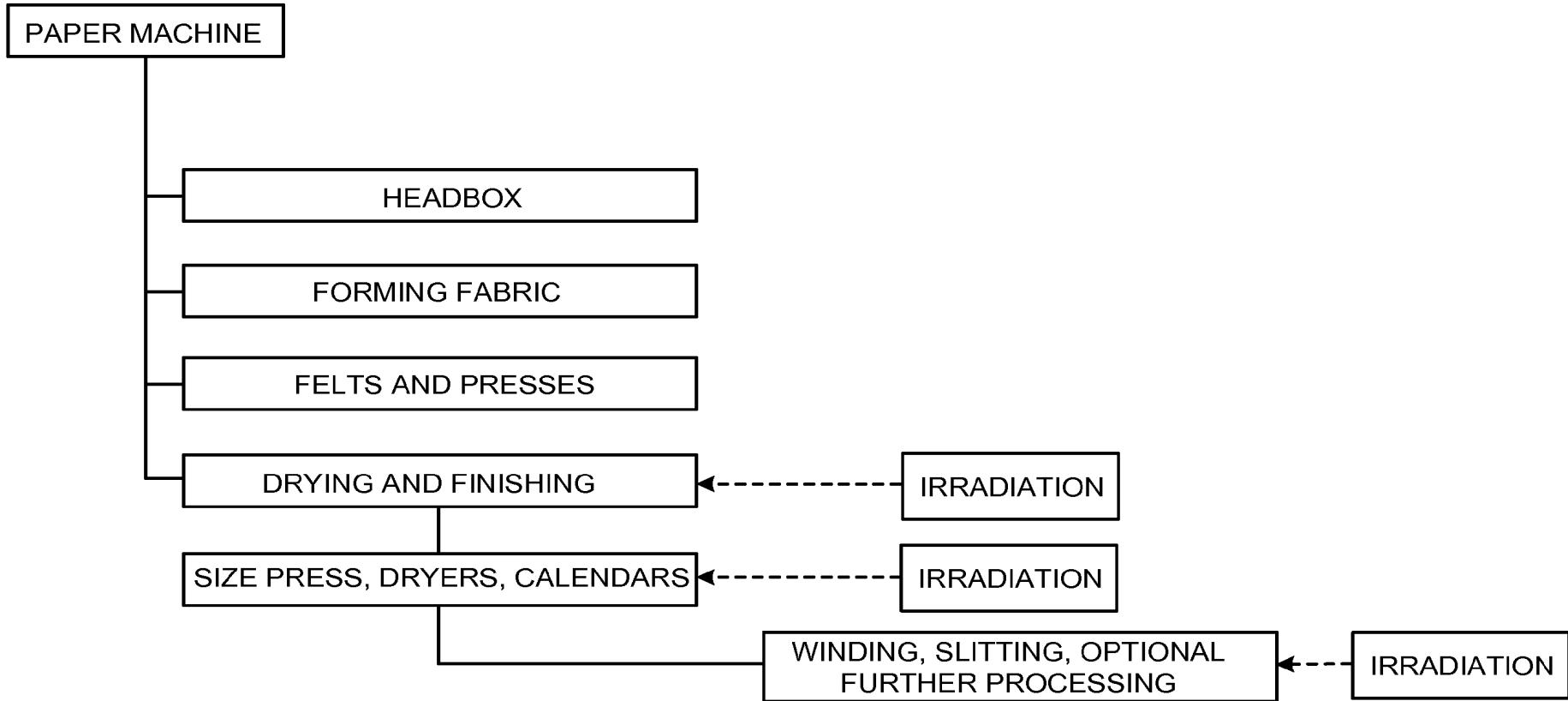


FIG. 2

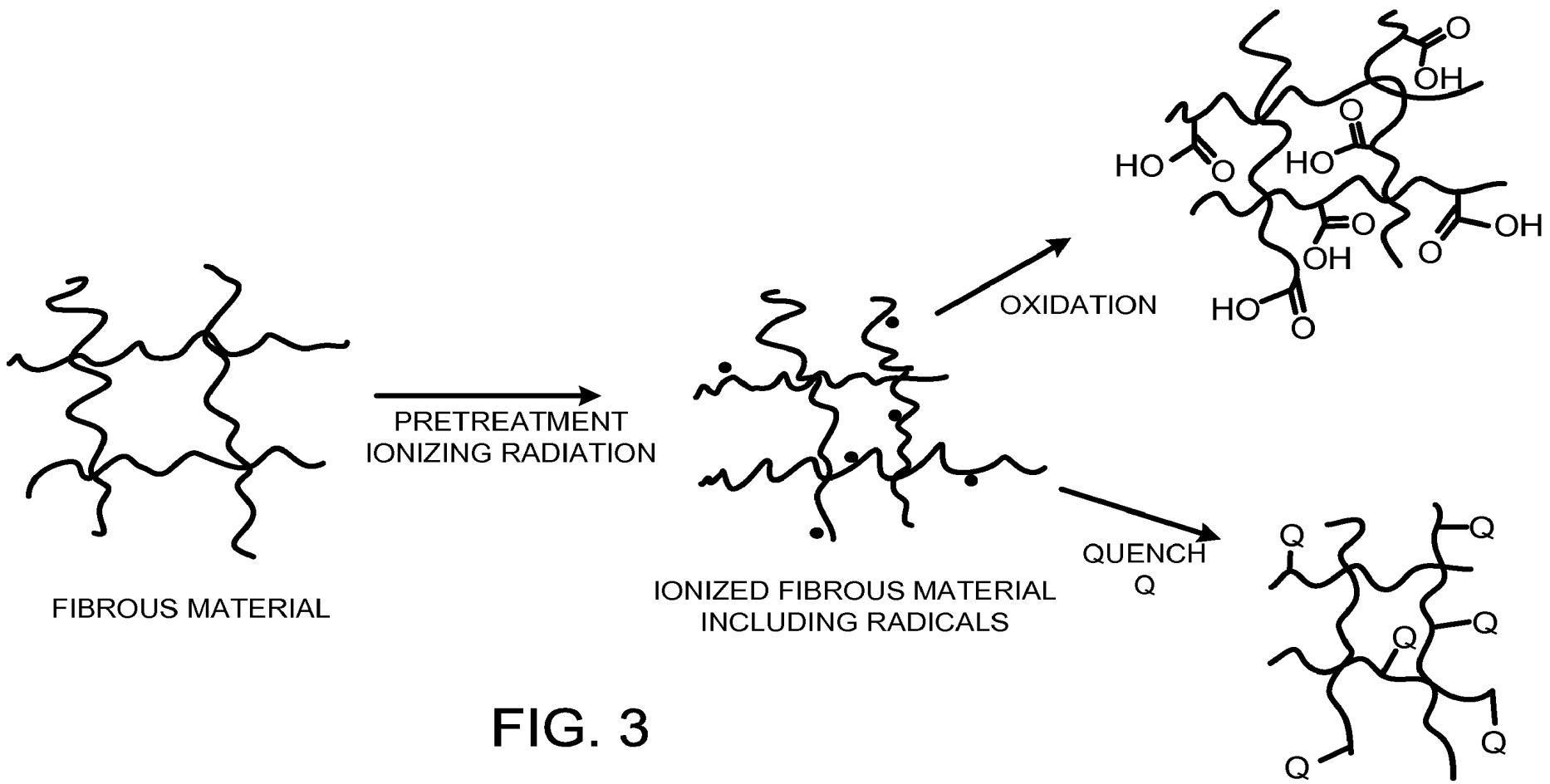


FIG. 3

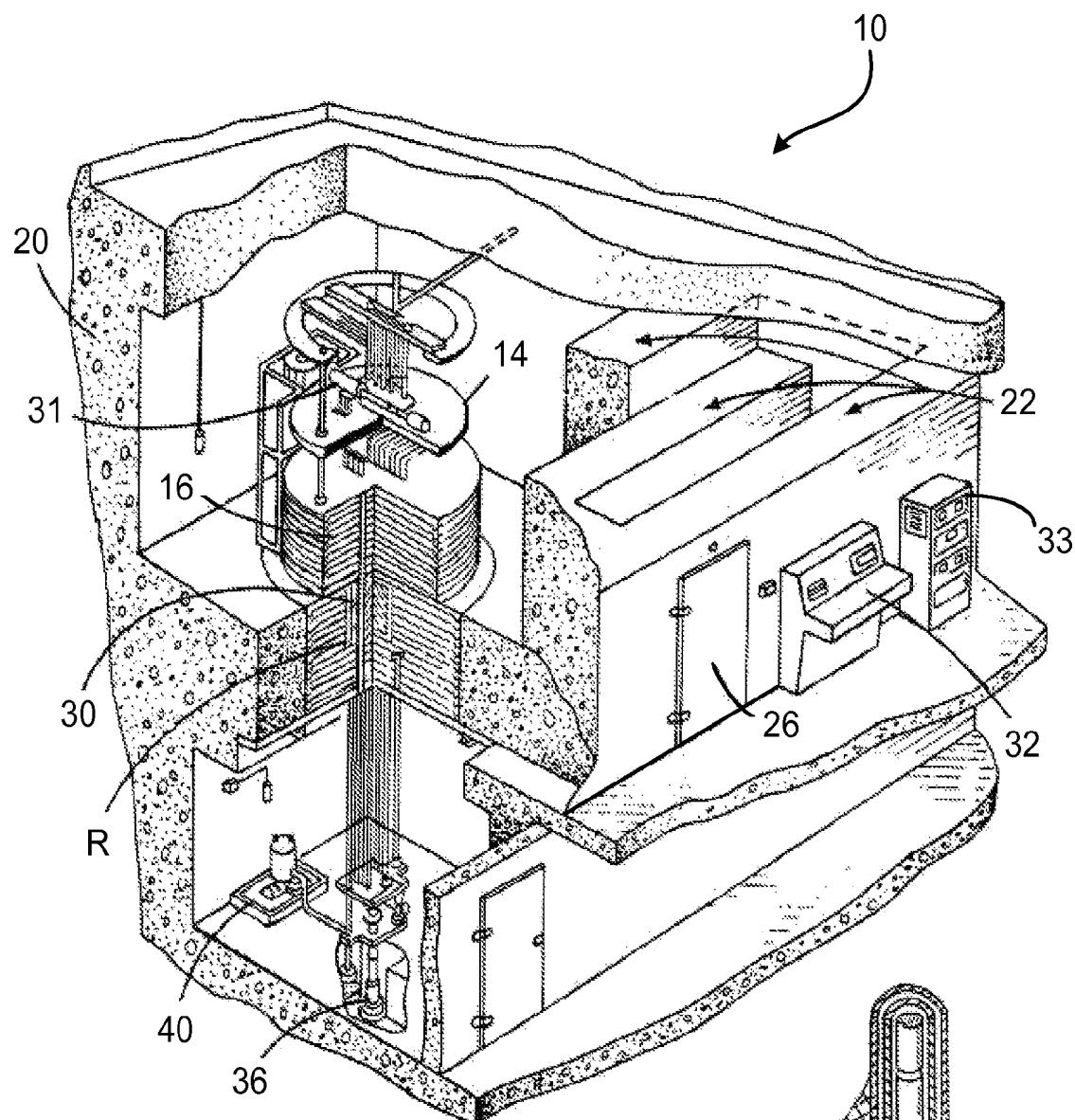


FIG. 4

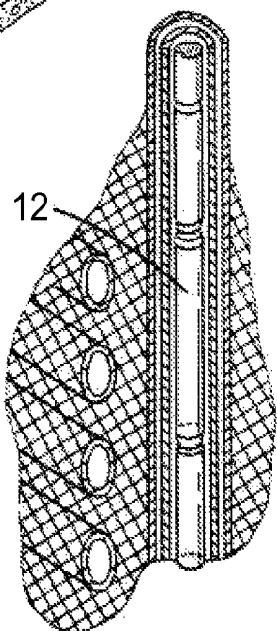


FIG. 5

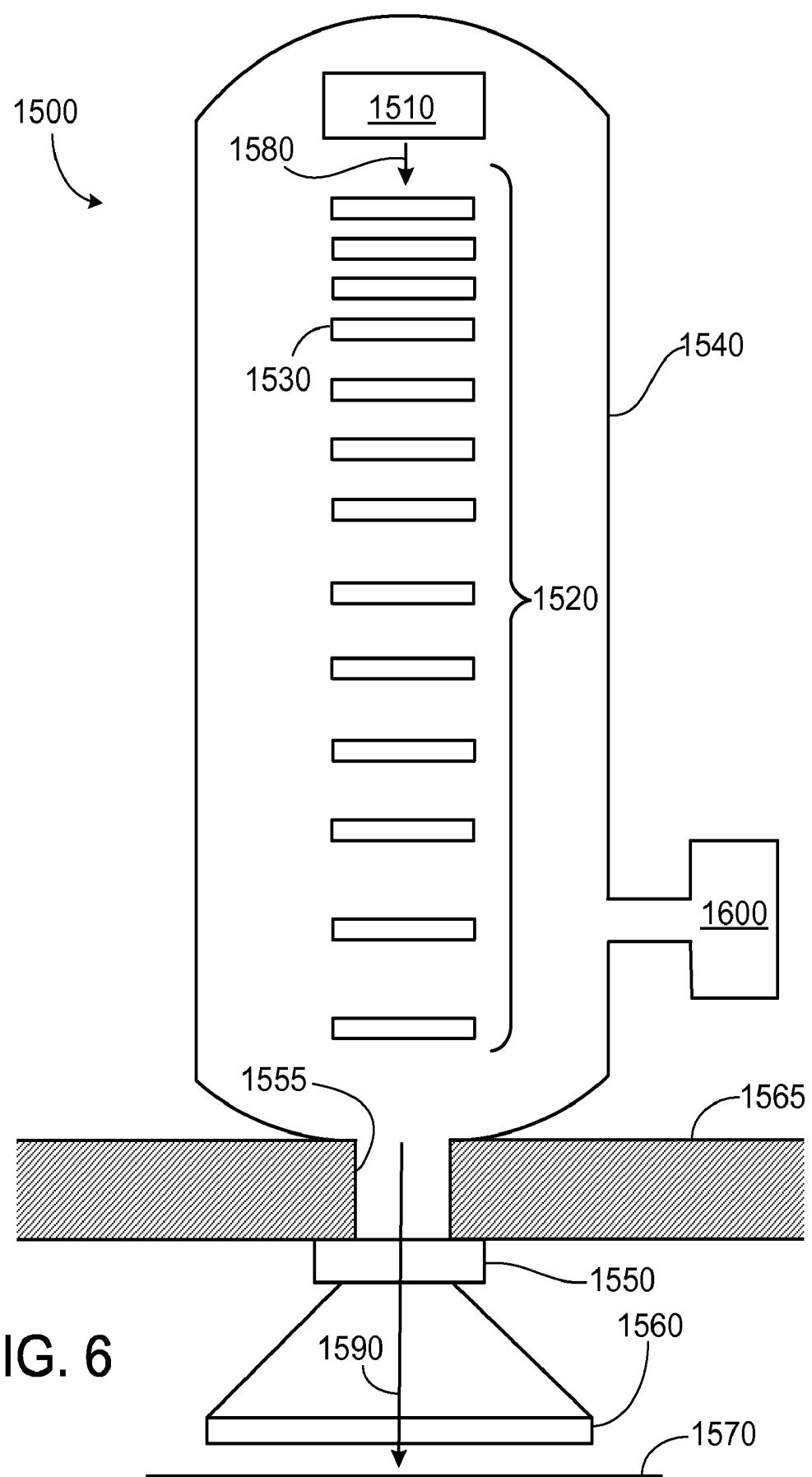


FIG. 6

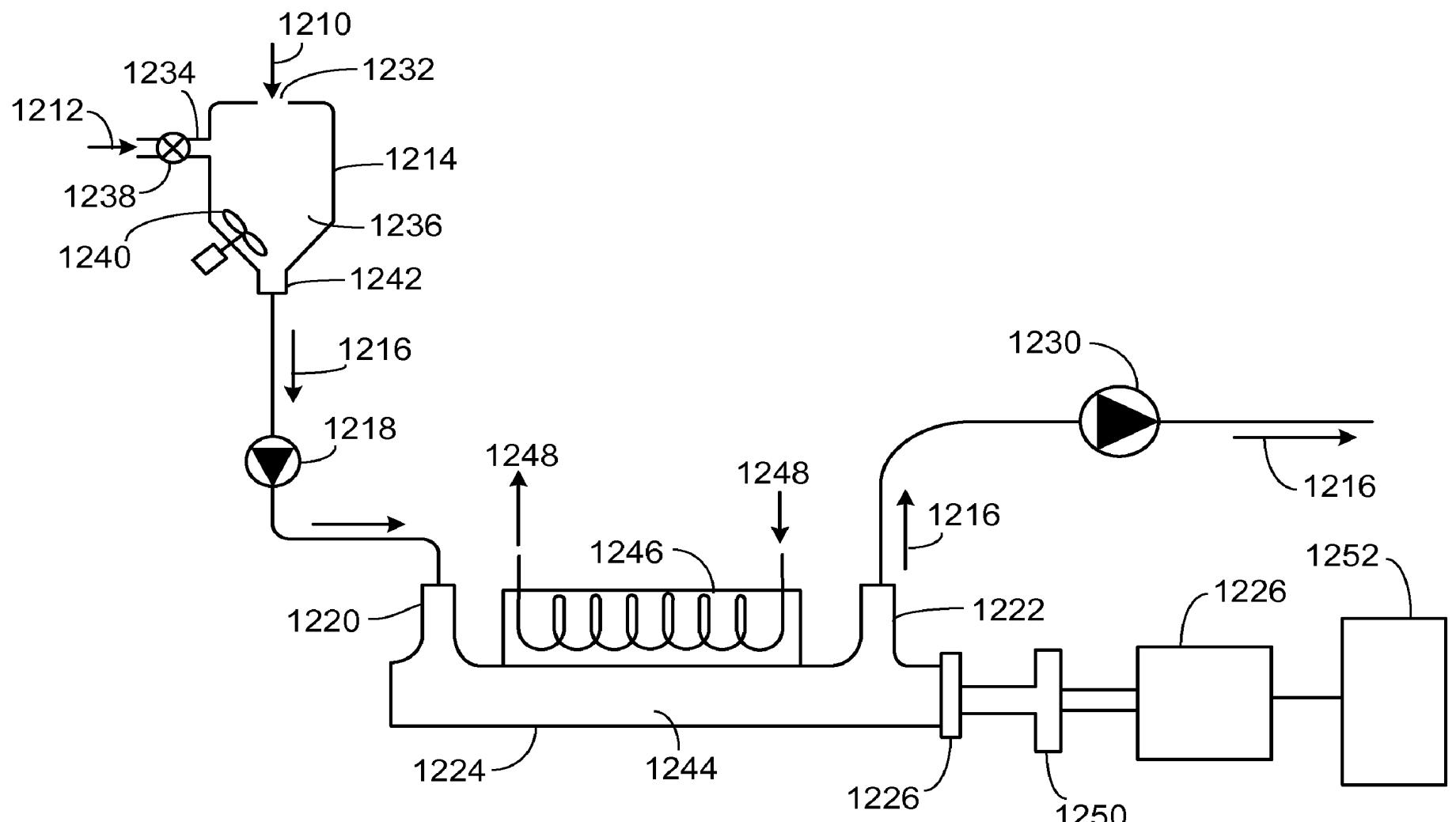


FIG. 7

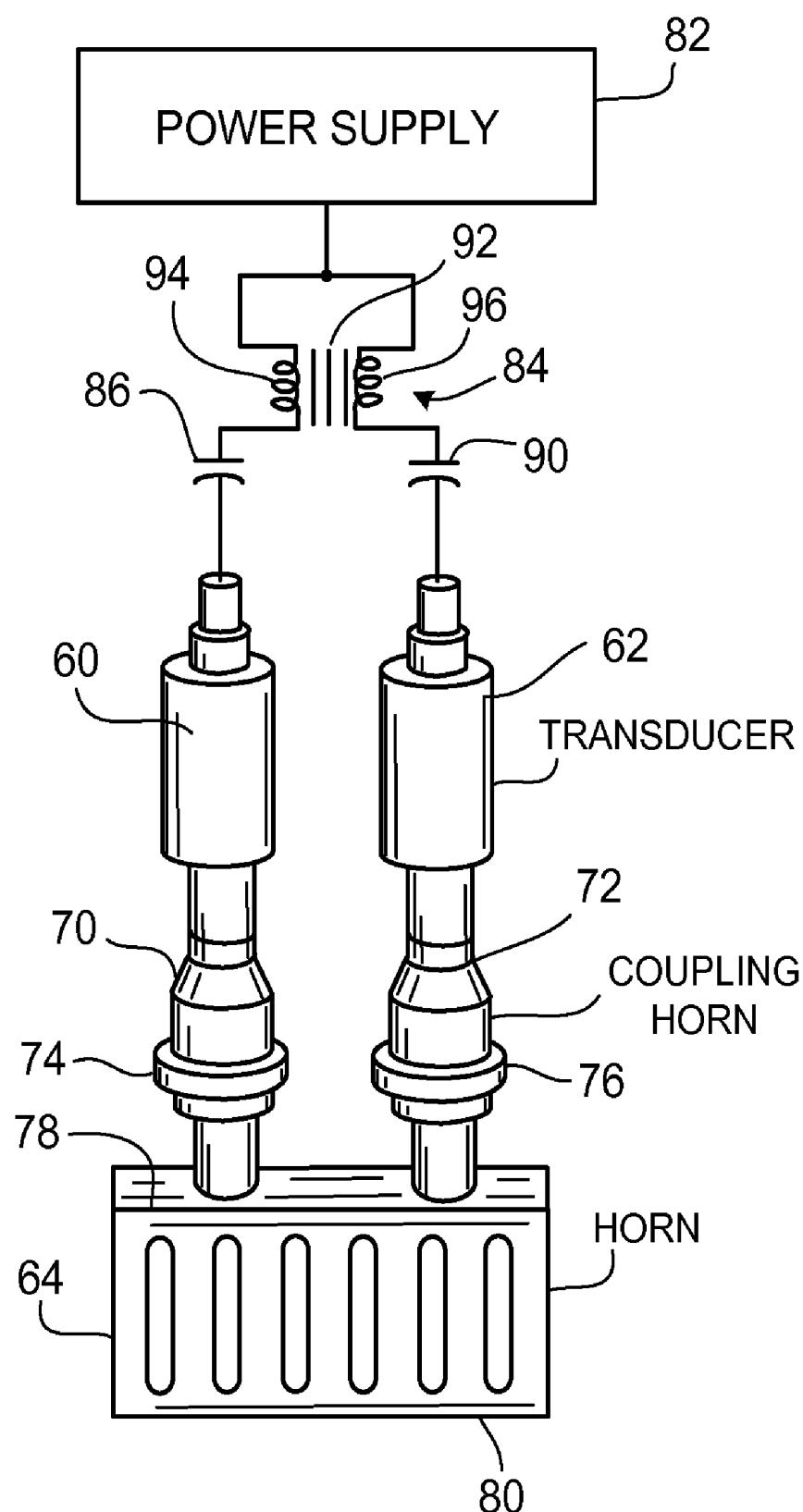


FIG. 8

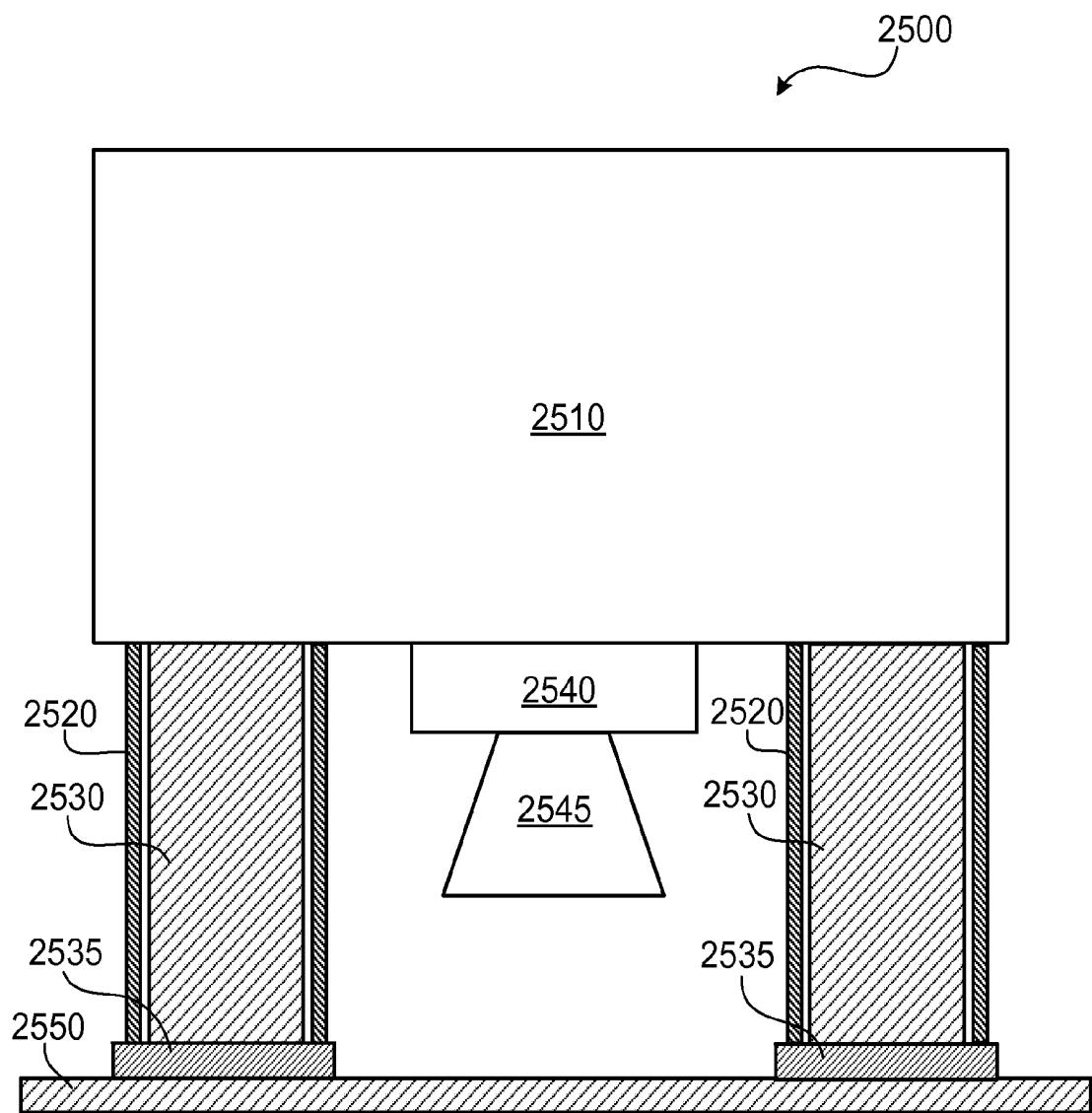


FIG. 9

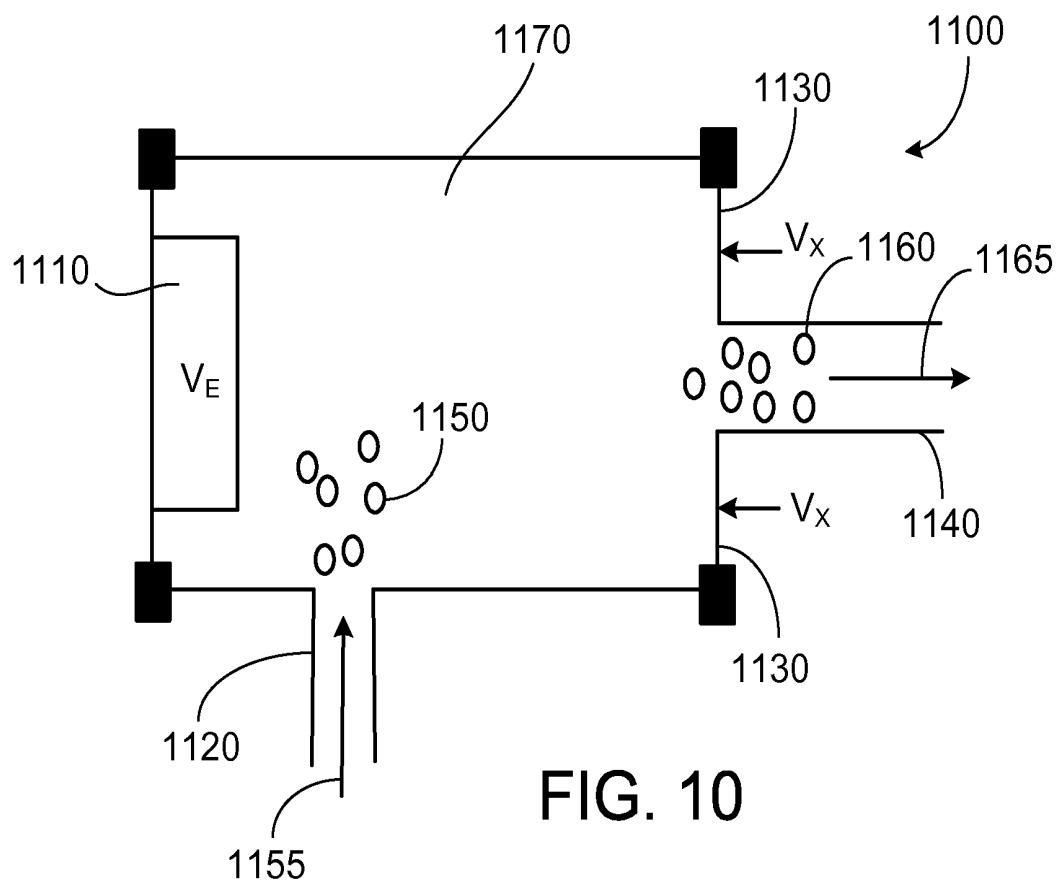


FIG. 10

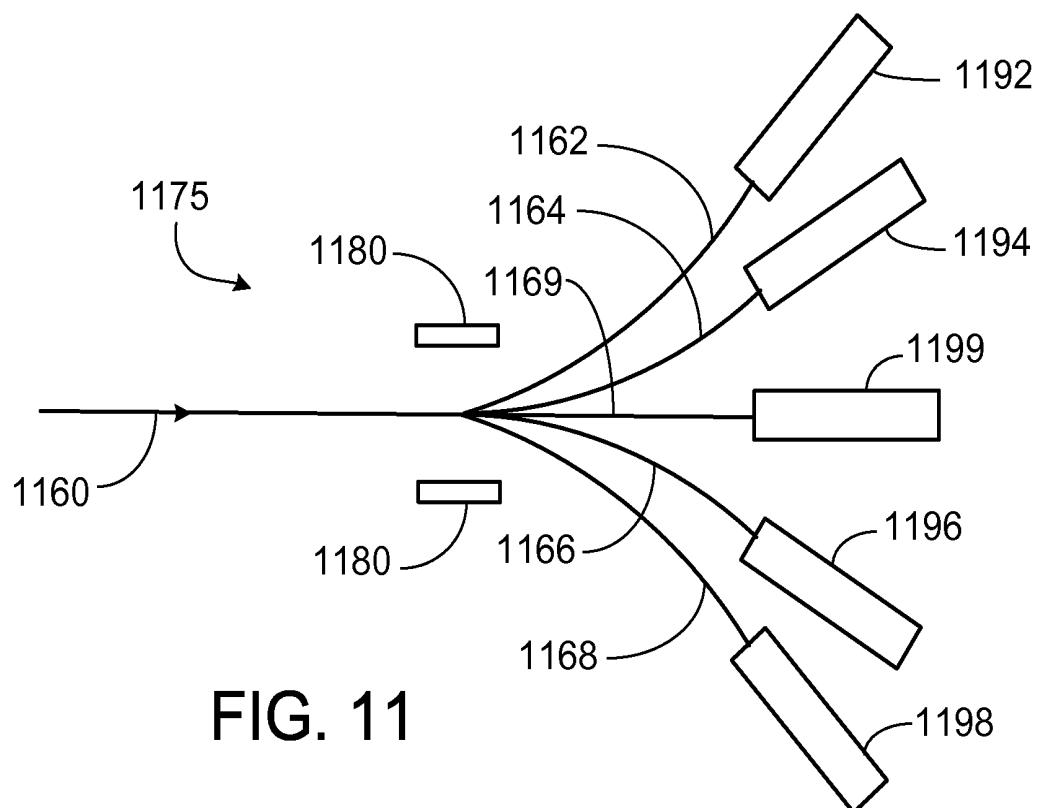


FIG. 11

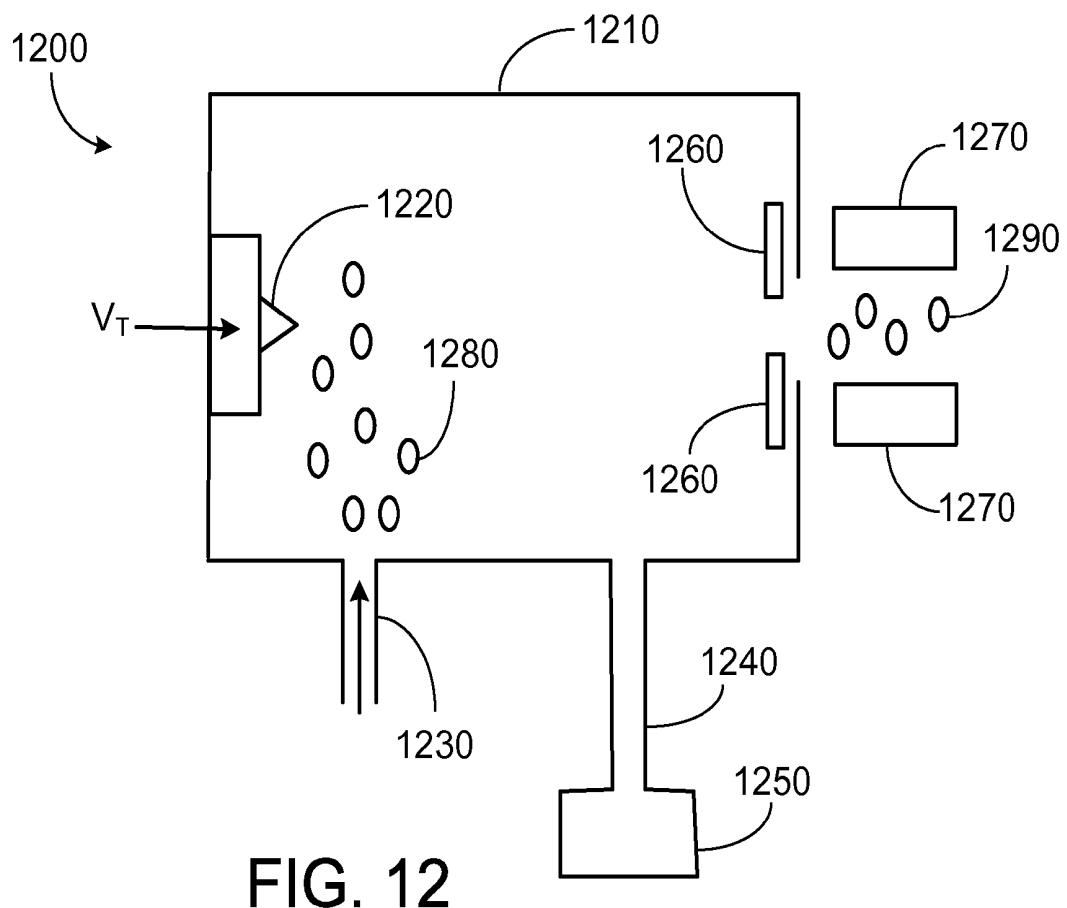


FIG. 12

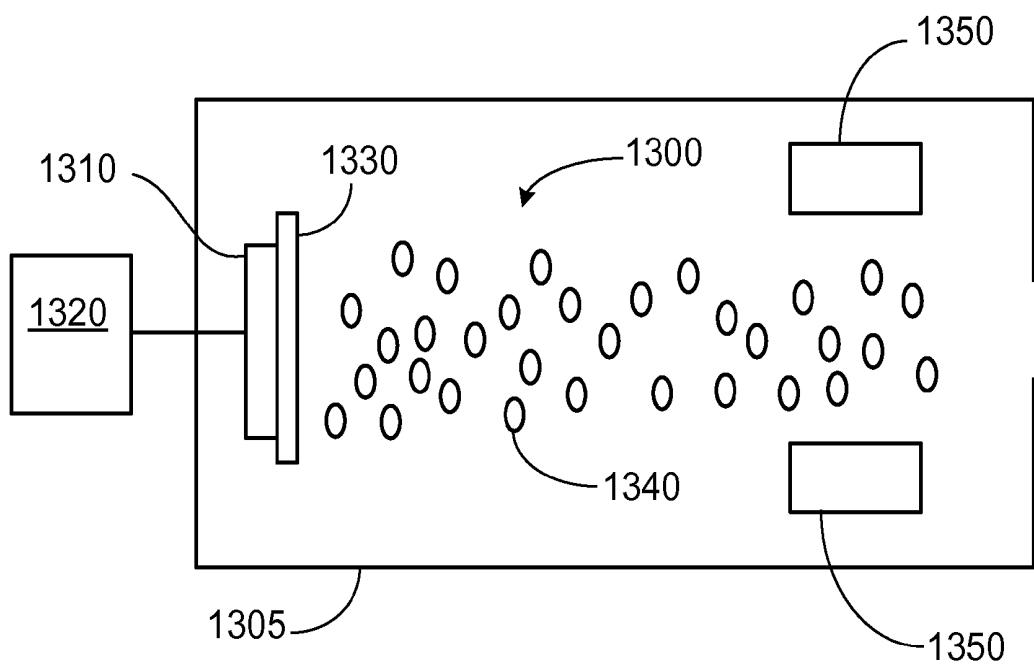


FIG. 13

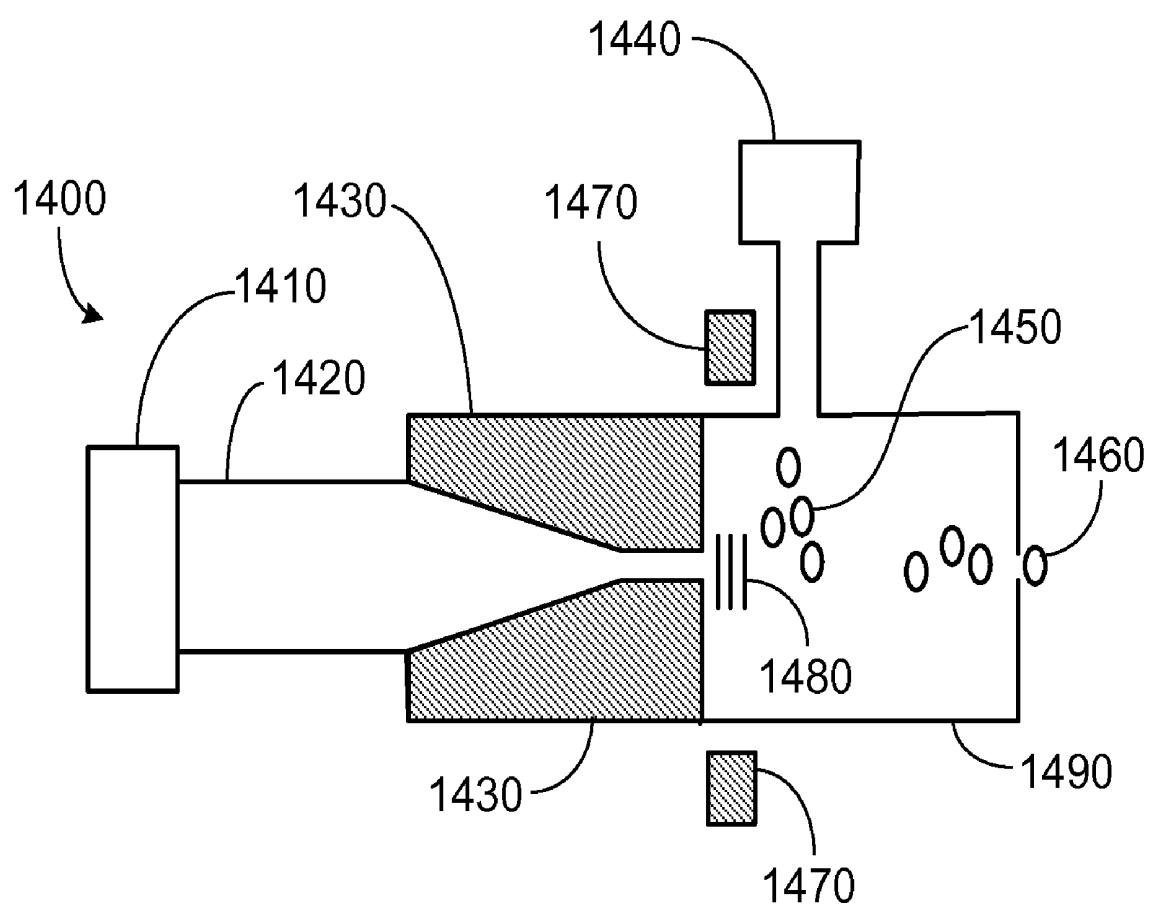
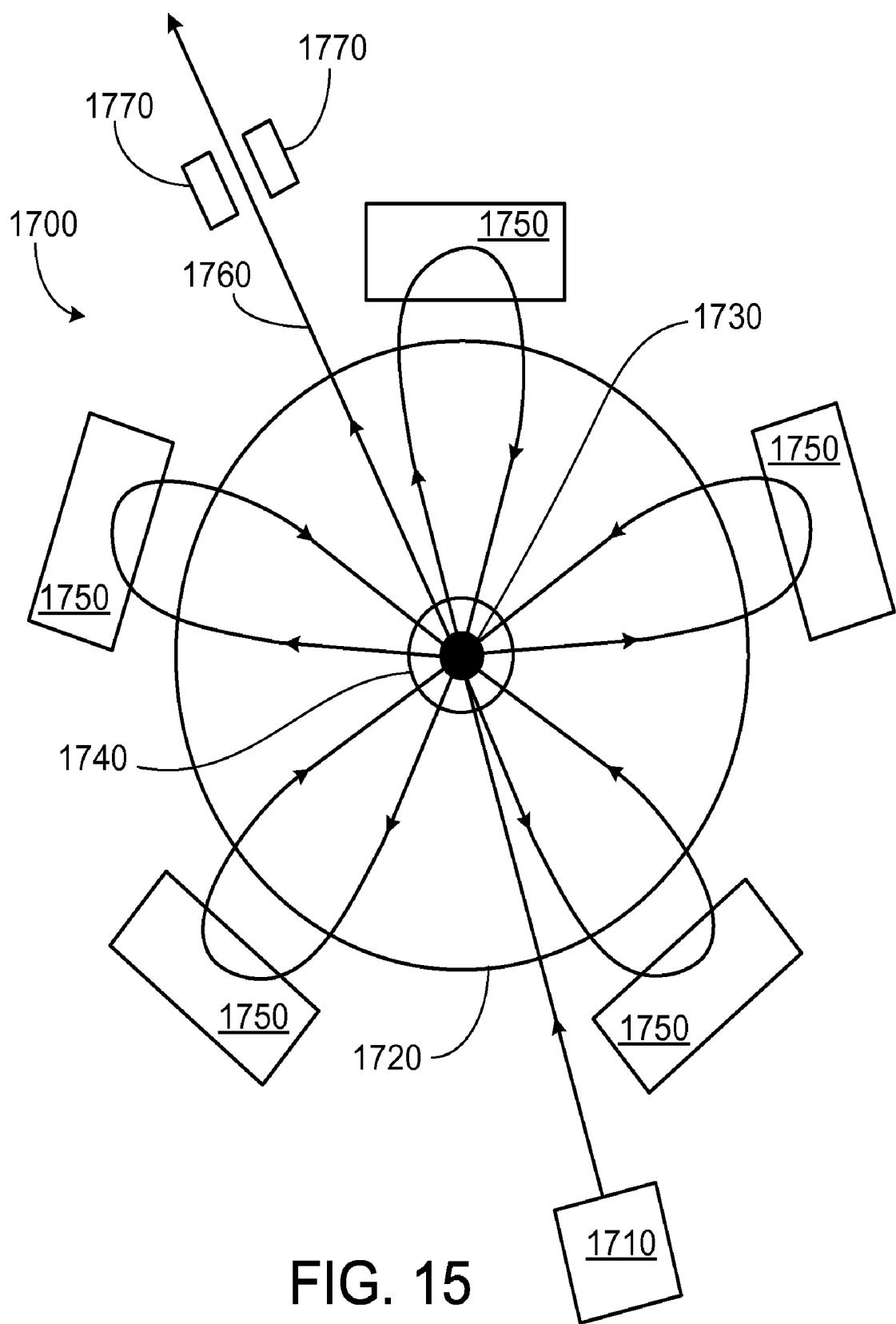


FIG. 14



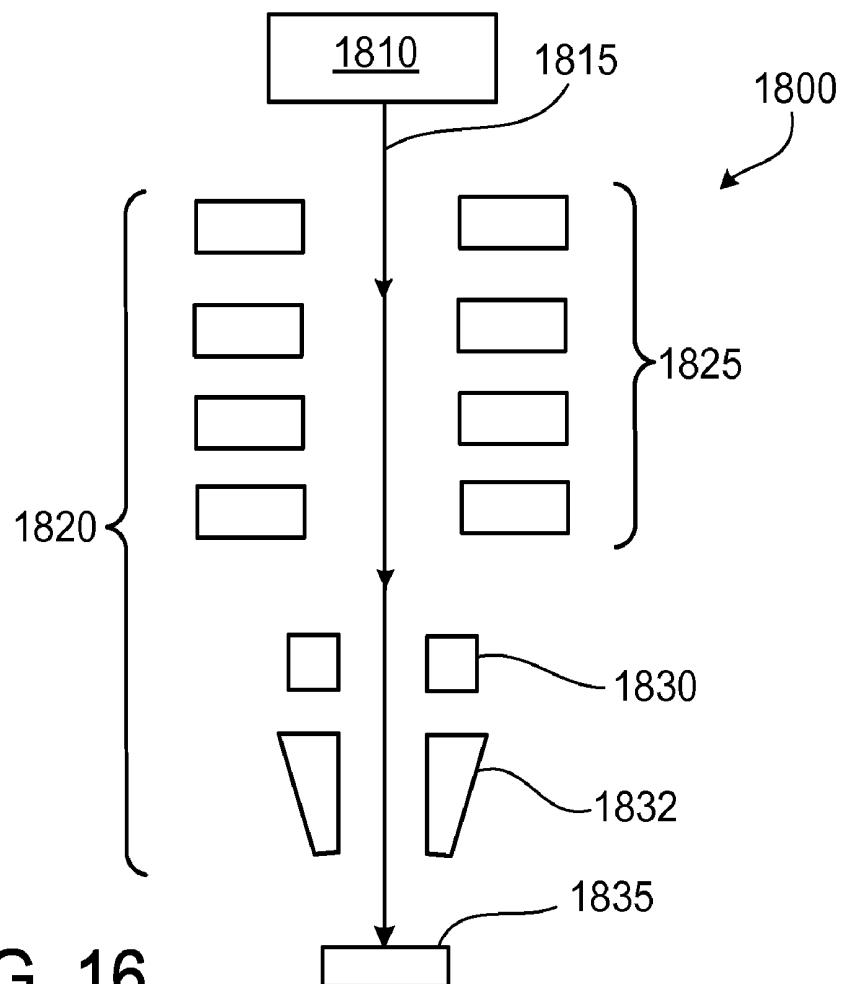


FIG. 16

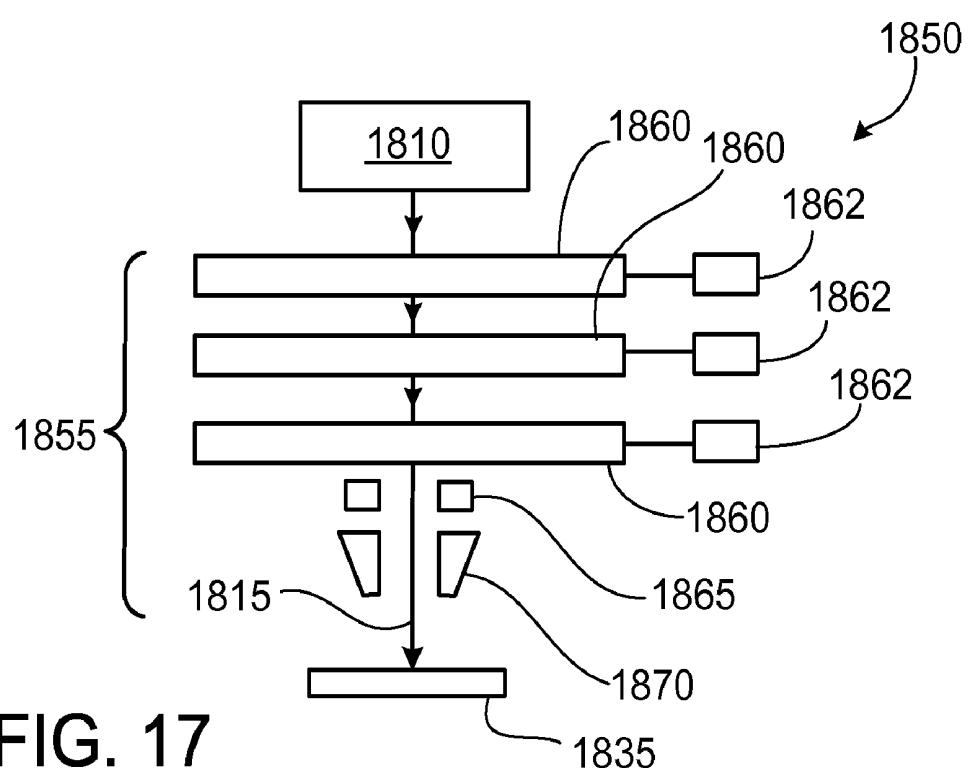
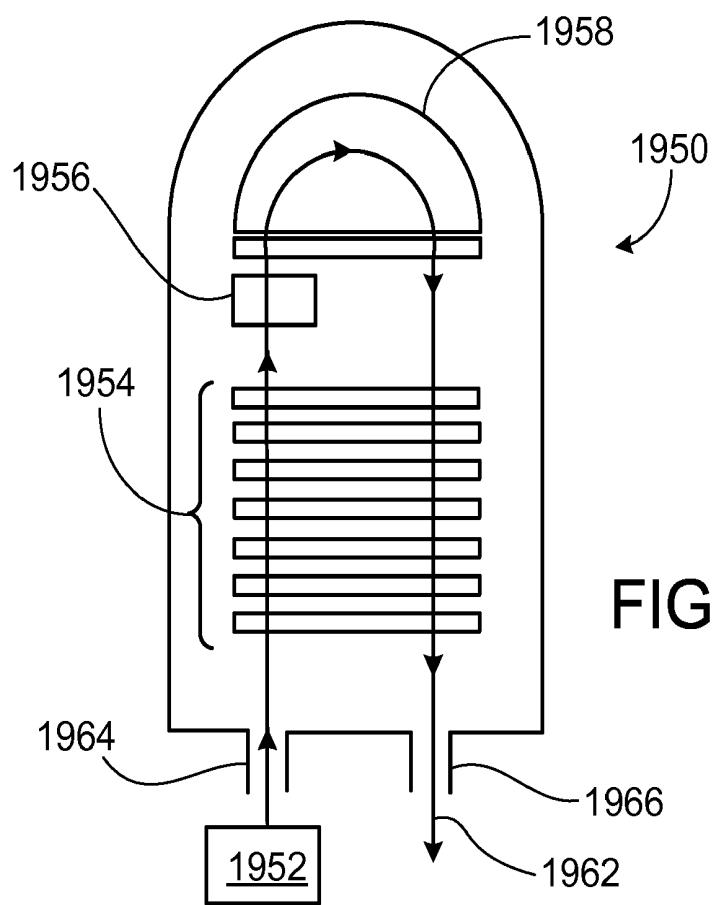
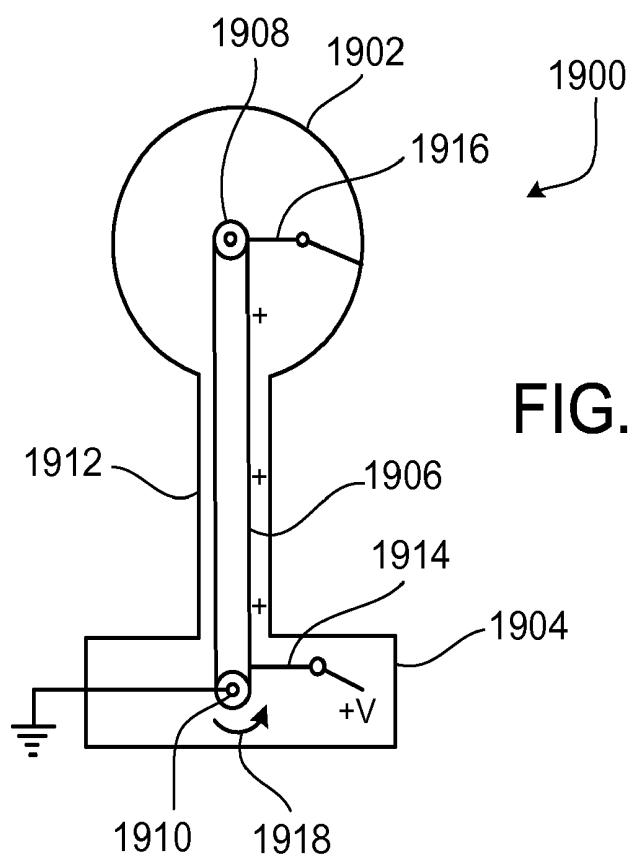


FIG. 17



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**PAPER PRODUCTS AND METHODS AND
SYSTEMS FOR MANUFACTURING SUCH
PRODUCTS**

RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application Ser. No. 61/049,391, filed Apr. 30, 2008. The complete disclosure of the provisional application is hereby incorporated by reference herein.

TECHNICAL FIELD

This invention relates to methods and systems for preparing paper products, and products produced by such methods and systems.

BACKGROUND

Paper, as that term is used herein, refers to the wide variety of cellulose-based sheet materials used for writing, printing, packaging, and other applications. Paper may be used, for example, but without limitation, in the following applications: as paper money, bank notes, stock and bond certificates, checks, and the like; in books, magazines, newspapers, and art; for packaging, e.g., paper board, corrugated cardboard, paper bags, envelopes, wrapping tissue, boxes; in household products such as toilet paper, tissues, paper towels and paper napkins; paper honeycomb, used as a core material in composite materials; building materials; construction paper; disposable clothing; and in various industrial uses including emery paper, sandpaper, blotting paper, litmus paper, universal indicator paper, paper chromatography, battery separators, and capacitor dielectrics.

Paper is generally produced by pulping a cellulosic material to form a pulp containing cellulosic fibers, amalgamating the cellulosic fibers to form a wet web, and drying the wet web. In the finished paper, the fibers are held together by mechanical interlocking and hydrogen bonding. Pulping may be accomplished in a number of ways, for example: using a chemical process (e.g., the Kraft process), a mechanical process (groundwood), or thermomechanical process (TMP). The amalgamating and drying steps are generally performed using a high speed paper machine.

The most common source of cellulosic fibers is wood pulp from trees. Pulp is also derived from recovered ("recycled") paper. Vegetable fiber materials, such as cotton, hemp, linen, and rice, are also used. Other non-wood fiber sources include, but are not limited to, sugarcane, bagasse, straw, bamboo, kenaf, jute, flax, and cotton. A wide variety of synthetic fibers, such as polypropylene and polyethylene, as well as other ingredients such as inorganic fillers, may be incorporated into paper as a means for imparting desirable physical properties.

For many applications, it is desirable that paper have high strength and tear resistance, even in very thin sheets, for example, when the paper is used in packaging, in industrial applications, as money, and in other applications that require strength and durability. It is also generally desirable that paper exhibit good printability characteristics, with the particular characteristics depending to some extent on the printing process in which the paper will be used.

SUMMARY

The invention is based, in part, on the discovery that by irradiating fibrous materials at appropriate levels, the physical characteristics of the fibrous material can be favorably

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altered. For example, the molecular weight, level of crosslinking, grafting sites, and/or functional groups of at least the cellulosic portions of the materials can be altered. Moreover, physical properties such as the tensile strength and shear strength of the fibrous material can be favorably affected. Relatively high doses of ionizing radiation can be used to reduce the molecular weight of at least the cellulosic portions of the fibrous material, assisting with transformation of a fibrous material to a pulp that is suitable for use in papermaking. Relatively lower doses of ionizing radiation can be used to increase the molecular weight of a paper product, enhancing its tensile strength and other mechanical properties. Ionizing radiation can also be used to control the functionalization of the fibrous material, i.e., the functional groups that are present on or within the material.

In one aspect, the invention features methods of producing a cellulosic or lignocellulosic material for use in papermaking. Some methods include treating a cellulosic or lignocellulosic dry feedstock having a first average molecular weight with at least 2.5 MRad of ionizing radiation to reduce the average molecular weight of the feedstock to a predetermined level.

Some implementations include one or more of the following features. The predetermined level is selected so that the treated feedstock is suitable for use as, or in forming, a pulp in a papermaking process. The methods further include subjecting the treated feedstock to a pulping process. The methods further include subjecting the treated feedstock to a mechanical disintegrating process. The methods can further include applying acoustic energy to the treated feedstock.

In some embodiments, the feedstock can include wood chips, and the dose of ionizing radiation can be about 2.5 to about 10 MRad. Treating can include irradiating with gamma radiation and/or irradiating with electron beam radiation. In certain embodiments, the electrons in the electron beam can have an energy of at least 0.25 MeV.

In another aspect, the invention features methods of making an irradiated paper product. Some methods include treating a paper product including a first carbohydrate-containing material having a first molecular weight with ionizing radiation to provide an irradiated paper product including a second carbohydrate-containing material having a second molecular weight higher than the first molecular weight.

Some implementations include one or more of the following features. The dose of ionizing radiation can be at least 0.10 MRad, e.g., at least 0.25 MRad. The dose of ionizing radiation can be controlled to a level of about 0.25 to about 5 MRad. Treating can include irradiating with gamma radiation, and/or with electron beam radiation. Electrons in the electron beam can have an energy of at least 0.25 MeV, e.g., from about 0.25 MeV to about 7.5 MeV. The methods can further include quenching the treated paper product. For example, quenching can be performed in the presence of a gas selected to react with radicals present in the treated paper product.

In yet a further aspect, the invention features methods of making an irradiated paper product that include treating a carbohydrate-containing pulp material with ionizing radiation such that the average molecular weight of the carbohydrate-containing pulp material is increased.

Some implementations of these methods can include one or more of the following features. Treating can occur during formation of the paper product. Forming can include amalgamating the pulp material into a wet paper web. Treating can be performed on the wet paper web or prior to formation of the wet paper web. Forming can further include drying the wet paper web, and treating can occur after drying.

In a further aspect, the invention features a paper, the paper comprising an irradiated lignocellulosic material, wherein the irradiated lignocellulosic material includes at least about 2 percent by weight lignin, such as at least about 2.5, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 or at least about 10.0 percent by weight lignin.

In some cases, the irradiated lignocellulosic material includes crosslinks, and the crosslinks occur in at least the lignin portion of the irradiated lignocellulosic material.

The invention also features a method of making a paper, the method including combining a cellulosic or lignocellulosic material with lignin and forming a paper from the combination.

In some cases the cellulosic or lignocellulosic material has been irradiated, and/or the combination is irradiated and then formed into a paper, and/or the formed paper is irradiated.

The invention also features pulp and paper products formed by irradiating cellulosic and lignocellulosic materials, e.g., using the methods described herein.

In one aspect, the invention features pulp materials including a treated cellulosic or lignocellulosic fibrous material having an average molecular weight of less than 500,000 and containing functional groups not present in a naturally occurring cellulosic or lignocellulosic fibrous materials from which the treated material was obtained. For example, in some embodiments, the functional groups include enol groups and/or carboxylic acid groups or salts or esters thereof. The functional groups can also be selected from the group consisting of aldehyde groups, nitroso groups, nitrile groups, nitro groups, ketone groups, amino groups, alkyl amino groups, alkyl groups, chloroalkyl groups, chlorofluoroalkyl groups, and carboxylic acid groups. In some cases the naturally occurring cellulosic or lignocellulosic fibrous materials can include wood chips.

In another aspect, the invention features paper products that include a treated cellulosic or lignocellulosic fibrous material, the treated cellulosic or lignocellulosic fibrous material containing functional groups not present in a naturally occurring cellulosic or lignocellulosic fibrous material from which the treated material was obtained.

The cellulosic or lignocellulosic material can be selected from the group consisting of paper waste, wood, particle board, sawdust, silage, grasses, rice hulls, bagasse, cotton, jute, hemp, flax, bamboo, sisal, abaca, straw, corn cobs, corn stover, switchgrass, alfalfa, hay, rice hulls, coconut hair, cotton, seaweed, algae, and mixtures thereof.

The term "dry feedstock" as used herein refers to a feedstock (e.g., woodchips or other cellulosic or lignocellulosic fibrous material) having a moisture content of less than 25%.

The full disclosures of each of the following U.S. Patent Applications, which are being filed concurrently herewith, are hereby incorporated by reference herein: Ser. Nos. 12/417,720, 12/417,699, 12/417,840, 12/417,731, 12/417,900, 12/417,800, 12,417,723, 12/417,786, and 12/417,904.

In any of the methods disclosed herein, radiation may be applied from a device that is in a vault.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All mentioned publications, patent applications, patents, and other references are incorporated herein by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In

addition, the materials, methods and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

DESCRIPTION OF DRAWINGS

FIG. 1A is a diagrammatic view of a pulping system.

FIG. 1B is a diagrammatic view of the pretreatment subsystem of the pulping system shown in FIG. 1A.

FIG. 2 is a diagrammatic view of a paper making system.

FIG. 3 is a diagram that illustrates changing a molecular and/or a supramolecular structure of a fibrous material.

FIG. 4 is a perspective, cut-away view of a gamma irradiator housed in a concrete vault.

FIG. 5 is an enlarged perspective view of region, R, of FIG. 4.

FIG. 6 is a schematic diagram of a DC accelerator.

FIG. 7 is a schematic view of a system for sonicating a process stream of cellulosic material in a liquid medium.

FIG. 8 is a schematic view of a sonicator having two transducers coupled to a single horn.

FIG. 9 is a schematic cross-sectional side view of a hybrid electron beam/sonication device.

FIG. 10 is a schematic diagram of a field ionization source.

FIG. 11 is a schematic diagram of an electrostatic ion separator.

FIG. 12 is a schematic diagram of a field ionization generator.

FIG. 13 is a schematic diagram of a thermionic emission source.

FIG. 14 is a schematic diagram of a microwave discharge ion source.

FIG. 15 is a schematic diagram of a recirculating accelerator.

FIG. 16 is a schematic diagram of a static accelerator.

FIG. 17 is a schematic diagram of a dynamic linear accelerator.

FIG. 18 is a schematic diagram of a van de Graaff accelerator.

FIG. 19 is a schematic diagram of a folded tandem accelerator.

DETAILED DESCRIPTION

As discussed above, the invention is based, in part, on the discovery that by irradiating fibrous materials, i.e., cellulosic and lignocellulosic materials, at appropriate levels, the molecular structure of at least a cellulosic portion of the fibrous material can be changed. For example, the change in molecular structure can include a change in any one or more of an average molecular weight, average crystallinity, surface area, polymerization, porosity, branching, grafting, and domain size of the cellulosic portion. These changes in molecular structure can in turn result in favorable alterations of the physical characteristics exhibited by the fibrous materials. Moreover, the functional groups of the fibrous material can be favorably altered.

For example, the following properties can be increased by 10, 20, 30, 40, 50, 75, or even 100% relative to the same properties prior to irradiation:

TAPPI T494 om-06 Tensile Properties of Paper and Paperboard (Using Constant Rate of Elongation Apparatus), including tensile strength and breaking length;

TAPPI Method T 414 om-04 Internal tearing resistance of paper (Elmendorf-type Method);

TAPPI Method T 403 om-02 Bursting strength of paper; and

TAPPI Method T 451 cm-84 Flexural properties of paper (Clark Stiffness).

Various cellulosic and lignocellulosic materials, their uses, and applications have been described in U.S. Pat. Nos. 7,307,108, 7,074,918, 6,448,307, 6,258,876, 6,207,729, 5,973,035 and 5,952,105; and in various patent applications, including "FIBROUS MATERIALS AND COMPOSITES," PCT/US2006/010648, filed on Mar. 23, 2006, and "FIBROUS MATERIALS AND COMPOSITES," U.S. Patent Application Publication No. 2007/0045456. The aforementioned documents are all incorporated by reference herein in their entireties. The cellulosic or lignocellulosic material can include, for example, paper waste, wood, particle board, sawdust, silage, grasses, rice hulls, bagasse, cotton, jute, hemp, flax, bamboo, sisal, abaca, straw, corn cobs, corn stover, switchgrass, alfalfa, hay, rice hulls, coconut hair, cotton, seaweed, algae, and mixtures thereof.

Relatively high doses of ionizing radiation can be used to reduce the molecular weight of the fibrous material, assisting with transformation of fibrous material to pulp that is suitable for use in papermaking. Thus, irradiation can be used to pre-treat a feedstock and thus facilitate a chemical, mechanical, or thermo-mechanical pulping process, or in some cases can be used to replace at least a portion of a conventional pulping process. Relatively high doses can also be applied to selected areas of a paper product or a precursor (e.g., a wet paper web) to form predetermined regions in which the paper is weakened, e.g., to create tear zones.

Relatively lower doses of ionizing radiation can be applied, at one or more stages of a papermaking process and/or to a finished paper product, to increase the molecular weight and the level of crosslinking of a paper product.

Ionizing radiation can also be used to control the functionalization of the fibrous material, i.e., the functional groups that are present on or within the material, which can increase solubility and/or dispersibility during pulping, and can favorably affect the surface properties of a paper product, e.g., the receptivity of the surface to coatings, inks and dyes.

Each of these processes will be discussed in detail below.

The irradiating steps discussed above can be combined in many ways. Some examples of processes including irradiation include the following:

(a) Irradiating only with a high dose of ionizing radiation, to reduce molecular weight and facilitate pulping. Irradiation can be performed prior to or during pulping.

(b) Irradiating only with a low dose of ionizing radiation, to increase molecular weight, and pulping conventionally. Irradiation can be performed at any stage of the papermaking process, or on the finished paper.

(c) Irradiating with a high dose of ionizing radiation, to break down molecular weight and facilitate pulping, followed by irradiation with a low dose of radiation, to increase molecular weight.

(d) Irradiating under conditions that favorably alter the functional groups present in the material. This can be accomplished during one of the steps discussed above, or as a separate step, as will be discussed in detail below.

(e) Irradiating selected areas of paper or a paper precursor with a relatively high dose of radiation to form predetermined weakened areas. This step can be performed alone, or in combination with any of the steps discussed in (a)-(d) above.

(f) Irradiating multiple times to achieve a given final dose, e.g., delivering a dose of 1 MRad repeated 10 times, to pro-

vide a final dose of 10 MRad. This may prevent overheating of the irradiated material, particularly if the material is cooled between doses.

Irradiating to Reduce Molecular Weight

Ionizing radiation can be applied to a cellulosic or lignocellulosic fibrous material that is suitable for use in making paper (e.g., wood chips) prior to or during pulping, at a dose that is sufficient to convert the starting material to pulp. In other words, irradiation with a dose of ionizing radiation that is selected to convert or to aid in converting the starting material to pulp can be used in place of conventional pulping processes such as chemical, mechanical, and thermomechanical pulping.

In this case, the dose is selected so that the molecular weight of the starting material is reduced to an extent similar to the extent by which molecular weight is reduced by conventional pulping. For example, in the case of converting wood chips to pulp, the dose would generally be selected to reduce the molecular weight from the starting molecular weight (1 million or greater) to about 20,000 to 500,000. The optimal dose will depend on the feedstock used, but will generally be in the range of 10 MRad to 1000 MRad, e.g., 25 MRad to 500 MRad, for conventional paper feedstocks such as wood-based materials.

Advantageously, in some implementations it is not necessary to remove lignin from the pulp, as is conventionally done during the pulping process. This is the case, for example, if the paper is irradiated with a low, molecular weight increasing, dose of ionizing radiation during or after the paper making process, as will be discussed below. In this case, the residual lignin may actually be useful, as the lignin acts as a filler, effectively reducing the amount of cellulosic material needed, and may be cross-linked by the low dose radiation.

In other implementations, instead of replacing conventional pulping with irradiation, ionizing radiation can be applied prior to or during a conventional pulping process, to facilitate or enhance the pulping process. For example, wood chips can be irradiated with a relatively high dose of ionizing radiation prior to the start of the pulping process. If desired, after irradiation, the wood chips can be subjected to a mechanical process prior to chemical pulping, such as further chipping, shearing, or pulverizing. Irradiating and, optionally, mechanically pulping of the irradiated feedstock, can initiate breakdown of the feedstock, in some cases allowing chemical pulping to be performed under less harsh conditions, e.g., using fewer chemicals, less energy, and/or less water.

Ionizing radiation can also be used in a paper recycling process, to re-pulp waste paper for use as starting material in recycled paper production. In this case, the dose of ionizing radiation delivered is selected to be sufficient to break down the hydrogen and mechanical bonding in the paper without deleteriously affecting the cellulosic and/or lignocellulosic fibers in the paper. The dose of ionizing radiation can, for example, be about 20% to 30% less than the dose used when the starting material is wood chips.

FIG. 1A shows a system 100 for converting cellulosic or lignocellulosic starting material, wood logs in the example shown, into pulp suitable for use in papermaking. System 100 includes a feed preparation subsystem 110, a pretreatment subsystem 114, a primary process subsystem 118, and a post-processing subsystem 122. Feed preparation subsystem 110 receives the starting material in its raw form (e.g., logs), and physically prepares the starting material for the downstream processes (e.g., reduces the size of the material and begins to homogenize the material). In the example shown, this is

accomplished by debarking and chipping the logs. Starting materials with significant cellulosic and lignocellulosic components can have a high average molecular weight and crystallinity that can make pulping difficult.

Pretreatment subsystem 114 receives feedstock (e.g., wood chips) from the feed preparation subsystem 110 and prepares the feedstock for use in primary production processes by, for example, reducing the average molecular weight and crystallinity, and changing the kind and degree of functionalization of the feedstock. This is accomplished, in the example shown, by irradiation with a relatively high dose of ionizing radiation, followed by an inline sonication (acoustic) process. Sonication will be discussed in detail below. A conveyor belt carries the feedstock from the feed preparation subsystem 110 to the pretreatment subsystem 114.

As shown in FIG. 1B, in the pretreatment subsystem 114, the feedstock is irradiated, e.g., using electron beam emitters 492, mixed with water to form a slurry, and subjected to the application of ultrasonic energy. As discussed above, irradiation of the feedstock changes the molecular structure (e.g., reduces the average molecular weight and the crystallinity) of the feedstock. Mixing the irradiated feedstock into a slurry and applying ultrasonic energy to the slurry further changes the molecular structure of the feedstock. Application of radiation and sonication in sequence can have synergistic effects in that the combination of techniques appears to achieve greater changes to the molecular structure (e.g., reduction of the average molecular weight and the crystallinity) than either technique can efficiently achieve on its own. Without wishing to be bound by theory, in addition to reducing the polymerization of the feedstock by breaking intramolecular bonds between segments of cellulosic and lignocellulosic components of the feedstock, the irradiation can make the overall physical structure of the feedstock more brittle. After the brittle feedstock is mixed into a slurry, the application of ultrasonic energy further changes the molecular structure (e.g., reduces the average molecular weight and the crystallinity) and also can reduce the particle size of the feedstock.

The conveyor belt 491 carrying the feedstock into the pretreatment subsystem distributes the feedstock into multiple feed streams (e.g., fifty feed streams), each leading to separate electron beam emitters 492. Preferably, the feedstock is irradiated while it is dry. For example, the feedstock may have a moisture content of less than 25%, preferably less than 20%, less than 15% or less than 10%. Each feed stream is carried on a separate conveyor belt to an associated electron beam emitter. Each irradiation feed conveyor belt can be approximately one meter wide. Before reaching the electron beam emitter, a localized vibration can be induced in each conveyor belt to evenly distribute the dry feedstock over the cross-sectional width of the conveyor belt.

Electron beam emitter 492 (e.g., electron beam irradiation devices commercially available from Titan Corporation, San Diego, Calif.) is, in one example, configured to apply a 100 kilo-Gray dose of electrons at a power of 300 kW. The electron beam emitters are scanning beam devices with a sweep width of 1 meter to correspond to the width of the conveyor belt. In some embodiments, electron beam emitters with large, fixed beam widths are used. A number of factors, including belt/beam width, desired dose, feedstock density, and power applied, govern the number of electron beam emitters required for the plant to process 2,000 tons per day of dry feedstock.

In some embodiments, sonication is omitted from the pretreatment system. In some embodiments, further mechanical processing, e.g., further chipping, replaces or is used in addition to sonication.

In some cases, the output of primary process subsystem 118 is directly useful as pulp, but in other cases, the output requires further processing, which is provided by post-processing subsystem 122. Post-processing subsystem 122 provides chemical pulping of the output of the primary process subsystem (e.g., pressure cooking and digestion, in the example shown). If the paper to be produced with the pulp is bleached, for example if the paper is bleached printing paper, a bleaching step is performed. This step can be omitted for pulp to be used for unbleached paper. In some embodiments, post-processing subsystem 122 utilizes other pulping processes, such as thermomechanical pulping, instead of chemical pulping. As shown, in some cases post-processing subsystem 122 can produce treated water to be recycled for use as process water in other subsystems, and/or can produce burnable waste that can be used as fuel for boilers producing steam and/or electricity.

Irradiating to Increase Molecular Weight

Relatively low doses of ionizing radiation can crosslink, graft, or otherwise increase the molecular weight of a carbohydrate-containing material, such as a cellulosic or lignocellulosic material (e.g., cellulose). In some embodiments, the starting number average molecular weight (prior to irradiation) of a paper product or a precursor to a paper product is from about 20,000 to about 500,000, e.g., from about 25,000 to about 100,000. The number average molecular weight after irradiation is greater than the starting number average molecular weight, for example by at least about 10%, 25%, 50%, 75%, 100%, 150%, 200%, 300%, or as much as 500%. For example, if the starting number average molecular weight is in the range of about 20,000 to about 100,000, the number average molecular weight after irradiation is, in some instances, from about 40,000 to about 200,000.

The new methods can be used to favorably alter properties of cellulose-based papers by applying radiation at one or more selected stages of the papermaking process. In some cases, irradiation will improve the strength and tear resistance of the paper, by increasing the strength of the cellulosic fibers of which the paper is made. In addition, treating the cellulosic material with radiation can sterilize the material, which may reduce the tendency of the paper to promote the growth of mold, mildew of the like. Irradiation is generally performed in a controlled and predetermined manner to provide optimal properties for a particular application, such as strength, by selecting the type or types of radiation employed and/or dose or doses of radiation applied.

A low dose of ionizing radiation can be applied to increase molecular weight, e.g., after pulping and before amalgamation of the pulped fibers into a web; to the wet fiber web; to the paper web during or after drying; or to the dried paper web, e.g., before, during, or after subsequent processing steps such as sizing, coating, and calendering. It is generally preferred that radiation be applied to the web when it has a relatively low moisture content. In the example shown in FIG. 2, irradiation can be performed during drying and finishing, e.g., between sizing, drying, pressing and calendering operations, or during post-processing, e.g., to the finished paper in roll, slit roll or sheet form.

As noted above, in some embodiments radiation is applied at more than one point during the manufacturing process. For example, ionizing radiation can be used at a relatively high dose to form or to help form the pulp, and then later at a relatively lower dose to increase the molecular weight of the fibers in the paper. As will be discussed in further detail below, radiation can also be applied to the finished paper in a manner so as to favorably affect the functional groups present within

and/or on the surface of the paper. High dose radiation can be applied to the finished paper at selected areas of the paper web to create locally weakened areas, e.g., to provide tear zones.

As a practical matter, using existing technology, it is generally most desirable to integrate the irradiation step into the papermaking process either after pulping and prior to introduction of the pulp to the papermaking machine, or after the web has exited the papermaking machine, typically after drying and sizing. However, as noted above, irradiation may be performed at any desired stage in the process.

If desired, various cross-linking additives can be added to the pulp to enhance cross-linking in response to irradiation. Such additives include materials that are cross-linkable themselves and materials that will assist with cross-linking. Cross-linking additives include, but are not limited to, lignin, starch, diacrylates, divinyl compounds, and polyethylene. In some implementations, such additives are included in concentrations of about 0.25% to about 2.5%, e.g., about 0.5% to about 1.0%.

Irradiating to Affect Material Functional Groups

After treatment with one or more ionizing radiations, such as photonic radiation (e.g., X-rays or gamma-rays), e-beam radiation or irradiation with particles heavier than electrons that are positively or negatively charged (e.g., protons or carbon ions), any of the carbohydrate-containing materials or mixtures described herein become ionized; that is, they include radicals at levels that are detectable, for example, with an electron spin resonance spectrometer. After ionization, any material that has been ionized can be quenched to reduce the level of radicals in the ionized material, e.g., such that the radicals are no longer detectable with the electron spin resonance spectrometer. For example, the radicals can be quenched by the application of sufficient pressure to the ionized material and/or by contacting the ionized material with a fluid, such as a gas or liquid, that reacts with (quenches) the radicals. Various gases, for example nitrogen or oxygen, or liquids, can be used to at least aid in the quenching of the radicals and to functionalize the ionized material with desired functional groups. Thus, irradiation followed by quenching can be used to provide pulp or paper with desired functional groups, including, for example, one or more of the following: aldehyde groups, enol groups, nitroso groups, nitrile groups, nitro groups, ketone groups, amino groups, alkyl amino groups, alkyl groups, chloroalkyl groups, chlorofluoroalkyl groups, and/or carboxylic acid groups. These groups increase the hydrophilicity of the region of the material where they are present. In some implementations, the paper web is irradiated and quenched, before or after processing steps such as coating and calendering, to affect the functionality within and/or at the surface of the paper and thereby affect the ink receptivity and other properties of the paper. In other implementations, the paper feedstock is irradiated with a relatively high dose of ionizing radiation, to facilitate pulping, and then later quenched to improve the stability of the ionized material in the pulp.

FIG. 3 illustrates changing a molecular and/or a supramolecular structure of fibrous material, such as paper feedstock, paper precursor (e.g., a wet paper web), or paper, by pretreating the fibrous material with ionizing radiation, such as with electrons or ions of sufficient energy to ionize the material, to provide a first level of radicals. As shown in FIG. 3, if the ionized material remains in the atmosphere, it will be oxidized, e.g., to an extent that carboxylic acid groups are generated by reaction with the atmospheric oxygen. In some instances, with some materials, such oxidation is desired, because it can aid in further breakdown in molecular weight

of the carbohydrate-containing material (for example, if irradiation is being used to facilitate pulping). However, since the radicals can "live" for some time after irradiation, e.g., longer than 1 day, 5 days, 30 days, 3 months, 6 months, or even longer than 1 year, material properties can continue to change over time, which in some instances can be undesirable.

Detecting radicals in irradiated samples by electron spin resonance spectroscopy and radical lifetimes in such samples is discussed in Bartolotta et al., Physics in Medicine and Biology, 46 (2001), 461-471 and in Bartolotta et al., Radiation Protection Dosimetry, Vol. 84, Nos. 1-4, pp. 293-296 (1999). As shown in FIG. 3, the ionized material can be quenched to functionalize and/or to stabilize the ionized material.

In some embodiments, quenching includes application of pressure to the ionized material, such as by mechanically deforming the material, e.g., directly mechanically compressing the material in one, two, or three dimensions, or applying pressure to fluid in which the material is immersed, e.g., isostatic pressing. In the case of paper that has been ionized, pressure may be applied, e.g., by passing the paper through a nip. In such instances, the deformation of the material itself brings radicals, which are often trapped in crystalline domains, into proximity close enough for the radicals to recombine, or react with another group. In some instances, pressure is applied together with application of heat, e.g. a quantity of heat sufficient to elevate the temperature of the material to above a melting point or softening point of a component of the ionized material, such as lignin, cellulose or hemicellulose. Heat can improve molecular mobility in the material, which can aid in quenching of radicals. When pressure is utilized to quench, the pressure can be greater than about 1000 psi, such as greater than about 1250 psi, 1450 psi, 3625 psi, 5075 psi, 7250 psi, 10000 psi, or even greater than 15000 psi.

In some embodiments, quenching includes contacting the ionized material with fluid, such as liquid or gas, e.g., a gas capable of reacting with the radicals, such as acetylene or a mixture of acetylene in nitrogen, ethylene, chlorinated ethylenes or chlorofluoroethylenes, propylene or mixtures of these gases. In other particular embodiments, quenching includes contacting the ionized material with liquid, e.g., a liquid soluble in, or at least capable of penetrating into, the ionized material and reacting with the radicals, such as a diene, such as 1,5-cyclooctadiene. In some specific embodiments, the quenching includes contacting the ionized material with an antioxidant, such as Vitamin E. If desired, the material can include an antioxidant dispersed therein, and quenching can come from contacting the antioxidant dispersed in the material with the radicals.

Other methods for quenching are possible. For example, any method for quenching radicals in polymeric materials described in Muratoglu et al., U.S. Patent Publication No. 2008/0067724 and Muratoglu et al., U.S. Pat. No. 7,166,650, the disclosures of which are incorporated herein by reference in their entireties, can be utilized for quenching any ionized material described herein. Furthermore, any quenching agent (described as a "sensitizing agent" in the above-noted Muratoglu disclosures) and/or any antioxidant described in either Muratoglu reference, can be utilized to quench any ionized material.

Functionalization can be enhanced by utilizing heavy charged ions, such as any of the heavier ions described herein. For example, if it is desired to enhance oxidation, charged oxygen ions can be utilized for the irradiation. If nitrogen functional groups are desired, nitrogen ions or any ion that

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includes nitrogen can be utilized. Likewise, if sulfur or phosphorus groups are desired, sulfur or phosphorus ions can be used in the irradiation.

In some embodiments, after quenching, any of the quenched ionized materials described herein can be further treated with one or more further doses of radiation, such as ionizing or non-ionizing radiation, sonication, pyrolysis, and oxidation for additional molecular and/or supramolecular structure change.

In some embodiments, the fibrous material is irradiated under a blanket of inert gas, e.g., helium or argon, prior to quenching.

The location of the functional groups can be controlled, e.g., by selecting a particular type and dose of ionizing particles. For example, gamma radiation tends to affect the functionality of molecules within paper, while electron beam radiation tends to preferentially affect the functionality of molecules at the surface.

In some cases, functionalization of the material can occur simultaneously with irradiation, rather than as a result of a separate quenching step. In this case, the type of functional groups and degree of oxidation can be affected in various ways, for example by controlling the gas blanketing the material to be irradiated, through which the irradiating beam passes. Suitable gases include nitrogen, oxygen, air, ozone, nitrogen dioxide, sulfur dioxide and chlorine.

In some embodiments, functionalization results in formation of enol groups in the fibrous material. When the fibrous material is paper, this can enhance receptivity of the paper to inks, adhesives, coatings, and the like, and can provide grafting sites. Enol groups can help break down molecular weight, especially in the presence of added base or acid. Thus, the presence of such groups can assist with pulping. In the finished paper product, generally the pH is close enough to neutral that these groups will not cause a deleterious decrease in molecular weight.

Particle Beam Exposure in Fluids

In some cases, the cellulosic or lignocellulosic materials can be exposed to a particle beam in the presence of one or more additional fluids (e.g., gases and/or liquids). Exposure of a material to a particle beam in the presence of one or more additional fluids can increase the efficiency of the treatment.

In some embodiments, the material is exposed to a particle beam in the presence of a fluid such as air. Particles accelerated in any one or more of the types of accelerators disclosed herein (or another type of accelerator) are coupled out of the accelerator via an output port (e.g., a thin membrane such as a metal foil), pass through a volume of space occupied by the fluid, and are then incident on the material. In addition to directly treating the material, some of the particles generate additional chemical species by interacting with fluid particles (e.g., ions and/or radicals generated from various constituents of air, such as ozone and oxides of nitrogen). These generated chemical species can also interact with the material, and can act as initiators for a variety of different chemical bond-breaking reactions in the material. For example, any oxidant produced can oxidize the material, which can result in molecular weight reduction.

In certain embodiments, additional fluids can be selectively introduced into the path of a particle beam before the beam is incident on the material. As discussed above, reactions between the particles of the beam and the particles of the introduced fluids can generate additional chemical species, which react with the material and can assist in functionalizing the material, and/or otherwise selectively altering certain properties of the material. The one or more additional fluids

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can be directed into the path of the beam from a supply tube, for example. The direction and flow rate of the fluid(s) that is/are introduced can be selected according to a desired exposure rate and/or direction to control the efficiency of the overall treatment, including effects that result from both particle-based treatment and effects that are due to the interaction of dynamically generated species from the introduced fluid with the material. In addition to air, exemplary fluids that can be introduced into the ion beam include oxygen, nitrogen, one or more noble gases, one or more halogens, and hydrogen.

Cooling Irradiated Materials

During treatment of the materials discussed above with ionizing radiation, especially at high dose rates, such as at rates greater than 0.15 Mrad per second, e.g., 0.25 Mrad/s, 0.35 Mrad/s, 0.5 Mrad/s, 0.75 Mrad/s or even greater than 1 Mrad/sec, the materials can retain significant quantities of heat so that the temperature of the material becomes elevated. While higher temperatures can, in some embodiments, be advantageous, e.g., when a faster reaction rate is desired, it is advantageous to control the heating to retain control over the chemical reactions initiated by the ionizing radiation, such as crosslinking, chain scission and/or grafting, e.g., to maintain process control.

For example, in one method, the material is irradiated at a first temperature with ionizing radiation, such as photons, electrons or ions (e.g., singularly or multiply charged cations or anions), for a sufficient time and/or a sufficient dose to elevate the material to a second temperature higher than the first temperature. The irradiated material is then cooled to a third temperature below the second temperature. If desired, the cooled material can be treated one or more times with radiation, e.g., with ionizing radiation. If desired, cooling can be applied to the material after and/or during each radiation treatment.

Cooling can in some cases include contacting the material with a fluid, such as a gas, at a temperature below the first or second temperature, such as gaseous nitrogen at or about 77 K. Even water, such as water at a temperature below nominal room temperature (e.g., 25 degrees Celsius) can be utilized in some implementations.

Types of Radiation

The radiation can be provided, e.g., by: 1) heavy charged particles, such as alpha particles; 2) electrons, produced, for example, in beta decay or electron beam accelerators; or 3) electromagnetic radiation, e.g., gamma rays, x-rays or ultraviolet rays. Different forms of radiation ionize the cellulosic or lignocellulosic material via particular interactions, as determined by the energy of the radiation.

Heavy charged particles primarily ionize matter via Coulomb scattering; furthermore, these interactions produce energetic electrons that can further ionize matter. Alpha particles are identical to the nucleus of a helium atom and are produced by alpha decay of various radioactive nuclei, such as isotopes of bismuth, polonium, astatine, radon, francium, radium, several actinides, such as actinium, thorium, uranium, neptunium, curium, californium, americium and plutonium.

Electrons interact via Coulomb scattering and bremsstrahlung radiation produced by changes in the velocity of electrons. Electrons can be produced by radioactive nuclei that undergo beta decay, such as isotopes of iodine, cesium, technetium and iridium. Alternatively, an electron gun can be used as an electron source via thermionic emission.

Electromagnetic radiation interacts via three processes: photoelectric absorption, Compton scattering and pair production. The dominating interaction is determined by the

energy of incident radiation and the atomic number of the material. The summation of interactions contributing to the absorbed radiation in cellulosic material can be expressed by the mass absorption coefficient.

Electromagnetic radiation is subclassified as gamma rays, x-rays, ultraviolet rays, infrared rays, microwaves or radio waves, depending on its wavelength.

For example, gamma radiation can be employed to irradiate the materials. Referring to FIGS. 4 and 5 (an enlarged view of region R), a gamma irradiator 10 includes gamma radiation sources 408, e.g., ^{60}Co pellets, a working table 14 for holding the materials to be irradiated and storage 16, e.g., made of a plurality iron plates, all of which are housed in a concrete containment chamber (vault) 20 that includes a maze entranceway 22 beyond a lead-lined door 26. Storage 16 defines a plurality of channels 30, e.g., sixteen or more channels, allowing the gamma radiation sources to pass through storage on their way proximate the working table.

In operation, the sample to be irradiated is placed on a working table. The irradiator is configured to deliver the desired dose rate and monitoring equipment is connected to an experimental block 31. The operator then leaves the containment chamber, passing through the maze entranceway and through the lead-lined door. The operator mans a control panel 32, instructing a computer 33 to lift the radiation sources 12 into working position using cylinder 36 attached to hydraulic pump 40.

Gamma radiation has the advantage of significant penetration depth into a variety of materials in the sample. Sources of gamma rays include radioactive nuclei, such as isotopes of cobalt, calcium, technetium, chromium, gallium, indium, iodine, iron, krypton, samarium, selenium, sodium, thallium and xenon.

Sources of x-rays include electron beam collision with metal targets, such as tungsten or molybdenum or alloys, or compact light sources, such as those produced commercially by Lyncean Technologies, Inc., of Palo Alto, Calif.

Sources for ultraviolet radiation include deuterium or cadmium lamps.

Sources for infrared radiation include sapphire, zinc or selenide window ceramic lamps.

Sources for microwaves include klystrons, Slevin type RF sources or atom beam sources that employ hydrogen, oxygen or nitrogen gases.

In some embodiments, a beam of electrons is used as the radiation source. A beam of electrons has the advantages of high dose rates (e.g., 1, 5, or even 10 MRad per second), high throughput, less containment and less confinement equipment. Electrons can also be more efficient at causing chain scission. In addition, electrons having energies of 4-10 MeV can have penetration depths of 5 to 30 mm or more, such as 40 mm.

Electron beams can be generated, e.g., by electrostatic generators, cascade generators, transformer generators, low energy accelerators with a scanning system, low energy accelerators with a linear cathode, linear accelerators, and pulsed accelerators. Electrons as an ionizing radiation source can be useful, e.g., for relatively thin materials, e.g., less than 0.5 inch, e.g., less than 0.4 inch, 0.3 inch, 0.2 inch, or less than 0.1 inch. In some embodiments, the energy of each electron of the electron beam is from about 0.25 MeV to about 7.5 MeV (million electron volts), e.g., from about 0.5 MeV to about 5.0 MeV, or from about 0.7 MeV to about 2.0 MeV. Electron beam irradiation devices may be procured commercially from Ion Beam Applications, Louvain-la-Neuve, Belgium or from Titan Corporation, San Diego, Calif. Typical electron energies can be 1, 2, 4.5, 7.5, or 10 MeV. Typical electron

beam irradiation device power can be 1, 5, 10, 20, 50, 100, 250, or 500 kW. Typical doses may take values of 1, 5, 10, 20, 50, 100, or 200 kGy.

Tradeoffs in considering electron beam irradiation device power specifications include operating costs, capital costs, depreciation and device footprint. Tradeoffs in considering exposure dose levels of electron beam irradiation would be energy costs and environment, safety, and health (ESH) concerns. Generators are typically housed in a vault, e.g., of lead or concrete.

The electron beam irradiation device can produce either a fixed beam or a scanning beam. A scanning beam may be advantageous with large scan sweep length and high scan speeds, as this would effectively replace a large, fixed beam width. Further, available sweep widths of 0.5 m, 1 m, 2 m or more are available.

In embodiments in which the irradiating is performed with electromagnetic radiation, the electromagnetic radiation can have an energy per photon (in electron volts) of, e.g., greater than 10^2 eV, e.g., greater than 10^3 , 10^4 , 10^5 , 10^6 or even greater than 10^7 eV. In some embodiments, the electromagnetic radiation has energy per photon of between 10^4 and 10^7 , e.g., between 10^5 and 10^6 eV. The electromagnetic radiation can have a frequency of, e.g., greater than 10^{16} Hz, greater than 10^{17} Hz, 10^{18} , 10^{19} , 10^{20} or even greater than 10^{21} Hz. In some embodiments, the electromagnetic radiation has a frequency of between 10^{18} and 10^{22} Hz, e.g., between 10^{19} to 10^{21} Hz.

One type of accelerator that can be used to accelerate ions produced using the sources discussed above is a Dynamitron® (available, for example, from Radiation Dynamics Inc., now a unit of IBA, Louvain-la-Neuve, Belgium). A schematic diagram of a Dynamitron® accelerator 1500 is shown in FIG. 6. Accelerator 1500 includes an injector 1510 (which includes an ion source) and an accelerating column 1520 that includes a plurality of annular electrodes 1530. Injector 1510 and column 1520 are housed within an enclosure 1540 that is evacuated by a vacuum pump 1600.

Injector 1510 produces a beam of ions 1580, and introduces beam 1580 into accelerating column 1520. The annular electrodes 1530 are maintained at different electric potentials, so that ions are accelerated as they pass through gaps between the electrodes (e.g., the ions are accelerated in the gaps, but not within the electrodes, where the electric potentials are uniform). As the ions travel from the top of column 1520 toward the bottom in FIG. 6, the average speed of the ions increases. The spacing between subsequent annular electrodes 1530 typically increases, therefore, to accommodate the higher average ion speed.

After the accelerated ions have traversed the length of column 1520, the accelerated ion beam 1590 is coupled out of enclosure 1540 through delivery tube 1555. The length of delivery tube 1555 is selected to permit adequate shielding (e.g., concrete shielding) to be positioned adjacent to column 1520, isolating the column. After passing through tube 1555, ion beam 1590 passes through scan magnet 1550. Scan magnet 1550, which is controlled by an external logic unit (not shown), can sweep accelerated ion beam 1590 in controlled fashion across a two-dimensional plane oriented perpendicular to a central axis of column 1520. As shown in FIG. 6, ion beam 1590 passes through window 1560 (e.g., a metal foil window or screen) and then is directed to impinge on selected regions of a sample 1570 by scan magnet 1550.

In some embodiments, the electric potentials applied to electrodes 1530 are static potentials, generated, e.g., by DC potential sources. In certain embodiments, some or all of the electric potentials applied to electrodes 1530 are variable

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potentials generated by variable potential sources. Suitable variable sources of large electric potentials include amplified field sources, e.g., such as klystrons. Accordingly, depending upon the nature of the potentials applied to electrodes 1530, accelerator 1500 can operate in either pulsed or continuous mode.

To achieve a selected accelerated ion energy at the output end of column 1520, the length of column 1520 and the potentials applied to electrodes 1530 are chosen based on considerations well-known in the art. However, it is notable that to reduce the length of column 1520, multiply-charged ions can be used in place of singly-charged ions. That is, the accelerating effect of a selected electric potential difference between two electrodes is greater for an ion bearing a charge of magnitude 2 or more than for an ion bearing a charge of magnitude 1. Thus, an arbitrary ion X^{2+} can be accelerated to final energy E over a shorter length than a corresponding arbitrary ion X^+ . Triply- and quadruply-charged ions (e.g., X^{3+} and X^{4+}) can be accelerated to final energy E over even shorter distances. Therefore, the length of column 1520 can be significantly reduced when ion beam 1580 includes primarily multiply-charged ion species.

To accelerate positively-charged ions, the potential differences between electrodes 1530 of column 1520 are selected so that the direction of increasing field strength in FIG. 6 is downward (e.g., toward the bottom of column 1520). Conversely, when accelerator 1500 is used to accelerate negatively-charged ions, the electric potential differences between electrodes 1530 are reversed in column 1520, and the direction of increasing field strength in FIG. 6 is upward (e.g., toward the top of column 1520). Reconfiguring the electric potentials applied to electrodes 1530 is a straightforward procedure, so that accelerator 1500 can be converted relatively rapidly from accelerating positive ions to accelerating negative ions, or vice versa. Similarly, accelerator 1500 can be converted rapidly from accelerating singly-charged ions to accelerating multiply-charged ions, and vice versa.

Doses

In some embodiments, the high dose irradiating, to reduce molecular weight (with any radiation source or a combination of sources), is performed until the material receives a dose of at least 2.5 MRad, e.g., at least 5.0, 7.5, 10.0, 100, or 500 MRad. In some embodiments, the irradiating is performed until the material receives a dose of between 3.0 MRad and 100 MRad, e.g., between 10 MRad and 100 MRad or between 25 MRad and 75 MRad. If gamma radiation is used, the dose will generally be towards the higher end of these ranges, while if electron beam radiation is used, the dose may, in some embodiments, be towards the lower end. Dosage rates will also be towards the lower end for some cellulosic materials which already have relatively low molecular weight, e.g., recycled paper.

In some embodiments, the low dose irradiating, to increase molecular weight (with any radiation source or a combination of sources), is performed until the material receives a dose of at least 0.05 MRad, e.g., at least 0.1, 0.25, 1.0, 2.5, or 5.0 MRad. In some embodiments, irradiating is performed until the material receives a dose of between 0.1 and 2.5 MRad. Other suitable ranges include between 0.25 MRad and 4.0 MRad, between 0.5 MRad and 3.0 MRad, and between 1.0 MRad and 2.5 MRad.

The doses discussed above, both high and low, are also suitable for functionalization of the material, with the degree of functionalization generally being higher the higher the dose.

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In some embodiments, the irradiating is performed at a dose rate of between 5.0 and 1500.0 kilorads/hour, e.g., between 10.0 and 750.0 kilorads/hour or between 50.0 and 350.0 kilorads/hours. When high throughput is desired, e.g., in a high speed papermaking process, radiation can be applied at, e.g., 0.5 to 3.0 MRad/sec, or even faster, using cooling to avoid overheating the irradiated material.

In some embodiments in which coated paper is irradiated, the paper coating includes resin that is cross-linkable, e.g., 10 diacrylate or polyethylene. As such, the resin crosslinks as the carbohydrate-containing material is irradiated to increase its molecular weight, which can provide a synergistic effect to optimize the scuff resistance and other surface properties of the paper. In these embodiments, the dose of radiation is 15 selected to be sufficiently high so as to increase the molecular weight of the cellulosic fibers, i.e., at least about 0.25 to about 2.5 MRad, depending on the material, while being sufficiently low so as to avoid deleteriously affecting the paper coating. The upper limit on the dose will vary depending on 20 the composition of the coating, but in some embodiments the preferred dose is less than about 5 MRad.

In some embodiments, two or more radiation sources are used, such as two or more ionizing radiations. For example, samples can be treated, in any order, with a beam of electrons, 25 followed by gamma radiation and/or UV light having wavelengths from about 100 nm to about 280 nm. In some embodiments, samples are treated with three ionizing radiation sources, such as a beam of electrons, gamma radiation, and energetic UV light.

30 Acoustic Energy

Radiation may be used in combination with acoustic energy, e.g., sonic or ultrasonic energy, to improve material throughput and/or characteristics, and/or to minimize energy usage. For example, acoustic energy can be used in combination with high dose radiation to enhance the pulping process.

Referring again to FIG. 1A, in the pretreatment system 114, a starting material that will be used to form the pulp, e.g., wood chips, can be subjected to an inline sonication step using acoustic energy.

FIG. 7 shows a general system in which cellulosic material stream 1210 (e.g., feedstock to make pulp) is mixed with water stream 1212 in reservoir 1214 to form process stream 1216. A first pump 1218 draws process stream 1216 from reservoir 1214 and toward flow cell 1224. Ultrasonic transducer 1226 transmits ultrasonic energy into process stream 1216 as the process stream flows through flow cell 1224. A second pump 1230 draws process stream 1216 from flow cell 1224 and toward subsequent processing.

Reservoir 1214 includes first intake 1232 and second intake 1234 in fluid communication with volume 1236. A conveyor (not shown) delivers cellulosic material stream 1210 to reservoir 1214 through first intake 1232. Water stream 1212 enters reservoir 1214 through second intake 1234. In some embodiments, water stream 1212 enters volume 1236 along a tangent establishing swirling flow within volume 1236. In certain embodiments, cellulosic material stream 1210 and water stream 1212 are introduced into volume 1236 along opposing axes to enhance mixing within the volume.

Valve 1238 controls the flow of water stream 1212 through second intake 1232 to produce a desired ratio of cellulosic material to water (e.g., approximately 10% cellulosic material, weight by volume). For example, 2000 tons/day of cellulosic material can be combined with 1 million to 1.5 million gallons/day, e.g., 1.25 million gallons/day, of water.

Mixing of cellulosic material and water in reservoir 1214 is controlled by the size of volume 1236 and the flow rates of cellulosic material and water into the volume. In some embodiments, volume 1236 is sized to create a minimum mixing residence time for the cellulosic material and water. For example, when 2000 tons/day of cellulosic material and 1.25 million gallons/day of water are flowing through reservoir 1214, volume 1236 can be about 32,000 gallons to produce a minimum mixing residence time of about 15 minutes.

Reservoir 1214 includes a mixer 1240 in fluid communication with volume 1236. Mixer 1240 agitates the contents of volume 1236 to disperse cellulosic material throughout the water in the volume. For example, mixer 1240 can be a rotating vane disposed in reservoir 1214. In some embodiments, mixer 1240 disperses the cellulosic material substantially uniformly throughout the water.

Reservoir 1214 further includes an exit 1242 in fluid communication with volume 1236 and process stream 1216. The mixture of cellulosic material and water in volume 1236 flows out of reservoir 1214 via exit 1242. Exit 1242 is arranged near the bottom of reservoir 1214 to allow gravity to pull the mixture of cellulosic material and water out of reservoir 1214 and into process stream 1216.

First pump 1218 (e.g., any of several recessed impeller vortex pumps made by Essco Pumps & Controls, of Los Angeles, Calif.) moves the contents of process stream 1216 toward flow cell 1224. In some embodiments, first pump 1218 agitates the contents of process stream 1216 such that the mixture of cellulosic material and water is substantially uniform at inlet 1220 of flow cell 1224. For example, first pump 1218 agitates process stream 1216 to create a turbulent flow that persists along the process stream between the first pump and inlet 1220 of flow cell 1224.

Flow cell 1224 includes a reactor volume 1244 in fluid communication with inlet 1220 and outlet 1222. In some embodiments, reactor volume 1244 is a stainless steel tube capable of withstanding elevated pressures (e.g., 10 bars). In addition or in the alternative, reactor volume 1244 defines a rectangular cross section.

Flow cell 1224 further includes a heat exchanger 1246 in thermal communication with at least a portion of reactor volume 1244. Cooling fluid 1248 (e.g., water) flows into heat exchanger 1246 and absorbs heat generated when process stream 1216 is sonicated in reactor volume 1244. In some embodiments, the flow rate and/or the temperature of cooling fluid 1248 into heat exchanger 1246 is controlled to maintain an approximately constant temperature in reactor volume 1244. In some embodiments, the temperature of reactor volume 1244 is maintained at 20 to 50° C., e.g., 25, 30, 35, 40 or 45° C. Additionally or alternatively, heat transferred to cooling fluid 1248 from reactor volume 1244 can be used in other parts of the overall process.

An adapter section 1226 creates fluid communication between reactor volume 1244 and booster 1250 coupled (e.g., mechanically coupled using a flange) to ultrasonic transducer 1226. For example, adapter section 1226 can include a flange and O-ring assembly arranged to create a leak tight connection between reactor volume 1244 and booster 1250. In some embodiments, ultrasonic transducer 1226 is a high-powered ultrasonic transducer made by Hielscher Ultrasonics, of Teltow, Germany.

In operation, generator 1252 delivers electricity to ultrasonic transducer 1252. Ultrasonic transducer 1226 includes a piezoelectric element that converts electrical energy into sound in the ultrasonic range. In some embodiments, the materials are sonicated using sound having a frequency of from about 16 kHz to about 110 kHz, e.g., from about 18 kHz

to about 75 kHz or from about 20 kHz to about 40 kHz (e.g., sound having a frequency of 20 kHz to 40 kHz). The ultrasonic energy is delivered to the working medium through booster 1248. Ultrasonic energy traveling through booster 1248 in reactor volume 1244 creates a series of compressions and rarefactions in process stream 1216 with intensity sufficient to create cavitation in process stream 1216. Cavitation disaggregates the cellulosic material dispersed in process stream 1216. Cavitation also produces free radicals in the water of process stream 1216. These free radicals act to further break down the cellulosic material in process stream 1216.

In general, 5 to 4000 MJ/m³, e.g., 10, 25, 50, 100, 250, 500, 750, 1000, 2000 or 3000 MJ/m³, of ultrasonic energy is applied to process stream 16 flowing at a rate of about 0.2 m³/s (about 3200 gallons/min). After exposure to ultrasonic energy in reactor volume 1244, process stream 1216 exits flow cell 1224 through outlet 1222. Second pump 1230 moves process stream 1216 to subsequent processing (e.g., any of several recessed impeller vortex pumps made by Essco Pumps & Controls, Los Angeles, Calif.).

While certain embodiments have been described, other embodiments are possible.

As an example, while process stream 1216 has been described as a single flow path, other arrangements are possible. In some embodiments, e.g., process stream 1216 includes multiple parallel flow paths (e.g., flowing at a rate of 10 gallon/min). In addition or in the alternative, the multiple parallel flow paths of process stream 1216 flow into separate flow cells and are sonicated in parallel (e.g., using a plurality of 16 kW ultrasonic transducers).

As another example, while a single ultrasonic transducer 1226 has been described as being coupled to flow cell 1224, other arrangements are possible. In some embodiments, a plurality of ultrasonic transducers 1226 are arranged in flow cell 1224 (e.g., ten ultrasonic transducers can be arranged in flow cell 1224). In some embodiments, the sound waves generated by each of the plurality of ultrasonic transducers 1226 are timed (e.g., synchronized out of phase with one another) to enhance cavitation acting upon process stream 1216.

As another example, while a single flow cell 1224 has been described, other arrangements are possible. In some embodiments, second pump 1230 moves process stream to a second flow cell where a second booster and ultrasonic transducer further sonicate process stream 1216.

As still another example, while reactor volume 1244 has been described as a closed volume, reactor volume 1244 is open to ambient conditions in certain embodiments. In such embodiments, sonication pretreatment can be performed substantially simultaneously with other pretreatment techniques. For example, ultrasonic energy can be applied to process stream 1216 in reactor volume 1244 while electron beams are simultaneously introduced into process stream 1216.

As another example, while a flow-through process has been described, other arrangements are possible. In some embodiments, sonication can be performed in a batch process. For example, a volume can be filled with a 10% (weight by volume) mixture of cellulosic material in water and exposed to sound with intensity from about 50 W/cm² to about 600 W/cm², e.g., from about 75 W/cm² to about 300 W/cm² or from about 95 W/cm² to about 200 W/cm². Additionally or alternatively, the mixture in the volume can be sonicated for about 1 hour to about 24 hours, e.g., for about 1.5 hours to about 12 hours or for about 2 hours to about 10 hours. In certain embodiments, the material is sonicated for a

pre-determined time, and then allowed to stand for a second predetermined time before sonicating again.

Referring now to FIG. 8, in some embodiments, two electroacoustic transducers are mechanically coupled to a single horn. As shown, a pair of piezoelectric transducers **60** and **62** is coupled to slotted bar horn **64** by respective intermediate coupling horns **70** and **72**, the latter also being known as booster horns. The mechanical vibrations provided by the transducers, responsive to high frequency electrical energy applied thereto, are transmitted to the respective coupling horns, which may be constructed to provide a mechanical gain, such as a ratio of 1 to 1.2. The horns are provided with a respective mounting flange **74** and **76** for supporting the transducer and horn assembly in a stationary housing.

The vibrations transmitted from the transducers through the coupling or booster horns are coupled to the input surface **78** of the horn and are transmitted through the horn to the oppositely disposed output surface **80**, which, during operation, is in forced engagement with a workpiece (not shown) to which the vibrations are applied.

The high frequency electrical energy provided by the power supply **82** is fed to each of the transducers, electrically connected in parallel, via a balancing transformer **84** and a respective series connected capacitor **86** and **90**, one capacitor connected in series with the electrical connection to each of the transducers. The balancing transformer is known also as "balun" standing for "balancing unit." The balancing transformer includes a magnetic core **92** and a pair of identical windings **94** and **96**, also termed the primary winding and secondary winding, respectively.

In some embodiments, the transducers include commercially available piezoelectric transducers, such as Branson Ultrasonics Corporation models 105 or 502, each designed for operation at 20 kHz and a maximum power rating of 3 kW. The energizing voltage for providing maximum motional excursion at the output surface of the transducer is 930 volt rms. The current flow through a transducer may vary between zero and 3.5 ampere depending on the load impedance. At 930 volt rms the output motion is approximately 20 microns. The maximum difference in terminal voltage for the same motional amplitude, therefore, can be 186 volt. Such a voltage difference can give rise to large circulating currents flowing between the transducers. The balancing unit **430** assures a balanced condition by providing equal current flow through the transducers, hence eliminating the possibility of circulating currents. The wire size of the windings must be selected for the full load current noted above and the maximum voltage appearing across a winding input is 93 volt.

As an alternative to using ultrasonic energy, high-frequency, rotor-stator devices can be utilized. This type of device produces high-shear, microcavitation forces that can disintegrate materials in contact with such forces. Two commercially available high-frequency, rotor-stator dispersion devices are the Supraton™ devices manufactured by Krupp Industrietechnik GmbH and marketed by Dorr-Oliver Deutschland GmbH of Connecticut, and the Dispax™ devices manufactured and marketed by Ika-Works, Inc. of Cincinnati, Ohio. Operation of such a microcavitation device is discussed in Stuart, U.S. Pat. No. 5,370,999.

While ultrasonic transducer **1226** has been described as including one or more piezoelectric active elements to create ultrasonic energy, other arrangements are possible. In some embodiments, ultrasonic transducer **1226** includes active elements made of other types of magnetostrictive materials (e.g., ferrous metals). Design and operation of such a high-powered ultrasonic transducer is discussed in Hansen et al., U.S. Pat.

No. 6,624,539. In some embodiments, ultrasonic energy is transferred to process stream **16** through an electrohydraulic system.

While ultrasonic transducer **1226** has been described as using the electromagnetic response of magnetostriuctive materials to produce ultrasonic energy, other arrangements are possible. In some embodiments, acoustic energy in the form of an intense shock wave can be applied directly to process stream **16** using an underwater spark. In some embodiments, ultrasonic energy is transferred to process stream **16** through a thermohydraulic system. For example, acoustic waves of high energy density can be produced by applying power across an enclosed volume of electrolyte, thereby heating the enclosed volume and producing a pressure rise that is subsequently transmitted through a sound propagation medium (e.g., process stream **1216**). Design and operation of such a thermohydraulic transducer is discussed in Hartmann et al., U.S. Pat. No. 6,383,152.

In some embodiments, it may be advantageous to combine irradiation and sonication devices into a single hybrid machine. For such a hybrid machine, multiple processes may be performed in close juxtaposition or even simultaneously, with the benefit of increasing pretreatment throughput and potential cost savings.

For example, consider the electron beam irradiation and sonication processes. Each separate process is effective in lowering the mean molecular weight of cellulosic material by an order of magnitude or more, and by several orders of magnitude when performed serially.

Both irradiation and sonication processes can be applied using a hybrid electron beam/sonication device as is illustrated in FIG. 8. Hybrid electron beam/sonication device **2500** is pictured above a shallow pool (depth 3-5 cm) of a slurry of cellulosic material **2550** dispersed in an aqueous, oxidant medium, such as hydrogen peroxide or carbamide peroxide. Hybrid device **2500** has an energy source **2510**, which powers both electron beam emitter **2540** and sonication horns **2530**.

Electron beam emitter **2540** generates electron beams that pass though an electron beam aiming device **2545** to impact the slurry **2550** containing cellulosic material. The electron beam aiming device can be a scanner that sweeps a beam over a range of up to about 6 feet in a direction approximately parallel to the surface of the slurry **2550**.

On either side of the electron beam emitter **2540** are sonication horns **2530**, which deliver ultrasonic wave energy to the slurry **2550**. The sonication horns **2530** end in a detachable endpiece **2535** that is in contact with the slurry **2550**.

The sonication horns **2530** are at risk of damage from long-term residual exposure to the electron beam radiation. Thus, the horns can be protected with a standard shield **2520**, e.g., made of lead or a heavy-metal-containing alloy such as Lipowitz metal, which is impervious to electron beam radiation. Precautions must be taken, however, to ensure that the ultrasonic energy is not affected by the presence of the shield. The detachable endpieces **2535**, are constructed of the same material and attached to the horns **2530**, are used to be in contact with the cellulosic material **2550** and are expected to be damaged. Accordingly, the detachable endpieces **2535** are constructed to be easily replaceable.

A further benefit of such a simultaneous electron beam and ultrasound process is that the two processes have complementary results. With electron beam irradiation alone, an insufficient dose may result in cross-linking of some of the polymers in the cellulosic material, which lowers the efficiency of the overall depolymerization process. Lower doses of electron beam irradiation and/or ultrasound radiation may also be used

to achieve a similar degree of depolymerization as that achieved using electron beam irradiation and sonication separately.

An electron beam device can also be combined with one or more of high-frequency, rotor-stator devices, which can be used as an alternative to ultrasonic energy devices, and performs a similar function.

Further combinations of devices are also possible. For example, an ionizing radiation device that produces gamma radiation emitted from, e.g., ^{60}Co pellets, can be combined with an electron beam source and/or an ultrasonic wave source. Shielding requirements may be more stringent in this case.

Ion Generation

Various methods may be used for the generation of ions suitable for ion beams which may be used in treating the cellulosic or lignocellulosic materials. After the ions have been generated, they are typically accelerated in one or more of various types of accelerators, and then directed to impinge on the cellulosic or lignocellulosic materials.

(i) Hydrogen Ions

Hydrogen ions can be generated using a variety of different methods in an ion source. Typically, hydrogen ions are introduced into an ionizing chamber of an ion source, and ions are produced by supplying energy to gas molecules. During operation, such chambers can produce large ion currents suitable for seeding a downstream ion accelerator.

In some embodiments, hydrogen ions are produced via field ionization of hydrogen gas. A schematic diagram of a field ionization source is shown in FIG. 10. Field ionization source 1100 includes a chamber 1170 where ionization of gas molecules (e.g., hydrogen gas molecules) occurs. Gas molecules 1150 enter chamber 1170 by flowing along direction 1155 in supply tube 1120. Field ionization source 1100 includes an ionization electrode 1110. During operation, a large potential V_E (relative to a common system ground potential) is applied to electrode 1110. Molecules 1150 that circulate within a region adjacent to electrode 1110 are ionized by the electric field that results from potential V_E . Also during operation, an extraction potential V_X is applied to extractors 1130. The newly-formed ions migrate towards extractors 1130 under the influence of the electric fields of potentials V_E and V_X . In effect, the newly-formed ions experience repulsive forces relative to ionization electrode 1110, and attractive forces relative to extractors 1130. As a result, certain of the newly-formed ions enter discharge tube 1140, and propagate along direction 1165 under the influence of potentials V_E and V_X .

Depending upon the sign of potential V_E (relative to the common ground potential), both positively and negatively charged ions can be formed. For example, in some embodiments, a positive potential can be applied to electrode 1110 and a negative potential can be applied to extractors 1130. Positively charged hydrogen ions (e.g., protons H^+) that are generated in chamber 1170 are repelled away from electrode 1110 and toward extractors 1130. As a result, discharged particle stream 1160 includes positively charged hydrogen ions that are transported to an injector system.

In certain embodiments, a negative potential can be applied to electrode 1110 and a positive potential can be applied to extractors 1130. Negatively charged hydrogen ions (e.g., hydride ions H^-) that are generated in chamber 1170 are repelled away from electrode 1110 and toward extractors 1130. Discharged particle stream 1160 includes negatively charged hydrogen ions, which are then transported to an injector system.

In some embodiments, both positive and negative hydrogen ions can be produced via direct thermal heating of hydrogen gas. For example, hydrogen gas can be directed to enter a heating chamber that is evacuated to remove residual oxygen and other gases. The hydrogen gas can then be heated via a heating element to produce ionic species. Suitable heating elements include, for example, arc discharge electrodes, heating filaments, heating coils, and a variety of other thermal transfer elements.

In certain embodiments, when hydrogen ions are produced via either field emission or thermal heating, various hydrogen ion species can be produced, including both positively and negatively charged ion species, and singly- and multiply-charged ion species. The various ion species can be separated from one another via one or more electrostatic and/or magnetic separators. FIG. 11 shows a schematic diagram of an electrostatic separator 1175 that is configured to separate a plurality of hydrogen ion species from one another. Electrostatic separator 1175 includes a pair of parallel electrodes 1180 to which a potential V_S is applied by a voltage source (not shown). Particle stream 1160, propagating in the direction indicated by the arrow, includes a variety of positively- and negatively-charged, and singly- and multiply-charged, ion species. As the various ion species pass through electrodes 1180, the electric field between the electrodes deflects the ion trajectories according to the magnitude and sign of the ion species. In FIG. 11, for example, the electric field points from the lower electrode toward the upper electrode in the region between electrodes 1180. As a result, positively-charged ions are deflected along an upward trajectory in FIG. 11, and negatively-charged ions are deflected along a downward trajectory. Ion beams 1162 and 1164 each correspond to positively-charged ion species, with the ion species in ion beam 1162 having a larger positive charge than the ion species in beam 1164 (e.g., due to the larger positive charge of the ions in beam 1162, the beam is deflected to a greater extent).

Similarly, ion beams 1166 and 1168 each correspond to negatively-charged ion species, with the ion species in ion beam 1168 having a larger negative charge than the ion species in ion beam 1166 (and thereby being deflected to a larger extent by the electric field between electrodes 1180). Beam 1169 includes neutral particles originally present in particle stream 1160; the neutral particles are largely unaffected by the electric field between electrodes 1180, and therefore pass undeflected through the electrodes. Each of the separated particle streams enters one of delivery tubes 1192, 1194, 1196, 1198, and 1199, and can be delivered to an injector system for subsequent acceleration of the particles, or steered to be incident directly on the cellulosic or lignocellulosic material. Alternatively, or in addition, any or all of the separated particle streams can be blocked to prevent ion and/or atomic species from reaching cellulosic or lignocellulosic material. As yet another alternative, certain particle streams can be combined and then directed to an injector system and/or steered to be incident directly on the cellulosic or lignocellulosic material using known techniques.

In general, particle beam separators can also use magnetic fields in addition to, or rather than, electric fields for deflecting charged particles. In some embodiments, particle beam separators include multiple pairs of electrodes, where each pair of electrodes generates an electric field that deflects particles passing therethrough. Alternatively, or in addition, particle beam separators can include one or more magnetic deflectors that are configured to deflect charged particles according to magnitude and sign of the particle charges.

(ii) Noble Gas Ions

Noble gas atoms (e.g., helium atoms, neon atoms, argon atoms) form positively-charged ions when acted upon by relatively strong electric fields. Methods for generating noble gas ions therefore typically include generating a high-intensity electric field, and then introducing noble gas atoms into the field region to cause field ionization of the gas atoms. A schematic diagram of a field ionization generator for noble gas ions (and also for other types of ions) is shown in FIG. 12. Field ionization generator 1200 includes a tapered electrode 1220 positioned within a chamber 1210. A vacuum pump 1250 is in fluid communication with the interior of chamber 1210 via inlet 1240, and reduces the pressure of background gases within chamber 1210 during operation. One or more noble gas atoms 1280 are admitted to chamber 1210 via inlet tube 1230.

During operation, a relatively high positive potential V_T (e.g., positive relative to a common external ground) is applied to tapered electrode 1220. Noble gas atoms 1280 that enter a region of space surrounding the tip of electrode 1220 are ionized by the strong electric field extending from the tip; the gas atoms lose an electron to the tip, and form positively charged noble gas ions.

The positively charged noble gas ions are accelerated away from the tip, and a certain fraction of the gas ions 1290 pass through extractor 1260 and exit chamber 1210, into an ion optical column that includes lens 1270, which further deflects and/or focuses the ions.

Electrode 1220 is tapered to increase the magnitude of the local electric field in the region near the apex of the tip. Depending upon the sharpness of the taper and the magnitude of potential V_T , the region of space in chamber 1210 within which ionization of noble gas atoms occurs can be relatively tightly controlled. As a result, a relatively well collimated beam of noble gas ions 1290 can be obtained following extractor 1260.

As discussed above in connection with hydrogen ions, the resulting beam of noble gas ions 1290 can be transported through a charged particle optical column that includes various particle optical elements for deflecting and/or focusing the noble gas ion beam. The noble gas ion beam can also pass through an electrostatic and/or magnetic separator, as discussed above in connection with FIG. 11.

Noble gas ions that can be produced in field ionization generator 1200 include helium ions, neon ions, argon ions, and krypton ions. In addition, field ionization generator 1200 can be used to generate ions of other gaseous chemical species, including hydrogen, nitrogen, and oxygen.

Noble gas ions may have particular advantages relative to other ion species when treating cellulosic or lignocellulosic material. For example, while noble gas ions can react with cellulosic or lignocellulosic materials, neutralized noble gas ions (e.g., noble gas atoms) that are produced from such reactions are generally inert, and do not further react with the cellulosic or lignocellulosic material. Moreover, neutral noble gas atoms do not remain embedded in the cellulosic or lignocellulosic material, but instead diffuse out of the material. Noble gases are non-toxic and can be used in large quantities without adverse consequences to either human health or the environment.

(iii) Carbon, Oxygen, and Nitrogen Ions

Ions of carbon, oxygen, and nitrogen can typically be produced by field ionization in a system such as field ionization source 1100 or field ionization generator 1200. For example, oxygen gas molecules and/or oxygen atoms (e.g., produced by heating oxygen gas) can be introduced into a chamber,

where the oxygen molecules and/or atoms are field ionized to produce oxygen ions. Depending upon the sign of the potential applied to the field ionization electrode, positively- and/or negatively-charged oxygen ions can be produced. The desired ion species can be preferentially selected from among various ion species and neutral atoms and molecules by an electrostatic and/or magnetic particle selector, as shown in FIG. 11.

As another example, nitrogen gas molecules can be introduced into the chamber of either field ionization source 1100 or field ionization generator 1200, and ionized to form positively- and/or negatively-charged nitrogen ions by the relatively strong electric field within the chamber. The desired ion species can then be separated from other ionic and neutral species via an electrostatic and/or magnetic separator, as shown in FIG. 11.

To form carbon ions, carbon atoms can be supplied to the chamber of either field ionization source 1100 or field ionization generator 1200, wherein the carbon atoms can be ionized to form either positively- and/or negatively-charged carbon ions. The desired ion species can then be separated from other ionic and neutral species via an electrostatic and/or magnetic separator, as shown in FIG. 11. The carbon atoms that are supplied to the chamber of either field ionization source 1100 or field ionization generator 1200 can be produced by heating a carbon-based target (e.g., a graphite target) to cause thermal emission of carbon atoms from the target. The target can be placed in relatively close proximity to the chamber, so that emitted carbon atoms enter the chamber directly following emission.

(iv) Heavier Ions

Ions of heavier atoms such as sodium and iron can be produced via a number of methods. For example, in some embodiments, heavy ions such as sodium and/or iron ions are produced via thermionic emission from a target material that includes sodium and/or iron, respectively. Suitable target materials include materials such as sodium silicates and/or iron silicates. The target materials typically include other inert materials such as beta-alumina. Some target materials are zeolite materials, and include channels formed therein to permit escape of ions from the target material.

FIG. 13 shows a thermionic emission source 1300 that includes a heating element 1310 that contacts a target material 1330, both of which are positioned inside an evacuated chamber 1305. Heating element 1310 is controlled by controller 1320, which regulates the temperature of heating element 1310 to control the ion current generated from target material 1330. When sufficient heat is supplied to target material 1330, thermionic emission from the target material generates a stream of ions 1340. Ions 1340 can include positively-charged ions of materials such as sodium, iron, and other relatively heavy atomic species (e.g., other metal ions). Ions 1340 can then be collimated, focused, and/or otherwise deflected by electrostatic and/or magnetic electrodes 1350, which can also deliver ions 1340 to an injector.

Thermionic emission to form ions of relatively heavy atomic species is also discussed, for example, in U.S. Pat. No. 4,928,033, entitled "Thermionic Ionization Sourced," the entire contents of which are incorporated herein by reference.

In certain embodiments, relatively heavy ions such as sodium ions and/or iron ions can be produced by microwave discharge. FIG. 14 shows a schematic diagram of a microwave discharge source 1400 that produces ions from relatively heavy atoms such as sodium and iron. Discharge source 1400 includes a microwave field generator 1410, a waveguide tube 1420, a field concentrator 1430, and an ionization chamber 1490. During operation, field generator 1410 produces a

microwave field which propagates through waveguide 1420 and concentrator 1430; concentrator 1430 increases the field strength by spatially confining the field, as shown in FIG. 14. The microwave field enters ionization chamber 1490. In a first region inside chamber 1490, a solenoid 1470 produces a strong magnetic field 1480 in a region of space that also includes the microwave field. Source 1440 delivers atoms 1450 to this region of space. The concentrated microwave field ionizes atoms 1450, and the magnetic field 1480 generated by solenoid 1470 confines the ionized atoms to form a localized plasma. A portion of the plasma exits chamber 1490 as ions 1460. Ions 1460 can then be deflected and/or focused by one or more electrostatic and/or magnetic elements, and delivered to an injector.

Atoms 1450 of materials such as sodium and/or iron can be generated by thermal emission from a target material, for example. Suitable target materials include materials such as silicates and other stable salts, including zeolite-based materials. Suitable target materials can also include metals (e.g., iron), which can be coated on an inert base material such as a glass material.

Microwave discharge sources are also discussed, for example, in the following U.S. Patents: U.S. Pat. No. 4,409,520, entitled "Microwave Discharge Ion Source," and U.S. Pat. No. 6,396,211, entitled "Microwave Discharge Type Electrostatic Accelerator Having Upstream and Downstream Acceleration Electrodes." The entire contents of each of the foregoing patents are incorporated herein by reference.

Particle Beam Sources

Particle beam sources that generate beams for use in irradiating cellulosic or lignocellulosic material typically include three component groups: an injector, which generates or receives ions and introduces the ions into an accelerator; an accelerator, which receives ions from the injector and increases the kinetic energy of the ions; and output coupling elements, which manipulate the beam of accelerated ions.

(i) Injectors

Injectors can include, for example, any of the ion sources discussed in the preceding sections above, which supply a stream of ions for subsequent acceleration. Injectors can also include various types of electrostatic and/or magnetic particle optical elements, including lenses, deflectors, collimators, filters, and other such elements. These elements can be used to condition the ion beam prior to entering the accelerator; that is, these elements can be used to control the propagation characteristics of the ions that enter the accelerator. Injectors can also include pre-accelerating electrostatic and/or magnetic elements that accelerate charged particles to a selected energy threshold prior to entering the accelerator. An example of an injector is shown in Iwata, Y. et al.

(ii) Accelerators

One type of accelerator that can be used to accelerate ions produced using the sources discussed above is a Dynamitron® (available, for example, from Radiation Dynamics Inc., now a unit of IBA, Louvain-la-Neuve, Belgium). A schematic diagram of a Dynamitron® accelerator 1500 is shown in FIG. 6 and discussed above.

Another type of accelerator that can be used to accelerate ions for treatment of cellulosic or lignocellulosic-based material is a Rhodotron® accelerator (available, for example, from IBA, Louvain-la-Neuve, Belgium). In general, Rhodotron-type accelerators include a single recirculating cavity through which ions that are being accelerated make multiple passes. As a result, Rhodotron® accelerators can be operated in continuous mode at relatively high continuous ion currents.

FIG. 15 shows a schematic diagram of a Rhodotron® accelerator 1700. Accelerator 1700 includes an injector 1710, which introduces accelerated ions into recirculating cavity 1720. An electric field source 1730 is positioned within an inner chamber 1740 of cavity 1720, and generates an oscillating radial electric field. The oscillation frequency of the radial field is selected to match the transit time of injected ions across one pass of recirculating cavity 1720. For example, a positively-charged ion is injected into cavity 1720 by injector 1710 when the radial electric field in the cavity has zero amplitude. As the ion propagates toward chamber 1740, the amplitude of the radial field in chamber 1740 increases to a maximum value, and then decreases again. The radial field points inward toward chamber 1740, and the ion is accelerated by the radial field. The ion passes through a hole in the wall of inner chamber 1740, crosses the geometrical center of cavity 1720, and passes out through another hole in the wall of inner chamber 1740. When the ion is positioned at the center of cavity 1720, the electric field amplitude inside cavity 1720 has been reduced to zero (or nearly zero). As the ion emerges from inner chamber 1740, the electric field amplitude in cavity 1720 begins to increase again, but the field is now oriented radially outward. The field magnitude during the second half of the ion's pass through cavity 1720 again reaches a maximum and then begins to diminish. As a result, the positive ion is again accelerated by the electric field as the ion completes the second half of a first pass through cavity 1720.

Upon reaching the wall of cavity 1720, the magnitude of the electric field in cavity 1720 is zero (or nearly zero) and the ion passes through an aperture in the wall and encounters one of beam deflection magnets 1750. The beam deflection magnets essentially reverse the trajectory of the ion, as shown in FIG. 15, directing the ion to re-enter cavity 1720 through another aperture in the wall of the chamber. When the ion re-enters cavity 1720, the electric field therein begins to increase in amplitude again, but is now once more oriented radially inward. The second and subsequent passes of the ion through cavity 1720 follow a similar pattern, so that the orientation of the electric field always matches the direction of motion of the ion, and the ion is accelerated on every pass (and every half-pass) through cavity 1720.

As shown in FIG. 15, after six passes through cavity 1720, the accelerated ion is coupled out of cavity 1720 as a portion of accelerated ion beam 1760. The accelerated ion beam passes through one or more electrostatic and/or magnetic particle optical elements 1770, which can include lenses, collimators, beam deflectors, filters, and other optical elements. For example, under control of an external logic unit, elements 1770 can include an electrostatic and/or magnetic deflector that sweeps accelerated beam 1760 across a two-dimensional planar region oriented perpendicular to the direction of propagation of beam 1760.

Ions that are injected into cavity 1720 are accelerated on each pass through cavity 1720. In general, therefore, to obtain accelerated beams having different average ion energies, accelerator 1700 can include more than one output coupling. For example, in some embodiments, one or more of deflection magnets 1750 can be modified to allow a portion of the ions reaching the magnets to be coupled out of accelerator 1700, and a portion of the ions to be returned to chamber 1720. Multiple accelerated output beams can therefore be obtained from accelerator 1700, each beam corresponding to an average ion energy that is related to the number of passes through cavity 1720 for the ions in the beam.

Accelerator 1700 includes 5 deflection magnets 1750, and ions injected into cavity 1720 make 6 passes through the

cavity. In general, however, accelerator **1700** can include any number of deflection magnets, and ions injected into cavity **1720** can make any corresponding number of passes through the cavity. For example, in some embodiments, accelerator **1700** can include at least 6 deflection magnets and ions can make at least 7 passes through the cavity (e.g., at least 7 deflection magnets and 8 passes through the cavity, at least 8 deflection magnets and 9 passes through the cavity, at least 9 deflection magnets and 10 passes through the cavity, at least 10 deflection magnets and 11 passes through the cavity).

Typically, the electric field generated by field source **1730** provides a single-cavity-pass gain of about 1 MeV to an injected ion. In general, however, higher single-pass gains are possible by providing a higher-amplitude electric field within cavity **1720**. In some embodiments, for example, the single-cavity-pass gain is about 1.2 MeV or more (e.g., 1.3 MeV or more, 1.4 MeV or more, 1.5 MeV or more, 1.6 MeV or more, 1.8 MeV or more, 2.0 MeV or more, 2.5 MeV or more).

The single-cavity-pass gain also depends upon the magnitude of the charge carried by the injected ion. For example, ions bearing multiple charges will experience higher single-pass-cavity gain than ions bearing single charges, for the same electric field within cavity. As a result, the single-pass-cavity gain of accelerator **1700** can be further increased by injecting ions having multiple charges.

In the foregoing description of accelerator **1700**, a positively-charged ion was injected into cavity **1720**. Accelerator **1700** can also accelerate negatively charged ions. To do so, the negatively charged ions are injected so that the direction of their trajectories is out of phase with the radial electric field direction. That is, the negatively charged ions are injected so that on each half pass through cavity **1720**, the direction of the trajectory of each ion is opposite to the direction of the radial electric field. Achieving this involves simply adjusting the time at which negatively-charged ions are injected into cavity **1720**. Accordingly, accelerator **1700** is capable of simultaneously accelerating ions having the same approximate mass, but opposite charges. More generally, accelerator **1700** is capable of simultaneously accelerating different types of both positively- and negatively-charged (and both singly- and multiply-charged) ions, provided that the transit times of the ions across cavity **1720** are relatively similar. In some embodiments, accelerator **1700** can include multiple output couplings, providing different types of accelerated ion beams having similar or different energies.

Other types of accelerators can also be used to accelerate ions for irradiation of cellulosic or lignocellulosic material. For example, in some embodiments, ions can be accelerated to relatively high average energies in cyclotron- and/or synchrotron-based accelerators. The construction and operation of such accelerators is well-known in the art. As another example, in some embodiments, Penning-type ion sources can be used to generate and/or accelerate ions for treating cellulosic or lignocellulosic-based material. The design of Penning-type sources is discussed in section 7.2.1 of Prelec (1997).

Static and/or dynamic accelerators of various types can also generally be used to accelerate ions. Static accelerators typically include a plurality of electrostatic lenses that are maintained at different DC voltages. By selecting appropriate values of the voltages applied to each of the lens elements, ions introduced into the accelerator can be accelerated to a selected final energy. FIG. 16 shows a simplified schematic diagram of a static accelerator **1800** that is configured to accelerate ions to treat cellulosic or lignocellulosic material **1835**. Accelerator **1800** includes an ion source **1810** that produces ions and introduces the ions into an ion column

1820. Ion column **1820** includes a plurality of electrostatic lenses **1825** that accelerate the ions generated by ion source **1810** to produce an ion beam **1815**. DC voltages are applied to lenses **1825**; the potentials of the lenses remain approximately constant during operation. Generally, the electrical potential within each lens is constant, and the ions of ion beam **1815** are accelerated in the gaps between the various lenses **1825**. Ion column **1820** also includes a deflection lens **1830** and a collimation lens **1832**. These two lenses operate to direct ion beam **1815** to a selected position on cellulosic or lignocellulosic material **1835**, and to focus ion beam **1815** onto the cellulosic or lignocellulosic material.

Although FIG. 16 shows a particular embodiment of a static accelerator, many other variations are possible and suitable for treating cellulosic or lignocellulosic material. In some embodiments, for example, the relative positions of deflection lens **1830** and collimation lens **1832** along ion column **1820** can be exchanged. Additional electrostatic lenses can also be present in ion column **1820**, and ion column **1820** can further include magnetostatic optical elements. In certain embodiments, a wide variety of additional elements can be present in ion column **1820**, including deflectors (e.g., quadrupole, hexapole, and/or octopole deflectors), filtering elements such as apertures to remove undesired species (e.g., neutrals and/or certain ionic species) from ion beam **1815**, extractors (e.g., to establish a spatial profile for ion beam **1815**), and other electrostatic and/or magnetostatic elements.

Dynamic linear accelerators—often referred to as LINACS—can also be used to generate an ion beam that can be used to treat cellulosic or lignocellulosic material. Typically, dynamic linear accelerators include an ion column with a linear series of radiofrequency cavities, each of which produces an intense, oscillating radiofrequency (RF) field that is timed to coincide with injection and propagation of ions into the ion column. As an example, devices such as klystrons can be used to generate the RF fields in the cavities. By matching the field oscillations to the injection times of ions, the RF cavities can accelerate ions to high energies without having to maintain peak potentials for long periods of time. As a result, LINACS typically do not have the same shielding requirements as DC accelerators, and are typically shorter in length. LINACS typically operate at frequencies of 3 GHz (S-band, typically limited to relatively low power) and 1 GHz (L-band, capable of significantly higher power operation). Typical LINACS have an overall length of 2-4 meters.

A schematic diagram of a dynamic linear accelerator **1850** (e.g., a LINAC) is shown in FIG. 17. LINAC **1850** includes an ion source **1810** and an ion column **1855** that includes three acceleration cavities **1860**, a deflector **1865**, and a focusing lens **1870**. Deflector **1865** and focusing lens **1870** function to steer and focus ion beam **1815** onto cellulosic or lignocellulosic material **1835** following acceleration, as discussed above. Acceleration cavities **1860** are formed of a conductive material such as copper, and function as a waveguide for the accelerated ions. Klystrons **1862**, connected to each of cavities **1860**, generate the dynamic RF fields that accelerate the ions within the cavities. Klystrons **1862** are individually configured to produce RF fields that, together, accelerate the ions in ion beam **1815** to a final, selected energy prior to being incident on cellulosic or lignocellulosic material **1835**.

As discussed above in connection with static accelerators, many variations of dynamic accelerator **1850** are possible and can be used to produce an ion beam for treating cellulosic or lignocellulosic material. For example, in some embodiments, additional electrostatic lenses can also be present in ion column **1855**, and ion column **1855** can further include magnetostatic optical elements. In certain embodiments, a wide

variety of additional elements can be present in ion column 1855, including deflectors (e.g., quadrupole, hexapole, and/or octopole deflectors), filtering elements such as apertures to remove undesired species (e.g., neutrals and/or certain ionic species) from ion beam 1815, extractors (e.g., to establish a spatial profile for ion beam 1815), and other electrostatic and/or magnetostatic elements. In addition to the specific static and dynamic accelerators discussed above, other suitable accelerator systems include, for example: DC insulated core transformer (ICT) type systems, available from Nissin High Voltage, Japan; S-band LINACS, available from L3-PSD (USA), Linac Systems (France), Mevex (Canada), and Mitsubishi Heavy Industries (Japan); L-band LINACS, available from Iotron Industries (Canada); and ILU-based accelerators, available from Budker Laboratories (Russia).

In some embodiments, van de Graaff-based accelerators can be used to produce and/or accelerate ions for subsequent treatment of cellulosic or lignocellulosic material. FIG. 18 shows an embodiment of a van de Graaff accelerator 1900 that includes a spherical shell electrode 1902 and an insulating belt 1906 that recirculates between electrode 1902 and a base 1904 of accelerator 1900. During operation, insulating belt 1906 travels over pulleys 1910 and 1908 in the direction shown by arrow 1918, and carries charge into electrode 1902. Charge is removed from belt 1906 and transferred to electrode 1902, so that the magnitude of the electrical potential on electrode 1902 increases until electrode 1902 is discharged by a spark (or, alternatively, until the charging current is balanced by a load current).

Pulley 1910 is grounded, as shown in FIG. 18. A corona discharge is maintained between a series of points or a fine wire on one side of belt 1906. Wire 1914 is configured to maintain the corona discharge in accelerator 1900. Wire 1914 is maintained at a positive potential, so that belt 1906 intercepts positive ions moving from wire 1914 to pulley 1910. As belt 1906 moves in the direction of arrow 1918, the intercepted charges are carried into electrode 1902, where they are removed from belt 1906 by a needle point 1916 and transferred to electrode 1902. As a result, positive charges accumulate on the surface of electrode 1902; these charges can be discharged from the surface of electrode 1902 and used to treat cellulosic or lignocellulosic material. In some embodiments, accelerator 1900 can be configured to provide negatively charged ions by operating wire 1914 and needle point 1916 at a negative potential with respect to grounded pulley 1910.

In general, accelerator 1900 can be configured to provide a wide variety of different types of positive and negative charges for treating cellulosic or lignocellulosic material. Exemplary types of charges include electrons, protons, hydrogen ions, carbon ions, oxygen ions, halogen ions, metal ions, and other types of ions.

In certain embodiments, tandem accelerators (including folded tandem accelerators) can be used to generate ion beams for treatment of cellulosic or lignocellulosic material. An example of a folded tandem accelerator 1950 is shown in FIG. 19. Accelerator 1950 includes an accelerating column 1954, a charge stripper 1956, a beam deflector 1958, and an ion source 1952.

During operation, ion source 1952 produces a beam 1960 of negatively charged ions, which is directed to enter accelerator 1950 through input port 1964. In general, ion source 1952 can be any type of ion source that produces negatively charged ions. For example, suitable ion sources include a source of negative ions by cesium sputtering (SNICS) source, a RF-charge exchange ion source, or a toroidal volume ion source (TORVIS). Each of the foregoing exemplary ion

sources is available, for example, from National Electrostatics Corporation (Middleton, Wis.).

Once inside accelerator 1950, the negative ions in beam 1960 are accelerated by accelerating column 1954. Typically, accelerating column 1954 includes a plurality of accelerating elements such as electrostatic lenses. The potential difference applied in column 1954 to accelerate the negative ions can be generated using various types of devices. For example, in some embodiments, (e.g., Pelletron® accelerators), the potential is generated using a Pelletron® charging device. Pelletron® devices include a charge-carrying belt that is formed from a plurality of metal (e.g., steel) chain links or pellets that are bridged by insulating connectors (e.g., formed from a material such as nylon). During operation, the belt 15 recirculates between a pair of pulleys, one of which is maintained at ground potential. As the belt moves between the grounded pulley and the opposite pulley (e.g., the terminal pulley), the metal pellets are positively charged by induction. Upon reaching the terminal pulley, the positive charge that has accumulated on the belt is removed, and the pellets are 20 negatively charged as they leave the terminal pulley and return to the ground pulley.

The Pelletron® device generates a large positive potential within column 1954 that is used to accelerate the negative ions of beam 1960. After undergoing acceleration in column 1954, beam 1960 passes through charge stripper 1956. Charge stripper 1956 can be implemented as a thin metal foil and/or a tube containing a gas that strips electrons from the negative ions, for example. The negatively charged ions are thereby converted to positively charged ions, which emerge from charge stripper 1956. The trajectories of the emerging positively charged ions are altered so that the positively charged ions travel back through accelerating column 1954, undergoing a second acceleration in the column before 35 emerging as positively charged ion beam 1962 from output port 1966. Positively charged ion beam 1962 can then be used to treat cellulosic or lignocellulosic material according to the various methods disclosed herein.

Due to the folded geometry of accelerator 1950, ions are 40 accelerated to a kinetic energy that corresponds to twice the potential difference generated by the Pelletron® charging device. For example, in a 2 MV Pelletron® accelerator, hydride ions that are introduced by ion source 1952 will be accelerated to an intermediate energy of 2 MeV during the first pass through column 1954, converted to positive ions (e.g., protons), and accelerated to a final energy of 4 MeV during the second pass through column 1954.

In certain embodiments, column 1954 can include elements in addition to, or as alternatives to, the Pelletron® charging device. For example, column 1954 can include static accelerating elements (e.g., DC electrodes) and/or dynamic acceleration cavities (e.g., LINAC-type cavities with pulse RF field generators for particle acceleration). Potentials applied to the various accelerating devices are selected to 50 accelerate the negatively charged ions of beam 1960.

Exemplary tandem accelerators, including both folded and non-folded accelerators, are available from National Electrostatics Corporation (Middleton, Wis.), for example.

In some embodiments, combinations of two or more of the 60 various types of accelerators can be used to produce ion beams that are suitable for treating cellulosic or lignocellulosic material. For example, a folded tandem accelerator can be used in combination with a linear accelerator, a Rhodotron® accelerator, a Dynamitron®, a static accelerator, or any other type of accelerator to produce ion beams. Accelerators can be used in series, with the output ion beam from one type of accelerator directed to enter another type of accelerator for

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additional acceleration. Alternatively, multiple accelerators can be used in parallel to generate multiple ion beams. In certain embodiments, multiple accelerators of the same type can be used in parallel and/or in series to generate accelerated ion beams.

In some embodiments, multiple similar and/or different accelerators can be used to generate ion beams having different compositions. For example, a first accelerator can be used to generate one type of ion beam, while a second accelerator can be used to generate a second type of ion beam. The two ion beams can then each be further accelerated in another accelerator, or can be used to treat cellulosic or lignocellulosic material.

Further, in certain embodiments, a single accelerator can be used to generate multiple ion beams for treating cellulosic or lignocellulosic material. For example, any of the accelerators discussed herein (and other types of accelerators as well) can be modified to produce multiple output ion beams by sub-dividing an initial ion current introduced into the accelerator from an ion source. Alternatively, or in addition, any one ion beam produced by any of the accelerators disclosed herein can include only a single type of ion, or multiple different types of ions.

In general, where multiple different accelerators are used to produce one or more ion beams for treatment of cellulosic or lignocellulosic material, the multiple different accelerators can be positioned in any order with respect to one another. This provides for great flexibility in producing one or more ion beams, each of which has carefully selected properties for treating cellulosic or lignocellulosic material (e.g., for treating different components in cellulosic or lignocellulosic material).

The ion accelerators disclosed herein can also be used in combination with any of the other treatment steps disclosed herein. For example, in some embodiments, electrons and ions can be used in combination to treat cellulosic or lignocellulosic material. The electrons and ions can be produced and/or accelerated separately, and used to treat cellulosic or lignocellulosic material sequentially (in any order) and/or simultaneously. In certain embodiments, electron and ion beams can be produced in a common accelerator and used to treat cellulosic or lignocellulosic material. For example, many of the ion accelerators disclosed herein can be configured to produce electron beams as an alternative to, or in addition to, ion beams. For example, Dynamitron® accelerators, Rhodotron® accelerators, and LINACs can be configured to produce electron beams for treatment of cellulosic or lignocellulosic material.

Moreover, treatment of cellulosic or lignocellulosic material with ion beams can be combined with other techniques such as sonication. In general, sonication-based treatment can occur before, during, or after ion-based treatment. Other treatments such as electron beam treatment can also occur in any combination and/or order with ultrasonic treatment and ion beam treatment.

Paper Additives

Any of the many additives and coatings used in the paper-making industry can be added to or applied to the fibrous materials, papers, or any other materials and products described herein. Additives include fillers such as calcium carbonate, plastic pigments, graphite, wollastonite, mica, glass, fiber glass, silica, and talc; inorganic flame retardants such as alumina trihydrate or magnesium hydroxide; organic flame retardants such as chlorinated or brominated organic compounds; carbon fibers; and metal fibers or powders (e.g., aluminum, stainless steel). These additives can reinforce,

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extend, or change electrical or mechanical properties, compatibility properties, or other properties. Other additives include starch, lignin, fragrances, coupling agents, antioxidants, opacifiers, heat stabilizers, colorants such as dyes and 5 pigments, polymers, e.g., degradable polymers, photostabilizers, and biocides. Representative degradable polymers include polyhydroxy acids, e.g., polylactides, polyglycolides and copolymers of lactic acid and glycolic acid, poly(hydroxybutyric acid), poly(hydroxyvaleric acid), poly[lactide-co-(*e*-caprolactone)], poly[glycolide-*co*-(*e*-caprolactone)], polycarbonates, poly(amino acids), poly(hydroxyalkanoate)s, polyanhydrides, polyorthoesters and blends of these polymers.

When additives are included, they can be present in 15 amounts, calculated on a dry weight basis, of from below about 1 percent to as high as about 80 percent, based on total weight of the fibrous material. More typically, amounts range from between about 0.5 percent to about 50 percent by weight, e.g., from about 0.5 percent to about 5 percent, 10 percent, 20 percent, 30 percent or more, e.g., 40 percent.

Any additives described herein can be encapsulated, e.g., spray dried or microencapsulated, e.g., to protect the additives from heat or moisture during handling.

Suitable coatings include any of the many coatings used in 25 the paper industry to provide specific surface characteristics, including performance characteristics required for particular printing applications.

As mentioned above, various fillers can be included in the 30 paper. For example, inorganic fillers such as calcium carbonate (e.g., precipitated calcium carbonate or natural calcium carbonate), aragonite clay, orthorhombic clays, calcite clay, rhombohedral clays, kaolin clay, bentonite clay, dicalcium phosphate, tricalcium phosphate, calcium pyrophosphate, insoluble sodium metaphosphate, precipitated calcium carbonate, magnesium orthophosphate, trimagnesium phosphate, hydroxyapatites, synthetic apatites, alumina, silica xerogel, metal aluminosilicate complexes, sodium aluminum silicates, zirconium silicate, silicon dioxide or combinations of the inorganic additives may be used. The fillers can have, 35 e.g., a particle size of greater than 1 micron, e.g., greater than 2, 5, 10, or 25 microns or even greater than 35 microns.

Nanometer scale fillers can also be used alone, or in combination with fibrous materials of any size and/or shape. The 40 fillers can be in the form of, e.g., particles, plates or fibers. For example, nanometer sized clays, silicon and carbon nanotubes, and silicon and carbon nanowires can be used. The fillers can have a transverse dimension less than 1000 nm, e.g., less than 900, 800, 750, 600, 500, 350, 300, 250, 200, or 100 nm, or even less than 50 nm.

50 In some embodiments, the nano-clay is a montmorillonite. Such clays are available from Nanocor, Inc. and Southern Clay products, and have been described in U.S. Pat. Nos. 6,849,680 and 6,737,464. The clays can be surface treated before mixing into, e.g., a resin or a fibrous material. For 55 example, the clay can be surface treated so that its surface is ionic in nature, e.g., cationic or anionic.

Aggregated or agglomerated nanometer scale fillers, or 60 nanometer scale fillers that are assembled into supramolecular structures, e.g., self-assembled supramolecular structures can also be used. The aggregated or supramolecular fillers can be open or closed in structure, and can have a variety of shapes, e.g., cage, tube or spherical.

Lignin Content

Paper can contain lignin, for example up to 1, 2, 3, 4, 5, 7.5, 65 10, 15, 20, or even 25% by weight of lignin.

This lignin content can be the result of the lignin present in the lignocellulosic material(s) used to manufacture the paper.

Alternatively, or in addition, lignin can be added to the paper as an additive, as mentioned above. In this case, the lignin can be added as a solid, e.g., as a powder or other particulate material, or can be dissolved or dispersed and added in liquid form. In the latter case, the lignin can be dissolved in solvent or a solvent system. The solvent or solvent system can be in the form of a single phase or two or more phases. Solvent systems for cellulosic and lignocellulosic materials include DMSO-salt systems. Such systems include, for example, DMSO in combination with a lithium, magnesium, potassium, sodium or zinc salt. Lithium salts include LiCl, LiBr, LiI, lithium perchlorate and lithium nitrate. Magnesium salts include magnesium nitrate and magnesium chloride. Potassium salts include potassium iodide and nitrate. Examples of sodium salts include sodium iodide and nitrate. Examples of zinc salts include zinc chloride and nitrate. Any salt can be anhydrous or hydrated. Typical loadings of the salt in the DMSO are between about 1 and about 50 percent, e.g., between about 2 and 25, between about 3 and 15 or between about 4 and 12.5 percent by weight.

In some cases, lignin will cross-link in the paper during irradiation, further enhancing the physical properties of the paper.

Paper Types

Paper is often characterized by weight. The weight assigned to a paper is the weight of a ream, 500 sheets, of varying "basic sizes," before the paper is cut into the size as sold to end customers. For example, a ream of 20 lb, 8½×11" paper weighs 5 pounds, because it has been cut from a larger sheet into four pieces. In the United States, printing paper is generally 20 lb, 24 lb, or 32 lb at most. Cover stock is generally 68 lb, and 110 lb or more.

In Europe the weight is expressed in grams per square meter (gsm or just g). Printing paper is generally between 60 g and 120 g. Anything heavier than 160 g is considered card stock. The weight of a ream therefore depends on the dimensions of the paper, e.g., one ream of A4 (210 mm×297 mm) size (approx 8.27"×11.7") weighs 2.5 kilograms (approx 5.5 pounds).

The density of paper ranges from 250 kg/m³ (16 lb/ft³) for tissue paper to 1500 kg/m³ (94 lb/ft³) for some specialty paper. In some cases the density of printing paper is about 800 kg/m³ (50 lb/ft³).

The processes described herein are suitable for use with all of these grades of paper, as well as other types of paper such as corrugated cardboard, paper board, and other paper products. The processes described herein may be used to treat paper that is used, for example, in any of the following applications: as stamps; as paper money, bank notes, securities, checks, and the like; in books, magazines, newspapers, and art; for packaging, e.g., paper board, corrugated cardboard, paper bags, envelopes, wrapping tissue, boxes; in household products such as toilet paper, tissues, paper towel sand paper napkins; paper honeycomb, used as a core material in composite materials; building materials; construction paper; disposable clothing; and in various industrial uses including emery paper, sandpaper, blotting paper, litmus paper, universal indicator paper, paper chromatography, battery separators, and capacitor dielectrics. The paper may be single or multi-layered paper.

The paper may be made of any desired type of fiber, including fiber derived from wood and recycled paper, as well as fiber derived from other sources. Vegetable fiber materials, such as cotton, hemp, linen, and rice, can be used alone or in combination with each other or with wood-derived fibers. Other non-wood fiber sources include, but are not limited to,

sugarcane, bagasse, straw, bamboo, kenaf, jute, flax, and cotton. A wide variety of synthetic fibers, such as polypropylene and polyethylene, as well as other ingredients such as inorganic fillers, may be incorporated into paper as a means for imparting desirable physical properties. It may be desirable to include these non-wood fibers in paper used in special application such as for paper money, fine stationary, art paper and other applications requiring particular strength or aesthetic characteristics.

The paper may be irradiated before or after printing. Radiation may be used to mark the paper, for example by increasing the number of carboxylic acid groups in the irradiated area. This may be useful, for example, in marking currency.

Process Water

In the processes disclosed herein, whenever water is used in any process, it may be grey water, e.g., municipal grey water, or black water. In some embodiments, the grey or black water is sterilized prior to use. Sterilization may be accomplished by any desired technique, for example by irradiation, steam, or chemical sterilization.

EXAMPLES

The following examples are not intended to limit the inventions recited in the claims.

Example 1

Methods of Determining Molecular Weight of Cellulosic and Lignocellulosic Materials by Gel Permeation Chromatography

This example illustrates how molecular weight is determined for the materials discussed herein. Cellulosic and lignocellulosic materials for analysis were treated as follows:

A 1500 pound skid of virgin bleached white Kraft board having a bulk density of 30 lb/ft³ was obtained from International Paper. The material was folded flat, and then fed into a 3 hp Flinch Baugh shredder at a rate of approximately 15 to 20 pounds per hour. The shredder was equipped with two 12 inch rotary blades, two fixed blades and a 0.30 inch discharge screen. The gap between the rotary and fixed blades was adjusted to 0.10 inch. The output from the shredder resembled confetti (as above). The confetti-like material was fed to a Munson rotary knife cutter, Model SC30. The discharge screen had ½ inch openings. The gap between the rotary and fixed blades was set to approximately 0.020 inch. The rotary knife cutter sheared the confetti-like pieces across the knife-edges. The material resulting from the first shearing was fed back into the same setup and the screen was replaced with a ¼ inch screen. This material was sheared. The material resulting from the second shearing was fed back into the same setup and the screen was replaced with a ⅓ inch screen. This material was sheared. The resulting fibrous material had a BET surface area of 1.6897 m²/g+/-0.0155 m²/g, a porosity of 87.7163 percent and a bulk density (@0.53 psia) of 0.1448 g/mL. An average length of the fibers was 0.824 mm and an average width of the fibers was 0.0262 mm, giving an average L/D of 32:1.

Sample materials presented in the following Tables 1 and 2 include Kraft paper (P), wheat straw (WS), alfalfa (A), and switchgrass (SG). The number "132" of the Sample ID refers to the particle size of the material after shearing through a ⅓ inch screen. The number after the dash refers to the dosage of radiation (MRad) and "US" refers to ultrasonic treatment. For

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example, a sample ID “P132-10” refers to Kraft paper that has been sheared to a particle size of 132 mesh and has been irradiated with 10 MRad.

TABLE 1

| Peak Average Molecular Weight of Irradiated Kraft Paper | | | | |
|---|-----------|----------------------------|-------------------------|-----------------------|
| Sample Source | Sample ID | Dosage ¹ (MRad) | Ultrasound ² | Average MW ± Std Dev. |
| Kraft Paper | P132 | 0 | No | 32853 ± 10006 |
| | P132-10 | 10 | " | 61398 ± 2468** |
| | P132-100 | 100 | " | 8444 ± 580 |
| | P132-181 | 181 | " | 6668 ± 77 |
| | P132-US | 0 | Yes | 3095 ± 1013 |

**Low doses of radiation appear to increase the molecular weight of some materials

¹Dosage Rate = 1 MRad/hour

²Treatment for 30 minutes with 20 kHz ultrasound using a 1000 W horn under re-circulating conditions with the material dispersed in water.

TABLE 2

| Peak Average Molecular Weight of Irradiated Materials | | | | |
|---|--------|----------------------------|-------------------------|-----------------------|
| Sample ID | Peak # | Dosage ¹ (MRad) | Ultrasound ² | Average MW ± Std Dev. |
| WS132 | 1 | 0 | No | 1407411 ± 175191 |
| | 2 | " | " | 39145 ± 3425 |
| | 3 | " | " | 2886 ± 177 |
| WS132-10* | 1 | 10 | " | 26040 ± 3240 |
| WS132-100* | 1 | 100 | " | 23620 ± 453 |
| A132 | 1 | 0 | " | 1604886 ± 151701 |
| | 2 | " | " | 37525 ± 3751 |
| | 3 | " | " | 2853 ± 490 |
| A132-10* | 1 | 10 | " | 50853 ± 1665 |
| | 2 | " | " | 2461 ± 17 |
| A132-100* | 1 | 100 | " | 38291 ± 2235 |
| | 2 | " | " | 2487 ± 15 |
| SG132 | 1 | 0 | " | 1557360 ± 83693 |
| | 2 | " | " | 42594 ± 4414 |
| | 3 | " | " | 3268 ± 249 |
| SG132-10* | 1 | 10 | " | 60888 ± 9131 |
| SG132-100* | 1 | 100 | " | 22345 ± 3797 |
| SG132-10-US | 1 | 10 | Yes | 86086 ± 43518 |
| | 2 | " | " | 2247 ± 468 |
| SG132-100-US | 1 | 100 | " | 4696 ± 1465 |

*Peaks coalesce after treatment

**Low doses of radiation appear to increase the molecular weight of some materials

¹Dosage Rate = 1 MRad/hour

²Treatment for 30 minutes with 20 kHz ultrasound using a 1000 W horn under re-circulating conditions with the material dispersed in water.

Gel Permeation Chromatography (GPC) is used to determine the molecular weight distribution of polymers. During GPC analysis, a solution of the polymer sample is passed through a column packed with a porous gel trapping small molecules. The sample is separated based on molecular size with larger molecules eluting sooner than smaller molecules. The retention time of each component is most often detected by refractive index (RI), evaporative light scattering (ELS), or ultraviolet (UV) and compared to a calibration curve. The resulting data is then used to calculate the molecular weight distribution for the sample.

A distribution of molecular weights rather than a unique molecular weight is used to characterize synthetic polymers. To characterize this distribution, statistical averages are utilized. The most common of these averages are the “number average molecular weight” (M_n) and the “weight average molecular weight” (M_w). Methods of calculating these values are described in the art, e.g., in Example 9 of WO 2008/073186.

The polydispersity index or PI is defined as the ratio of M_w/M_n . The larger the PI, the broader or more disperse the

36

distribution. The lowest value that a PI can be is 1. This represents a monodisperse sample; that is, a polymer with all of the molecules in the distribution being the same molecular weight.

5 The peak molecular weight value (M_P) is another descriptor defined as the mode of the molecular weight distribution. It signifies the molecular weight that is most abundant in the distribution. This value also gives insight to the molecular weight distribution.

10 Most GPC measurements are made relative to a different polymer standard. The accuracy of the results depends on how closely the characteristics of the polymer being analyzed match those of the standard used. The expected error in reproducibility between different series of determinations, calibrated separately, is about 5-10% and is characteristic to the limited precision of GPC determinations. Therefore, GPC results are most useful when a comparison between the molecular weight distribution of different samples is made during the same series of determinations.

15 The lignocellulosic samples required sample preparation prior to GPC analysis. First, a saturated solution (8.4% by weight) of lithium chloride (LiCl) was prepared in dimethyl acetamide (DMAc). Approximately 100 mg of the sample was added to approximately 10 g of a freshly prepared saturated LiCl/DMAc solution, and the mixture was heated to approximately 150° C.-170° C. with stirring for 1 hour. The resulting solutions were generally light- to dark-yellow in color. The temperature of the solutions were decreased to approximately 100° C. and heated for an additional 2 hours. The temperature of the solutions were then decreased to approximately 50° C. and the sample solution was heated for approximately 48 to 60 hours. Of note, samples irradiated at 100 MRad were more easily solubilized as compared to their untreated counterpart. Additionally, the sheared samples (denoted by the number 132) had slightly lower average molecular weights as compared with uncut samples.

20 The resulting sample solutions were diluted 1:1 using DMAc as solvent and were filtered through a 0.45 µm PTFE filter. The filtered sample solutions were then analyzed by GPC. The peak average molecular weight (M_p) of the samples, as determined by Gel Permeation Chromatography (GPC), are summarized in Tables 1 and 2, above. Each sample was prepared in duplicate and each preparation of the sample was analyzed in duplicate (two injections) for a total of four injections per sample. The EasiCal® polystyrene standards PS1A and PS1B were used to generate a calibration curve for the molecular weight scale from about 580 to 7,500,00 Dalton. GPC analysis conditions are recited in Table 3, below.

TABLE 3

| GPC Analysis Conditions | |
|------------------------------|---|
| Instrument: | Waters Alliance GPC 2000 |
| Columns (3): | Pfgel 10µ Mixed-B |
| | S/N's: 10M-MB-148-83; 10M-MB-148-84; 10M-MB-174-129 |
| Mobile Phase (solvent): | 0.5% LiCl in DMAc (1.0 mL/min.) |
| Column/Detector Temperature: | 70° C. |
| Injector Temperature: | 70° C. |
| Sample Loop Size: | 323.5 µL |

Example 2

Electron Beam Processing Cardboard Samples

Brown cardboard samples 0.050 inches thick were treated with a beam of electrons using a vaulted Rhodotron® TT200 continuous wave accelerator delivering 5 MeV electrons at 80 kW output power. Table 4 describes the nominal parameters for the TT200. Table 5 reports the nominal doses (in MRad) and actual doses (in kgy) delivered to the samples.

TABLE 4

| Rhodotron ® TT 200 Parameters | |
|---|---|
| Beam | |
| Beam Produced: | Accelerated electrons |
| Beam energy: | Nominal (maximum): 10 MeV (+0 keV-250 keV) |
| Energy dispersion at 10 Mev: | Full width half maximum (FWHM) 300 keV |
| Beam power at 10 MeV: | Guaranteed Operating Range 1 to 80 kW |
| Power Consumption | |
| Stand-by condition (vacuum and cooling ON): | <15 kW |
| At 50 kW beam power: | <210 kW |
| At 80 kW beam power: | <260 kW |
| RF System | |
| Frequency: | 107.5 ± 1 MHz |
| Tetrode type: | Thomson TH781 |
| | Scanning Horn |
| Nominal Scanning Length (measured at 25-35 cm from window): | |
| Scanning Range: | From 30% to 100% of Nominal Scanning Length |
| Nominal Scanning Frequency (at max. scanning length): | 100 Hz ± 5% |
| Scanning Uniformity (across 90% of Nominal Scanning Length) | ±5% |

TABLE 5

| Dosages Delivered to Samples | |
|---|--------------------------------------|
| Total Dosage (MRad) (Number Associated with Sample ID) | Delivered Dose (kgy) ¹ |
| 1 | 9.9 |
| 3 | 29.0 |
| 5 | 50.4 |
| 7 | 69.2 |
| 10 | 100.0 |
| 15 | 150.3 |
| 20 | 198.3 |
| 30 | 330.9 |
| 50 | 529.0 |
| 70 | 695.9 |
| 100 | 993.6 |

¹For example, 9.9 kgy was delivered in 11 seconds at a beam current of 5 mA and a line speed of 12.9 feet/minute. Cool time between 1 MRad treatments was about 2 minutes.

The cardboard samples treated below 7 MRad were stiffer to the touch than untreated controls, but otherwise appeared visibly identical to the controls. Samples treated at about 10 MRad were of comparable stiffness to the controls to the touch, while those treated with higher doses were more flexible under manipulation. Extensive material degradation was visibly apparent for samples treated above 50 Mrad.

Other Embodiments

It is to be understood that while the invention has been described in conjunction with the detailed description

thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

What is claimed is:

1. A method of making an irradiated paper product, the method comprising
 - treating a paper product comprising a carbohydrate-containing material with from about 0.25 to about 10 MRad of ionizing radiation having an energy of from about 0.25 to 7.5 MeV, without the addition of cross-linking additives, so as to self-crosslink the carbohydrate-containing material and thereby increase the molecular weight of the carbohydrate-containing material, providing an irradiated paper product.
 2. The method of claim 1 wherein the dose of ionizing radiation is from about 0.25 to about 2.5 MRad.
 3. The method of claim 1 wherein treating comprises irradiating with gamma radiation.
 4. The method of claim 1 wherein treating comprises irradiating with electron beam radiation.
 5. The method of claim 1 further comprising quenching the treated paper product.
 6. The method of claim 5 wherein quenching is performed in the presence of a gas selected to react with radicals present in the treated paper product.
 7. The method of claim 1 wherein the dose of ionizing radiation is from about 0.25 to about 5 MRad.

* * * * *

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(54) Title: A METHOD FOR PRODUCING MODIFIED CELLULOSE

(57) Abstract: The present invention provides a method for producing modified nanofibrillated cellulose characterized by bringing cellulosic material into a fiber suspension, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto fibers in said fiber suspension under special conditions and subjecting the obtained fiber suspension derivative to mechanical disintegration. A modified nanofibrillated cellulose obtainable by a method of the present invention is provided. Furthermore, the invention relates to the use of said modified nanofibrillated cellulose.

A METHOD FOR PRODUCING MODIFIED CELLULOSE

FIELD OF THE INVENTION

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The present invention relates to a method for producing modified nanofibrillated cellulose characterized by steps of preparing a suspension containing fibers from cellulosic material, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under special conditions and subjecting 10 the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration. The invention also relates to modified nanofibrillated cellulose obtainable by a method of the present invention. The invention provides a paper containing the modified nanofibrillated cellulose and method and use thereof. Furthermore, the invention relates to the use of said 15 modified nanofibrillated cellulose in paper, food products, composite materials, concrete, oil drilling products, coatings, cosmetic products and pharmaceutical products. The invention also provides a use of the present method for producing modified nanofibrillated cellulose energy efficiently.

20

BACKGROUND OF THE INVENTION

Cellulose-based nano-sized fibrils provide new possibilities for producing light and strong materials. For example increasing environmental requirements promote more 25 extensive utilization of new natural fiber based biomaterials in the future. Nanosized materials can provide properties which can not be achieved with larger sized particles. The smaller the particle, the larger the surface area is and more possibilities for desired interactions with other materials exist.

30

Cellulose fibers (width 30-40 µm, length 2-3 mm) can be dismantled into nanosized structures (width about 5-30 nm, length several µms). Microfibrillated cellulose (MFC) has been produced by combining enzymatic or chemical treatments to mechanical treatments. Microfibrils provide even in minor proportion conventional paper products increased toughness and strength. International patent publication WO 2007/091942 35 discloses a method for manufacturing microfibrillated cellulose using enzymatic treatment.

Properties of the cellulose fibers used for producing paper can be modified by adding polymers to the fiber suspension. Suitable additive polymers include for example starch-based polymers, such as cationized starch, or synthetic polymers such as polyacryl polymers, polyamineamide-, polyamine- and acrylamino-epichlorohydrine polymers, cellulose derivatives or anionic polymers containing carboxyl groups or carboxylate ions in the form of alkali metals of ammonium salts, for example carboxymethyl polysaccharides, such as carboxymethyl cellulose (CMC). International patent publications WO 01/66600 and WO 00/47628 disclose derivatized microfibrillar polysaccharides, such as cellulose and production methods thereof.

10

CMC or sodium carboxymethyl cellulose is a water-soluble anionic polymer achieved by introducing carboxymethyl groups along the cellulose chain. The functional properties of CMC depend on the degree of substitution on the cellulose structure (i.e. how many of the hydroxyl groups have taken part in the substitution reaction), and 15 also on the chain length of the cellulose backbone. The degree of substitution (DS) of CMC is usually in the range from 0.6 to 0.95 derivatives per monomer unit.

20

CMC can be used as an additive during the grinding of paper pulp (B. T. Hofreiter in "Pulp and Paper Chemistry and Chemical Technology", Chapter 14, Volume III, 3rd. edition, New York, 1981; W. F. Reynolds in "Dry strength additives", Atlanta 1980; D. Eklund and T. Lindström in "Paper Chemistry - an introduction", Grankulla, Finland 1991; J. C. Roberts in "Paper Chemistry"; Glasgow and London 1991).

25

CMC has a low affinity for cellulose fibers, since both are anionically charged. CMC can still be attached irreversibly to pulp fibres and it increases the surface charge density of pulp fibres.

30

US patents 5,061,346 and 5,316,623 disclose the addition of CMC to pulp in paper making processes. Publications WO 2004/055268 and WO 2004/055267 present fiber suspensions comprising cellulose enzyme-treated microfibrillar sulphate pulp (eMFC) and carboxymethyl cellulose (CMC) as raw material for packages and for surface application in paperboard and paper production, respectively.

35

CMC is used as thickener to modify the rheology. CMC has also been used as a dispersion agent. Furthermore, CMC has been used as binder. US patent US 5,487,419 discloses CMC as dispersion agent. US patent US 6,224,663 discloses use of CMC as an additive in a cellulose composition. Publication WO 95/02966 discloses the use of

CMC to modify microcrystalline cellulose and in some cases microfibrillated MCC by mixing the two components and the use of this mixture in food compositions.

CMC sorption is known in the art. US Patent 6,958,108 and international patent publication WO 99/57370 disclose a method for producing a fiber product, wherein alkali soluble CMC is added to the pulp under alkali conditions. International patent publication WO 01/021890 discloses a method for modifying cellulose fibers with a cellulose derivative such as CMC. Publication WO 2009/126106 relates to attachment of amphoteric CMC polymers to cellulose fibres before homogenization.

The following articles by Laine et al. disclose modification of cellulosic fibers with CMC: Nord Pulp Pap Res J, 15:520-526 (2000); Nord Pulp Pap Res J, 17:50-56 (2002); Nord Pulp Pap Res J, 17:57-60 (2002); Nord Pulp Pap Res J, 18:316-325 (2003); Nord Pulp Pap Res J, 18:325-332 (2003).

Despite the ongoing research and development in the manufacturing of microfibrillated cellulose there is still a continuing need in the industry to improve the processes. One problem is high energy consumption and thus there is a need for an energy efficient method. There is also a need for a process, wherein the properties of paper are improved. The present invention provides a method for overcoming the problems associated with the prior art.

SUMMARY OF THE INVENTION

The present invention relates to a method for producing modified nanofibrillated cellulose. The method comprises preparing a suspension containing fibers from cellulosic material, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under special conditions and subjecting the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration to obtain modified nanofibrillated cellulose modified with said cellulose derivative or polysaccharide or polysaccharide derivative. The present invention also relates to modified nanofibrillated cellulose obtainable by the method of the present invention and characterized by that a diameter of modified nanofibrillated cellulose is less than 1 μm .

A significant advance of the present invention is reduced consumption of refining energy compared to the prior art methods. A novel and efficient method for producing modified nanofibrillated cellulose energy efficiently is thus provided.

- 5 Additives such as cellulose derivatives or polysaccharides or polysaccharide derivatives are usually added to already fibrillated material i.e. by addition to suspension after mechanical disintegration.

- In the present invention the cellulose derivative or polysaccharide or polysaccharide derivative is added prior and/or during mechanical disintegration. This results in the decreased consumption of energy and better fibrillation. In the present invention a cellulose derivative or polysaccharide or polysaccharide derivative is used in a novel way while adsorbed to cellulosic material under special conditions. Cellulosic material is brought into a fiber suspension and a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed to said fiber suspension. The fiber suspension containing the adsorbed cellulose derivative or polysaccharide or polysaccharide derivative is then subjected to mechanical disintegration. The cellulose derivative or polysaccharide or polysaccharide derivative is anionic or non-ionic.
- 10
15
20
- The present invention further relates to a paper comprising the modified nanofibrillated cellulose prepared according to the method of the present invention.

One of the advantages of the invention is an improvement of the paper properties.

- 25 The present invention further relates to the use of said nanofibrillated cellulose in paper, food products, composite materials, concrete, oil drilling products, coatings, cosmetic products or pharmaceutical products.

- 30 The present invention further relates to use of a method for producing nanofibrillated cellulose energy efficiently and use of a method for producing paper with improved properties.

BRIEF DESCRIPTION OF THE DRAWINGS

35

Figure 1 shows the Scott Bond (J/m^2) i.e. the internal strength of a paper sheet, measured on Scott Bond Tester as a function of drainage time, measured using a

dynamic drainage analyzer. From this figure it is evident that by adding the nanofibrillated cellulose (NFC) prepared according to this invention (10 min + CS + CMC modified NFC, filled sphere) to only slightly refined pulp almost fivefold increase in internal strength is achieved without severe loss in dewatering efficiency.

5

Soft wood (pine) pulp was refined for 10 minutes and the pulp was washed to sodium form. A cationic starch (CS; Raisamyl 50021, DS =0.035, Ciba Specialty Chemicals) was used as an additive in some of the cases (10 min + CS + CMC modified NFC, filled sphere; 10 min + CS + unmodified NFC open sphere). The NFC was dispersed with 10 ultrasound microtip sonication prior to use. All experiments were done in a solution of deionised water containing 1 mM NaHCO₃ and 9 mM NaCl.

Pulp was first mixed with cationic starch (CS, 25 mg/g dry pulp) for 15 min, then the dispersed nanofibrillated cellulose (NFC, 30 mg/g dry pulp) was added and the 15 suspension was mixed for another 15 min. In the cases where no CS was used (10 min + unmodified NFC; triangle) only NFC (30 mg/g) was added and the suspension was mixed for 15 min before sheet making. The sheets were prepared in laboratory sheet former (SCAN-C26:76) and dried under restrain. For comparison the effect of refining is shown by the black squares. In this series the pulp has been refined for 10, 20 15, 20 and 30 minutes, respectively, as shown by black squares. The CMC modified NFC in this example was prepared by sorption of Finnfix WRM CMC and 3 passes through the friction grinder with addition of the same CMC before the second and third pass. Abbreviations: CS, cationic starch; NFC, nanofibrillated cellulose; CMC, Carboxy methyl cellulose.

25

Figure 2 depicts optical microscopy images of CMC modified nanofibrillated cellulose. CMC (Finnfix WRM, high molecular weight CMC) was added during fibrillation in fluidizer. **Figure 2a** shows modified nanofibrillated cellulose after 1+1 passes through the fluidizer. **Figure 2b** shows modified nanofibrillated cellulose after 1+2 passes through the fluidizer. **Figure 2c** shows modified nanofibrillated cellulose after 1+3 passes through the fluidizer. The decrease in the amount of large particles can be observed.

Figure 3 depicts optical microscopy images of samples after 1+3 passes through the fluidizer. **Figure 3a** shows the image of unmodified nanofibrillated cellulose (NFC). **Figure 3b** shows the image of NFC modified according to this invention by addition of 10 mg/g dry pulp Finnfix, WRM high molecular weight CMC before each pass (a total

of 40 mg/g after 1+3 passes). **Figure 3c** shows the image of NFC modified according to this invention by addition of 10 mg/g dry pulp Finnfix, BW low molecular weight CMC before each pass (a total of 40 mg/g after 1+3 passes).

- 5 **Figure 4a** depicts a schematic diagram of CMC pre-sorption onto the fibre prior to mechanical disintegration. **Figure 4b** depicts a schematic diagram of CMC addition to the pulp suspension prior to and/or during mechanical disintegration. In contrast to the method shown in Figure 4a CMC is allowed to adsorb during the whole disintegration process.

10

Figure 5 shows the Scott Bond as a function of passes through Masuko or Fluidizer. The corresponding microscopy images are of the Fluidizer samples after 2, 3 and 4 passes through the fluidizer, respectively.

15

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method for producing modified nanofibrillated cellulose by adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto fibers in a fiber suspension under special conditions and subjecting the fiber suspension comprising a cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration. By combining the adsorption of a cellulose derivative or polysaccharide or polysaccharide derivative onto fibers under special conditions and mechanical disintegration the number of passes through a disintegration device needed to refine the pulp is reduced and the energy demanded is decreased. Special conditions according to the present invention include temperature, presence of monovalent or polyvalent cations, adsorption time and/or mixing. It has surprisingly been found that the amount of refining energy needed in the process is decreased. The present invention provides significant advances compared to the prior art by decreasing the energy consumption during fibrillation. The modification of nanofibrillated cellulose with a cellulose derivative or polysaccharide or polysaccharide derivative prior to and/or during the mechanical disintegration surprisingly increases the processing efficiency.

35 Furthermore, the modified nanofibrillated cellulose improves the paper properties more than unmodified nanofibrillated cellulose. None of the prior art methods results in the similar strength properties for paper when compared to modified nanofibrillated

cellulose according to the present invention. Nanofibrillated cellulose modified with a cellulose derivative or polysaccharide or polysaccharide derivative contains up to five times more nanofibrils than the unmodified nanocellulose prepared from the same pulp. The strength of paper produced from the modified nanofibrillated cellulose using the special conditions of the present invention is already after the initial pass through the friction grinder considerably increased as compared to unmodified fibrils. Thus, mechanical treatment to obtain modified nanofibrillated cellulose can be reduced to one fifth, while still achieving considerably improved paper qualities. Nanofibrillated cellulose together with a modification by a cellulose derivative or polysaccharide or polysaccharide derivative under special conditions provides a synergistic effect, which can be utilized in paper produced from said modified nanocellulose.

Unless otherwise specified, the terms, which are used in the specification and claims, have the meanings commonly used in the pulp and paper industry. Specifically, the following terms have the meanings indicated below:

The term "nanofibrillated cellulose" or NFC" refers to very refined cellulose where most of the fibrils have been fully liberated from the fibers and occur as individual threads, which are 5 nm – 1 µm thick and several µms long. Conventionally the fibrils having a diameter of less than 1 µm are called nanofibrils and fibrils having a diameter of more than 1 µm and length of several micrometers are called microfibrils.

The term "mechanical disintegration" or "fibrillation" or "grinding" in the present invention relates to producing nanofibrillated cellulose from larger fiber material.

Mechanical disintegration includes also for example refining, beating and homogenization. Mechanical disintegration can be carried out with suitable equipment such as a refiner, grinder, homogenizer, colloider, friction grinder, fluidizer such as microfluidizer, macrofluidizer or fluidizer-type homogenizer.

The term "cellulosic material" refers to nonwoody and wood cellulosic materials used. As cellulosic material for the method and process of the present invention almost any kind of cellulosic raw materials is suitable, as described below.

The term "special conditions" in the present invention refers to a specified temperature, presence of monovalent or polyvalent cations, adsorption time and/or mixing which are defined according to the present invention.

The term "chemical pulp" refers to all types of chemical wood-based pulps, such as bleached, half-bleached and unbleached sulphite, sulphate and soda pulps, kraft pulps together with unbleached, half-bleached and bleached chemical pulps and mixtures thereof.

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The term "paper", as used herein, includes not only paper and production thereof, but also other web-like products, such as nonwoven, board and paperboard, and the production thereof.

- 10 The present invention provides a method for producing modified nanofibrillated cellulose wherein the method comprises steps of preparing a suspension containing fibers from cellulosic material, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under specified conditions and subjecting the fiber suspension comprising said cellulose derivative or
15 polysaccharide or polysaccharide derivative to mechanical disintegration to obtain modified nanofibrillated cellulose modified with said cellulose derivative or polysaccharide or polysaccharide derivative.

According to an embodiment of the present invention a cellulose derivative or
20 polysaccharide or polysaccharide derivative is adsorbed onto the fibers either prior to mechanical disintegration (sorption) or by adding a cellulose derivative or polysaccharide or polysaccharide derivative during the mechanical disintegration (addition) under special conditions. In still another embodiment of the invention the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the
25 fibers both prior to and during the mechanical disintegration.

In a preferred embodiment of the invention as cellulosic material for the method of the present invention almost any kind of cellulosic raw materials is suitable. The cellulosic material which is used in the present invention includes pulp such as a chemical pulp,
30 mechanical pulp, thermo mechanical pulp (TMP) or chemi-thermo mechanical pulp (CTMB) produced from wood, non-wood material or recycled fibers. Wood can be from softwood tree such as spruce, pine, fir, larch, douglas-fir or hemlock, or from hardwood tree such as birch, aspen, poplar, alder, eucalyptus or acacia, or from a mixture of softwoods and hardwoods. Non-wood material can be from agricultural residues, grasses or other plant substances such as straw, leaves, bark, seeds, hulls, flowers, vegetables or fruits from cotton, corn, wheat, oat, rye, barley, rice, flax,

hemp, manila hemp, sisal hemp, jute, ramie, kenaf, bagasse, bamboo or reed. Non-wood material can also be from algae or fungi or of bacterial origin.

In a preferred embodiment of the invention as a cellulose derivative for the purposes
5 of the present invention almost any kind of cellulose derivative is suitable. A cellulose derivative can be carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, ethylhydroxyethyl cellulose, carboxymethylcellulose, carboxymethylhydroxyethyl cellulose, hydroxypropylhydroxyethyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose, carboxymethylmethyl cellulose, or hydrophobically modified variants thereof, or cellulose acetate, cellulose sulfate, cellulose phosphate, cellulose phosphonate, cellulose vinyl sulfate, or nitrocellulose or other derivatives known by the person skilled in the art can be applied. The present invention is exemplified by using carboxymethyl cellulose (CMC) for producing modified nanofibrillated cellulose. Preferably anionic CMC is used. Even
10 though CMC represents a preferred embodiment, it should be noted, that other cellulose derivatives known by the person skilled in the art can be used.
15

In a preferred embodiment of the invention a polysaccharide or polysaccharide derivative can be selected from guar gums, chitins, chitosans, galactans, glucans,
20 xantan gums, mannans or dextrans ,which are given here by the way of examples. It should be noted, that other polysaccharides or polysaccharide derivatives known by the person skilled in the art can be used.

The amount of added cellulose derivative or polysaccharide or polysaccharide derivative is at least 5 mg/g of fiber suspension, preferably from 10 to 50 mg/g of fiber suspension, more preferably about 15 mg/g, 20 mg/g, 25mg/g, 30 mg/g, 35 mg/g or 40 mg/g of fiber suspension, the upper limit being 1000 mg/g of fiber suspension, preferably the upper limit is 100 mg/g of fiber suspension.
25

30 In an embodiment where CMC is used as the cellulose derivative, different commercially available CMC grades having a suitable degree of substitution and molar mass can be used for carrying out the invention. Typically high molecular weight CMC has suitable characteristics for mechanical disintegration or fibrillation and typically low molecular weight CMC can penetrate the fiber wall, which also increases the
35 amount of adsorbed CMC.

In a preferred embodiment of the invention a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers at a temperature of at least 5°C, preferably at a temperature of at least 20°C, the upper limit being 180°C. In a more preferred embodiment of the invention temperature is from 75°C to 80°C.

5

In a preferred embodiment of the invention a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers for at least 1 minute, preferably for at least 1 hour, preferably for 2 hours. Preferably the adsorption is aided by sufficient mixing.

10

In a preferred embodiment of the present invention the absorption is made in the presence of monovalent or polyvalent cations such as aluminium, calcium and/or sodium salts containing Al³⁺, Ca²⁺ and/or Na⁺, respectively, preferably for example CaCl₂. High valencies are advantageous for the adsorption. Generally a higher concentration of electrolyte and a higher valence of the cation increase the affinity of an anionic cellulose derivative, such as CMC, to the pulp. Generally, however, an optimum exists. The preferred concentration interval for salts with divalent cations such as CaCl₂ is between 0 and 1 M, preferably about 0.05 M.

15

In a preferred embodiment of the invention the pH value of the fiber suspension is at least pH 2, preferably from about pH 7.5 to 8, the upper limit being pH 12. A suitable base or acid is used for setting the pH. The pH value is dependent on the origin of the fibers in the mass.

20

The sorption at specified conditions ensures that a cellulose derivative or polysaccharide or polysaccharide derivative is irreversibly attached to the pulp prior to disintegration. The addition at low temperature during disintegration does not facilitate sorption but indicates the effect of a cellulose derivative or polysaccharide or polysaccharide derivative in solution on fibrillation efficiency.

25

The present invention comprises a step of mechanical disintegration. In a preferred embodiment of the invention the mechanical disintegration is carried out with a refiner, grinder, homogenizer, colloider such as a supermass colloid, friction grinder, fluidizer such as microfluidizer, macrofluidizer or any fluidizer-type homogenizer known by the person skilled in the art without, however, not limiting to these examples. Typically the fiber suspension is passed through mechanical disintegration at least once, preferably 1, 2, 3, 4 or 5 times.

This enables the reduction of mechanical treatment by up to one fifth, while at the same time considerable improvement for example in paper quality is achieved. It is shown in the Examples that the energy consumption during friction grinding of pulp

5 modified with a cellulose derivative, such as CMC, is lower compared to friction grinding of same pulp without a cellulose derivative, such as CMC adsorbed. The energy consumption of producing the modified nanocellulose of the present invention is lower compared to unmodified pulp. The energy needed to obtain roughly the same amount of nanofibrillated material is halved.

10

In a preferred embodiment of the invention the fiber suspension containing the cellulose derivative or polysaccharide or polysaccharide derivative is redispersed in water to a concentration of at least 0,1%, preferably at least 1%, more preferably at least 2%, 3%, 4% or 5%, up to 10% prior to mechanical disintegration. In a preferred 15 embodiment using the friction grinder for the mechanical disintegration the fiber suspension containing the cellulose derivative or polysaccharide or polysaccharide derivative is redispersed in water to 3% consistency. Preferably 1-5 passes are run.

20

The present invention also relates to nanofibrillated cellulose prepared according to the method of any of the claims.

In nanosized structure the surface area of cellulose is maximized and the structure has more chemically functional groups than cellulose in general. This means that nanocellulose fibers attach strongly to surrounding substances. This provides the 25 paper produced from the nanocellulose with good strength properties. Using the modified nanocellulose according to the present invention even higher strength properties than with unmodified nanocellulose are obtained.

30

The present invention relates to the use of modified nanofibrillated cellulose according to the present invention in paper. The present invention also relates to a paper containing the modified nanofibrillated cellulose of the present invention. In a preferred embodiment the amount of modified nanofibrillated cellulose is at least 0,2%, preferably at least 1%, 2%, 3%, 4% or 5%, up to 20% by weight of the paper.

Other ingredients in paper are such that are known to the person skilled in the art. 35 The paper is prepared using the standard methods used in the field and known by the person skilled in the art. The technical paper properties of both fibril sheets of the present invention and paper sheets containing modified nanofibrillated cellulose of the

present invention are tested using standard methods known by the person skilled in the art.

Adsorbed cellulose derivative or polysaccharide or polysaccharide derivative of the present invention is used in a novel way. Combining the adsorption of the cellulose derivative or polysaccharide or polysaccharide derivative and mechanical disintegration provides novel and surprising advantages. It is noted that in the present process, energy savings are achieved. Another advantage of the modification is the new properties of the modified fibrils that can be used for example to improve the properties of paper. The strength of the paper produced from the modified nanofibrillated cellulose of the present invention is already after the initial pass through the refiner considerably increased as compared to unmodified fibrils. Thus, mechanical treatment can be reduced to up to one fifth, while at the same time considerable improvement for example in paper quality is achieved.

15

The efficiency of the mechanical disintegration or fibrillation is determined by gravimetrically measuring the amount of nano-size particles after each pass through the homogenizing device.

20

Application areas for the modified nanofibrillated cellulose of the present invention include, but are not restricted to paper, food products, composite materials, concrete, oil drilling products, coatings, cosmetic products and pharmaceutical products. Other possible application areas of the modified nanocellulose of the present invention include for example the use as a thickener, use in composites for vehicles, consumables and furniture, in new materials for electronics and use in moldable light weight and high strength materials.

25

The following example is given to further illustrate the invention and is not intended to limit the scope thereof. Based on the above description, a person skilled in the art will be able to modify the invention in many ways.

Examples

Example 1

35

Materials

Pulp

Bleached, never-dried kraft birch pulps provided by UPM-Kymmene Oyj were used.

CMC

Two different CMC grades were used: the high molecular weight Finnfix WRM or low
5 molecular weight Finnfix BW (DS 0.52-0.51) (CP Kelco, Äänekoski, Finland).

CMC adsorption was carried out with two strategies: either treating the pulp prior to fibrillation with CMC in specific conditions (sorption) or adding the CMC during the fibrillation (addition). The third strategy was to adsorb CMC both prior to fibrillation
10 and during fibrillation.

CMC sorption

The pulp (never dried hardwood) was first washed with deionised water prior to sorption. A slurry with pulp consistency of 30 g/l containing 0.05 M CaCl₂ and 0.01 M
15 NaHCO₃ was prepared and heated to 75-80°C. 20 mg carboxymethyl cellulose (CMC) was added per gram of pulp (o.d). The pH was adjusted to pH 7.5-8 with 1M NaOH. The slurry was mixed for 2h at 75-80°C. After sorption the pulp was washed with deionised water, excess water was removed by filtration and the moist pulp cakes were stored in cold room until fibrillation. Batches corresponding to about 20-25 l of
20 3% CMC sorbed pulp were prepared for fibrillation with friction grinder and batches of about 5 l of 3% CMC sorbed pulp were prepared for fluidizer runs. Sorption is presented in Figure 4a.

CMC addition

25 The CMC was dissolved carefully the day before fibrillation into 2% consistency. After dispersing the pulp the addition was done before each pass by adding the CMC solution calculated as 10 mg per dry gram of fibre for one pass. One to four additions corresponding to total additions of 10-40 mg/g were performed. Between the additions the slurry was mixed 15 minutes without heating. In this case the cellulose derivative adsorption was going on during fibrillation.
30

Fibrillation

Fibrillation was done with either friction grinder (Masuko Supermass colloider, Masuko Sangyo, Japan) or a laboratory scale fluidizer (Microfluidics M110Y, Microfluidics Corp.,
35 USA).

Friction grinding

In friction grinding the CMC sorbed pulp was redispersed in water to 3% consistency using the grinder with 200µm gap. Subsequently 1 to 5 passes were run through the friction grinder with a gap of roughly 100-160 µm and power around 3 kW and samples were taken after each pass. In the cases where CMC was also added during

- 5 fibrillation, the slurry was heated to 60-80°C for 30 min and mixed for 10 min after CMC addition prior to passing through the colloider.

The following experiments were carried out with friction grinder:

1. Reference, unmodified pulp was passed five times through the friction grinder.
- 10 2. High molecular weight CMC (WRM) was sorbed onto pulp, the pulp was washed prior to refining and one to five passes were run through the friction grinder.
3. High molecular weight CMC (WRM) was sorbed onto pulp, the pulp was washed prior to refining. 20 mg/g CMC (WRM) was added to suspension (adsorption) before each pass through the friction grinder. The pulp was run one to three
- 15 times through the refiner.
4. Low molecular weight CMC (BW) was sorbed to the pulp and the pulp was washed prior to refining, one to five passes were run through the friction grinder.

- 20 The concentration of nanofibrils in each of the above listed experiments are presented in the upper part of Table 2, "Masuko Supermass Colloider".

Fluidizer

In the experiments carried out with the fluidizer the well beaten pulp (hardwood pulp) was diluted to 2% consistency and pre-dispersed with a Polytron mixer before first run through the fluidizer. The sample was first passed through the wider chamber pair with diameters of 400 and 200µm at 950 bar and then 1 to 3 times through the smaller chamber pair with diameters of 200 and 100µm at 1350 bar.

- 30 The following experiments were carried out with a fluidizer:

1. Reference: unmodified pulp – only fibrillation.
2. Presorption of CMC (high molecular weight, WRM or low molecular weight, BW) prior to fibrillation
3. Presorption of CMC (high molecular weight, WRM or low molecular weight, BW) prior to fibrillation + addition (adsorption) of CMC during fibrillation.
- 35 4. Addition (adsorption) of CMC during fibrillation only (WRM or BW).

The concentrations of nanofibrils in each of the above listed experiments are presented in the lower part of Table 2, "Microfluidics fluidizer".

Amount of nanosized material

- 5 The proportion of nanosized material in the nanofibrillated cellulose (NFC) was estimated by centrifugation. The more there were unsettled fibrils in the supernatant after centrifugation the more efficient the fibrillation had been. Solids content was determined gravimetrically after drying the samples before and after drying them in oven (105°C). Based on the value, the samples are diluted into constant (ca. 1.7
10 g/ml) consistency and dispersed with ultrasound microtip (Branson Digital Sonifier D-450) for 10 min, 25 % amplitude setting. After sonification, samples are centrifuged (Beckman Coulter L-90K) for 45 min at 10 000 G. From clear supernatant, 5 ml is carefully taken with a pipette. Two parallel measurements (10 ml) are combined for gravimetric analysis and results are given as an average value for two measurements.

15

Optical microscopy imaging

- Fibrous material was stained with 1% Congo red (Merck L431640) in order to improve contrast in light microscopy. Staining liquid was centrifuged (13 00 rpm, 2 min) prior to use to remove insoluble material. For microscopical examination a fibre sample
20 (150µl) was mixed with Congo red solution at a ratio of 1:1 in an eppendorf tube and about 100 µl of stained fibre slurry was spread with 50 µl of distilled water on microscope slide and covered with a cover slip. The samples were examined using bright field settings under Olympus BX61 microscope equipped with ColorView 12 camera (Olympus). Images were taken with magnifications of 40 x and 100 x using
25 Analysis Pro 3.1 image processing program (Soft Imaging System GmbH).

Preparation of fibril sheets

- To demonstrate the efficiency of the present invention sheets containing 85% NFC and 15 % unrefined soft wood pulp were prepared according to the standard method using
30 a normal laboratory sheet former (SCAN-C26:76).

Preparation of paper sheets with fibrils as additives

- Softwood pulp was refined for 10 minutes, and the pulp was washed to sodium form. A cationic starch (Raisamyl 50021, DS =0.035, Ciba Specialty Chemicals) was used as
35 an additive. A 2 g/l starch stock solution was prepared fresh every day. The NFC was dispersed with ultrasound microtip sonication prior to use. All experiments were done in a solution of deionised water containing 1 mM NaHCO₃ and 9 mM NaCl.

Pulp was first mixed with cationic starch (CS) for 15 min and then the dispersed nanofibrillated cellulose (NFC) was added and the suspension was mixed for another 15 min. The sheets were prepared in laboratory sheet former (SCAN-C26:76) and
5 dried under restrain.

The paper technical properties of both fibril sheets and paper sheets containing modified NFC were tested using standard methods.

10 Results

Energy consumption during production

The energy consumption during friction grinding of CMC sorbed pulp is illustrated in Table 1. Furthermore, average solids content after fibrillation and estimated amount of
15 nanosized material are presented.

Table 1. Energy consumption for the fibrillation of pulp after CMC sorption using friction grinder.

| Sample | Passes | Cumulative total refining energy (MW*h/t) | Average solids content [%] | Nanomaterial (upper phase) [g/l] |
|--------------|--------|---|----------------------------|----------------------------------|
| Reference | 1 | 1.84 | | Too low to determine |
| Reference | 3 | 6.63 | | Too low to determine |
| Reference | 5 | 12.75 | | 0.099 |
| WRM sorption | 1 | 1.59 | 2.74 | 0.164 |
| WRM sorption | 2 | 3.16 | 2.44 | 0.110 |
| WRM sorption | 3 | 5.30 | 2.04 | 0.117 |
| WRM sorption | 4 | 7.95 | | Not determined |
| WRM sorption | 5 | 11.06 | 1.75 | 0.110 |

Effect of CMC modification on amount of nanosized material**Table 2.** Concentration of nanofibrils in upper phase after centrifugation.

| sample ID | Nanomaterial conc (g/l) |
|--|----------------------------|
| Masuko supermass colloider | |
| unmodified hardwood, 5 pass | 0.099 |
| CMC (WRM) sorption only prior to fibrillation, 1 pass | 0.16 |
| CMC (WRM) sorption only prior to fibrillation, 3 pass | 0.12 |
| CMC (WRM) sorption only prior to fibrillation, 5 pass | 0.11 |
| CMC (WRM) sorption + addition during fibrillation, 2 pass | 0.18 |
| CMC (WRM) sorption + addition during fibrillation, 3 pass | 0.17 |
| CMC (BW) sorption only prior to fibrillation, 1 pass | 0.015 |
| CMC (BW) sorption only prior to fibrillation, 3 pass | not determined |
| CMC (BW) sorption only prior to fibrillation, 5 pass | 0.035 |
| Microfluidics Fluidizer | |
| Unmodified hard wood, 1 + 1 pass | 0.339 |
| Unmodified hard wood, 1 + 2 pass | 0.348 |
| Unmodified hard wood, 1 + 3 pass | 0.452 |
| CMC (BW) sorption only prior to fibrillation, 1 + 1 pass | 0.154 |
| CMC (BW) sorption only prior to fibrillation, 1 + 2 pass | 0.169 |
| CMC (BW) sorption only prior to fibrillation, 1 + 3 pass | 0.218 |
| CMC (BW) addition during fibrillation, 1 + 1 pass | 0.322 |
| CMC (BW) addition during fibrillation, 1 + 2 pass | 0.343 |
| CMC (BW) addition during fibrillation, 1 + 3 pass | 0.415 |
| CMC (BW) sorption + addition during fibrillation, 1 + 1 pass | 0.218 |
| CMC (BW) sorption + addition during fibrillation, 1 + 2 pass | 0.290 |
| CMC (BW) sorption + addition during fibrillation, 1 + 3 pass | 0.196 |
| CMC (WRM) sorption only prior to fibrillation, 1 + 1 pass | 0.129 |

| | |
|---|-------|
| CMC (WRM) sorption only prior to fibrillation, 1 + 2 pass | 0.124 |
| CMC (WRM) sorption only prior to fibrillation, 1 + 3 pass | 0.123 |
| CMC (WRM) addition during fibrillation, 1 + 1 pass | 0.418 |
| CMC (WRM) addition during fibrillation, 1 + 2 pass | 0.407 |
| CMC (WRM) addition during fibrillation, 1 + 3 pass | 0.492 |
| CMC (WRM) sorption + addition during fibrillation, 1 + 1 pass | 0.112 |
| CMC (WRM) sorption + addition during fibrillation, 1 + 2 pass | 0.184 |
| CMC (WRM) sorption + addition during fibrillation, 1 + 3 pass | 0.179 |

Abbreviations: CMC, carboxymethyl cellulose;

BW, low molecular weight CMC (Finnfix BW, CP Kelco, Äänekoski, Finland, DS 0.51);

WRM, high molecular weight CMC (Finnfix WRM, CP Kelco, Äänekoski, Finland)

5

CMC sorption increases the efficiency of the fibrillation (Table 2). Tests using friction grinding indicates that sorption prior to fibrillation in combination with addition during fibrillation gives the highest concentration of fibrils in upper phase after centrifugation. In these cases the total amount of CMC used is also highest, since 20 mg/g was added
10 three times i.e. in total of 60 mg.

However, when fluidizer was used an effective way was to add CMC only during the disintegration.

15 It was thus observed that the upper phase of the CMC modified nanofibrillated cellulose sample contained five times more nanofibrils than the unmodified nanofibrillated cellulose prepared from the same mass.

Effect of CMC modification on strength of test sheets

20 The potential of the modified nanofibrillated cellulose (NFC) as a strength additive is illustrated below. In Table 3 the paper properties of test sheets containing 85% NFC and 15% long fibers are compared. A clear increase in paper strength was observed using the modified NFC as compared to unmodified NFC (reference hardwood). Noteworthy is that the density of the paper produced using modified NFC did not
25 increase although the tensile strength was clearly higher than for unmodified NFC. Satisfying results were obtained already after 1 pass through the friction grinder (Masuko colloider).

Table 3. NFC Paper Sheet Characteristics.

| | TestPoint | Grammage g/m² | Apparent density kg/m³ | Tensile strength kNm/kg | Tear Index Jm/kg | Bending stiffness mNm |
|-------------|------------------|---|--|--|-----------------------------------|--|
| CMC-treated | WRM sorpt. 1p | 66.1 | 991 | 93.17 | 4.51 | 0.104 |
| | WRM sorpt. 3p | 66.2 | 999 | 84.40 | 3.29 | 0.112 |
| | WRM sorpt. 5p | 66.5 | 987 | 84.89 | 2.99 | 0.126 |
| | BW sorpt. 1p | 66.2 | 991 | 86.11 | 3.69 | 0.115 |
| | BW sorpt. 2p | 66.1 | 1000 | 88.04 | 3.20 | 0.107 |
| | BW sorpt. 3p | 67 | 1030 | 84.89 | 2.70 | 0.125 |
| Ref. | hardwood 5p | 67.4 | 1010 | 64.84 | 3.75 | 0.089 |

Abbreviations:

- 5 WRM sorpt., nanofibril sample modified with high molecular weight CMC (WRM);
 BW sorpt., nanofibril sample modified with low molecular weight CMC (BW);
 1p, 2p, 3p and 5p, the amount of the passes through the refiner (refining cycles);
 Ref., hardwood 5p, the corresponding unmodified fiber suspension from hardwood
 passed five times through the friction grinder.
- 10 It was found that the strength of the paper produced from the modified NFC already
 after the initial pass through the refiner, was considerably increased as compared to
 unmodified fibrils. Thus, mechanical treatment can be reduced to one fifth, while still
 achieving considerably improved paper qualities (Table 3).
- 15 The effect of NFC on sheet properties was also studied using NFC as an additive. The
 results are shown in Table 4 and in Figure 1. In these experiments cationic starch (CS,
 25 mg/g) was added to fractionated softwood pulp and adsorbed for 15 minutes,
 whereupon either unmodified or modified NFC was added (30 mg/g) and adsorbed for
 20 15 minutes and sheets were made. Scott Bond is a measure of the internal strength of
 the sheet, measured on Scott Bond Tester, expressed in J/m². In Table 4 the paper
 properties achieved using NFC prepared according to the present method using
 Masuko Mass colloider are shown.
- 25 **Table 4.** Paper Technical paper properties of sheets made from pulp, cationic starch
 (CS) and nanofibrillated cellulose (NFC) at constant ionic strength, pH and after fines

have been removed. NFC was modified using friction grinder (Masuko super colloider). Reference sample contained pulp only or pulp and cationic starch.

| Sample | | NFC | CS + NFC | NFC | CS + NFC |
|-------------------------------|--------|----------------------|----------------------|--------------------------------|--------------------------------|
| | Passes | Tensile index (Nm/g) | Tensile index (Nm/g) | Scott Bond (J/m ²) | Scott Bond (J/m ²) |
| Reference | 5 | 64.6 | 83.37 | 194 | 320 |
| CMC sorption (WRM) | 1 | 70.15 | 90.2 | 180 | 405 |
| CMC sorption (WRM) | 3 | 68.97 | 84.16 | 193 | 531 |
| CMC sorption (WRM) | 5 | 68.26 | 89.49 | 204 | 400 |
| CMC sorption + addition (WRM) | 1 | 67.77 | 85.08 | 211 | 446 |
| CMC sorption + addition (WRM) | 3 | 66.42 | 86.76 | 190 | 559 |

5 Abbreviations:

CS, cationic starch; NFC, nanofibrillated cellulose; CMC, carboxymethyl cellulose; WRM, high molecular weight CMC; BW, low molecular weight CMC

The efficiency of the fibrillation

10

The efficiency of the fibrillation made according to this invention is illustrated by optical microscopy images in Figures 2 and 3. The scale bars in the figures are 500 µm. The decrease in the amount of dark thick fibers shows the efficiency of fibrillation. The finest nanosized material is obviously not visible in optical microscopy.

15

CMC (Finnfix WRM, high molecular weight CMC) was added during fibrillation in fluidizer. In Figure 2 the samples after different amount of passes, 1+1, 1+2 and 1+3 passes, respectively, through the fluidizer are compared, (Figures 2a, 2b and 2c). The decrease in the amount of large particles can be observed.

20

In Figure 3 CMC-modified samples (Figure 3b and 3c) are compared to a sample of unmodified nanofibrillated cellulose (Figure 3a) after 1 + 3 passes through the fluidizer. NFC was modified according to this invention by addition of 10 mg/g dry pulp Finnfix, WRM high molecular weight CMC before each pass (a total of 40 mg/g after 25 1+3 passes) (Figure 3b). The image of NFC modified according to this invention by

addition of 10 mg/g dry pulp Finnfix, BW low molecular weight CMC before each pass (a total of 40 mg/g after 1+3 passes) is shown in Figure 3c. Clearly there are much less large particles left in the samples modified according to this invention than in an unmodified sample.

5

Example 2

Materials

10 Pulps

Bleached softwood kraft pulp made from Scots Pine (*Pinus sylvestris*) was acquired from UPM-Kymmene Oyj, Kaukas pulp mill in air dry sheets. The dry pulp samples were swollen in deionized water and beaten in a Valley beater according to standard 15 SCAN-C 25:76. Unless otherwise stated the beating time was 10 min. Thereafter any remaining metal ions were removed by acid treatment, and the fibres were washed into their Na-form according to method described by Swerin et al. (1990). Finally the samples were dewatered and stored in a refrigerator at ca. 20 % consistency. Prior to 20 use the samples were diluted to desired consistency and cold disintegrated according to standard SCAN-C 18:65. The salt concentration of the suspensions was adjusted to 9 mM NaCl and 1 mM NaHCO₃, and the pH was adjusted to 8.0.

Polyelectrolytes

Two different CMC (carboxymethyl cellulose) grades from CP Kelco Oy (Äänekoski, 25 Finland) were used for preparation of modified NFC. They are hereafter referred to as WRM (high molecular weight) CMC and BW (low molecular weight) CMC.

In sheet preparation and dewatering experiments cationic starch (CS, Raisamyl 50021 from Ciba Specialty Chemicals Ltd), of which degree of substitution (D.S.) ca 0.035, 30 and charge density of ca. 0.2 meq/g was used to enhance the retention of the NFC on the fibres.

Nanofibrillar cellulose

Different grades of modified NFC were used. The NFC was prepared from never dried 35 birch pulp, obtained from UPM-Pietarsaari and grinded to SR 90. NFC samples were prepared either using the Masuko Mass Colloider (Masuko Sangyo Co., Kawaguchi,

Japan) or the laboratory scale fluidizer (M-110Y, Microfluidics Corp.). As a reference a sample prepared by passing the pulp 5 times through the Masuko colloider was used.

Electrolytes (NaCl and NaHCO₃) were of analytical grade and dissolved in deionized

5 water. Analytical grade HCl and NaOH solutions were used for pH adjustments. The used water was deionized.

Methods

10 Sheet forming

The pH and electrolyte concentration of the fibre suspension was kept constant using 1 mM NaHCO₃ and 9 mM NaCl. Polyelectrolyte (cationic starch or PDADMAC) was first added to the fibre suspension and the suspension was vigorously mixed for 15 min.

15 The NFC was dispersed using ultrasound, added to polyelectrolyte treated pulp and the suspension was mixed for another 15 min. Sheets were formed in a laboratory sheet former, Lorentzen & Wettre AB, Sweden (ISO 5269-1) with a 100 mesh wire. The grammage of sheets was adjusted to about 60 g/m² by dilution of the suspension when necessary. The sheets were wet pressed under 4.2 bars for 4 minutes and dried

20 in a frame to avoid shrinkage during drying (105°C for 3 minutes). The samples were conditioned over night in 50% humidity and 20°C according to the standard SCAN_P 2:75 before testing.

Sheet testing

25 All the sheet properties were measured according to SCAN or ISO standards. Grammage (ISO 536:1995(E)), thickness and bulk were determined with Lorentzen & Wettre micrometer (ISO 534:2005(E)). The Scott Bond was determined using Huygen Internal bond tester) and Tensile strength, fracture toughness index and TEA were measured with Lorentzen & Wettre tearing tester (SE009 Elmendorf, SCAN-P 11:73).

30

Results

Strength of sheets

35 In Tables 5 and 6 the sheet properties of sheets made using NFC prepared with Masuko supermass colloider (Table 5) or microfluidics fluidizer (Table 6) are summarized. Cationic starch, CS, Raisamyl 50021 was used in the experiments presented in table 5 and 6.

Table 5. Sheet properties of sheets made from pulp, cationic starch (CS, 25 mg/g)) and nanofibrillated cellulose (NFC, 30 mg/g). NFC was prepared with Masuko supermass colloider. Reference sample contains only pulp.

| NFC grade | Passes | Grammage (g/m ²) | Density (kg/m ³) | Tensile index (Nm/g) | Scott Bond (J/m ²) |
|-------------------------|--------|------------------------------|------------------------------|----------------------|--------------------------------|
| Reference | No NFC | 60,8 | 558 | 58,35 | 132 |
| WRM sorption | 1 | 58 | 579 | 90,2 | 405 |
| WRM sorption | 3 | 58,3 | 599 | 84,16 | 531 |
| WRM sorption | 5 | 56,4 | 573 | 89,49 | 400 |
| WRM sorption + addition | 1 | 59 | 584 | 85,08 | 446 |
| WRM sorption + addition | 3 | 61,4 | 608 | 86,76 | 559 |
| BW sorption | 1 | 59 | 564 | 76,26 | 347 |
| BW sorption | 3 | 59,5 | 582 | 84,62 | 426 |
| BW sorption | 5 | 59,8 | 603 | 85,77 | 470 |

5

Abbreviations: WRM, high molecular weight CMC; BW, low molecular weight CMC

Table 6. Sheet properties of sheets made from pulp, cationic starch (CS, 25 mg/g)) and nanofibrillated cellulose (NFC, 30 mg/g). NFC was prepared with microfluidics fluidizer. Reference sample contains pulp, cationic starch (CS) and unmodified NFC.

| NFC grade | Passes | Grammage (g/m ²) | Density (kg/m ³) | Tensile index (Nm/g) | Scott Bond (J/m ²) |
|-------------------------|--------|------------------------------|------------------------------|----------------------|--------------------------------|
| BW sorption | 4 | 62,4 | 575 | 79,26 | 383 |
| BW addition | 4 | 62,8 | 597 | 85,16 | 520 |
| WRM addition | 4 | 62,6 | 589 | 82,68 | 427 |
| WRM sorption | 4 | 62,8 | 592 | 79,91 | 520 |
| REF no CMC | 4 | 62,3 | 572 | 82,97 | 411 |
| BW sorption + addition | 2 | 65,1 | 589 | 74,21 | 480 |
| BW sorption + addition | 3 | 63,5 | 583 | 78,1 | 446 |
| BW sorption + addition | 4 | 66 | 608 | 84,59 | 517 |
| WRM sorption + addition | 2 | 62,9 | 574 | 84,63 | 380 |
| WRM sorption + addition | 3 | 62,6 | 593 | 82,65 | 434 |
| WRM sorption + addition | 4 | 63,3 | 608 | 83,1 | 561 |

Abbreviations: WRM, high molecular weight CMC; BW, low molecular weight CMC

In Figure 5 both the way of preparing NFC and the effect of passes through the Fluidizer are compared. The corresponding microscopy images show that the fibril size is decreasing with the passes through the Fluidizer. No clear difference between

5 Masuko and Fluidizer samples are found in this case. Compared to the reference at 132 J/m², the Scott Bond increases clearly and also compared to unmodified NFC (411 J/m² after 4 passes) CMC modified NFC gives higher Scott Bond.

The present invention has been described herein with reference to specific
10 embodiments. It is, however clear to a person skilled in the art that the process(es) may be varied within the bounds of the claims.

CLAIMS

1. A method for producing modified nanofibrillated cellulose, **characterized** by the steps of
 - 5 - preparing a suspension containing fibers from cellulosic material;
 - adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under special conditions; and
 - subjecting the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration;
 - 10 to obtain modified nanofibrillated cellulose modified with said cellulose derivative or polysaccharide or polysaccharide derivative.
2. The method according to claim 1, **characterized** in that the cellulosic material is a pulp such as a chemical pulp, mechanical pulp, thermo mechanical pulp or chemi-
 - 15 thermo mechanical pulp produced from wood, non-wood material or recycled fibers.
3. The method according to claim 2, **characterized** in that wood is from softwood tree, hardwood tree, or a mixture of softwoods and hardwoods.
- 20 4. The method according to any of the preceding claims, **characterized** in that the cellulose derivative is carboxymethyl cellulose.
5. The method according to claims 1 to 4, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers
 - 25 prior to or during mechanical disintegration.
6. The method according to claims 1 to 5, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers both prior to and during mechanical disintegration.
- 30 7. The method according to any of the preceding claims, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers at a temperature of at least 5°C, preferably at a temperature of at least 20°C, the upper limit being 180°C.

8. The method according to any of the preceding claims, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers at a temperature of 75°C - 80°C.

5 9. The method according to any of the preceding claims, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers for at least 1 minute, preferably for at least 1 hour, preferably for 2 hours.

10 10. The method according to any of the preceding claims, **characterized** in that the method takes place in the presence of monovalent or polyvalent cations such as aluminium, calcium and/or sodium salts, preferably CaCl₂.

15 11. The method according to any of the preceding claims, **characterized** in that the pH value of the fiber suspension is at least pH 2, preferably from pH 7.5 to 8, the upper limit being pH 12.

20 12. The method according to any of the preceding claims, **characterized** in that the amount of added cellulose derivative or polysaccharide or polysaccharide derivative is at least 5 mg/g of fiber suspension, preferably from 10 to 50 mg/g, preferably 20 mg/g, the upper limit being 1000 mg/g of fiber suspension.

25 13. The method according to any of the preceding claims, **characterized** in that mechanical disintegration is carried out with a refiner, grinder, homogenizer, colloider, friction grinder, fluidizer such as microfluidizer, macrofluidizer or fluidizer-type homogenizer.

30 14. The method according to any of the preceding claims, **characterized** in that the fiber suspension is passed through mechanical disintegration at least once, preferably 2, 3, 4 or 5 times.

35 15. The method according to any of the preceding claims, **characterized** in that the fiber suspension containing the cellulose derivative or polysaccharide or polysaccharide derivative is redispersed in water to a concentration of at least 0,1%, preferably at least 1%, more preferably at least 2%, 3%, 4% or 5%, up to 10% prior to mechanical disintegration.

16. A modified nanofibrillated cellulose obtainable by a method according to any of claims 1 to 15 and characterized by that a diameter of nanofibrillated cellulose is less than 1 μm .

5 17. Use of modified nanofibrillated cellulose according to claim 16 in food products, composite materials, concrete, oil drilling products, coatings, cosmetic products, pharmaceutical products or paper.

18. A paper containing the modified nanofibrillated cellulose of claim 16.

10

19. A paper according to claim 18, **characterized** in that the amount of modified nanofibrillated cellulose is at least 0,2%, preferably at least 1%, 2%, 3%, 4% or 5%, up to 20% by weight of the paper.

15

20. Use of a method according to claims 1 to 15 for producing modified nanofibrillated cellulose energy efficiently.

21. Use of a method according to claims 1 to 15 for producing paper with improved properties.

20

22. A method for manufacturing paper with improved properties **characterized** by the steps of

- preparing a fiber suspension from cellulosic material; and
- adding modified nanofibrillated cellulose according to claim 16 to the fiber suspension.

25

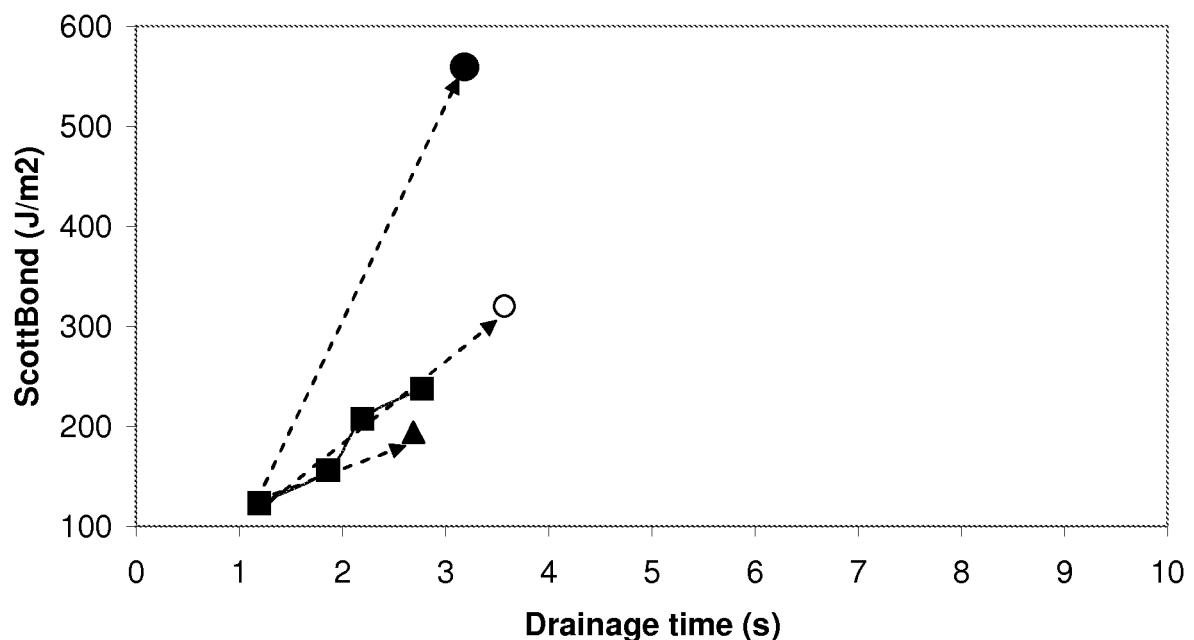


Fig. 1

2 / 5



2c



2b



2a

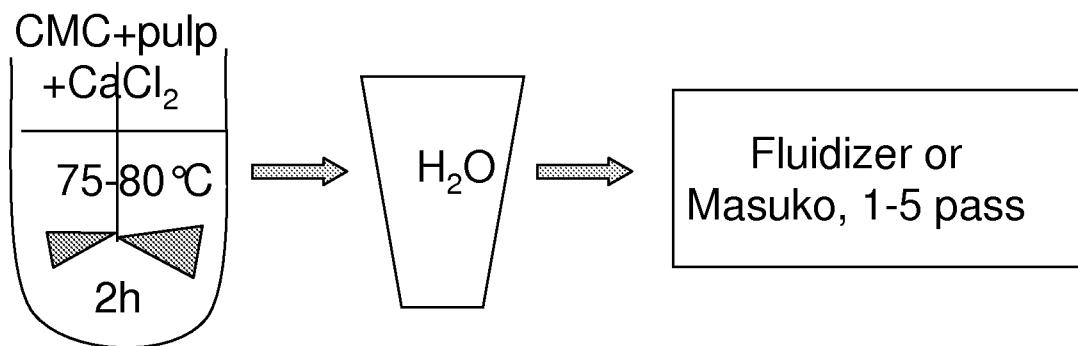
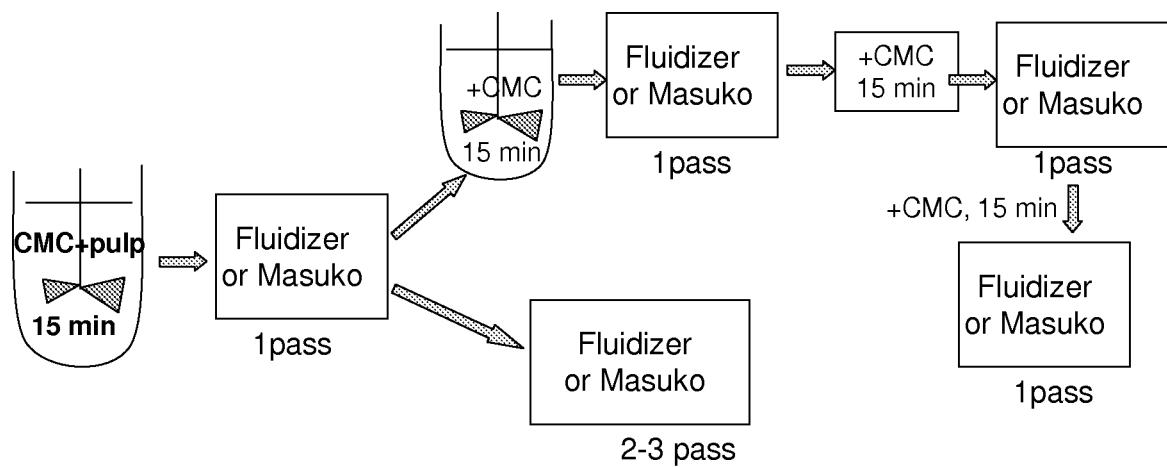
Fig. 2

3 / 5



Fig. 3

4 / 5

**Fig. 4 A****Fig. 4 B**

5 / 5

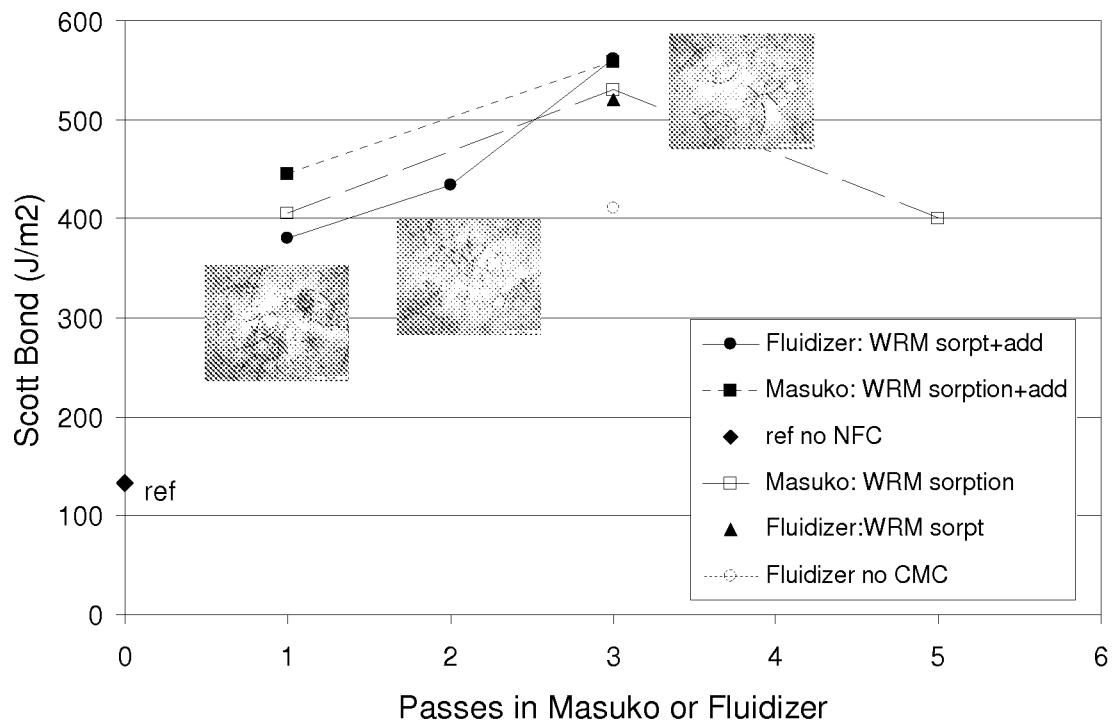


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2010/050096

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: D21H, D21D, D21C, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI, XPESP

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | US 2005272836 A1 (YAGINUMA YOSHIHITO et al.) 08 December 2005 (08.12.2005) claims 10-13, paragraphs [0012]-[0034], [0049], [0047], [0070], [0078], [0083] | 1-17 |
| A | WO 2007001229 A1 (AKZO NOBEL NV et al.) 04 January 2007 (04.01.2007) page 1, line 28 - page 2, line 29; page 3, line 33 - page 4, line 34; example 3 | |
| E | WO 2009126106 A1 (STFI PACKFORSK AB et al.) 15 October 2009 (15.10.2009) the whole document | 1-5, 7-18, 20, 21 |

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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- "P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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|--|---|
| Date of the actual completion of the international search 17 June 2010 (17.06.2010) | Date of mailing of the international search report 22 June 2010 (22.06.2010) |
| Name and mailing address of the ISA/FI National Board of Patents and Registration of Finland P.O. Box 1160, FI-00101 HELSINKI, Finland Facsimile No. +358 9 6939 5328 | Authorized officer Heimo Koskinen Telephone No. +358 9 6939 500 |

INTERNATIONAL SEARCH REPORT

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|---|
| International application No. PCT/FI2010/050096 |
|---|

| Patent document cited in search report | Publication date | Patent family members(s) | Publication date |
|--|------------------|--|--|
| US 2005272836 A1 | 08/12/2005 | TW 231819B B WO 2004007558 A1 EP 1553103 A1 CN 1668646 A AU 2003281045 A1 JP 2004041119 A | 01/05/2005 22/01/2004 13/07/2005 14/09/2005 02/02/2004 12/02/2004 |
| WO 2007001229 A1 | 04/01/2007 | NZ 564484 A NO 20080479 A KR 20080023739 A MX 2007015340 A AR 055978 A1 ZA 200711043 A RU 2008102975 A JP 2008544112T T EP 1896508 A1 CN 101208358 A CA 2612065 A1 AU 2006262963 A1 | 30/04/2010 28/03/2008 14/03/2008 11/02/2008 12/09/2007 24/06/2009 10/08/2009 04/12/2008 12/03/2008 25/06/2008 04/01/2007 04/01/2007 |
| WO 2009126106 A1 | 15/10/2009 | SE 0800807 A | 11/10/2009 |

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International application No.
PCT/FI2010/050096

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Published:

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/66600 A1

(54) Title: STABILIZED MICROFIBRILLAR CELLULOSE

(57) Abstract: A derivatized microfibrillar cellulose, derivatized to contain a substituent that provides cationic charge. A method for producing a derivatized microfibrillar cellulose to include a substituent that provides cationic charge, which may include derivatizing a microfibrillar cellulose to obtain a derivatized microfibrillar cellulose, microfibrillizing a derivatized non-microfibrillar cellulose to produce a derivatized microfibrillar cellulose, or microfibrillizing and derivatizing a non-microfibrillar cellulose substantially simultaneously. A method of modifying the rheological properties of a composition of matter using derivatized microfibrillar cellulose. Methods of improving coatings, paper manufacture, and the stability of emulsions, dispersions, and foams using a derivatized microfibrillar cellulose. Compositions that include derivatized microfibrillar cellulose, including paper compositions, comestible compositions, non-comestible spreadable compositions, and emulsions, dispersion, and foams.

DescriptionSTABILIZED MICROFIBRILLAR CELLULOSEFIELD OF THE INVENTION

5 The present invention relates to stabilized microfibrillar cellulose. More specifically, the present invention relates to microfibrillar cellulose that is electrostatically stabilized by cationic groups.

BACKGROUND OF THE INVENTION

10 Polysaccharides are often found in nature in forms having fibrous morphology. Polysaccharides which are not found in nature in fibrous form can often be transformed into fibrous morphologies using fiber-spinning techniques. Whether the fibrous morphology is of natural or artificial origin, the polysaccharide will often be present in such a form that the fibers can be reduced to fibrillar and microfibrillar sub-morphologies through the application of energy.

15 Fibrillar and microfibrillar cellulose obtained in this manner have been considered for use in applications, including use as additives to aqueous-based systems in order to affect rheological properties, such as viscosity. The use level of these materials in aqueous systems is often on the order of about 2% by weight, below which these materials have a tendency to poorly occupy volume,

20 and to exhibit gross inhomogeneities in distribution.

Microfibrillated cellulose and its manufacture are discussed in U.S. Patent Nos. 4,500,546; 4,487,634; 4,483,743; 4,481,077; 4,481,076; 4,464,287; 4,452,722; 4,452,721; 4,378,381; 4,374,702; and 4,341,807, the disclosures of which are hereby incorporated by reference thereto. These documents, in part, purport to describe microfibrillated cellulose in stable, homogenous suspensions, characterized as useful in end use products including foods, cosmetics, pharmaceuticals, paints, and drilling muds.

Cellulose nanofibrils are characterized in WO 98/02486 (PCT/FR97/01290), WO 98/02487 (PCT/FR97/01291), and WO 98/02499 (PCT/FR97/01297), the disclosures of which are hereby incorporated by

reference. Nanofibrils are characterized as having diameters in the range of about 2 to about 10 nanometers.

EP 845495 discusses cationic cellulose particulate which is characterized as insoluble, positively charged, and used in water treatment, specifically to treat water in a paper manufacturing plant. In papermaking this cationic particulate is said to remove anionic trash from the water. The particles are obtained by milling, which is stated to reduce particle size uniformly such that particles are typically round as described by a length/diameter ratio of approximately 1.

Particle size is stated to be 0.001 mm (i.e., 1 μm), and preferably 0.01 mm (10 μm).

EP 859011 ("EP '011") is directed to a process for obtaining cationic cellulose microfibrils or their soluble derivatives. The process is described as including making a cationic cellulose derivative and processing the derivative through a high-pressure homogenizer to form transparent gels. The product can be dehydrated and rehydrated. Viscosity measurements are reported on the product at a concentration of 2% in water. EP '011 indicates that the degree of substitution ("DS") of the cellulose can range from 0.1 to 0.7, with a DS of between 0.2 and 0.7, 0.3 and 0.6, and 0.5 and 0.6 characterized as representing increasing orders of preference. The examples show cellulose with a DS ranging from a low of 0.24 up to 0.72. Gelling is reported to occur above a microfibril concentration of 10 g/L, or above 1%, in water. EP '011 defines gelling as occurring when $G' > G''$, where G' is the dynamic storage modulus and G'' is the dynamic loss modulus.

Microfibrillated chitosan is reported to form uniplanar, oriented sheets upon drying by H. Yokata, J. Polymer Sci., Part C: Polymer Letters, **24**:423-425 (1986). This article mentions that at a level of 4% chitosan in water, a gel is formed having a viscosity of 26,600 cps (Brookfield, 20° C, rotor #7, 10rpm). The microfibrillated chitosan is made by homogenization of commercial chitosan flakes in a Gaulin homogenizer. The commercial chitosan is deacetylated using sodium hydroxide.

JP 59 [1984]-84938 discusses a method for producing a chitosan suspension. Commercial chitosan separated and purified from crabs and lobsters is pulverized to pieces having maximum length of about 1-2 mm. The pieces are then suspended in water at up to 15% chitosan, and are run in multiple passes

5 through a high-pressure homogenizer at between 3,000 and 8,000 psi.

It would be desirable to obtain microfibrillar cellulose capable of forming a gel at concentrations of 1% or less, thereby providing economy and ease of formulation, while still providing necessary rheological behavior and homogeneity of distribution.

10 In addition, there is a continuing need in industry to improve the stability of commercial emulsions, such as paper sizing emulsions. At present, one method for stabilizing such emulsions is the addition of charged materials, such as cationic starches, which may be added in amounts equal to 10-20% by weight of the size component. Interaction with anionic components, such as sulfonates, can

15 also improve stability. However, emulsion failure still takes place in such emulsions, either through density-driven separation, also referred to as creaming, or through gellation. It would accordingly be desirable to develop a material that could be added to emulsions to provide long-term stability.

SUMMARY OF THE INVENTION

20 The present invention is directed to a derivatized microfibrillar cellulose which is derivatized to include a substituent that provides cationic charge and is capable of forming a gel in water at a concentration of less than 1%. The cellulose used to prepare the derivatized microfibrillar cellulose may be obtained from any suitable source, including but not limited to chemical pulps, mechanical

25 pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.

Preferably the cellulose is obtained from purified, optionally bleached wood

pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; or vegetables.

The substituent which provides cationic charge to the derivatized microfibrillar cellulose may be, or include, an amine. A quaternary amine is
5 particularly preferred.

The derivatized microfibrillar cellulose may form a gel in water throughout the concentration range of between about 0.01 % and about 100%, or throughout the concentration range of between about 0.01 % and about 50 %, in water.

Moreover, the derivatized microfibrillar cellulose may form a gel at a
10 concentration of less than about 1% in water, and preferably forms a gel at least one point in the concentration range of from about 0.05 % up to about 0.99% in water.

The derivatized microfibrillar cellulose of the present invention may include a solvent in which the derivatized microfibrillar cellulose is substantially
15 insoluble. Suitable solvents include water, alcohol, or oil, with water being preferred.

The derivatized microfibrillar cellulose may have a degree of substitution of less than about 0.5, or of less than about 0.35, or of less than about 0.2, or of less than about 0.18, or of less than about 1.15. Preferably the degree of substitution
20 is between about 0.02 and about 0.5, and more preferably between about 0.05 and about 0.2.

A particularly preferred embodiment of the present invention is microfibrillar 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose having a degree of substitution of less than about 2.0, preferably of less than
25 about 0.35, more preferably of between about 0.02 and about 0.20, and most preferably between about 0.1 and about 0.2.

The derivatized microfibrillar cellulose may form part of a comestible composition of matter, including but not limited to a low fat, reduced fat, or fat-free mayonnaise, or a salad dressing. When it forms part of a comestible
30 composition of matter, the derivatized microfibrillar cellulose may include a

Cash et al 2

Description

STABILIZED MICROFIBRILLAR CELLULOSE

FIELD OF THE INVENTION

5 The present invention relates to stabilized microfibrillar cellulose. More specifically, the present invention relates to microfibrillar cellulose that is electrostatically stabilized by cationic groups.

BACKGROUND OF THE INVENTION

10 Polysaccharides are often found in nature in forms having fibrous morphology. Polysaccharides which are not found in nature in fibrous form can often be transformed into fibrous morphologies using fiber-spinning techniques. Whether the fibrous morphology is of natural or artificial origin, the polysaccharide will often be present in such a form that the fibers can be reduced to fibrillar and microfibrillar sub-morphologies through the application of energy.

15 Fibrillar and microfibrillar cellulose obtained in this manner have been considered for use in applications, including use as additives to aqueous-based systems in order to affect rheological properties, such as viscosity. The use level of these materials in aqueous systems is often on the order of about 2% by weight, below which these materials have a tendency to poorly occupy volume,

20 and to exhibit gross inhomogeneities in distribution.

Microfibrillated cellulose and its manufacture are discussed in U.S. Patent Nos. 4,500,546; 4,487,634; 4,483,743; 4,481,077; 4,481,076; 4,464,287; 4,452,722; 4,452,721; 4,378,381; 4,374,702; and 4,341,807, the disclosures of which are hereby incorporated by reference thereto. These documents, in part,

25 purport to describe microfibrillated cellulose in stable, homogenous suspensions, characterized as useful in end use products including foods, cosmetics, pharmaceuticals, paints, and drilling muds.

Cellulose nanofibrils are characterized in WO 98/02486 (PCT/FR97/01290), WO 98/02487 (PCT/FR97/01291), and WO 98/02499 (PCT/FR97/01297), the disclosures of which are hereby incorporated by

pharmaceutically active ingredient, and may at least partially provide for the controlled, sustained, or delayed release of the pharmaceutically active ingredient.

Alternatively, the derivatized microfibrillar cellulose may form part of a

5 non-comestible composition of matter, such as, by way of non-limiting example, a wound care product. Suitable wound care products include, without limitation, wound dressings and ostomy rings. In another embodiment, the non-comestible composition of matter may be a skin care lotion or cream, a sunscreen lotion or cream, or an oral care composition, such as a toothpaste.

10 The non-comestible composition of matter may further be or include an agricultural composition, such as a fertilizer, herbicide, fungicide, or pesticide. The derivatized microfibrillar cellulose may provide at least partially for the controlled, sustained, or delayed release of the fertilizer, herbicide, or pesticide.

15 In an alternative embodiment, the non-comestible composition of matter may be a drilling fluid.

In another embodiment, the present invention is directed to a paper composition which contains the derivatized microfibrillar cellulose described herein.

20 The present invention further includes a method for producing the derivatized microfibrillar cellulose described herein, which involves at least one of the following steps:

- (a) a derivatizing step of treating a microfibrillar cellulose to obtain a derivatized microfibrillar cellulose;
- (b) a microfibrillizing step of treating a derivatized non-microfibrillar cellulose to produce a derivatized microfibrillar cellulose; or,
- (c) microfibrillizing and derivatizing a non-microfibrillar cellulose substantially simultaneously.

25 In the above method, the derivatized microfibrillar cellulose is derivatized to include a substituent that contains cationic charge, as for example by the

presence of amine groups. Preferably the derivatizing step involves derivatizing the cellulose with a quaternary amine reagent, such that the derivatized microfibrillar cellulose includes quaternary amine functionalized cellulose.

The derivatizing step of the above method may include contacting a non-

5 microfibrillar cellulose with a swelling agent. This contact may occur under alkaline conditions, and the swelling agent may be an anionic reagent. Moreover, the alkaline conditions may include contacting the cellulose with the anionic reagent in the presence of an alkaline reagent which is at least one of sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an
10 alkali silicate, an alkali aluminate, an alkali carbonate, an amine, ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof. The derivatizing step may further take place at high solids.

In a preferred method, the derivatized microfibrillar cellulose is obtained by:

- 15 (a) derivatizing cellulose with 3-chloro-2-hydroxypropyl trimethylammonium chloride under alkaline conditions to produce 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose;

(b) suspending the 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose in water to form a suspension; and

20 (c) homogenizing the suspension to produce microfibrillated 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose.

The microfibrillizing step of the above method may include applying energy to the cellulose under conditions sufficient to produce microfibrillar cellulose, and the cellulose may be treated with enzyme prior to microfibrillizing.

25 Any suitable approach may be used to apply sufficient energy to the cellulose to obtain microfibrillar cellulose, including, without limitation, one or more of homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, and milling. Use of a homogenizer is preferred, and preferred homogenization
30 conditions include passing the non-microfibrillar cellulose through a pressure

differential of at least about 3,000 psi, and more preferably passing the non-microfibrillar cellulose through the homogenizer at least three times.

Preferably, the derivatized microfibrillar cellulose obtained by the above methods forms a gel throughout a concentration range of from about 0.01 % to 5 about 100% in water, and more preferably throughout a concentration range of between about 0.01 % and about 50 % in water. Alternatively, the derivatized microfibrillar cellulose should form a gel at at least one point in the concentration range of from about 0.05 % to about 0.99% in water. In a particularly preferred embodiment, the derivatized microfibrillar cellulose forms a gel at a 10 concentration of about 0.9% in water.

The present invention extends to derivatized microfibrillar cellulose produced by the above-described method, including it's the described variations of the method.

In yet another embodiment, the present invention includes a method of 15 modifying the rheological properties of a composition of matter by incorporating the derivatized microfibrillar cellulose into the composition of matter, which may be a liquid, such as water. The derivatized microfibrillar cellulose may be used in an amount which is effective to provide scale control and/or corrosion control.

Alternatively, the derivatized microfibrillar cellulose may be used to modify one 20 or more of the viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention of the composition of matter. Compositions whose rheological properties may be modified in this manner include foods, pharmaceuticals, neutraceuticals, personal care products, fibers, papers, paints, coatings, and construction compositions. More 25 specifically, possible compositions include oral care products; creams or lotions for epidermal application, including moisturizing, night, anti-age, or sunscreen creams or lotions; food spreads, including reduced fat, low fat, or fat free food spreads (for example, mayonnaise); and drilling fluids.

Alternatively, the derivatized microfibrillar cellulose may be incorporated 30 into a coating composition in order to improve its physical and/or mechanical

properties. Those properties may include one or more of film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

The derivatized microfibrillar cellulose may further be incorporated into the manufacture of paper and paper products in order to improve at least one of sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, absorbency, film formation, membrane formation, and polyelectrolyte complexation during manufacture. Microfibrillated quaternary amine functionalized cellulose is particularly preferred for use in this method.

In one embodiment of this method, the microfibrillated quaternary amine functionalized cellulose may be used to increase the rate of drainage and/or dewatering during paper manufacture. In another embodiment, the microfibrillated quaternary amine functionalized cellulose may be used for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture. Representative dispersed particles which may be retained in this manner include pulp fines, fillers, sizing agents, pigments, clays, detrimental organic particulate materials, detrimental inorganic particulate materials, and combinations thereof. In a yet further embodiment, the microfibrillated quaternary amine functionalized cellulose may be used in a papermaking machine to improve the uniformity of formation of a sheet of paper during its manufacture. Additionally, the microfibrillated quaternary amine functionalized cellulose may be used in a papermaking machine to improve the strength of a sheet of paper produced on a paper machine.

In each of the embodiments described in the above paragraph, the microfibrillated quaternary amine functionalized cellulose may be used in the presence of one or more of the following: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.

The derivatized microfibrillar cellulose may further be used in a method for improving the stability of an emulsion, dispersion, or foam system, by including the derivatized microfibrillar cellulose in the system. Where the system being treated is an emulsion, the emulsion may be produced by processing of an emulsion formulation, in which case the derivatized microfibrillar cellulose may be added to the emulsion formulation prior to completion of processing of the emulsion formulation. In one variation, a non-microfibrillated derivatized cellulose is added to the emulsion formulation prior to completion of processing, and the emulsion formulation is then processed under conditions sufficient to 5 microfibrillate the non-microfibrillated derivatized cellulose. In another variation, a microfibrillated non-derivatized cellulose is added to the emulsion formulation prior to completion of processing, and the emulsion formulation is then processed under conditions sufficient to derivatize the microfibrillated non-derivatized cellulose. In yet a third variation, a non-microfibrillated, non-10 derivatized cellulose is added to the emulsion formulation prior to completion of processing, and the emulsion formulation is further processed under conditions sufficient to both microfibrillate and derivatize the non-microfibrillated, non-derivatized cellulose.

15

Emulsion systems which may be treated in this manner include water-in-oil and oil-in-water emulsions. The present invention includes the system produced by the above method.

In a yet further embodiment, the present invention extends to a system comprising an emulsion, dispersion, or foam containing a the derivatized microfibrillar cellulose.

25 In another embodiment, the present invention includes a polyelectrolyte complex containing the derivatized microfibrillar cellulose.

The derivatized microfibrillar cellulose of the present invention may also be used in a method for treating wastewater, which includes the step of adding, to the wastewater, a amount of the derivatized microfibrillar cellulose sufficient to 30 treat the wastewater. Materials being treated by this method in the wastewater

may include, by way of non-limiting example only, anionic contaminants and color bodies.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the dynamic mechanical spectra of Sample 1 from Table 4.

5 Fig. 2 shows the dynamic mechanical spectra of Sample 2 from Table 4.

Fig. 3 shows the dynamic mechanical spectra of Sample 3 from Table 4.

Fig. 4 shows the dynamic mechanical spectra of Sample 4 from Table 4.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises stabilized microfibrillar cellulose. Sources

10 of cellulose for use in this invention include the following: (a) wood fibers, such as from chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint; (b) seed fibers, such as from cotton; (c) seed hull fiber, such as from soybean hulls, pea hulls, corn hulls;

(d) bast fibers, such as from flax, hemp, jute, ramie, kenaf; (e) leaf fibers, such as

15 from manila hemp, sisal hemp; (f) stalk or straw fibers, such as from bagasse,

corn, wheat; (g) grass fibers, such as from bamboo; (h) cellulose fibers from

algae, such as velonia; (i) bacteria or fungi; and (j) parenchymal cells, such as

from vegetables and fruits, and in particular sugar beets, and citrus fruits such as

lemons, limes, oranges, grapefruits. Microcrystalline forms of these cellulose

20 materials may also be used. The cellulose may be used as is, or spinning may be

used to generate or improve fibrous structure. Preferred cellulose sources are (1)

purified, optionally bleached, wood pulps produced from sulfite, kraft (sulfate),

or prehydrolyzed kraft pulping processes; (2) purified cotton linters; and, (3)

fruits and vegetables, in particular sugar beets and citrus fruits. The source of the

25 cellulose is not limiting, and any source may be used, including synthetic

cellulose or cellulose analogs.

Cellulose is found in nature in several hierarchical levels of organization

and orientation. Cellulose fibers comprise a layered secondary wall structure

within which macrofibrils are arranged. Macrofibrils comprise multiple

30 microfibrils which further comprise cellulose molecules arranged in crystalline

and amorphous regions. Cellulose microfibrils range in diameter from about 5 to about 100 nanometers for different species of plant, and are most typically in the range of from about 25 to about 35 nanometers in diameter. The microfibrils are present in bundles which run in parallel within a matrix of amorphous
5 hemicelluloses (specifically xyloglucans), pectinic polysaccharides, lignins, and hydroxyproline rich glycoproteins (includes extensin). Microfibrils are spaced approximately 3-4 nm apart with the space occupied by the matrix compounds listed above. The specific arrangement and location of the matrix materials and how they interact with the cellulose microfibrils is not yet fully known. Further
10 background on the structure, functions, and biogenesis of native cellulose may be found in Haigler, C.H., Cellular Chemistry and Its Applications, Nevell, pp. 30-83 (1985), the entirety of which is hereby incorporated by reference.

For purposes of the present invention microfibrils refer to small diameter, high length-to-diameter ratio substructures which are comparable in dimensions
15 to those of cellulose microfibrils occurring in nature. By way of non-limiting example, cellulose microfibrils may have diameters in the range of about 5 to about 100 nanometers, combined with lengths providing high aspect ratios, such as in excess of 100, in excess of 500, or in excess of 1,000. While the present specification and claims refer to microfibrils and microfibrillation, the scope of
20 the present invention also includes nanofibrils, and the rheology modification, stabilization, and other properties that may be obtained with microfibrils by practicing the present invention may also be obtained using nanofibrils, either alone or in combination with microfibrils.

The derivatized microfibrillar cellulose of the present invention is
25 characterized by being in microfibrillar form, and by the presence of cationic substituents that provide electrostatic functionality. The amount of substituent present may be quantified by the degree of substitution, or DS. The degree of substitution, which will vary with the molecular weight of the cellulose, is the average number of substituted hydroxyl groups per anhydroglucose unit, while
30 the molar substitution is the average number of substituent groups added per

anhydroglucose unit. The DS determines the solubility of the derivatized cellulose, and may be readily adjusted to obtain a derivatized cellulose that is substantially insoluble in the environment of use, whether aqueous or non-aqueous. While the environment of use will frequently be aqueous, the 5 derivatized microfibrillar cellulose of the present invention has utility in applications having other solvents or liquid carriers, such as paints, coating, lacquers, oil-rich foods, inks (including but not limited to ink-jet inks), and water-in-oil emulsions.

Any suitable method may be used to obtain the derivatized microfibrillar 10 cellulose. In particular, the steps of microfibrillation and derivatization to impart electrostatic functionality to the cellulose may be carried out separately or combined to arrive at the end result. Therefore, a non-microfibrillar cellulose starting material may be derivatized with cationic groups and then microfibrillated, or may first be microfibrillated and then derivatized. 15 Alternatively, if the starting material is microfibrillar cellulose, only the derivatizing step would be necessary, whereas if the starting material is a cellulose that has already been properly derivatized with cationic groups, only the microfibrillation step is required.

The degree of substitution of the cellulose should be sufficiently low so that 20 the derivatized microfibrillar cellulose will be substantially insoluble in the solvent or carrier that is present in the intended environment of use. In many applications the solvent or carrier will be water, and in such applications the degree of substitution should be such that the derivatized microfibrillar cellulose is substantially insoluble in water. However, in other applications a polar solvent 25 or carrier (such as an alcohol) may be used having different solubility characteristics, or a non-polar solvent or carrier (such as an oil) may be used, and in such cases the degree of substitution should be adjusted to obtain a derivatized microfibrillar cellulose that is substantially insoluble in the solvent or carrier used in the application of interest, which, for purposes of convenience, will 30 hereafter be referred to as the "solvent of use". Functionally, the derivatized

microfibrillar cellulose should be sufficiently insoluble in the environment of use to provide the desired properties in the intended application.

The presence of substantially insoluble material may be confirmed by observation of a 1-5% suspension of the material in question in the solvent or carrier of use under a light microscope at sufficient magnification to see insoluble material. A size determination may be made by preparing a suspension of the material under consideration at approximately 0.1-0.01% in a liquid non-solvent which is effective in dispersing microfibrils. This suspension is then dried on a transmission electron microscope (TEM) grid; the sample is coated to protect it from electron beam damage, and examined at sufficient magnification and focus to observe structure in the 1-1000 nanometer range. If microfibrillar elements are present they can be detected under these conditions, and the combination of insolubility under the light microscope and microfibrillar structure under the TEM will indicate the presence of substantially insoluble microfibrillar material.

For purposes of simplicity, unless specifically indicated otherwise the term "substituents" shall be used herein to mean chemical species that provide electrostatic functionality to the cellulose through cationic charge. In addition, "electrostatic" means cationic charge. "Derivatization" refers not only to chemical reactions resulting in covalent bonds, but to any process whereby the substituents become sufficiently associated with the cellulose to provide the rheological and other benefits of the present invention, and may include, for example, adsorption. However, "derivatized" does not include the naturally-occurring, de minimis presence of groups that would only provide the electrostatic functionality required by the present invention at concentrations higher than those found in nature.

The sequence of steps used to arrive at the derivatized microfibrillar cellulose of the present invention is not critical. Therefore, the starting material used to make the derivatized microfibrillar cellulose may be in microfibrillar or non-microfibrillar form. Similarly, the starting material may already be derivatized with electrostatic substituents, or not. If the starting material is non-

microfibrillar, substituents may be placed on the cellulose followed by microfibrillation, or the microfibrillation may be carried out first, followed by the placement of the substituents onto the resulting microfibrils. It is also acceptable to process cellulose into fibrils, place the substituents on the fibrils, and then 5 further process the fibrils into microfibrils. Similarly, any non-microfibrillar form of cellulose which already contains such substituents may be processed into microfibrillar form. Moreover, derivatization and microfibrillation may be carried out simultaneously.

It will be understood that most, if not all, cellulose will contain some 10 quantity of both microfibrillar and non-microfibrillar structure both before and after processing, and that the ratio between the two structures may range from cellulose that is substantially completely microfibrillar, to cellulose that is substantially completely non-microfibrillar. As used herein, the terms "microfibrillar", "microfibrillated", and the like include celluloses that are 15 substantially completely microfibrillated, and those which may be substantially microfibrillated while containing minor but significant amounts of non-microfibrillar structure, provided the cellulose is sufficiently microfibrillated to confer the benefits afforded by the present invention.

Processes which minimize the energy needed to produce microfibrils from 20 non-microfibrillar starting material, and/or which reduce the amount of water extracted during the process or at its end, are preferred. In this regard, it should be noted that while the derivatized microfibrillar cellulose of the present invention can be made by derivatizing a microfibrillated cellulose, the microfibrillation process generally requires less energy, and/or is more efficient, 25 if the cellulose has already been derivatized. Without being bound by theory, this may be because the presence of electrostatic functionalities on the cellulose 'loosens' the structure of fibril bundles.

The ability to use less energy not only offers cost savings, but results in less breakage of the cellulose microfibrils. Therefore, microfibrillating a cellulose 30 that has already been derivatized may result in a derivatized microfibrillar

cellulose with relatively longer microfibrils as compared to effecting derivatization after microfibrillation. This is particularly significant because the energy required for microfibrillation can be significantly reduced by amounts of derivatization which are below the level that would render the resulting

5 derivatized microfibrillar cellulose freely soluble in water. For example, derivatization of cellulose resulting in a DS on the order of 0.1 or 0.2 will 'loosen' the fibril bundles enough to permit microfibrillation using conventional shearing devices such as a homogenizer, impingement mixer, or ultrasonicator. These low DS cellulose microfibrils have diameters on the order of 50 nanometers

10 combined with lengths of up to 500 microns, resulting in aspect ratios in excess of 1,000. While the low DS allows microfibrillation, it is too low to allow the resulting material to be fully soluble in the solvent or carrier of use at the concentrations of interest. Without being bound by theory, the presence of insoluble regions in the fibers may explain the data showing maximum gel

15 formation at low DS's. These gels may be strengthened by weak association of the more hydrophobic unsubstituted regions.

The stabilization or derivatization is accomplished by the generation or placement of substituents onto the fibril and/or microfibril. It appears that the substituents become associated predominantly with the surface regions of the

20 fibrils or microfibrils. Regardless of the precise mechanism, in functional terms microfibril-microfibril contact is inhibited by electrostatic mechanisms or forces. The presence of the substituents also causes the microfibrils to occupy more volume than when they are not derivatized, possibly due to inhibition of contact along at least part of the length of the microfibrils. Rheological performance of

25 the resulting derivatized microfibrillar cellulose is enhanced at low concentration since volume is better occupied and the materials are distributed more homogeneously.

Without being bound by theory, the surfaces of the derivatized microfibrils appear to have some areas free of the substituents such that some limited interaction between microfibrils still takes place. Limited interaction may even

be necessary to facilitate network formation, and may be a cause of the rheological attributes of interest such as yield stress, shear reversible gelation, and insensitivity of the modulus to temperature. It also appears that the length/diameter ratio, or aspect ratio, of the fibrils and microfibrils also
5 contributes to the performance of the materials of the present invention.

Any suitable process may be used to generate or place the substituents on the cellulose. For convenience, the possible processes will generally be referred to collectively as "derivatization" herein; however, within the context of this invention, derivatization is used to mean any process which results in a cellulose
10 (including fibrillar and microfibrillar cellulose) having the substituents sufficiently associated with the cellulose to provide the desired benefit(s), and includes not only chemical reactions resulting in covalent bonding, but also physical adsorption. In addition, the present application will refer both to "derivatization" and to "stabilization". Chemically, both terms refer to the same
15 type of process, namely, the placement or generation of substituents on the cellulosic substrate. Functionally, "derivatization" is generally the broader term, as "stabilization" implies a functionality which is usually observed primarily or exclusively when the cellulose is in microfibrillar form.

Possible derivatization processes include any synthetic method(s) which
20 may be used to associate the substituents with the cellulose. More generally, the stabilization or derivatization step may use any process or combination of processes which promote or cause the placement or generation of the substituents. For example, the conditions for treating non-microfibrillar cellulose should generally include both alkalinity and swelling of the cellulose, in order to
25 make the surface of the fibrils more accessible to the placement or generation of the substituents. Alkalinity and swelling may be provided by separate agents, or the same agent may both provide alkalinity and cause swelling of the cellulose. In particular, alkaline agents often serve multiple purposes, in that they may catalyze the reaction between the cellulose and the substituent, optionally de-

protonate the derivative, and swell open the cellulose structure to allow access of the reagents to carry out the derivatization.

Specific chemical methods which may be used to achieve the present invention include but are not limited to generation of cationic groups, such as quaternary amine and/or amine, on or near the surface of the particulate cellulose. Alkaline conditions are preferably obtained by using sodium hydroxide. Any material that functions as a swelling agent for the cellulose may be used, and alternative alkaline agents include alkali metal or alkaline earth metal oxides or hydroxides; alkali silicates; alkali aluminates; alkali carbonates; amines, including aliphatic hydrocarbon amines, especially tertiary amines; ammonium hydroxide; tetramethyl ammonium hydroxide; lithium chloride; N-methyl morpholine N-oxide; and the like. In addition to catalytic amounts of alkaline agent, swelling agents may be added to increase access for derivatization. Interfibrillar and intercrystalline swelling agents are preferred, particularly swelling agents used at levels which give interfibrillar swelling, such as sodium hydroxide at an appropriately low concentration.

These derivatization reactions, if carried out on the original fibrous cellulose structure, may require specific conditions to maximize the efficiency of location of the derivatization onto the surface of the cellulose. For example, in the case of cellulose from wood pulp the concentration of the swelling agent used appears to have an effect on the performance of the final cellulose. In particular, in using sodium hydroxide it has been determined that the level of the sodium hydroxide can have a significant effect on the rheological performance.

It is preferred that derivatization of these fibrous celluloses be performed in a manner which limits the formation of microfibrils which are soluble in the intended end use composition, as these may not contribute significantly to the desired rheological performance. This typically limits the degree of derivatization which can be made where derivatization at higher levels would make the cellulose soluble in the end use composition. Specific limits may be readily determined based on the application in question, but as a matter of

general guidance it is preferred that the degree of substitution (DS) be below about 0.5, or below about 0.35, or below about 0.2, or below about 0.18, or below about 0.15.

The derivatization may be carried out in any suitable manner, including but
5 not limited to suspension in water; in organic solvent, either alone or in mixtures
with water; in solution; and in high solids, either with water alone or with water
and a minor amount of organic solvent. (For purposes of the present disclosure,
"high solids" refers to a polysaccharide content of greater than about 25%).

Optional derivatizations or functionalities which may also be placed on the
10 cellulose include but are not limited to short chain aliphatic and other
hydrophobic-type substitutions; oligomeric and polymeric substitutions;
uncharged substitutions, as for example short chain ethylene and propylene
glycols; other associative-type functionality; surfactant-like functionality;
methyl; ethyl; propyl; and combinations of these. These substitutions are
15 optional in that they may not be intended for stabilization of the cellulose, and
will instead provide additional functionality such as surface activity,
emulsification power, adsorption characteristics, and the like.

The method for processing a non-microfibrillar form of cellulose into the
microfibrillar form may be carried out before, during, or after the derivatization
20 reaction. The preferred method involves the use of a homogenizer on a dilute
suspension of the non-microfibrillar cellulose in an aqueous medium. The
aqueous medium optionally may have additives such as swelling agents, in
particular interfibrillar and/or intercrystalline swelling agents, for example
sodium hydroxide, to aid in improving the ease of microfibril generation. A
25 more preferred method of microfibrillation involves the use of mechanical energy
on an aqueous suspension of derivatized cellulose which has not been dried.
Other microfibrillation processes include, by way of non-limiting example, use of
an impingement mixer; heat; steam explosion; pressurization-depressurization
cycle; freeze-thaw cycle; impact; grinding (such as a disc grinder); pumping;
30 mixing; ultrasound; microwave explosion; and milling. Combinations of these

may also be used, such as milling followed by homogenization. Essentially any method of reducing particle size may be used, but methods for reducing particle size while preserving a high aspect ratio in the cellulose are preferred. As described previously, the degree of substitution of the cellulose also affects the 5 ease of processing the cellulose to microfibrillar form.

The process to generate the particulate may either be run by the consumer in the final application such that the particulate is generated in situ, or be run as described above in aqueous media, the material dehydrated, and the resulting particulate dried. The dried particulate of this invention, hereafter referred to as 10 the ready-to-gel or RTG form, can be rehydrated readily in polar solvents to obtain the desired rheological attributes. Dehydration can be accomplished by displacing water with less polar solvents and drying.

In terms of general properties, applications where the derivatized 15 microfibrillar celluloses of the present invention have particular utility include those where the desired rheological attributes include at least one of yield stress, shear reversible gelation, and a modulus which is insensitive to temperature. The ability to provide the rheological attributes described herein also makes it possible to provide stabilization of mixtures of liquids and solids having different densities; gel-like properties; pumpable gels; stabilization at elevated 20 temperatures; and, control of hydration and diffusion.

In terms of more specific applications or fields of use, the utility of the 25 present derivatized microfibrillar cellulose includes, without limitation, foods, personal care products, household products, pharmaceuticals, neutraceuticals, paper manufacture and treatment, coating compositions, water and wastewater treatment, drilling fluids, agriculture, construction, and spill control and/or recovery. Use in food applications is also possible, subject to satisfactory resolution of any concern regarding introduction of cationic materials into substances intended for consumption.

In food applications, the derivatized microfibrillar celluloses of the present 30 invention may be useful as rheology modifiers; as stabilizers, such as by

inhibiting creaming or settling in suspensions; and as non-digestible dietary fiber.

They may also be used to control ice crystal growth during, for example, ice cream manufacture and storage.

In personal care products, the derivatized microfibrillar cellulose may be
5 used to stabilize emulsions, dispersions, suspensions, and foams, and may find
use in creams, lotions, gels, and pastes, including those intended for epidermal
application (it should be noted that the derivatized microfibrillar cellulose of the
present invention has substantivity to biological surfaces, including but not
limited to skin, hair, and nails). Representative but not exhaustive examples
10 include sunscreens; moisturizing or anti-aging creams and lotions; cleaning soaps
or gels; antiperspirants and deodorants, including those in stick, pump spray,
aerosol, and roll-on form; fragrance releasing gels; lipsticks, lip glosses, and
liquid makeup products; oral care products, including toothpastes, tooth polishing
and whitening agents, and denture care products such as cleaners and adhesives,
15 and further including use in sorbitol, sorbitol-water mixtures, and glycerol-water
mixtures; products where controlled, sustained, or delayed release of an
ingredient would be desirable; wound care products, such as ointments (including
anesthetic, antiseptic, and antibiotic ointments), dressings, and products such as
ostomy rings where good liquid retention is desirable; and absorbent products,
20 such as diapers. The present invention may have particular utility, not only in
personal care products but in other applications, with products dispersed by a
pumping action. The shear-reversible gelation exhibited by the derivatized
microfibrillar cellulose is well suited for pump dispensing, and may be
advantageously combined with its ability to stabilize emulsions, dispersions, and
25 foams to improve the uniform delivery of product.

In the area of household products, the rheological properties of the present
derivatized microfibrillar celluloses, and their ability to stabilize emulsions,
dispersions, and foams, provide utility in areas such as detergents, shampoos,
cleaners, and air fresheners. Specific examples include, without limitation,
30 laundry products (including detergents, pre-spotting cleaners, and fabric

treatment compositions, such as softeners); rug and upholstery shampoos; toilet bowl cleaners (particularly those dispensed in liquid or gel form); air fresheners; and general purpose cleaning agents, including liquids, gels, pastes, and foams used in cleaning and/or disinfecting household surfaces.

5 In pharmaceutical applications, the derivatized microfibrillar cellulose may have utility in controlled, sustained, or delayed release formulations (including epidermal patches used for slow and/or prolonged release of one or more active ingredients); as disintegrants; as dietary fiber; in wound care, particularly in applications (such as ostomy rings) where liquid-holding ability is important; and
10 as rheology modifiers.

In the area of paper manufacture and treatment, the derivatized microfibrillar cellulose of the present invention has utility in emulsion modification and/or stabilization; sizing; retention; clarification; absorbence; drainage; formation (such as by functioning as a flocculation aid); deposit or
15 scale control (by inhibiting the formation and/or growth of inorganic deposits); water and wastewater treatment; dewatering; film and membrane formation; polyelectrolyte cross-linking; removal of detrimental organic and/or inorganic materials; in paper coatings; and in improving properties such as stiffness, wet strength, absorbancy, softness, toughness, tear resistance, and fold resistance.

20 In the context of paper manufacture, scale control refers to the prevention of calcium carbonate and calcium oxalate deposits forming during the pulping process. Scale control can be achieved by dispersion of salt crystals in the medium to prevent growth and deposition, inhibition of nucleation, or modification of the crystal growth mechanism to prevent the formation of crystal
25 forms that will lead to deposits. The use of derivatized microfibrillar cellulose having micron and smaller particle size, stabilized with appropriate functional groups, would serve to control scale deposit because such microcarriers inhibit the crystal growth which leads to deposition. Moreover, cellulosic materials would be easier to recover from the pulping process due to their organic nature.
30 Preferred functional groups would include amines. Alternative functional groups

and appropriate use levels may be readily determined by those of ordinary skill in the art, based on the particular environment of use.

The derivatized microfibrillar cellulose may also be used in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture; to retain organic and/or inorganic dispersed particles (such as pulp fines, fillers, sizing agents, pigments, and/or clays); to retain detrimental organic and inorganic particulate materials; to improve the uniformity of formation of a sheet of paper; and to improve the strength of a sheet of paper. With particular regard to drainage, drainage aids are additives that increase the rate at which water is removed from a paper slurry on a paper machine. These additives increase machine capacity, and hence profitability, by allowing faster sheet formation. Charged microfibrillar cellulosic derivatives are capable of greatly increasing drainage, either alone or in combination with other charged polymers.

15 The derivatized microfibrillar cellulose of the present invention may also be used in coated papers, where cellulose derivatives may be used to control the rheology of the color coating and to provide water retention, thereby controlling the amount of liquid that permeates into the base sheet.

20 In coating compositions, such as paints and inks, the derivatized microfibrillar cellulose can provide rheology modification, improving properties such as spatter, leveling, sag resistance, flooding, and floating, and may have particular utility in gel paints. It may also improve pigment dispersion and/or stabilization, and function as charge control or flow control agents, including in inks, such as ink jet inks.

25 In the area of water treatment, the derivatized microfibrillar cellulose of the present invention can provide scale control, that is, inhibiting the formation and/or growth of inorganic deposits in aqueous systems; clarification; flocculation; sedimentation; coagulation; charge delivery; and softening.

In drilling fluids, the present derivatized microfibrillar cellulose can provide rheology modification, reduce or prevent fluid loss, and improve secondary oil recovery.

5 In agricultural applications, the derivatized microfibrillar cellulose of the present invention can be used in soil treatment, and may provide moisture retention, erosion resistance, frost resistance, and controlled, sustained, or delayed release of agricultural materials such as fertilizers, pesticides, fungicides, and herbicides. It may also be used for crop protection, such as to minimize or prevent frost damage.

10 In construction, derivatized microfibrillar cellulose can be used in dry wall muds, caulk, water-soluble adhesives, and board manufacture.

15 In other areas, derivatized microfibrillar cellulose can be used for control and cleanup of liquid spills; as absorbents for oil; as stabilizers for emulsions, dispersions, and foams (including but not limited to oil-in-water and water-in-oil emulsions); and for emulsification. Stability of commercial emulsions, such as paper size emulsions, is a recurring issue in industry. Current commercial emulsions include those which generally consist of an oil, waxy, or rosin phase dispersed in water. These dispersions are generally stabilized by the addition of charged materials such as cationic starches, sodium lignin sulfonate, and 20 aluminum sulfate. Such materials are generally added in amounts equal to about 10-20% by weight of the size component. The resulting dispersions are typically 0.2 to 2 micron particles, thought to be stabilized by charge repulsion, for example, with the positively charged starches on particle surfaces repelling each other.

25 One cause of emulsion failure is density-driven separation. This can be limited by increasing viscosity, or internal structure within the fluid. For example, an emulsion which maintains a viscosity of less than about 20 centipoise throughout a standard aging test might have its viscosity increased initially by as much as 100 centipoise through addition of a viscosifier to the

formulation, and still be within acceptable commercial viscosity, provided that the viscosity did not then increase over time to exceed acceptable limits.

One method to accomplish this result would be to use a viscosifying agent that does not cause a substantial increase in viscosity when first added to an emulsion formulation, but which does provide an increase in viscosity during normal processing of the emulsion formulation to produce the emulsion. This can be accomplished by including, as an additive to the emulsion formulation, cellulose that has been derivatized as described herein but not yet microfibrillated. When the emulsion formulation is then subjected to energy, typically high shear, during the processing used to turn the emulsion formulation into an emulsion, the shear will also microfibrillize the derivatized cellulose, resulting in the derivatized microfibrillar cellulose of the present invention, which will be present as part of the emulsion. The gel produced by the derivatized microfibrillar cellulose will then thin under shear stress but re-form when shear stops. Moreover, the insolubility of such low DS cellulose may cause it to concentrate at the oil/water interface of oil-and-water emulsions, rather than the aqueous bulk phase, which may be desirable.

Effectively the same result may be achieved by adding the derivatized microfibrillar cellulose of the present invention to an emulsion formulation, or to the final emulsion, or at any point during production of the emulsion. Further variations would include introducing derivatized cellulose that is only partially microfibrillated into the emulsion-making process at a point where subsequent processing would provide sufficient energy to complete the microfibrillation. It may also be possible to accomplish some or all of the derivatization as part of the emulsion production process; for example, the emulsion formulation may include a charged species that will adsorb onto the cellulose microfibrils, or such a species may be added during processing of the emulsion formulation, separately or in combination with the cellulose. Therefore, the derivatized microfibrillar cellulose of the present invention may serve as a stabilizing additive to

emulsions, with several process routes being available to accomplish this end result.

While the choice of method may cause some variation in the properties of the resulting emulsion, the basic benefit of improved emulsion stability should be achieved by any procedure which has, as its final result, the presence of the derivatized microfibrillar cellulose of the present invention in the final emulsion.

Commercially, it may be desirable to supply customers with derivatized, non-microfibrillated cellulose as a powder which, when added to a formulation and subjected to high shear or other appropriate forms of energy, will microfibrillate and yield the derivatized microfibrillar cellulose of the present invention.

This improved emulsion stability may enable use of emulsion formulations which would not perform satisfactorily in the absence of the derivatized microfibrillar cellulose. Other benefits may include improved retention in paper, improved drainage of water from paper systems due to association of fillers and pulp fines with the retained microfibrils, and resistance to emulsion breakage in the presence of high salt concentrations.

The subject electrostatically derivatized materials of this invention have also been discovered to provide rheology to aqueous systems over a wide range of pH and ionic strength. This insensitivity to pH and ionic strength facilitates use in areas where low pH and high salt conditions exist, such as in personal care creams and lotions, food products, and the like.

In addition to the above, the derivatized microfibrillar cellulose of the present invention represent a vehicle for providing cationic charge to a given environment. This may include utility in water and wastewater treatment, where charged particles may be used to remove color bodies and to flocculate particulates and other contaminants. Thus, by way of non-limiting example, a suitable amount of the derivatized microfibrillar cellulose may be added to water (or to an aqueous system) that is contaminated with anionic material and/or color bodies; allowed to bind or complex with the contaminants, optionally with mixing and/or heating; and physical, chemical, and/or other conventional

separation techniques may then be used to separate the bound or complexed cellulose/contaminant combination from the water. While any amount of derivatized microfibrillar cellulose would facilitate removal of some amount of contaminant from the water, in order to have the most effect the amount of derivatized microfibrillar cellulose should preferably be at least equal to the stoichiometric equivalent necessary to bind or complex with the measured or estimated concentration of the contaminant whose separation or removal is desired.

The following examples indicate various possible methods for making and using the derivatized microfibrillar cellulose of the present invention. These examples are merely illustrative, and are not to be construed as limiting the present invention to particular compounds, processes, conditions, or applications. Throughout this description, "gelling" is defined to occur when $G' > G''$, where G' is the dynamic storage modulus and G'' is the dynamic loss modulus. This is the functional definition used in EP '011; for general background, see Ferry, J.D., Viscoelastic Properties of Polymers, John E. Wiley & Sons, NY, 1980.

The following examples indicate various possible methods for making and using the derivatized microfibrillar cellulose of present invention. These examples are merely illustrative, and are not to be construed as limiting the present invention to particular compounds, processes, conditions, or applications.

Example 1

Preparation Of A Quaternary Amine Functionalized Cellulose (QAC).

Isopropanol (IPA) and deionized (DI) water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. Bleached sulfate wood pulp (approximately 400 μm length, 5.2% moisture)(Weyerhaeuser Company) was added to the reactor, the mixture slurry was agitated for 10 minutes, after which

the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15°C.

The reactor was then inerted, and aqueous NaOH (50% NaOH) was slowly added to the reactor while maintaining the mixture slurry's temperature at or

5 below 15°C. The slurry was agitated for 1 hour after completion of caustic addition. Dow Quat 188 (3-chloro-2-hydroxypropyl trimethylammonium chloride, Dow Chemical Company, Midland, MI) (65% in water) was slowly added to the reactor by addition funnel while maintaining reaction slurry temperature at 15° C. After Dow Quat addition, the reaction slurry was heated to
10 70° C and held for 1 hour. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80% methanol for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two
15 more times.

The wetcake obtained from the previous three washes was slurried in 1000g of pure methanol using an air driven stirrer and a grounded stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was broken into small particles
20 using a rubber spatula and then dried in a Lab-Line fluidized bed dryer (model number 23852) for 35 minutes. (Air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes). The product was ground using a Retsch Grinding Mill (model 2M1) with a 1mm screen.

25 Table 1: QAC Recipes
(all weights in grams)

| Quaternary Amine Functionalized Cellulose | | | | | | | |
|---|------------------|-------------------------------|---------|----------------------|-------------------|---------------------------------|------|
| Sample # | Cellulose Length | Wt. Cellulose (dry wt. Basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. Dow Quat 188 (65% aq. Soln) | DS |
| 1 | ~400 μm | 65 | 750 | 110 | 18.46 | 58.02 | 0.02 |

| Quaternary Amine Functionalized Cellulose | | | | | | | |
|---|------------------|-------------------------------|---------|----------------------|-------------------|---------------------------------|------|
| Sample # | Cellulose Length | Wt. Cellulose (dry wt. Basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. Dow Quat 188 (65% aq. Soln) | DS |
| 2 | ~400 µm | 65 | 750 | 110 | 13.84 | 43.52 | 0.03 |
| 3 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.03 |
| 4 | ~200 µm | 65 | 750 | 110 | 18.46 | 58.02 | 0.07 |
| 5 | ~200 µm | 65 | 750 | 110 | 18.46 | 58.02 | 0.08 |
| 6 | ~200 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.11 |
| 7 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.11 |
| 8 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.11 |
| 9 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.12 |
| 10 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.13 |
| 11 | ~200 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.14 |
| 12 | ~400 µm | 65 | 750 | 110 | N/A | N/A | 0.25 |

Slurry preparation: An 800 g 1% slurry was made from each Sample in Table 1 using the following materials:

| | | <u>Weight</u> | <u>Weight%</u> |
|----|--|---------------|----------------|
| 5 | QAC | 8.00 grams | 1.0 ± |
| | 0.06% | | |
| | Germaben ® II biocide (Sutton Laboratories, New Jersey) | 4.00 grams | 0.5% |
| | Deionized water | 788.00 grams | 98.5 ± |
| 10 | <u>0.06%</u> | | |
| | Total | 800.00 grams | |

The container was closed and shaken to wet and disperse the QAC solids. The solids will settle if left standing, so the container was shaken just prior to pouring the slurry into the homogenizer.

15 **Homogenization of QAC slurries:** The suspension was processed in the homogenizer equipped with an agitated feed pot as follows: the homogenizer was turned on before the slurry was loaded. An 800-gram slurry was processed for about 20 minutes at about 3000 psi by recycling the discharged stream from the homogenizer to the feed pot. Pressure was monitored and appropriate

adjustments made to the primary stage handwheel to keep the total pressure at about 3000 psi. After the processing was completed, the discharge tube was redirected so that the sample was collected and stored in a capped jar.

Rheological testing of microfibrillated QAC: each microfibrillated QAC sample prepared in Example 1 was then tested for rheological properties. Data was collected on a Bohlin CS Rheometer (Bohlin Instruments, Cranbury, New Jersey). Dynamic mechanical properties were measured including the dynamic storage modulus, the dynamic loss modulus, complex viscosity, and yield stress.

Rheometer Test Conditions

10 **Temperature Sweep:** Measuring System: PP 40; 25° C - 65° C; Shear Stress: automatic; Frequency: 1 Hz; Temperature Ramp Rate: 5° C/60 seconds; Measurement Interval: 20 seconds; Gap: 1 mm.

15 **Yield Stress Test:** Measuring System: CP 4/40; Stress: 6.0E-02 - 1.0E+02; Sweep Time: 60.0 seconds; Number of Steps: 30; Temperature: Manual (25° C); No of measurements: 1; Measurement Interval: 5 seconds.

Stress Sweep Test: Measuring System: PP 40; Temperature: Manual (25 °C); Number of Measurements: 1; Gap: 1 mm; Measurement Interval: 5 seconds; Frequency: 1 Hz.

Table 2: Rheology of Microfibrillated QAC

| Sample # | Cellulose Length | DS of Quat-Cellulose | YIELD STRESS(Pa) | G' @ 5.75 Pa(Pa) | G' @25° C/50° C(Pa) | Homogenizer Processing Time(minutes) |
|----------|------------------|----------------------|------------------|------------------|---------------------|--------------------------------------|
| 1 | ~400 µm | 0.02 | NONE | | | 20 |
| 2 | ~400 µm | 0.03 | NONE | | | 20 |
| 3 | ~400 µm | 0.03 | NONE | | | 20 |
| 4 | ~200 µm | 0.07 | 38.0 | 572 | 619/633 | 25 |
| 5 | ~200 µm | 0.08 | 44.7 | 489 | 468/450 | 30 |
| 6 | ~200 µm | 0.11 | 51.4 | 480 | 505/530 | 25 |
| 7 | ~400 µm | 0.11 | 38.0 | 622 | 621/646 | 15 |
| 8 | ~400 µm | 0.11 | 34.7 | 482 | | 20 |
| 9 | ~400 µm | 0.12 | 68.0 | 500 | 488/487 | 20 |
| 10 | ~400 µm | 0.13 | 18.1 | 420 | | 20 |
| 11 | ~200 µm | 0.14 | 21.4 | 497 | 577/592 | 15 |
| 12 | ~400 µm | 0.25 | 51.4 | 106 | 119/131 | 30 |

Example 2**Ready-To-Gel(RTG) Process For Quaternary Amine Cellulose**

- 5 Gels are made as described in the "Slurry preparation" and "Homogenization of QAC Slurries" steps in Example 1. The gels are then processed as follows:

The following description pertains to Sample #1 in the data table. A similar procedure was used for all of the other samples.

- 10 Approximately 2800 ml of IPA was added to a grounded 12-quart stainless steel (SS) beaker. The IPA was stirred at the top speed of an overhead stirrer driven by house air. A SS cowls blade on an SS shaft was used to stir the IPA. Next, approximately 1400 grams of 1% QAC gel was slowly added to the stirring IPA. The material ratio is 2 ml IPA/1 gram gel. The beaker was covered with
15 Saran Wrap and the slurry was stirred for ten minutes.

When ten minutes had passed, the slurry was filtered through a synthetic straining cloth. The slurry was filtered using gravity. The slurry was covered with Saran Wrap during the filtration to reduce IPA evaporation. Occasionally the gel on the cloth was stirred with a plastic spatula to help speed filtration. When it

appeared that the filtration had gone about as far as it could, the wet cake was transferred back to the 12 quart SS beaker.

A fresh amount of approximately 2800 ml IPA was added to the beaker and the slurry was again stirred for ten more minutes with the cowls blade/air stirrer.

5 The slurry was then filtered on a 20 cm Buchner funnel with #415 VWR filter paper. The wet cake was transferred to a glass crystallization dish. The dish containing the wet cake was placed into an 80° C oven under vacuum overnight for drying. The sample was dried to constant weight, and the solids were ground in a Waring Blender.

10 The dehydrated gels were examined by rehydration as follows: a premix of deionized water and Germaben II was prepared.

| | <u>Weight</u> | <u>Weight%</u> |
|---------------------|---------------|----------------|
| Deionized water | 788.00 grams | 99.49% |
| Germaben II biocide | 4.00 grams | 0.51% |

15 The water/Germaben II solution was then weighed into a small Waring blender cup along with the ready-to-gel dry QAC.

| | <u>Weight</u> | <u>Weight%</u> |
|------------------|---------------|----------------|
| water/Germaben | 29.70 grams | 99.0% |
| Ready-to-gel QAC | 0.30 grams | 1.0% |

The blender cup was covered and the sample was mixed until it appeared to be homogeneous. The resulting gel was transferred to a glass jar. It was then shaken on a vortex mixer.

Rheological testing: Same as described in example 1.

25 Table 3: Rheology of RTG QAC

| Sample # | DS of QAC | YIELD STRESS (Pa) | G' @ 5.75 Pa (Pa) |
|-------------|--------------|----------------------|----------------------|
| 1 | 0.09 | 61.4 | 385 |

Rheological properties as a function of concentration: a series of gels were prepared from a 1% QAC (DS 0.09) by diluting with DI water.

Table 4: Rheology of RTG QAC by Concentration

| Sample # | QAC Concentration (wt%) | G' @ 5.75 Pa (Pa) |
|----------|-------------------------|-------------------|
| 1 | 1 | 246 |
| 2 | 0.5 | 35.6 |
| 3 | 0.25 | 0.475 |
| 4 | 0.1 | 0.136 |

G' > G" in all samples (1 - 4); see Figures 1 to 4, respectively.

Stable water/oil emulsions containing QAC: cetyl trimethyl ammonium

- 5 bromide was mixed with deionized water. The CTAB solution was added to 1% quaternary amine (DS=0.15) functionalized microfibrillated cellulose gel prepared as in Example 1. The mixture was stirred in a Waring Blender for 3 minutes on high speed. The sample remained a gel. This gel was processed through a Gaulin homogenizer, 1 pass at 4000 psi. Ten percent (10%) miglyol emulsions were prepared from the gels by adding miglyol and deionized water to the gel and mixing with a rotary mixer for 4 minutes. The resulting emulsions were aged in a 50° C oven.
- 10

Table 5: Stability of Water/Oil Emulsions

| 10% Miglyol Emulsion | Stability at 50° C |
|-----------------------|--------------------|
| 0.45% QAC/0.008% CTAB | > 3 weeks |
| 0.90% QAC/0.016% CTAB | > 3 weeks |

- 15 **Use in paper sizing compositions:** the following examples relate to use of QAC as made in example 1 having a DS of about 0.10 in connection with compositions used in paper sizing.

Example 3

- A 600 ml beaker was used to combine 66.0 grams of Precis® 787 ketene dimer (available from Hercules Incorporated, Wilmington, Delaware; Precis is a registered trademark of Hercules Incorporated), 1.5g of QAC, and 232.5 grams of deionized (DI) water. The mixture was stirred, and then passed through a
- 20

Microfluidics Corporation Model M110 Series impingement mixer (Microfluidics Corp.) with its pressure set at 5000 PSI. The emulsion was collected, and a second pass was made. The second pass product was collected in a clean jar, a stir bar was added, the jar was capped, and then cooled in a 5 to 15° C water bath.

Example 4

Three grams of QAC were dispersed in 465g of DI water for 5 minutes using a Tekmar Ultra-turax SD45 rotor-stator high shear mixer (Tekmar Company, Cincinnati, Ohio) at a power setting of 50. The resulting materials 10 was then given three passes through the impingement mixer at 5000 psi. As in Example 3, 66.0 g of Precis were combined with 234.0 g of QAC in DI water gel, stirred using the high shear mixer at a power setting of 50, then given two passes through the impingement mixer at 5000 psi and cooled in a 5 to 15° C water bath.

Example 5.

15 Four (4.0) grams of QAC was dispersed in 400g of DI water for 5 minutes using the high shear mixer at a power setting of 50, then given three passes through the impingement mixer at 5000 psi to create a gel. A 44% emulsion of Precis ketene dimer was made by combining 176.0 grams of Precis 787 ketene dimer with 224.0 grams of DI water in a wide mouth jar; the pre-mix was sheared 20 in a high shear mixer for 5 minutes at a power setting of 50, the resulting material was quickly poured into the feed chamber of the impingement mixer, and, with mechanical stirring set at about 250 RPM, the premix was passed twice through the impingement mixer set at 5000 psi. Next, 150.0 g of the QAC gel was combined with 150.0 g of the Precis ketene dimer 44% emulsion and stirred for 5 25 minutes using the high shear mixer at a power setting of 50.

The following table provides testing results for the sample emulsions using TAPPI standard Method T560:

Table 6: Surface Sizing of Example 3 through Example 5 Size Emulsions
 (formulation weight in grams)

| | | | (Pre-shear) |
|--------------------------|---|------------|-------------|
| Designation | | (MF gel) | (MF gel) |
| Example | 3 | 4 | 5 |
| Precis 787 | 66.00 | 66.00 | 66.00 |
| QAC | 1.50 | 1.50 | 1.50 |
| DI Water | 232.50 | 232.50 | 232.50 |
| | | | |
| Total | 300.0 | 300.0 | 300.0 |
| | | | |
| Tekmar Shearing cond. | 2 min.@ 50 | 2 min.@ 50 | 2 min.@ 50 |
| Microfluidizer shearing | 2X @ 5kpsi | 2X @ 5kpsi | |
| Tekmar Gel Shearing | | 5 min.@ 50 | 5 min.@ 50 |
| Microfluidizer Gel Shear | | 3X @ 5kpsi | 3X @ 5kpsi |
| | | | |
| Calc. % Actives | 22.00 | 22.00 | 22.00 |
| IRAQ % Actives | NA | 14.9 | NA |
| pH | 2.42 | 2.60 | 2.75 |
| @temp | 20.7 | 21.0 | 26.80 |
| Particle size | 0.75 | 0.97 | Failed |
| Particle size Sonicated | 0.70 | 0.63 | Failed |
| Zeta Potential | -58.3 | -57.9 | Failed |
| Brookfield Visc. | Failed | 119.3 | Failed |
| | "Failed" means emulsion broke prior to testing. | | |

Drainage Aids in Paper Manufacture: the following examples

- 5 demonstrate the effectiveness of derivatized microfibrillar cellulose as a drainage-improvement aid.

Drainage measurements were performed on a Canadian Standard Freeness (CSF) tester, using a bleached kraft pulp consisting of 70% hardwood and 30% softwood. All freeness testing was performed in hard water having a pH of 7.95-10 8.05, alkalinity of 50 ppm (as calcium carbonate), and hardness of 100 ppm (as calcium carbonate) using TAPPI method T 227 om-92. A pulp consistency of 0.3% was used. Higher CSF values indicate better (faster) drainage.

The following results were obtained using microfibrillated quaternary amine cellulose (MFQAC), alone and in combination with microfibrillar

carboxymethyl cellulose (MFCMC). The preparation of MFCMC is described in U.S. patent application serial number 09/248,246, filed February 10, 1999, the disclosure of which is hereby incorporated in its entirety by reference thereto. The MFQAC had a degree of substitution of about 0.09, while the MFCMC had a 5 degree of substitution of about 0.17 charge group per anhydroglucose unit. All loadings are calculated as percent of additive (dry basis) relative to pulp.

Example 6

MFQAC alone.

| | <u>% MFQAC</u> | <u>CSF</u> |
|----|----------------|------------|
| 10 | 0.00 | 211 |
| | 0.05 | 264 |
| | <u>% MFQAC</u> | <u>CSF</u> |
| 15 | 0.10 | 315 |
| | 0.20 | 388 |
| | 0.30 | 451 |
| | 0.40 | 491 |
| | 0.50 | 509 |

Example 7

MFQAC (0.2% loading) with Hercules Reten®1523H anionic polyacrylamide resin:

| | <u>% Reten®1523H</u> | <u>CSF</u> |
|----|----------------------|------------|
| 25 | 0.000 | 464 |
| | 0.003 | 464 |
| | 0.006 | 503 |
| | 0.009 | 513 |
| | 0.012 | 526 |

Example 8

MFQAC with MFCMC

| | % MFQAC <u>(based on pulp)</u> | CSF VALUES | |
|---|-----------------------------------|--------------------|-----------------------|
| | | 0% <u>MFCMC</u> | 0.05% <u>MFCMC</u> |
| 5 | 0.00 | 211 | N/A |
| | 0.10 | 315 | 432 |
| | 0.20 | 388 | 518 |
| | 0.40 | 491 | 612 |

10

In addition to the examples provided above, QAC may be produced with a range of alternative cellulose sources, including Avicel® pH-101NF (-90); Solka® Floc (grade 300 FCC), which may be obtained from Fiber Sales & Development Corp., Urbana, Ohio; and Bleached CTMP (Chemical

15 Thermomechanical Pulp) Fluff, which may be obtained from SCA Graphic Sundsvall AB, Timra, Sweden.

The present invention has of necessity been discussed herein by reference to certain specific methods and materials. The enumeration of these methods and materials was merely illustrative, and in no way constitutes any limitation on the 20 scope of the present invention. It is to be expected that those skilled in the art may discern and practice variations of or alternatives to the specific teachings provided herein, without departing from the scope of the present invention.

WHAT I/WE CLAIM IS:

1. A derivatized microfibrillar cellulose, derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.
2. The derivatized microfibrillar cellulose of claim 1, wherein said cellulose is obtained from at least one of chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.
3. The derivatized microfibrillar cellulose of claim 2, wherein said cellulose is obtained from at least one of purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.
4. The derivatized microfibrillar cellulose of claim 1, wherein said substituent comprises an amine.
5. The derivatized microfibrillar cellulose of claim 4, wherein said substituent comprises a quaternary amine.
6. The derivatized microfibrillar cellulose of claim 1, wherein said derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 100% in water.
7. The derivatized microfibrillar cellulose of claim 6, wherein said derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 50 % in water.
8. The derivatized microfibrillar cellulose of claim 1, wherein said derivatized microfibrillar cellulose forms a gel at a concentration of less than about 1% in water.

9. The derivatized microfibrillar cellulose of claim 8, wherein said derivatized microfibrillar cellulose forms a gel at at least one point in the concentration range of from about 0.05 % up to about 0.99% in water.

10. The derivatized microfibrillar cellulose of claim 1, further
5 comprising a solvent, wherein said derivatized microfibrillar cellulose is substantially insoluble in said solvent.

11. The derivatized microfibrillar cellulose of claim 10, wherein said solvent is water, alcohol, or oil.

12. The derivatized microfibrillar cellulose of claim 11, wherein said
10 solvent is water.

13. The derivatized microfibrillar cellulose of claim 1, having a degree of substitution of less than about 0.5.

14. The derivatized microfibrillar cellulose of claim 13, wherein said degree of substitution is less than about 0.35.

15. The derivatized microfibrillar cellulose of claim 14, wherein said degree of substitution is less than about 0.2.

16. The derivatized microfibrillar cellulose of claim 15, wherein said degree of substitution is less than about 0.18.

17. The derivatized microfibrillar cellulose of claim 16, wherein said
20 degree of substitution is less than about 1.15.

18. The derivatized microfibrillar cellulose of claim 13, wherein said degree of substitution is between about 0.02 and about 0.5.

19. The derivatized microfibrillar cellulose of claim 18, wherein said degree of substitution is between about 0.05 and about 0.2.

25 20. Microfibrillar 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose having a degree of substitution of between about 0.10 and about 0.20.

21. A comestible composition of matter comprising derivatized microfibrillar cellulose derivatized to comprise a substituent that provides

cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

22. The comestible composition of matter of claim 21, in the form of a low fat, reduced fat, or fat-free mayonnaise.

5 23. The comestible composition of matter of claim 22, in the form of a salad dressing.

24. The comestible composition of matter of claim 21, further comprising a pharmaceutically active ingredient.

10 25. The comestible composition of claim 24, wherein said derivatized microfibrillar cellulose at least partially provides controlled, sustained, or delayed release of said pharmaceutically active ingredient.

15 26. A non-comestible composition of matter comprising derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

27. The non-comestible composition of matter of claim 26, in the form of a wound care product.

28. The non-comestible composition of matter of claim 27, wherein said wound care product is a wound dressing.

20 29. The non-comestible composition of matter of claim 27, wherein said wound care product is an ostomy ring.

30. The non-comestible composition of matter of claim 26, in the form of a skin care lotion or cream.

25 31. The non-comestible composition of matter of claim 26, in the form of a sunscreen lotion or cream.

32. The non-comestible composition of matter of claim 26, in the form of an oral care composition.

33. The non-comestible composition of matter of claim 32, wherein said oral care product is a toothpaste.

34. The non-comestible composition of matter of claim 26, in the form of a hair care composition.

35. The non-comestible composition of matter of claim 26, further comprising a fertilizer, herbicide, fungicide, or pesticide.

5 36. The non-comestible composition of matter of claim 35, wherein said derivatized microfibrillar cellulose at least partially provides controlled, sustained, or delayed release of said fertilizer, herbicide, or pesticide.

37. The non-comestible composition of matter of claim 26, in the form of a drilling fluid.

10 38. A paper composition comprising derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 39. The paper composition of claim 38, wherein said derivatized microfibrillar cellulose is microfibrillar 2-hydroxy-3-(trimethylammonium chloride) – propylcellulose.

40. A method for producing derivatized microfibrillar cellulose, said method comprising at least one of the following:

20 a) a derivatizing step of treating a microfibrillar cellulose to obtain a derivatized microfibrillar cellulose;

b) a microfibrillizing step of treating a derivatized non-microfibrillar cellulose to produce a derivatized microfibrillar cellulose; or,

c) a step of microfibrillizing and derivatizing a non-microfibrillar cellulose substantially simultaneously,

25 wherein said derivatized microfibrillar cellulose is derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

41. The method of claim 40, wherein said cellulose is obtained from 30 at least one of chemical pulps, mechanical pulps, thermal mechanical pulps,

chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.

5 42. The method of claim 41, wherein said cellulose is obtained from at least one of purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.

10 43. The method of claim 40, comprising the steps of:
a) derivatizing cellulose with 3-chloro-2-hydroxypropyl trimethylammonium chloride under alkaline conditions to produce 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose;
b) suspending the 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose in water to form a suspension; and
15 c) homogenizing said suspension to produce microfibrillated 2-hydroxy-3-(trimethylammonium chloride) – propylcellulose.

44. The method of claim 40, wherein said derivatizing step comprises contacting a non-microfibrillar cellulose with a swelling agent.

45. The method of claim 44, further wherein said contacting takes place under alkaline conditions.

46. The method of claim 44, wherein said swelling agent is an anionic reagent.

47. The method of claim 46, further wherein said alkaline conditions comprise contacting the cellulose with said anionic reagent in the presence of an alkaline reagent which is at least one of sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an alkali silicate, an alkali aluminate, an alkali carbonate, an amine, ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof.

48. The method of claim 40, wherein said derivatizing step takes place at high solids.

49. The method of claim 40, wherein said cationic charge comprises the presence of amine groups.

50. The method of claim 40, wherein said derivatizing step comprises derivatizing the cellulose with a quaternary amine reagent.

51. The method of claim 40, wherein said derivatized microfibrillar cellulose comprises quaternary amine cellulose.

52. The method of claim 40, wherein said microfibrillizing step comprises applying energy to said cellulose under conditions sufficient to produce microfibrillar cellulose.

10 53. The method of claim 52, further comprising enzyme-treating said non-microfibrillar cellulose prior to said microfibrillizing step

54. The method of claim 52, comprising applying at least one of homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, and 15 milling to said non-microfibrillar cellulose.

55. The method of claim 54, comprising passing said non-microfibrillar cellulose through a homogenizer under conditions sufficient to produce microfibrillar cellulose.

56. The method of claim 55, wherein said conditions comprise passing 20 said non-microfibrillar cellulose through a pressure differential of at least about 3,000 psi.

57. The method of claim 56, further comprising passing said non-microfibrillar cellulose through said homogenizer at least three times.

58. The method of claim 40, wherein said derivatized microfibrillar 25 cellulose forms a gel throughout a concentration range of from about 0.01 % to about 100% in water.

59. The method of claim 58, wherein said derivatized microfibrillar cellulose forms a gel throughout a concentration range of between about 0.01 % and about 50 % in water.

60. The method of claim 40, wherein said derivatized microfibrillar cellulose forms a gel at at least one point in the concentration range of from about 0.05 % to about 0.99% in water.

5 61. The method of claim 60, wherein said derivatized microfibrillar cellulose forms a gel at a concentration of about 0.9% in water.

62. The method of claim 40, wherein said derivatized microfibrillar cellulose is substantially insoluble in the solvent of use.

63. The method of claim 62, wherein the solvent of use is water.

10 64. The method of claim 63, wherein said derivatized microfibrillar cellulose is derivatized microfibrillar cellulose having a degree of substitution of less than about 0.5.

65. The method of claim 64, wherein said degree of substitution is less than about 0.35.

15 66. The method of claim 65, wherein said degree of substitution is less than about 0.2.

67. The method of claim 66, wherein said degree of substitution is less than about 0.18.

68. The method of claim 67, wherein said degree of substitution is less than about 1.15.

20 69. The method of claim 64, wherein said derivatized microfibrillar cellulose has a degree of substitution of between about 0.02 and about 0.5.

70. The method of claim 69, wherein said degree of substitution is between about 0.05 and about 0.2.

25 71. The method of claim 43, wherein said 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose has a degree of substitution of less than about 2.0.

72. The method of claim 71, wherein said degree of substitution is less than about 0.35.

30 73. The method of claim 72, wherein said degree of substitution is between about 0.02 and about 2.0.

74. The method of claim 73, wherein said degree of substitution is between about 0.1 and about 0.2.

75. Derivatized microfibrillar cellulose produced by the method of claim 40.

5 76. Derivatized microfibrillar cellulose produced by the method of claim 43.

77. The derivatized microfibrillar cellulose of claim 40, wherein said cationic charge comprises the presence of amine groups.

10 78. A method of modifying the rheological properties of a composition of matter, said method comprising the step of incorporating, into said composition of matter, derivatized microfibrillar cellulose that is derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 79. The method of claim 78, wherein said composition comprises a liquid.

80. The method of claim 79, wherein said liquid is water.

20 81. The method of claim 80, comprising using said derivatized microfibrillar cellulose in an amount effective to provide scale control and/or corrosion control.

82. The method of claim 78, wherein said rheological properties are at least one of viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention.

25 83. The method of claim 78, wherein said composition of matter is a food, pharmaceutical, pharmaceutical, personal care, fiber, paper, paint, coating, or construction composition.

84. The method of claim 83, wherein said composition of matter is an oral care product.

30 85. The method of claim 83, wherein said composition of matter is a cream or lotion for epidermal application.

86. The method of claim 85, wherein said composition of matter is moisturizing, night, anti-age, or sunscreen cream or lotion.

87. The method of claim 83, wherein said composition of matter is a food spread.

5 88. The method of claim 87, wherein said food spread is a reduced fat, low fat, or fat free food spread.

89. The method of claim 88, wherein said food spread is a reduced fat, low fat, or fat free mayonnaise.

10 90. The method of claim 83, wherein said composition of matter is a drilling fluid.

91. A method of improving the physical and/or mechanical properties of a coating composition by incorporating, into said coating composition, an effective amount of a derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 92. The method of claim 91, wherein said physical and/or mechanical properties include at least one of film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

20 93. The method of claim 92, wherein said derivatized microfibrillar cellulose complexes, adsorbs, precipitates, or otherwise renders inactive dissolved detrimental substances.

94. A method of improving at least one of sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, adsorbency, 25 film formation, membrane formation, and polyelectrolyte complexation during paper manufacture, said method comprising the step of using a derivatized microfibrillar cellulose during said manufacture, wherein said derivatized microfibrillar cellulose is derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

95. The method of claim 94, wherein said derivatized microfibrillar cellulose is used as a drainage aid and/or as a component of a sizing agent.

96. The method of claim 94, wherein said derivatized microfibrillar cellulose is microfibrillated quaternary amine functionalized cellulose.

5 97. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture.

10 98. The method of claim 97, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.

15 99. The method of claim 97, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

20 100. The method of claim 97, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

25 101. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture

30 102. The method of claim 101, wherein said dispersed particles comprise at least one of pulp fines, fillers, sizing agents, pigments, clays,

detrimental organic particulate materials, detrimental inorganic particulate materials, and combinations thereof.

103. The method of claim 101, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one
5 of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.

10 104. The method of claim 101, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

15 105. The method of claim 101, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

20 106. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine to improve the uniformity of formation of a sheet of paper during its manufacture.

25 107. The method of claim 106, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.
30

108. The method of claim 106, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or 5 inorganic species; and combinations thereof.

109. The method of claim 106, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or 10 vinylamine; and combinations thereof.

110. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine to improve the strength of a sheet of paper produced on a paper machine.

111. The method of claim 110, further wherein said microfibrillated 15 quaternary amine functionalized cellulose is used in the presence of at least one of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing 20 carboxylic acid functionality; and combinations thereof.

112. The method of claim 110, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or 25 inorganic species; and combinations thereof.

113. The method of claim 110, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or 30 vinylamine; and combinations thereof.

114. A method for improving the stability of an emulsion, dispersion, or foam system, said method comprising the step of including, in the system, a derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar 5 cellulose is capable of forming a gel in water at a concentration of less than 1%.

115. The method of claim 114, wherein said system comprises an emulsion, further wherein said emulsion is produced by processing of an emulsion formulation.

116. The method of claim 115, further wherein said derivatized 10 microfibrillar cellulose is added to said emulsion formulation prior to completion of processing of said emulsion formulation.

117. The method of claim 115, wherein a non-microfibrillated derivatized cellulose is added to said emulsion formulation prior to completion of processing of said emulsion formulation and said emulsion formulation is 15 processed under conditions sufficient to microfibrillate said non-microfibrillated derivatized cellulose, whereby said derivatized microfibrillar cellulose is produced.

118. The method of claim 115, wherein a microfibrillated non-derivatized cellulose is added to said emulsion formulation prior to completion of 20 processing of said emulsion formulation, and said emulsion formulation is further processed under conditions sufficient to derivatize said microfibrillated non-derivatized cellulose.

119. The method of claim 115, wherein a non-microfibrillated, non-derivatized cellulose is added to said emulsion formulation prior to completion of 25 processing of said emulsion formulation, and said emulsion formulation is further processed under conditions sufficient to microfibrillate and derivatize said non-microfibrillated, non-derivatized cellulose.

120. The method of claim 114, wherein said system is a water-in-oil or oil-in-water emulsion.

30 121. The system produced by the method of claim 114.

122. A system comprising an emulsion, dispersion, or foam containing
a derivatized microfibrillar cellulose, wherein said derivatized microfibrillar
cellulose is derivatized to comprise a substituent that provides cationic charge,
yet further wherein said derivatized microfibrillar cellulose is capable of forming
5 a gel in water at a concentration of less than 1%.

123. A polyelectrolyte complex comprising a derivatized microfibrillar
cellulose comprising a substituent that provides cationic charge, yet further
wherein said derivatized microfibrillar cellulose is capable of forming a gel in
water at a concentration of less than 1%.

10 124. A method for treating wastewater comprising the step of adding,
to the wastewater, a sufficient amount of a derivatized microfibrillar cellulose
derivatized to comprise a substituent that provides cationic charge, wherein said
derivatized microfibrillar cellulose is capable of forming a gel in water at a
concentration of less than 1%.

15 125. The method of claim 124, wherein said wastewater contains at
least one of anionic contaminants and color bodies.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/03458

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08B11/20 C08B11/145

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| X | US 4 676 904 A (JOBST SCHRÖDER) 30 June 1987 (1987-06-30) column 1, line 55 - line 66 --- | 1-20 -/- |

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| (74) Agent: EDWARDS, David; Hercules Incorporated, 1313 North Market Street, Wilmington, DE 19894-0001 (US). | |

(54) Title: DERIVATIZED MICROFIBRILLAR POLYSACCHARIDE

(57) Abstract

A method for producing derivatized microfibrillar polysaccharide, including but not limited to cellulose, derivatized by steric and/or electrostatic forces, where the electrostatic forces are provided by anionic charge or by a combination of both anionic and cationic charge, by stabilizing and/or microfibrillating a polysaccharide starting material. A method of modifying the rheological properties of a composition of matter using derivatized microfibrillar polysaccharide. Method of improving coatings, paper manufacture, and the stability of emulsions, dispersions, and foams using a derivatized microfibrillar polysaccharide. Compositions that include derivatized microfibrillar polysaccharide, including paper compositions, comestible compositions, non-comestible spreadable compositions, and emulsions, dispersion, and foams.

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DERIVATIZED MICROFIBRILLAR POLYSACCHARIDE

FIELD OF THE INVENTION

5 The present invention relates to derivatized microfibrillar polysaccharide. More specifically, the present invention relates to microfibrillar polysaccharide stabilized by steric and/or electrostatic forces, where the electrostatic forces are provided by anionic charge, or by a combination of both anionic and cationic charge.

BACKGROUND OF THE INVENTION

10 Polysaccharides are often found in nature in forms having fibrous morphology. Polysaccharides which are not found in nature in fibrous form can often be transformed into fibrous morphologies using fiber spinning techniques. Whether the fibrous morphology is of natural or artificial origin, the polysaccharide will often be present such that the fibers can be reduced to fibrillar and microfibrillar sub-morphologies
15 through the application of energy.

 Fibrillar and microfibrillar cellulose obtained in this manner have been considered for use in applications, including use as additives to aqueous-based systems in order to affect rheological properties, such as viscosity. The use level of these materials in aqueous systems is often on the order of about 2% by weight, below which these
20 materials have a tendency to poorly occupy volume, and to exhibit gross inhomogeneities in distribution.

 Microfibrillated cellulose and its manufacture are discussed in U.S. Patent Nos. 4,500,546; 4,487,634; 4,483,743; 4,481,077; 4,481,076; 4,464,287; 4,452,722; 4,452,721; 4,378,381; 4,374,702; and 4,341,807, the disclosures of which are hereby
25 incorporated by reference thereto. These documents, in part, purport to describe microfibrillated cellulose in stable, homogenous suspensions, characterized as useful in end use products including foods, cosmetics, pharmaceuticals, paints, and drilling muds.

 Cellulose nanofibrils are characterized in WO 98/02486 (PCT/FR97/01290), WO
30 98/02487 (PCT/FR97/01291), and WO 98/02499 (PCT/FR97/01297), the disclosures of which are hereby incorporated by reference. Nanofibrils are characterized as having diameters in the range of about 2 to about 10 nanometers.

EP 845495 discusses cationic cellulose particulate which is characterized as insoluble, positively charged, and used in water treatment, specifically to treat water in a paper manufacturing plant. In paper making this cationic particulate is said to remove anionic trash from the water. The particles are obtained by milling, which is stated to 5 reduce particle size uniformly such that particles are typically round as described by a length/diameter ratio of approximately 1. Particle size is stated to be 0.001 mm (i.e., 1 μm), and preferably 0.01 mm (10 μm)

EP 859011 ("EP '011") is directed to a process for obtaining cationic cellulose microfibrils or their soluble derivatives. The process is described as including making a 10 cationic cellulose derivative and processing the derivative through a high pressure homogenizer to form transparent gels. The product can be dehydrated and rehydrated. Viscosity measurements are reported on the product at a concentration of 2% in water. EP '011 indicates that the degree of substitution ("DS") of the cellulose can range from 15 0.1 to 0.7, with a DS of between 0.2 and 0.7, 0.3 and 0.6, and 0.5 and 0.6 characterized as representing increasing orders of preference. The examples show cellulose with a DS ranging from a low of 0.24 up to 0.72. Gelling is reported to occur above a microfibril concentration of 10 g/L, or above 1%, in water. EP '011 defines gelling as occurring when $G' > G''$, where G' is the dynamic storage modulus and G'' is the dynamic loss modulus.

Microfibrillated chitosan is reported to form uniplanar, oriented sheets upon 20 drying by H. Yokata, J. Polymer Sci., Part C: Polymer Letters, 24:423-425 (1986). This article mentions that at a level of 4% chitosan in water, a gel is formed having a viscosity of 26,600 cps (Brookfield, 20° C, rotor #7, 10rpm). The microfibrillated chitosan is made by homogenization of commercial chitosan flakes in a Gaulin 25 homogenizer. The commercial chitosan is deacetylated using sodium hydroxide.

JP 59 [1984]-84938 discusses a method for producing a chitosan suspension. Commercial chitosan separated and purified from crabs and lobsters is pulverized to pieces having maximum length of about 1-2 mm. The pieces are then suspended in water at up to 15% chitosan, and are run in multiple passes through a high pressure 30 homogenizer at between 3,000 and 8,000 psi.

It would be desirable to obtain microfibrillar polysaccharides whose viscosity-affecting properties are achieved without the presence of cationic functionalities, at least

in part because of the general lack of suitability of cationic materials for use in foods. It would also be desirable to obtain microfibrillar polysaccharides that are capable of forming a gel at concentrations of 1% or less, thereby providing economy and ease of formulation, while still providing necessary rheological behavior and homogeneity of distribution.

In addition, there is a continuing need in industry to improve the stability of commercial emulsions, such as paper sizing emulsions. At present, one method for stabilizing such emulsions is the addition of charged materials, such as cationic starches, which may be added in amounts equal to 10-20% by weight of the size component.

Interaction with anionic components, such as sulfonates, can also improve stability. However, emulsion failure still takes place in such emulsions, either through density-driven separation, also referred to as creaming, or through gellation. It would accordingly be desirable to develop a material that could be added to emulsions to provide long-term stability.

15 SUMMARY OF THE INVENTION

The present intention is directed to derivatized microfibrillar polysaccharide, methods for its production, and applications for its use. The derivatized microfibrillar polysaccharides is derivatized to contain substituents that provide electrostatic and/or steric functionality; where electrostatic functionality is present, it includes, but is not necessarily limited to, the presence of anionic charge.

Polysaccharides suitable for use in the present invention include cellulose, hemicellulose, chitin, chitosan, guar gum, pectin, alginate, agar, xanthan, starch, amylose, amylopectin, alternan, gellan, mutan, dextran, pullulan, fructan, locust bean gum, carrageenan, glycogen, glycosaminoglycans, murein, bacterial capsular polysaccharides, and derivatives thereof. Mixtures of these may be employed.

Preferred polysaccharides are cellulose, chitin, chitosan, pectin, agar, starch, carrageenan, and derivatives thereof, used singly or in combination, with cellulose being most preferred. The cellulose may be obtained from any available source, including, by way of example only, chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose,

vegetables, and fruits. Preferred sources of cellulose include purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.

The derivatized microfibrillar polysaccharides that may be obtained using cellulose include, but are not limited to, hydroxyethyl cellulose, ethylhydroxyethyl cellulose, carboxymethylcellulose, carboxymethylhydroxyethyl cellulose, hydroxypropylhydroxyethyl cellulose, methyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose, carboxymethylmethyl cellulose, hydrophobically modified carboxymethylcellulose, hydrophobically modified hydroxyethyl cellulose, hydrophobically modified hydroxypropyl cellulose, hydrophobically modified ethylhydroxyethyl cellulose, hydrophobically modified carboxymethylhydroxyethyl cellulose, hydrophobically modified hydroxypropylhydroxyethyl cellulose, hydrophobically modified methyl cellulose, hydrophobically modified methylhydroxypropyl cellulose, hydrophobically modified methylhydroxyethyl cellulose, hydrophobically modified carboxymethylmethyl cellulose, nitrocellulose, cellulose acetate, cellulose sulfate, cellulose vinyl sulfate, cellulose phosphate, and cellulose phosphonate.

The derivatized microfibrillar cellulose of the present invention may form a gel in water throughout the concentration range of between about 0.01 % and about 100%, or throughout the concentration range of between about 0.01 % and about 50 % in water, or at at least one point in the concentration range of from about 0.05 % up to about 0.99% in water. In an alternative embodiment, the derivatized microfibrillar cellulose of the present invention forms a gel in water at a concentration of about 0.95%.

The derivatized microfibrillar polysaccharide may be used in the presence of a solvent, in which it is substantially insoluble. Examples of solvents include water, alcohol, and oil.

In the case of derivatization with groups that provide electrostatic functionality, the derivatized microfibrillar polysaccharides of the present invention may have a degree of substitution of less than about 0.5, less than about 0.35, less than about 0.2, less than about 0.18, or less than about 0.1. A preferred range for the degree of substitution is between about 0.02 and about 0.5, with a range of between about 0.05 and about 0.2 being more preferred. When the derivatized microfibrillar polysaccharide

is derivatized to comprise substituents that provide electrostatic functionality in the form of anionic charge, the degree of substitution representing those substituents which provide electrostatic functionality in the form of anionic charge is preferably least about 0.05. Anionic charge may be provided, for example, by carboxyl, sulfate, sulfonate, 5 phosphonate, or phosphate groups, or combinations thereof. Where cationic charge is also present, both charges may be provided by the same groups or substituent (i.e., the substituent may be amphoteric or zwitterionic); or, the derivatized microfibrillar polysaccharide may be derivatized to contain both substituents that contain anionic charge and substituents that contain cationic charge. In addition, the derivatized 10 microfibrillar polysaccharides of the present invention may be obtained by blending two or more separate derivatized microfibrillar polysaccharides, where at least one has been derivatized to provide anionic charge, and at least one other has been derivatized to provide anionic charge, cationic charge, or both.

When the derivatized microfibrillar polysaccharide of the present invention is 15 derivatized to contain substituents that provide steric functionality, the derivatized microfibrillar polysaccharides may have a molar substitution of less than about 3.0, or of less than about 1.5, or of less than about 1.0, or of less than about 0.5. The range of molar substitution may be from about 0.5 to about 3.0. Steric functionality may be provided, by way of non-limiting example, by hydroxyethyl groups, hydroxypropyl 20 groups, methyl groups, ethyl groups; straight- or branched-chain alkyl, alkenyl, or alkynyl groups having from about 4 to about 30 carbons; and/or aryl, arylalkyl, arylalkenyl, cyclic, and heterocyclic hydrocarbons having from about 4 to about 30 carbons.

In a preferred embodiment the derivatized microfibrillar polysaccharide contains 25 carboxymethylcellulose, and has a degree of substitution of less than about 0.35, or of less than about 2.0. The range of degree of substitution may be from about 0.02 to about 0.2, with a range of from about 0.10 to about 0.2 being preferred.

The derivatized microfibrillar cellulose of the present invention may form a gel at a concentration of less than about 1% in water.

30 In a further embodiment, the present invention is directed to a comestible composition of matter containing the derivatized microfibrillar polysaccharide of the present invention. The comestible composition of matter may, by way of non-limiting

example, be a low fat, reduced fat, or fat-free food spread, such as a mayonnaise, or a salad dressing. Alternatively, the comestible composition may contain a pharmaceutically active ingredient. The derivatized microfibrillar polysaccharide may be used to provide or improve a controlled, sustained, or delayed release of a component of the comestible composition, including in particular a pharmaceutically active ingredient.

In yet another embodiment, the derivatized microfibrillar polysaccharides of the present invention may be used in non-comestible, spreadable compositions of matter, such as skin care lotions or creams, or sunscreen lotions or creams.

The present invention is further directed to a paper composition containing the derivatized microfibrillar cellulose, and particularly, though not exclusively, microfibrillar carboxymethylcellulose.

The derivatized microfibrillar polysaccharide may be produced by using a derivatizing step to treat a microfibrillar polysaccharide to obtain the derivatized microfibrillar polysaccharide. Alternatively, a derivatized polysaccharide may be microfibrillated to produce the derivatized microfibrillar polysaccharide. In another method, the steps of microfibrillation and derivatization may take place at substantially the same time. In a preferred embodiment, cellulose is first derivatized with monochloroacetic acid or a salt thereof under alkaline conditions to produce carboxymethylcellulose; the carboxymethylcellulose is suspended in water; and the resulting suspension is homogenized to produce microfibrillated carboxymethylcellulose.

The derivatizing step may include contacting a non-microfibrillar polysaccharide with a swelling agent, such as an anionic reagent, and may take place under alkaline conditions. These alkaline conditions may include contacting the cellulose with the anionic reagent in the presence of an alkaline reagent which is sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an alkali silicate, an alkali aluminate, an alkali carbonate, an amine, ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof. The derivatization may take place at high solids.

Microfibrillation may be accomplished by applying energy to a non-microfibrillar polysaccharide under conditions sufficient to produce microfibrillar polysaccharide. The non-microfibrillar may optionally be enzyme-treated before microfibrillizing. More

specifically, microfibrillation may be accomplished using homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, milling, and combinations of these. In a preferred embodiment the non-microfibrillar polysaccharide is passed through a homogenizer under conditions sufficient to produce microfibrillar cellulose; those conditions may include a pressure differential of at least about 3,000 psi, and passing the non-microfibrillar polysaccharide through the homogenizer at least three times.

The method should be conducted to yield a derivatized microfibrillar polysaccharide that is substantially insoluble in the solvent of use. Water is a preferred solvent of use, but other solvents, including but not limited to alcohols and oils, are contemplated for various applications.

The present invention extends to derivatized microfibrillar polysaccharide produced by the above methods.

In an alternative embodiment the present invention is directed to a method of modifying the rheological properties of a liquid composition of matter by incorporating the derivatized microfibrillar polysaccharides of the present invention into the liquid composition of matter.

This may be accomplished by incorporating the derivatized microfibrillar polysaccharide into a water-containing system, where it may be used, for example, to provide scale control and/or corrosion control. The rheological properties which may be modified by the derivatized microfibrillar polysaccharide include viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention.

Liquid compositions which may be rheologically modified include, as non-limiting examples, foods, pharmaceuticals, neutraceuticals, personal care products, fibers, papers, paints, coatings, and construction compositions. These include oral care products; creams or lotions for epidermal application (such as moisturizing, night, anti-age, or sunscreen creams or lotions); food spreads, including reduced fat, low fat, or fat free food spreads (such as mayonnaises); and drilling fluids.

The present invention further extends to a method of improving the physical and/or mechanical properties of a coating composition by incorporating, into the coating composition, an effective amount of the derivatized microfibrillar polysaccharide. The

physical and/or mechanical properties that may be improved in this manner include film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

The present invention has particular utility in the field of paper manufacture and treatment. For example, derivatized microfibrillar cellulose may be used to improve one or more of sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, adsorbency, film formation, membrane formation, and polyelectrolyte complexation during paper manufacture. As a particular example, the derivatized microfibrillar cellulose may be used as a drainage aid and/or as a sizing agent. A polyelectrolyte complex containing the derivatized microfibrillar polysaccharide is also within the scope of the present invention.

Microfibrillated carboxymethylcellulose is a particularly preferred embodiment for use in paper applications. During the process of paper manufacture, the derivatized microfibrillar cellulose may be used, by way of further example, in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture; for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture; to improve the uniformity of formation of a sheet of paper during its manufacture; and to improve the strength of a sheet of paper. The derivatized microfibrillar cellulose may be used in combination with any of the additives and performance enhancers conventionally used in paper manufacture, including cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and, at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof. In the context of retention of organic and/or inorganic dispersed particles, the particles so retained may include one or more of pulp fines, fillers, sizing agents, pigments, clays, detrimental organic particulate materials, and detrimental inorganic particulate materials.

In another embodiment, the stability of an emulsion, dispersion, or foam system may be improved by including, in the system, the derivatized microfibrillar polysaccharide of the present invention. The derivatized microfibrillar polysaccharide may be added to an existing system; added to a formulation which will be processed into such a system; or added during processing of such a formulation. Where addition takes place before completion of processing of a formulation into an emulsion, dispersion, or foam system, the processing conditions used to form the emulsion, dispersion, or foam may be used to produce the derivatized microfibrillar polysaccharide as well. Thus, a derivatized non-microfibrillated polysaccharide (where "non-microfibrillated" includes an incompletely microfibrillated polysaccharide) may be added to a formulation prior to completion of processing, and subsequent processing may then be conducted in a manner that will microfibrillate the polysaccharide. Alternatively, a microfibrillated polysaccharide may be added to the formulation, with subsequent processing conducted so as to derivatize the microfibrillated polysaccharide.

In another variation, both derivatization and microfibrillation may take place during processing. Systems which may be treated in this manner include water-in-oil and oil-in-water emulsions.

The present invention also extends to emulsion, dispersion, and foam systems produced by the above methods; and, to emulsion, dispersion, or foam systems that contain the derivatized microfibrillar polysaccharide of the present invention.

BRIEF DESCRIPTION OF THE FIGURES

- Figure 1 shows the dynamic mechanical spectra of Example 7, Sample 1.
- Figure 2 shows the dynamic mechanical spectra of Example 7, Sample 2.
- Figure 3 shows the dynamic mechanical spectra of Example 7, Sample 3.
- Figure 4 shows the dynamic mechanical spectra of Example 7, Sample 4.
- Figure 5 shows the dynamic mechanical spectra of Example 7, Sample 5.
- Figure 6 shows the dynamic mechanical spectra of Example 13, Sample 1.
- Figure 7 shows the dynamic mechanical spectra of Example 13, Sample 2.
- Figure 8 shows the dynamic mechanical spectra of Example 13, Sample 3.
- Figure 9 is a transmission electron micrograph of a sample microfibrillar carboxymethylcellulose prepared as in example 3 below, with a degree of substitution of about 0.17, negative stained with urinal acetate, at a magnification of 10,000X.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises derivatized microfibrillar polysaccharide.

Suitable polysaccharides for use in the present invention include, without limitation, cellulose, hemicellulose, chitin, chitosan, guar gum, pectin, alginate, agar, xanthan, starch, amylose, amylopectin, alerman, gellan, mutan, dextran, pullulan, fructan, locust bean gum, carrageenan, glycogen, glycosaminoglycans, murein, bacterial capsular polysaccharides, and derivatives thereof, with cellulose being preferred. The polysaccharide may be used as is, or spinning may be used to generate or improve fibrous structure.

Cellulose is a preferred polysaccharide for use in the present invention. Sources of cellulose for use in this invention include the following: (a) wood fibers, such as from chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint; (b) seed fibers, such as from cotton; (c) seed hull fiber, such as from soybean hulls, pea hulls, corn hulls; (d) bast fibers, such as from flax, hemp, jute, ramie, kenaf; (e) leaf fibers, such as from manila hemp, sisal hemp; (f) stalk or straw fibers, such as from bagasse, corn, wheat; (g) grass fibers, such as from bamboo; (h) cellulose fibers from algae, such as velonia; (i) bacteria or fungi; and (j) parenchymal cells, such as from vegetables and fruits, and in particular sugar beets, and citrus fruits such as lemons, limes, oranges, grapefruits. Microcrystalline forms of these cellulose materials may also be used. Preferred cellulose sources are (1) purified, optionally bleached, wood pulps produced from sulfite, kraft (sulfate), or prehydrolyzed kraft pulping processes, (2) purified cotton linters, and (3) fruits and vegetables, in particular sugar beets and citrus fruits. The source of the cellulose is not limiting, and any source may be used, including synthetic cellulose or cellulose analogs.

Cellulose is found in nature in several hierarchical levels of organization and orientation. Cellulose fibers comprise a layered secondary wall structure within which macrofibrils are arranged. Macrofibrils comprise multiple microfibrils which further comprise cellulose molecules arranged in crystalline and amorphous regions. Cellulose microfibrils range in diameter from about 5 to about 100 nanometers for different species of plant, and are most typically in the range of from about 25 to about 35 nanometers in diameter. The microfibrils are present in bundles which run in parallel within a matrix of amorphous hemicelluloses (specifically xyloglucans), pectinic polysaccharides, lignins, and

hydroxyproline rich glycoproteins (includes extensin). Microfibrils are spaced approximately 3-4 nm apart with the space occupied by the matrix compounds listed above. The specific arrangement and location of the matrix materials and how they interact with the cellulose microfibrils is not yet fully known.

5 For purposes of the present invention polysaccharide microfibrils refer to small diameter, high length-to-diameter ratio substructures which are comparable in dimensions to those of cellulose microfibrils occurring in nature. By way of non-limiting example, polysaccharide microfibrils may have diameters in the range of about 20 to about 100 nanometers, combined with lengths providing high aspect ratios, such
10 as in excess of 100, in excess of 500, or in excess of 1,000. While the present specification and claims refer to microfibrils and microfibrillation, the scope of the present invention also includes nanofibrils (cellulosic or otherwise), and the rheology modification, stabilization, and other properties that may be obtained with microfibrils by practicing the present invention may also be obtained using nanofibrils, either alone
15 or in combination with microfibrils.

In nature many polysaccharides are not present in microfibril arrangements, however, by using fiber spinning techniques it is possible to manufacture fibers from these polysaccharides. In one embodiment of this invention it is contemplated that fibers spun from polysaccharides can be derivatized and microfibrillated into fibrous
20 structures having dimensions on the order of those found naturally in cellulose. Further background on the structure, functions, and biogenesis of native cellulose may be found in Haigler, C.H., Cellular Chemistry and Its Applications, Nevell, pp. 30-83 (1985), the entirety of which is hereby incorporated by reference.

The derivatized microfibrillar polysaccharide of the present invention is
25 characterized by being in microfibrillar form, and by the presence of substituents that provide steric and/or electrostatic functionality. The amount of substituent present may be quantified by the degree of substitution, or DS, in the case of some anionic and cationic substituents, and by the molar substitution, or MS, in the case of steric substituents. The degree of substitution, which will vary with the molecular weight of
30 the polysaccharide, is the average number of substituted hydroxyl groups per anhydrosaccharide unit, while the molar substitution is the average number of substituent groups added per anhydrosaccharide unit. The DS and MS determine the

solubility of the derivatized polysaccharide, and may be readily adjusted to obtain a derivatized polysaccharide that is substantially insoluble in the environment of use, whether aqueous or non-aqueous. While the environment of use will frequently be aqueous, the derivatized microfibrillar polysaccharides of the present invention have 5 utility in applications having other solvents or liquid carriers, such as paints, coating, lacquers, oil-rich foods, inks (including but not limited to ink-jet inks), personal care products, cosmetics, and water-in-oil emulsions.

Any suitable method may be used to obtain the derivatized microfibrillar polysaccharide. In particular, the steps of microfibrillation and derivatization to impart 10 steric and/or electrostatic functionality to the polysaccharide may be carried out separately or combined to arrive at the end result. Therefore, a non-microfibrillar polysaccharide starting material may either be derivatized with anionic groups, with both anionic and cationic groups, or with a blend or mixture of anionic groups and cationic groups, and then microfibrillated, or may first be microfibrillated and then 15 derivatized. Alternatively, if the starting material is microfibrillar polysaccharide, only the derivatizing step would be necessary, whereas if the starting material is a polysaccharide that has already been properly derivatized with anionic or both anionic and cationic groups, only the microfibrillation step is required.

The degree of substitution (for electrostatic derivatization), and/or of molar 20 substitution (for steric derivatization), of the polysaccharide should be sufficiently low so that the derivatized microfibrillar polysaccharide will be substantially insoluble in the solvent or carrier that is present in the intended environment of use. In many applications the solvent or carrier will be water, and in such applications the degree of substitution and/or the molar substitution should be such that the derivatized 25 microfibrillar polysaccharide is substantially insoluble in water. However, in other applications a polar solvent or carrier (such as an alcohol) may be used having different solubility characteristics, or a non-polar solvent or carrier (such as an oil) may be used, and in such cases the degree of substitution and/or the molar substitution should be adjusted to obtain a derivatized microfibrillar polysaccharide that is substantially 30 insoluble in the solvent or carrier used in the application of interest, which, for purposes of convenience, will hereafter be referred to as the "solvent of use". Functionally, the

derivatized microfibrillar polysaccharide should be sufficiently insoluble in the environment of use to provide the desired properties in the intended application.

The presence of substantially insoluble material may be confirmed by observation of a 1-5% suspension of the material in question in the solvent or carrier of use under a light microscope at sufficient magnification to see insoluble material. A size determination may be made by preparing a suspension of the material under consideration at approximately 0.1-0.01% in a liquid non-solvent which is effective in dispersing microfibrils. This suspension is then dried on a transmission electron microscope (TEM) grid, the sample is coated to protect it from electron beam damage, and examined at sufficient magnification and focus to observe structure in the 1-1000 nanometer range. If microfibrillar elements are present they can be detected under these conditions, and the combination of insolubility under the light microscope and microfibrillar structure under the TEM will indicate the presence of substantially insoluble microfibrillar material. See Figure 9 for an example transmission electron micrograph of a microfibrillar carboxymethylcellulose prepared as in example 3 below, having a DS of about 0.17

For purposes of simplicity, unless specifically indicated otherwise the term "substituents" shall be used herein to mean chemical species that provide steric stabilization to the polysaccharide; chemical species that provide electrostatic functionality to the polysaccharide through anionic charge; chemical species that provide electrostatic functionality to the polysaccharide through a combination of both anionic and cationic charge; and combinations of the foregoing. In addition, "electrostatic" means either anionic charge, or a combination of both anionic and cationic charge, whether as groups both present on a single substituent, or as groups provided separately on two or more substituents. "Derivatization" refers not only to chemical reactions resulting in covalent bonds, but to any process whereby the substituents become sufficiently associated with the polysaccharide to provide the rheological and other benefits of the present invention, and may include, for example, adsorption. Finally, references to the combination of both anionic and cationic charge on the polysaccharide include the use of substituents that contain both types of charge (i.e., amphoteric and/or zwitterionic substituents); the combined use of substituents which individually contain only anionic or only cationic charge, resulting in derivatized

polysaccharide with a distribution of substituents that includes both anionic groups and cationic groups; and, blending of two or more derivatized polysaccharides where at least one derivatized polysaccharide includes at least anionic substituents and at least one other derivatized polysaccharide includes at least cationic substituents, resulting in a
5 blend that contains both anionically derivatized polysaccharide and cationically derivatized polysaccharide. However, "derivatized" does not include the naturally- occurring, de minimis presence of groups that would only provide the steric and/or electrostatic functionality required by the present invention at concentrations higher than those found in nature. For example, naturally-occurring cellulose may contain very low
10 levels of anionic charge, which may still be present after microfibrillation. However, such microfibrillated cellulose is not "derivatized" as that term is used in the present application, both because its degree of substitution has not been changed from its natural state, and because the amount of charge present in such microfibrillated cellulose would not provide the benefits of the present invention.

15 The sequence of steps used to arrive at the derivatized microfibrillar polysaccharide of the present invention is not critical. Therefore, the starting material used to make the derivatized microfibrillar polysaccharide may be in microfibrillar or non-microfibrillar form. Similarly, the starting material may already be derivatized with steric and/or electrostatic substituents, or not. If the starting material is non-
20 microfibrillar polysaccharide, substituents may be placed on the polysaccharide followed by microfibrillation, or the microfibrillation may be carried out first, followed by the placement of the substituents onto the resulting microfibrils. It is also acceptable to process polysaccharide into fibrils, place the substituents on the fibrils, and then further process the fibrils into microfibrils. Similarly, any non-microfibrillar form of
25 polysaccharide which already contains such substituents may be processed into microfibrillar form. Moreover, derivatization and microfibrillation may be carried out simultaneously.

It will be understood that most, if not all, polysaccharides will contain some quantity of both microfibrillar and non-microfibrillar structure both before and after
30 processing, and that the ratio between the two structures may range from polysaccharide that is substantially completely microfibrillar, to polysaccharide that is substantially completely non-microfibrillar. As used herein, the terms "microfibrillar",

"microfibrillated", and the like include polysaccharides that are substantially completely microfibrillated, and those which may be substantially microfibrillated while containing minor but significant amounts of non-microfibrillar structure, provided the polysaccharide is sufficiently microfibrillated to confer the benefits afforded by the 5 present invention.

Processes which minimize the energy needed to produce microfibrils from non-microfibrillar starting material, and/or which reduce the amount of water extracted during the process or at its end, are preferred. In this regard, it should be noted that while the derivatized microfibrillar polysaccharide of the present invention can be made 10 by derivatizing a microfibrillated polysaccharide, the microfibrillation process generally requires less energy, and/or is more efficient, if the polysaccharide has already been derivatized. Without being bound by theory, this may be because the presence of the steric and/or electrostatic functionalities on the polysaccharide 'loosens' the structure of fibril bundles.

15 The ability to use less energy not only offers cost savings, but results in less breakage of the polysaccharide microfibrils. Therefore, microfibrillating a polysaccharide that has already been derivatized may result in a derivatized microfibrillar polysaccharide with relatively longer microfibrils as compared to effecting derivatization after microfibrillation. This is particularly significant because 20 the energy required for microfibrillation can be significantly reduced by amounts of derivatization which are below the level that would render the resulting derivatized microfibrillar polysaccharide freely soluble in water. For example, derivatization of cellulose resulting in a DS on the order of 0.1 or 0.2 will 'loosen' the fibril bundles in cellulose enough to permit microfibrillation using conventional shearing devices such as 25 a homogenizer, impingement mixer, or ultrasonicator. These low DS cellulose microfibrils have diameters on the order of 50 nanometers combined with lengths of up to 500 microns, resulting in aspect ratios in excess of 1,000. While the low DS allows microfibrillation, it is too low to allow the resulting material to be fully soluble in the solvent or carrier of use at the concentrations of interest. Without being bound by 30 theory, the presence of insoluble regions in the fibers may explain the data showing maximum gel formation at low DS's. These gels may be strengthened by weak association of the more hydrophobic unsubstituted regions.

The stabilization or derivatization is accomplished by the generation or placement of substituents onto the fibril and/or microfibril. It appears that the substituents become associated predominantly with the surface regions of the fibrils or microfibrils.

Regardless of the precise mechanism, in functional terms microfibril-microfibril contact
5 is inhibited by steric and/or electrostatic mechanisms or forces. The presence of the substituents also causes the microfibrils to occupy more volume than when they are not derivatized, possibly due to inhibition of contact along at least part of the length of the microfibrils. Rheological performance of the resulting derivatized microfibrillar polysaccharide is enhanced at low concentration since volume is better occupied and the materials are distributed more homogeneously.
10

With regard to use of steric force, steric functionality or stabilization is provided by the formation of a protective barrier or sheath around a particle (such as a cellulose fibril or microfibril) to prevent flocculation. For example, it may be achieved by a material, such as a polymer, being physically adsorbed on the surface of the particle,
15 thereby preventing two particles from coming closer than a distance that is twice the sum of the radius of the particle and the thickness of the adsorbed layer. As two particles approach and the distance between them approaches the distance noted above, the adsorbed layers on two particles interact. This interaction, which as noted may be a polymer-polymer interaction, results in forces, such as osmotic and/or entropic forces,
20 that repel the particles. This prevents flocculation of the two particles, providing stabilization. Because steric forces are generally provided by the size and/or configuration of the substituent, a substituent used to provide the polysaccharide with steric functionality or stabilization may be neutral, anionic, cationic, amphiphilic, amphoteric, and/or zwitterionic.

Without being bound by theory, the surfaces of the derivatized microfibrils appear
25 to have some areas free of the substituents such that some limited interaction between microfibrils still takes place. Limited interaction may even be necessary to facilitate network formation, and may be a cause of the rheological attributes of interest such as yield stress, shear reversible gelation, and insensitivity of the modulus to temperature. It
30 also appears that the length/diameter ratio, or aspect ratio, of the fibrils and microfibrils also contributes to the performance of the materials of the present invention.

Any suitable process may be used to generate or place the substituents on the polysaccharide. For convenience, the possible processes will generally be referred to collectively as "derivatization" herein; however, within the context of this invention, derivatization is used to mean any process which results in a polysaccharide (including 5 fibrillar and microfibrillar polysaccharide) having the substituents sufficiently associated with the polysaccharide to provide the desired benefit(s), and includes not only chemical reactions resulting in covalent bonding, but also physical adsorption. In addition, the present application will refer both to "derivatization" and to "stabilization". Chemically, both terms refer to the same type of process, namely, the placement or 10 generation of substituents on the cellulosic substrate. Functionally, "derivatization" is generally the broader term, as "stabilization" implies a functionality which is usually observed primarily or exclusively when the polysaccharide is in microfibrillar form.

Possible derivatization processes include any synthetic method(s) which may be used to associate the substituents with the polysaccharide. More generally, the 15 stabilization or derivatization step may use any process or combination of processes which promote or cause the placement or generation of the substituents. For example, the conditions for treating non-microfibrillar polysaccharide should generally include both alkalinity and swelling of the polysaccharide, in order to make the surface of the fibrils more accessible to the placement or generation of the substituents. Alkalinity and 20 swelling may be provided by separate agents, or the same agent may both provide alkalinity and cause swelling of the polysaccharide. In particular, alkaline agents often serve multiple purposes, in that they may catalyze the reaction between the polysaccharide and the substituent, optionally de-protonate the derivative, and swell 25 open the polysaccharide structure to allow access of the reagents to carry out the derivatization.

Specific chemical methods which may be used to achieve the present invention include but are not limited to generation of anionic groups (such as carboxyl, sulfate, sulfonate, phosphonate, and/or phosphate); generation of both anionic and cationic groups (such as quaternary amine and/or amine); and generation of steric groups, on or 30 near the surface of the particulate polysaccharide. Alkaline conditions are preferably obtained by using sodium hydroxide. Any material that functions as a solvent for the polysaccharide of choice may be used, and alternative alkaline agents include alkali

metal or alkaline earth metal oxides or hydroxides; alkali silicates; alkali aluminates; alkali carbonates; amines, including aliphatic hydrocarbon amines, especially tertiary amines; ammonium hydroxide; tetramethyl ammonium hydroxide; lithium chloride; N-methyl morpholine N-oxide; and the like. In addition to catalytic amounts of alkaline agent, swelling agents may be added to increase access for derivatization. Interfibrillar and intercrystalline swelling agents are preferred, particularly swelling agents used at levels which give interfibrillar swelling, such as sodium hydroxide at an appropriately low concentration.

These derivatization reactions, if carried out on the original fibrous polysaccharide structure, may require specific conditions to maximize the efficiency of location of the derivatization onto the surface of the polysaccharide. For example, in the case of cellulose from wood pulp the concentration of the swelling agent used appears to have an effect on the performance of the final cellulose. In particular, in using sodium hydroxide it has been determined that the level of the sodium hydroxide can have a significant effect on the rheological performance.

It is preferred that derivatization of these fibrous polysaccharides be performed in a manner which limits the formation of microfibrils which are soluble in the intended end use composition, as these may not contribute significantly to the desired rheological performance. This typically limits the degree of derivatization which can be made where derivatization at higher levels would make the polysaccharide soluble in the end use composition. Specific limits may be readily determined based on the application in question, but as a matter of general guidance it is preferred that the degree of substitution (DS) be below about 0.5, or below about 0.35, or below about 0.2, or below about 0.18, or below about 0.1.

The derivatization may be carried out in any suitable manner, including but not limited to suspension in water; in organic solvent, either alone or in mixtures with water; in solution; and in high solids, either with water alone or with water and a minor amount of organic solvent. (For purposes of the present disclosure, "high solids" refers to a polysaccharide content of greater than about 25%).

Optional derivatizations or functionalities which may also be placed on the polysaccharide include but are not limited to short chain aliphatic and other hydrophobic-type substitutions; oligomeric and polymeric substitutions; uncharged

substitutions, as for example short chain ethylene and propylene glycols; other associative-type functionality; surfactant-like functionality; methyl; ethyl; propyl; and combinations of these. These substitutions are optional in that they may not be intended for stabilization of the polysaccharide, and will instead provide additional functionality
5 such as surface activity, emulsification power, adsorption characteristics, and the like.

The method for processing a non-microfibrillar form of polysaccharide into the microfibrillar form may be carried out either before or after the derivatization reaction. The preferred method involves the use of a homogenizer on a dilute suspension of the non-microfibrillar polysaccharide in an aqueous medium. The aqueous medium
10 optionally may have additives such as swelling agents, in particular interfibrillar and/or intercrystalline swelling agents, for example sodium hydroxide, to aid in improving the ease of microfibril generation. A more preferred method of microfibrillation involves the use of mechanical energy on an aqueous suspension of derivatized polysaccharide which has not been dried. Other microfibrillation processes include, by way of non-limiting example, use of an impingement mixer; heat; steam explosion; pressurization-depressurization cycle; freeze-thaw cycle; impact; grinding (such as a disc grinder); pumping; mixing; ultrasound; microwave explosion; and milling. Combinations of
15 these may also be used, such as milling followed by homogenization. Essentially any method of reducing particle size may be used, but methods for reducing particle size while preserving a high aspect ratio in the polysaccharide are preferred. As described previously, the degree of substitution of the polysaccharide also affects the ease of
20 processing the polysaccharide to microfibrillar form.

The process to generate the particulate may either be run by the consumer in the final application such that the particulate is generated in situ, or be run as described
25 above in aqueous media, the material dehydrated, and the resulting particulate dried. The dried particulate of this invention, hereafter referred to as the ready-to-gel or RTG form, can be rehydrated readily in polar solvents to obtain the desired rheological attributes. Dehydration can be accomplished by displacing water with less polar
30 solvents and drying, and can be accelerated by protonation or shielding of charged groups if they are present.

In terms of general properties, applications where the derivatized microfibrillar polysaccharide of the present invention have particular utility include those where the

desired rheological attributes include at least one of yield stress, shear reversible gelation, and a modulus which is insensitive to temperature. The ability to provide the rheological attributes described herein also makes it possible to provide stabilization of mixtures of liquids and solids having different densities; gel-like properties, including 5 mouth feel; pumpable gels; stabilization at elevated temperatures; and, control of hydration and diffusion.

In terms of more specific applications or fields of use, the utility of the present derivatized microfibrillar polysaccharides includes, without limitation, foods, personal care products, household products, pharmaceuticals, neutraceuticals, paper manufacture 10 and treatment, coating compositions, water treatment, drilling fluids, agriculture, construction, and spill control and/or recovery.

In food applications, the derivatized microfibrillar polysaccharides of the present invention may be useful as rheology modifiers; as stabilizers, such as by inhibiting creaming or settling in suspensions; and as non-digestable dietary fiber. They may also 15 be used to control ice crystal growth during, for example, ice cream manufacture and storage.

In personal care products, the derivatized microfibrillar polysaccharides may be used to stabilize emulsions, dispersions, suspensions, and foams, and may find use in creams, lotions, gels, and pastes, including those intended for epidermal application. 20 Representative but not exhaustive examples include sunscreens; moisturizing or anti-aging creams and lotions; cleaning soaps or gels; antiperspirants and deodorants, including those in stick, pump spray, aerosol, and roll-on form; fragrance releasing gels; lipsticks, lip glosses, and liquid makeup products; oral care products, including toothpastes, tooth polishing and whitening agents, and denture care products such as 25 cleaners and adhesives, and further including use in sorbitol, sorbitol-water mixtures, and glycerol-water mixtures; products where controlled, sustained, or delayed release of an ingredient would be desirable; wound care products, such as ointments (including anesthetic, antiseptic, and antibiotic ointments), dressings, and products such as ostomy rings where good liquid retention is desirable; and absorbent products, such as diapers. 30 The present invention may have particular utility, not only in personal care products but in other applications, with products dispersed by a pumping action. The shear-reversible gelation exhibited by the derivatized microfibrillar polysaccharide is well

suited for pump dispensing, and may be advantageously combined with its ability to stabilize emulsions, dispersions, and foams to improve the uniform delivery of product.

In the area of household products, the rheological properties of the present derivatized microfibrillar polysaccharides, and their ability to stabilize emulsions, 5 dispersions, and foams, provide utility in areas such as detergents, shampoos, cleaners, and air fresheners. Specific examples include, without limitation, laundry products (including detergents, pre-spotting cleaners, and fabric treatment compositions, such as softeners); rug and upholstery shampoos; toilet bowl cleaners (particularly those dispensed in liquid or gel form); air fresheners; and general purpose cleaning agents, 10 including liquids, gels, pastes, and foams used in cleaning and/or disinfecting household surfaces.

In pharmaceutical applications, the derivatized microfibrillar polysaccharides may have utility in controlled, sustained, or delayed release formulations; as disintegrants; as dietary fiber; in wound care, particularly in applications (such as ostomy rings) where 15 liquid-holding ability is important; and as rheology modifiers.

In the area of paper manufacture and treatment, the derivatized microfibrillar polysaccharides of the present invention have utility in emulsion modification and/or stabilization; sizing; retention; clarification; absorbence; drainage; formation (such as by functioning as flocculation aids); deposit or scale control (by inhibiting the formation 20 and/or growth of inorganic deposits); water treatment; dewatering; film and membrane formation; polyelectrolyte cross-linking; removal of detrimental organic and/or inorganic materials; in paper coatings; and in improving properties such as stiffness, wet strength, absorbancy, softness, toughness, tear resistance, and fold resistance.

In the context of paper manufacture, scale control refers to the prevention of 25 calcium carbonate and calcium oxalate deposits forming during the pulping process. Scale control can be achieved by dispersion of salt crystals in the medium to prevent growth and deposition, inhibition of nucleation, or modification of the crystal growth mechanism to prevent the formation of crystal forms that will lead to deposits. The use of derivatized microfibrillar cellulose having micron and smaller particle size, stabilized 30 with appropriate functional groups, would serve to control scale deposit because such microcarriers inhibit the crystal growth which leads to deposition. Moreover, cellulosic materials would be easier to recover from the pulping process due to their organic

nature. Preferred functional groups would include phosphate/phosphonate groups, carboxylate groups, and sulfate/sulfonate groups. Alternative functional groups and appropriate use levels may be readily determined by those of ordinary skill in the art, based on the particular environment of use.

5 The derivatized microfibrillar cellulose may also be used in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture; to retain organic and/or inorganic dispersed particles (such as pulp fines, fillers, sizing agents, pigments, and/or clays); to retain detrimental organic and inorganic particulate materials; to improve the uniformity of formation of a
10 sheet of paper; and to improve the strength of a sheet of paper. With particular regard to drainage, drainage aids are additives that increase the rate at which water is removed from a paper slurry on a paper machine. These additives increase machine capacity, and hence profitability, by allowing faster sheet formation.
15 Anionically charged microfibrillar cellulosic derivatives are capable of greatly increasing drainage, either alone or in combination with other charged polymers.

The derivatized microfibrillar cellulose of the present invention may also be used in coated papers, where cellulose derivatives may be used to control the rheology of the color coating and to provide water retention, thereby controlling the amount of liquid that permeates into the base sheet.

20 In coating compositions, such as paints and inks, the derivatized microfibrillar polysaccharides can provide rheology modification, improving properties such as spatter, leveling, sag resistance, flooding, and floating, and may have particular utility in gel paints. They may also improve pigment dispersion and/or stabilization, and function as charge control or flow control agents, including in inks, such as ink jet inks.

25 In the area of water treatment, the derivatized microfibrillar polysaccharides of the present invention can provide scale control, that is, inhibiting the formation and/or growth of inorganic deposits in aqueous systems; clarification; flocculation; sedimentation; coagulation; charge delivery; and softening.

30 In drilling fluids, the present derivatized microfibrillar polysaccharides can provide rheology modification, reduce or prevent fluid loss, and improve secondary oil recovery.

In agricultural applications, the derivatized microfibrillar polysaccharides of the present invention can be used in soil treatment, and may provide moisture retention, erosion resistance, frost resistance, and controlled, sustained, or delayed release of agricultural materials such as fertilizers, pesticides, fungicides, and herbicides. They 5 may also be used for crop protection, such as to minimize or prevent frost damage.

In construction, the derivatized microfibrillar polysaccharides can be used in dry wall muds, caulk, water-soluble adhesives, and board manufacture.

In other areas, the derivatized microfibrillar polysaccharides can be used for control and cleanup of liquid spills, as absorbents for oil; in general, as stabilizers for 10 emulsions, dispersions, and foams (including but not limited to oil-in-water and water-in-oil emulsions); and for emulsification. Stability of commercial emulsions, such as paper size emulsions, is a recurring issue in industry. Current commercial emulsions include those which generally consist of an oil, waxy, or rosin phase dispersed in water. These dispersions are generally stabilized by the addition of charged materials such as 15 cationic starches, sodium lignin sulfonate, and aluminum sulfate. Such materials are generally added in amounts equal to about 10-20% by weight of the size component. The resulting dispersions are typically 0.2 to 2 micron particles, thought to be stabilized by charge repulsion, for example, with the positively charged starches on particle surfaces repelling each other.

20 One cause of emulsion failure is density-driven separation. This can be limited by increasing viscosity, or internal structure within the fluid. For example, an emulsion which maintains a viscosity of less than about 20 centipoise throughout a standard aging test might have its viscosity increased initially by as much as 100 centipoise through addition of a viscosifier to the formulation, and still be within acceptable commercial 25 viscosity, provided that the viscosity did not then increase over time to exceed acceptable limits.

One method to accomplish this result would be to use a viscosifying agent that does not cause a substantial increase in viscosity when first added to an emulsion 30 formulation, but which does provide an increase in viscosity during normal processing of the emulsion formulation to produce the emulsion. This can be accomplished by including, as an additive to the emulsion formulation, polysaccharide that has been derivatized as described herein but not yet microfibrillated. When the emulsion

formulation is then subjected to energy, typically high shear, during the processing used to turn the emulsion formulation into an emulsion, the shear will also microfibrillize the derivatized polysaccharide, resulting in the derivatized microfibrillar polysaccharide of the present invention, which will be present as part of the emulsion. The gel produced by the derivatized microfibrillar polysaccharide will then thin under shear stress but reform when shear stops. Moreover, the insolubility of such low DS/MS polysaccharide may cause it to concentrate at the oil/water interface of oil-and-water emulsions, rather than the aqueous bulk phase, which may be desirable.

Effectively the same result may be achieved by adding the derivatized microfibrillar polysaccharide of the present invention to an emulsion formulation, or to the final emulsion, or at any point during production of the emulsion. Further variations would include introducing derivatized polysaccharide that is only partially microfibrillated into the emulsion-making process at a point where subsequent processing would provide sufficient energy to complete the microfibrillation. It may also be possible to accomplish some or all of the derivatization as part of the emulsion production process; for example, the emulsion formulation may include a charged species that will adsorb onto the polysaccharide microfibrils, or such a species may be added during processing of the emulsion formulation, separately or in combination with the polysaccharide. Therefore, the derivatized microfibrillar polysaccharides of the present invention may serve as stabilizing additives to emulsions, with several process routes being available to accomplish this end result.

While the choice of method may cause some variation in the properties of the resulting emulsion, the basic benefit of improved emulsion stability should be achieved by any procedure which has, as its final result, the presence of the derivatized microfibrillar polysaccharide of the present invention in the final emulsion.

Commercially, it may be desirable to supply customers with derivatized, non-microfibrillated polysaccharide as a powder which, when added to a formulation and subjected to high shear or other appropriate forms of energy, will microfibrillate and yield the derivatized microfibrillar polysaccharide of the present invention.

This improved emulsion stability may enable use of emulsion formulations which would not perform satisfactorily in the absence of the derivatized microfibrillar polysaccharide. Other benefits may include improved retention in paper, improved

drainage of water from paper systems due to association of pulp and filler fines with the retained microfibrils, and resistance to emulsion breakage in the presence of high salt concentrations.

The subject electrostatically derivatized materials of this invention have also been discovered to provide rheology to aqueous systems over a wide pH range (namely from about 2.5 to 10 or higher) and ionic strength. This insensitivity to pH and ionic strength facilitates use in areas where low pH and high salt conditions exist, such as in personal care creams and lotions, food products, and the like.

In addition to the above, the derivatized microfibrillar polysaccharides of the present invention represent a vehicle for providing charge, whether anionic, cationic, or both, to a given environment. This may, as a representative example, have utility in water treatment, where charged particles are used to flocculate particulates and other contaminates.

The following examples indicate various possible methods for making and using the derivatized microfibrillar cellulose of present invention. These examples are merely illustrative, and are not to be construed as limiting the present invention to particular compounds, processes, conditions, or applications. Throughout this description, "gelling" is defined to occur when $G' > G''$, where G' is the dynamic storage modulus and G'' is the dynamic loss modulus. This is the functional definition used in EP '011; for general background, see Ferry, J.D., Viscoelastic Properties of Polymers, John E. Wiley & Sons, NY, 1980.

Example 1 (Comparative): Microfibrillated, Non-Derivatized Cellulose.

The following three components were weighed into a one gallon jar at the following wt% levels:

| | | <u>Weight</u> | <u>Weight%</u> | <u>Dry Wt. Basis</u> |
|----|--|---------------|----------------|----------------------|
| | Bleached sulfate wood pulp (5.2% moisture) (Weyerhaeuser Company) | 74.82g | 2.11 | 2.00 |
| 30 | Germaben® II biocide (Sutton Laboratories, New Jersey) | 17.50g | 0.49 | 0.49 |
| | Deionized (DI) water | 3445.58g | 97.39 | 97.50 |

The cellulose quickly settled to the bottom of the jar when there was no agitation of the slurry. The jar was shaken to disperse the solids. The slurry was then processed in a dual stage Gaulin Model 15MR homogenizer. The secondary stage was set at about 1000psi and the primary stage was adjusted so that the total pressure was about 8000psi. The 5 slurry was processed for a total of 3.5 hours. The resulting slurry had a much thicker consistency and the cellulose remained suspended. When this suspension was diluted to 1.0% solids in DI water, the resulting suspension was a viscous slurry which did not exhibit gel properties. Over time the 1% suspension settled, leaving free water on the surface.

10 **Example 2: Preparation and Microfibrillation of Carboxymethylcellulose I (CMC I).**

Isopropanol (IPA) and DI water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. 15 Sulfate wood pulp (approximately 400 µm length) was added to the reactor and the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15° C. The reactor was inerted. Aqueous 50% NaOH was slowly added to the reactor while maintaining the mixture slurry's temperature at about 15° C. The slurry was agitated for 1 hour after 20 completion of caustic addition. Aqueous monochloroacetic acid (80% MCA) was slowly added to the reactor by funnel while maintaining reaction slurry temperature at about 15°C. After MCA addition, the reaction slurry was heated to 70° C and held for 1.5 hours. The reaction slurry was cooled below 30° C and glacial acetic acid was added to the reactor. The reaction mixture was then aspirator vacuum filtered with a 25 sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80% methanol for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three washes was slurried in 1000g of pure methanol using an air driven stirrer and a grounded 30 stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in a Lab-Line fluidized bed dryer (model number 23852) for 35 minutes (air-dry for 5 minutes, heat-

dry at 50° C for 10 minutes, and heat-dry at 70° C for an additional 20 minutes) The carboxymethylcellulose (CMC) product was ground using a Retsch Grinding Mill (model 2M1) with a 1mm screen. (Although the examples herein show washing of the product, the need for, or amount of, washing will depend on the intended application.)

5

Table 1: CMC I Recipes

(all weights in grams)

| Sample # | Cellulose Length | Wt. Cellulose (dry wt. Basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. 80% MCA (aq) | Wt. Glacial Acetic Acid | DS |
|----------|------------------|-------------------------------|---------|----------------------|-------------------|------------------|-------------------------|------|
| 1 | ~400 µm | 61.36 | 729 | 73.6 | 60 | 11.8 | 32.2 | 0.16 |
| 2 | ~400 µm | 61.36 | 729 | 73.6 | 60 | 11.8 | 32.2 | 0.18 |

Preparation of CMC slurry: An 800 g 1% CMC slurry was made from each Sample in Table 1 using the following materials:

10

| | <u>Weight</u> | <u>Weight%</u> |
|------------------------|---------------------|---------------------|
| CMC | 8.00 grams | 1.0 ± 0.06% |
| Germaben ® II biocide | 4.00 grams | 0.5% |
| <u>Deionized water</u> | <u>788.00 grams</u> | <u>98.5 ± 0.06%</u> |
| Total | 800.00 grams | |

15 The container was closed and shaken to wet and disperse the CMC solids. The solids will settle if left standing, so the container was shaken just prior to pouring the slurry into the homogenizer.

20 **Homogenization of CMC slurries:** The suspension was processed in the homogenizer equipped with an agitated feed pot as follows: the homogenizer was turned on before the slurry was loaded. An 800 gram slurry was processed for about 20 minutes at about 3000 psi by recycling the discharged stream from the homogenizer to the feed pot. Pressure was monitored and appropriate adjustments made to the primary stage handwheel to keep the total pressure at about 3000 psi. After the processing was completed, the discharge tube was redirected so that the sample was collected and stored 25 in a capped jar.

Rheological testing of microfibrillated CMC I: Each microfibrillated CMC sample prepared in Example 2 was then tested for rheological properties. Data was collected on a Bohlin CS Rheometer (Bohlin Instruments, Cranbury, New Jersey).

Dynamic mechanical properties were measured including the dynamic storage modulus, the dynamic loss modulus, complex viscosity, and yield stress.

Rheometer Test Conditions

Temperature Sweep: Measuring System: PP 40; 25° C - 65° C; Shear Stress: automatic;

5 Frequency: 1 Hz; Temperature Ramp Rate: 5° C/60 seconds; Measurement Interval: 20 seconds; Gap: 1 mm.

Yield Stress Test: Measuring System: CP 4/40; Stress: 6.0E-02 - 1.0E+02; Sweep Time: 60.0 seconds; Number of Steps: 30; Temperature: Manual (25° C); No of measurements: 1; Measurement Interval: 5 seconds.

10 Stress Sweep Test: Measuring System: PP 40; Temperature: Manual (25 °C); Number of Measurements: 1; Gap: 1 mm; Measurement Interval: 5 seconds; Frequency: 1 Hz.

Table 2: Rheology of Microfibrillated CMC I

| Sample # | Cellulose Length | DS of CMC I | Yield Stress (Pa) | G' @ 5.75 Pa (Pa) |
|----------|------------------|-------------|-------------------|-------------------|
| 1 | ~400 µm | 0.16 | 8.08 | 256 |
| 2 | ~400 µm | 0.18 | Not Tested | 192 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 15 1 is given in Figure 1.

Example 3: Preparation and Microfibrillation of Carboxymethylcellulose II (CMC II).

Isopropanol (IPA) and DI water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing 20 addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple.

Sulfate wood pulp (approximately 400 µm length) was added to the reactor, the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15° C. The reactor was inerted. Aqueous 50% NaOH was slowly added to the reactor maintaining the mixture slurry's 25 temperature at about 15° C. The slurry was agitated for 1 hour after completion of caustic addition. Aqueous monochloroacetic acid (80% MCA) was slowly added to the reactor by funnel while maintaining reaction slurry temperature at about 15°C. After MCA addition, the reaction slurry was heated to about 70° C and held for 1.5 hours. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered

with a sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80% methanol for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three washes
 5 was slurried in 1000g of pure methanol using an air driven stirrer and a grounded stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in a Lab-Line fluidized bed dryer (model number 23852) for 35 minutes (air-dry for 5 minutes, heat-dry at 50° C for 10 minutes, and heat-dry at 70° C for an additional 20 minutes). The
 10 carboxymethylcellulose (CMC) product was ground using a Retsch Grinding Mill (model 2M1) with a 1mm screen.

Table 3: CMC II Recipes(all weights in grams)

| Sample # | Cellulose Length | Wt Cellulose (dry wt. basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. 80% MCA (aq) | DS |
|----------|------------------|------------------------------|---------|----------------------|-------------------|------------------|------|
| 1 | ~400 µm | 77.11 | 937.5 | 141.64 | 12.50 | 8.63 | 0.04 |
| 2 | ~400 µm | 61.69 | 750 | 113.32 | 10.00 | 6.90 | 0.06 |
| 3 | ~400 µm | 77.11 | 937.5 | 141.64 | 25.00 | 17.25 | 0.13 |
| 4 | ~400 µm | 61.91 | 750 | 113.09 | 20.00 | 13.95 | 0.15 |
| 5 | ~400 µm | 61.30 | 750 | 113.71 | 20.00 | 13.86 | 0.16 |
| 6 | ~400 µm | 61.91 | 750 | 113.09 | 20.00 | 13.79 | 0.17 |
| 7 | ~400 µm | 61.43 | 750 | 113.58 | 23.60 | 16.27 | 0.19 |
| 8 | ~400 µm | 61.62 | 750 | 109.38 | 28.00 | 19.32 | 0.23 |
| 9 | ~400 µm | 61.88 | 750 | 108.12 | 30.00 | 20.70 | 0.28 |
| 10 | ~400 µm | 61.43 | 750 | 106.08 | 35.00 | 24.15 | 0.31 |
| 11 | ~400 µm | 61.43 | 750 | 108.58 | 30.00 | 20.70 | 0.34 |
| 12 | ~200 µm | 62.60 | 750 | 116.41 | 12.00 | 8.28 | 0.10 |
| 13 | ~200 µm | 62.60 | 750 | 112.91 | 19.00 | 13.11 | 0.17 |

Slurry preparation and homogenizer processing were performed as in example 2.

15 Rheological testing was performed as described in example 2.

Table 4: Rheology of Microfibrillated CMC II

| Sample # | Cellulose Length | DS of CMC I | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) | G' @25 °C/50 °C(Pa) |
|----------|------------------|-------------|------------------|------------------|---------------------|
| 1 | ~400 µm | 0.04 | Not Tested | 125 | 145/168 |
| 2 | ~400 µm | 0.06 | Not Tested | 139 | 161/160 |
| 3 | ~400 µm | 0.13 | 18.0 | 467 | 508/493 |
| 4 | ~400 µm | 0.15 | Not Tested | 467 | 441/429 |
| 5 | ~400 µm | 0.16 | 18.1 | 474 | 436/450 |
| 6 | ~400 µm | 0.17 | 34.7 | 436 | 452/462 |
| 7 | ~400 µm | 0.19 | 28.1 | 306 | 331/352 |
| 8 | ~400 µm | 0.23 | 21.4 | 148 | 137/145 |
| 9 | ~400 µm | 0.28 | 18.0 | 114 | Not Tested |
| 10 | ~400 µm | 0.31 | 14.7 | 12.9 | 12.3/12.6 |
| 11 | ~400 µm | 0.34 | 11.4 | 19 | 23.4/24.9 |
| 12 | ~200 µm | 0.10 | 8.08 | 339 | Not Tested |
| 13 | ~200 µm | 0.17 | 16.1 | 354 | Not Tested |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 3 is given in Figure 2.

5 **Example 4: Preparation and Microfibrillation of Carboxymethylcellulose III (CMC III).**

Isopropanol and DI water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. 10 Sulfate wood pulp (approximately 400 µm length) was added to the reactor, the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to about 15° C. The reactor was inerted. Aqueous NaOH (50% NaOH) was slowly added to the reactor maintaining the mixture slurry's temperature at about 15 ° C. The slurry was agitated for 1 hour after completion 15 of caustic addition. Aqueous sodium monochloroacetate was prepared by mixing 80% MCA, 50% aqueous NaOH and DI water. This solution was slowly added to the reactor by addition funnel while maintaining reaction slurry temperature at about 15° C. After MCA addition, the reaction slurry was heated to about 70° C and held for 1.5 hours. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered 20 with a sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80%

methanol for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three washes was slurried in 1000g of pure methanol using an air driven stirrer and a grounded

5 stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was broken into small particles using a rubber spatula and then dried in the fluidized bed dryer for 35 minutes. (Air-dry for 5 minutes, heat-dry at 50 ° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes) The product was ground using the Retsch mill with a 1mm

10 screen.

Table 5: CMC III Recipes

(all weights in grams)

| Sample # | Cellulose Length | Wt Cellulose (dry wt. basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | NaMCA Solution | | | DS |
|----------|------------------|------------------------------|---------|----------------------|-------------------|----------------|----------|------------------|------|
| | | | | | | 80% MCA | 50% NaOH | H ₂ O | |
| 1 | ~400 µm | 61.88 | 750 | 117.12 | 6.39 | 8.28 | 5.61 | 3.0 | 0.06 |
| 2 | ~400 µm | 61.88 | 750 | 114.32 | 9.38 | 12.14 | 8.22 | 5.0 | 0.12 |
| 3 | ~400 µm | 61.62 | 750 | 113.38 | 12.58 | 16.27 | 11.02 | 10.0 | 0.16 |
| 4 | ~400 µm | 61.62 | 750 | 108.38 | 15.98 | 20.70 | 14.02 | 10.0 | 0.24 |
| 5 | ~400 µm | 61.62 | 750 | 105.88 | 18.64 | 24.15 | 16.36 | 10.0 | 0.29 |
| 6 | ~400 µm | 61.88 | 750 | 102.47 | 21.31 | 27.60 | 18.69 | 10.0 | 0.31 |
| 7 | ~200 µm | 62.60 | 750 | 116.41 | 6.39 | 8.28 | 5.61 | 10.0 | 0.08 |
| 8 | ~200 µm | 62.60 | 750 | 112.91 | 10.12 | 13.11 | 8.88 | 10.0 | 0.16 |
| 9 | ~200 µm | 62.60 | 750 | 110.61 | 12.57 | 16.28 | 11.03 | 10.0 | 0.21 |
| 10 | ~200 µm | 62.60 | 750 | 117.12 | 15.67 | 20.30 | 13.75 | 10.0 | 0.26 |

Slurry preparation and homogenizer processing were performed as in example 2 except

15 for Sample #7, which was processed for 30 minutes. Rheological testing was performed as described in example 2.

Table 6: Rheology of Microfibrillated CMC III

| Sample # | Cellulose Length | DS of CMC III | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) | G' @ 25°C/50°C(Pa) |
|----------|------------------|---------------|------------------|------------------|--------------------|
| 1 | ~400 µm | 0.06 | 14.7 | 281 | 316/310 |
| 2 | ~400 µm | 0.12 | 51.4 | 568 | 520/586 |
| 3 | ~400 µm | 0.16 | 28.1 | 564 | 607/649 |
| 4 | ~400 µm | 0.24 | 18.1 | 457 | 414/474 |
| 5 | ~400 µm | 0.29 | 21.4 | 298 | 292/303 |
| 6 | ~400 µm | 0.31 | 44.7 | 288 | Not Tested |
| 7 | ~200 µm | 0.08 | 4.70 | 238 | Not Tested |
| 8 | ~200 µm | 0.16 | 29.5 | 483 | Not Tested |
| 9 | ~200 µm | 0.21 | 18.1 | 339 | Not Tested |
| 10 | ~200 µm | 0.26 | 21.4 | 288 | Not Tested |

¹ 30 minute homogenizer processing time.

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 3 is given in Figure 3.

5 Example 5: CMC Preparation with Water Washing of Wetcake.

Isopropanol and DI water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. Sulfate wood pulp (approximately 400 µm length) was added to the reactor, the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15° C. The reactor was inerted. Aqueous NaOH (50% NaOH) was slowly added to the reactor maintaining the mixture slurry's temperature at about 15° C. The slurry was agitated for 1 hour after completion of caustic addition. Aqueous sodium monochloroacetate was prepared by mixing 80% MCA, 50% aqueous NaOH and DI water. This solution was slowly added to the reactor by addition funnel while maintaining reaction slurry temperature at about 15° C. After MCA addition, the reaction slurry was heated to about 70° C and held for 1.5 hours. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 650g of DI water for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated one additional time. The wetcake obtained from the previous two washes was slurried in 1000g DI water using an air driven stirrer and a grounded stainless steel

beaker for 15 minutes and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in the fluidized bed dryer for 35 minutes (air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes). The product was ground using the Retsch mill with a 1mm screen.

Table 7: Water Washed CMC Recipes

(all weights in grams)

| Sample # | Wt Cellulose (dry wt. Basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | NaMCA Solution | | | DS |
|----------|------------------------------|---------|----------------------|-------------------|----------------|----------|------------------|------|
| | | | | | 80% MCA | 50% NaOH | H ₂ O | |
| 1 | 61.88 | 750 | 110.5 | 10.12 | 13.11 | 8.88 | 10.0 | 0.10 |
| 2 | 60.06 | 750 | 110.5 | 10.12 | 13.11 | 8.88 | 10.0 | 0.13 |

Slurry preparation, homogenizer processing, and rheological testing were performed as described in example 2.

Table 8 Rheology of Water Washed CMC Samples

| Sample | DS of CMC | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) |
|--------|-----------|------------------|------------------|
| 1 | 0.10 | 37.4 | 724 |
| 2 | 0.13 | 34.7 | 855 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 2 is given in Figure 4.

15 Example 6: High Solids Reactions.

Sulfate wood pulp (about 200 µm length) was charged to an Abbey Ribbon Blender (model 0 RM, Paul O. Abbe, Inc., Little Falls, New Jersey) equipped with a spray nozzle. The reactor was sealed and the system was inerted with nitrogen under slow agitation. Agitation was increased to approximately 125 rpm and a solution of 20 50% aqueous NaOH and DI water was sprayed into the reactor. The mixture was mixed for one hour at ambient temperature. An aqueous solution of sodium monochloroacetate (NaMCA) was sprayed into the reactor and the reactor temperature was increased to 75° C and held for 2 hours. Glacial acetic acid was sprayed into the reactor and the reactor was cooled to approximately 30° C. The product was slurried in 3 liters of water for 15 25 minutes and filtered using a rubber dam. This slurry/filtration process was repeated

three additional times. The final filter cake was dried in the fluidized bed dryer and ground in the Retsch mill using a 1 mm screen.

Table 9: High Solids Recipes

(all weights in grams)

| Sample | Wt. Cellulose (dry wt. Basis) | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. NaMCA (NaMCA/H ₂ O) | Acetic Acid | DS |
|--------|-------------------------------------|----------------------|----------------------|---------------------------------------|----------------|------|
| 1 | 500 | 93 | 62.8 | 105/128.3 | 0 | 0.10 |
| 2 | 180 | 64.8 | 43.2 | 45.3/55.4 | 8.6 | 0.17 |

5 Slurry preparation: As in Example 2, except that Sample #2 (DS = 0.17) was worked up as a 10% solids slurry in water. This slurry was then mixed with more water and Germaben® II to make the new slurry which was processed in the homogenizer.

| | | <u>Weight</u> | <u>Weight%</u> |
|----|------------------------|---------------------|----------------|
| 10 | 10% CMC slurry | 80.07 grams | 10.00% |
| | Germaben® II biocide | 4.01 grams | 0.50% |
| | <u>Deionized water</u> | <u>716.88 grams</u> | <u>89.50%</u> |
| | Total | 800.96 grams | |

Since the final slurry is 10% by weight of a 10% CMC slurry, the actual CMC level is 15 the normal 1% by weight. Homogenization was performed as in Example 2 except that Sample #1 was processed for 25 minutes, and rheological testing was performed as in example 2.

Table 10: Rheology of High Solids Samples

| Sample | DS of CMC | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) |
|--------|--------------|---------------------|---------------------|
| 1 | 0.10 | 18.1 | 248 |
| 2 | 0.17 | 31.4 | 427 |

20 A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 2 is given in Figure 5.

Example 7: Preparation of Ready-to-Gel Microfibrillated CMC.

Gels were made as described in the slurry preparation and homogenization processing steps in Example 2 using CMC II as made in example 3 (DS about 0.16).

25 The gels were then processed as follows (the following description pertains to Sample #1 in Table 11, and a similar procedure was used for all of the other samples):

Approximately 2800 ml of isopropyl alcohol was added to a grounded 12 quart stainless steel (SS) beaker. The IPA was stirred at the top speed of an overhead stirrer driven by house air. A SS cowls blade on a SS shaft was used to stir the IPA. about 1400 grams of 1% CMC II gel was slowly added to the stirring IPA. The material ratio 5 was 2 ml IPA/1 gram gel. It took about 5 minutes to add the gel to the IPA. The beaker was covered with plastic film and the slurry was stirred for ten minutes.

When ten minutes had passed, the slurry was filtered through a synthetic straining cloth. The slurry was filtered using gravity. The slurry was covered with plastic film during the filtration to reduce IPA evaporation. Occasionally the gel on the cloth was 10 stirred with a plastic spatula to help speed filtration. When it appeared that the filtration had gone about as far as it could, the wet cake was transferred back to the 12 quart SS beaker.

Approximately 2800 ml of fresh IPA was added to the beaker and the slurry was again stirred for ten more minutes with the cowls blade/air stirrer. The slurry was then 15 filtered on a 20 cm Büchner funnel with #415 VWR filter paper. The wet cake was transferred to a glass crystallization dish. The dish and wet cake were placed into an 80° C oven under vacuum overnight for drying. The sample was dried to constant weight. The solids were ground in a Waring Blender.

The dehydrated gels were examined by rehydration as follows: a premix of DI 20 water and Germaben® II was prepared.

| | <u>Weight</u> | <u>Weight%</u> |
|----------------------|---------------|----------------|
| Deionized water | 788.00 grams | 99.49% |
| Germaben® II biocide | 4.00 grams | 0.51% |

The water/Germaben® II solution was then weighed into a small Waring blender cup along with the Ready-to-gel dry CMC according to the recipes in Table 11. The blender 25 cup was covered and the sample was mixed until it appeared to be homogeneous. The resulting gel was transferred to a glass jar. It was then shaken on a vortex mixer.

Rheological testing was performed as described in example 2.

Table 11: Rheology of RTG CMC

| Sample | Wt. % water/Germaben® II | Wt% RTG CMC | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) |
|--------|--------------------------|-------------|------------------|------------------|
| 1 | 99.75 | 0.25 | 2.4 | 5.61 |
| 2 | 99.5 | 0.50 | 10.7 | 68.6 |
| 3 | 99.0 | 1.00 | 25.7 | 328 |
| 4 | 98.5 | 1.50 | 51.0 | 731 |
| 5 | 98.0 | 2.00 | 95.3 | 1400 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 1 through 5 are given in Figures 6 through 10, respectively.

5 **Example 8A: Acid Process for Preparation of Ready-to-Gel Microfibrillar CMC.**

A gel as prepared in example 3 was acidified using HCl to adjust the pH to about 2.7. The gel was centrifuged to remove about 60% of the water. The concentrated gel was then converted to RTG form by mixing with IPA equivalent to 2 times the weight of the gel, followed by filtration on a Büchner funnel and a second mix with another 2 times weight of IPA. The wet cake was dried in a vacuum oven.

10 The dried solids were rehydrated at 1% in water/Germaben® II biocide. A small amount of baking soda was added and the sample was mixed on the blender. Viscosity rose gradually with stirring and the sample became gel-like. The pH was about 6.9.

Rheological testing was performed as described in example 2. G' @ 5.75 Pa: 15 226 Pa, Yield Stress: 17.4 Pa. A copy of the dynamic mechanical spectra (obtained by the stress sweep test) is given in Figure 11.

Example 8B: Acid Process for Preparation of Ready-to-Gel Microfibrillar CMC.

A second batch of gel as made in example 3 had its pH adjusted to about 2.7 with concentrated HCl. The sample was centrifuged and about 62% of the water was removed. About 97g of concentrated gel was slurried with 150 ml IPA. The pH was adjusted to 7.0 during the stirring of the slurry by addition of a small amount of baking soda. The slurry was filtered on a Büchner funnel, and half of the wet cake (Sample A) was weighed into a crystallization dish for drying. For Sample B, the other half of the wet cake was reslurried in about 75 ml IPA. This wet cake was filtered on a Büchner funnel and was pressed with rubber dam to remove as much IPA as possible. Both wet

cakes were dried to constant weight under vacuum, and the solids were ground up in a Waring blender.

Sample A was mixed with water for a total solids level of 1%, and gelled quickly. The pH was about 5.8. Sample B gelled quickly when stirred in water at a solids level of 5 1%.

Rheological testing was performed as described in example 2.

Sample A: G' @ 5.75 Pa: 471 Pa, Yield Stress: 34.0 Pa. A copy of the dynamic mechanical spectra (obtained by the stress sweep test) is given in Figure 12.

Sample B: G' @ 5.75 Pa: 403 Pa, Yield Stress: 35.7 Pa. A copy of the dynamic 10 mechanical spectra (obtained by the stress sweep test) is given in Figure 13.

Example 9: Derivatization of Microfibrillar Cellulose.

Isopropanol (602.8g) and DI water (86.4g) were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and 15 thermocouple. Microfibrillated cellulose of Example 1 was vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80% isopropanol (IPA) for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three 20 washes was slurried in 1000g of pure IPA using an air driven stirrer and a grounded stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The resulting wet cake, comprised of 36g microfibrillated cellulose, 228g IPA, and 36g DI water was added to the reactor, the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15° C. The reactor was 25 inerted. Aqueous 50% NaOH (10.52g) was slowly added to the reactor maintaining the mixture slurry's temperature at about 15° C. The slurry was agitated for 1 hour after completion of caustic addition. Aqueous monochloroacetic acid (7.26g of 80% aq MCA) was slowly added to the reactor by funnel while maintaining reaction slurry 30 temperature at about 15° C. After MCA addition, the reaction slurry was heated to about 70° C and held for 1.5 hours. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The

wetcake was slurried in 565g of 80% methanol for 15 minutes using an air driven stirrer and a ground stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three washes was slurried in 1000g of pure methanol using an air driven stirrer and a ground stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in the fluidized bed dryer for 35 minutes (air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes). The product was ground using the Retsch mill with a 1mm screen. DS of the resulting material was 0.14.

A 1% aqueous suspension of the product was mixed in a Waring blender for 15 minutes. This produced a viscous suspension which did not settle with time.

Slurry preparation: Same as in example 2. Homogenization was performed as in example 2, except where otherwise stated, and rheological testing was performed as in example 2.

Yield Stress: 5.75 Pa, G' @ 5.75 Pa: 363 Pa. A copy of the dynamic mechanical spectra (obtained by the stress sweep test) is given in Figure 14.

Example 10: Alternative Cellulose.

CMC was produced as in example 3 using the cellulose source and recipe in Table 12.

20

Table 12: Alternative Cellulose Recipe

(all weights in grams)

| Sample | Cellulose Source | Wt Cellulose (dry wt. basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. 80% MCA (aq) | DS |
|--------|------------------------|------------------------------|---------|----------------------|-------------------|------------------|------|
| 1 | Avicel® pH-101NF (-90) | 62.01 | 750 | 113.49 | 19.00 | 13.11 | 0.16 |
| 2 | Solka® Floc (1) | 61.23 | 750 | 114.27 | 19.00 | 13.11 | 0.19 |
| 3 | CTMP (2) | 54.5 | 750 | 121 | 19.00 | 13.11 | 0.22 |

(1) Solka Floc (grade 300 FCC) obtained from Fiber Sales & Development Corp.,

Urbana, Ohio.

25 (2) Bleached CTMP (Chemical Thermomechanical Pulp) Fluff obtained from SCA Graphic Sundsvall AB, Timra, Sweden

Slurry preparation of the Solka Floc sample (Sample 2) was prepared as in Example 2. Homogenizer processing was performed as in Example 2, and rheological testing was performed as in Example 2.

Table 13: Rheology

| Sample | Cellulose Source | DS of CMC | Yield Stress ¹ (Pa) | G' @ 5.75 Pa(Pa) |
|--------|------------------|-----------|--------------------------------|------------------|
| 2 | Solka Floc | 0.19 | 22.4 | 141 |

5 ¹ From yield stress test/ from stress sweep test.

A copy of the dynamic mechanical spectra of sample 2 is given in Figure 15.

Example 11: Microfibrillation of CMC with Impingement Mixer.

The samples used were 0.5%, 1.0% and 1.5% suspensions of low DS CMC prepared as in Example 3. Each slurry weighed a total of 100 grams. No Germaben® II biocide was used in the samples processed in the impingement mixer. The slurries were prepared by weighing the components into four ounce glass jars. The jars were capped and shaken to wet and disperse the CMC solids.

| | <u>Sample #1 (0.5%)</u> | <u>Sample #2 (1.0%)</u> | <u>Sample #3 (1.5%)</u> |
|----------|-------------------------|-------------------------|-------------------------|
| CMC | 0.50 grams | 1.0 grams | 1.5 grams |
| DI water | 99.5 grams | 99.0 grams | 98.5 grams |

A Microfluidics Corporation Model M110 Series impingement mixer was flushed with DI water prior to use. The pressure was adjusted to the desired setting as the water was pumped. The impingement mixer was run such that the DI water was pumped until it was just at the bottom of the charge funnel. A heating bath used to control the temperature of the impingement mixer piping was set at 50° C.

The sample jar was shaken again just before charging the sample funnel. The sample was charged into the funnel. An electric overhead stirrer was in the sample funnel. This was turned on to help keep the CMC homogeneously suspended. After the first pass, the stirrer is not needed. The sample was pumped through the microfluidizer and out into a collection jar. The material initially collected which contains the initial DI residue was discarded. Processing was then continued until the entire sample had been processed for 1 pass through the equipment.

The 0.5% solids gel was processed at 6000 psi for 4 passes. The 1.0% solids gel was processed under the same conditions. The 1.5% solids gel was processed at 6000 psi for just 3 passes.

Table 14: Rheology of Impingement Mixer Microfibrillated CMC

| Sample | Cellulose Length | DS of CMC | Yield Stress(Pa) | G' @ 5.75 Pa (Pa) | G' @ 25°C/50°C (Pa) |
|--------|---------------------------|-----------|------------------|-------------------|---------------------|
| 1 | ~400 µm(0.5% solids gel) | 0.17 | 4.82 | 79.3 | 97/109 |
| 2 | ~400 µm(1.0% solids gel) | 0.17 | Not Tested | 270 | 222/242 |
| 3 | ~400 µm (1.5% solids gel) | 0.17 | Not Tested | 522 | 363/434 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Samples 1 through 3 are given in Figures 16 through 18.

5 **Example 12: Microfibrillated Hydrophobically Modified Carboxymethyl Cellulose (HMCMC)**

Tert-butyl alcohol (TBA, 750 g) and Hercules CMC 7H (DS of about 0.7, 100 g) were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. The mixture was nitrogen sparged for 1 hour at 25 ° C. Aqueous NaOH (54 g of 7.5% NaOH) was slowly added to the reactor maintaining the mixture slurry's temperature at about 25° C. The slurry cooled to about 15° C and was agitated for 1 hour at about 15° C. A 50% solution of cetyl glycidal ether (40 g of solution) was slowly added to the reactor by addition funnel while maintaining reaction slurry temperature at about 15° C. The reaction slurry was heated to about 80° C and held for 3.25 hours. The reaction slurry was cooled down to about 50° C and 9 g of 70% nitric acid was added. The mixture was cooled to about 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 1000 g of 85% acetone for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two additional times. The wetcake obtained from the previous three washes was slurried in 1000g of 100% acetone using an air driven stirrer and a grounded stainless steel beaker for 15 minutes and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in the fluidized bed dryer for 35 minutes. (Air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes)

The product was ground using the Retsch mill with a 1mm screen. The cetyl content of the resulting product was \leq 0.03 wt.%.

Slurry preparation, homogenizer processing, and rheological testing were performed as described in example 2. G' @ 5.75 Pa: 319 Pa, Yield Stress: 14 Pa. A copy of the dynamic mechanical spectra (obtained by the stress sweep test) is given in Figure 19.

While the use of hydrophobically modified derivatized microfibrillar cellulose has been demonstrated herein by a particular example, for purposes of the present invention a derivatized microfibrillar cellulose may be hydrophobically modified by carbon groups having from about 4 to about 30 carbons.

10 **Example 13: Microfibrillated Hydroxyethylcellulose (HEC).**

Sulfate wood pulp, tert-butyl alcohol (TBA), acetone, isopropanol (IPA) and DI water were charged to a nitrogen sparged, agitated Chemco reactor (3 pint reactor, Chemco, Tulsa, OK). The reactor was inerted with nitrogen and the reaction slurry temperature was adjusted to 20° C. Aqueous NaOH (50% NaOH) was added to the reactor and the mixture was agitated for 45 minutes at 20 ° C. Ethylene oxide (EO) was charged to the reactor over a period of about 5 minutes, maintaining the reaction slurry at 20° C. After EO addition, the reaction slurry was heated to 50° C and maintained at 50° C with agitation for about 45 minutes. The reaction slurry was then heated to about 90° C and maintained at 90° C with agitation for 30 minutes. The reaction slurry was cooled to about 50° C and 70% nitric acid was added. The reaction slurry was cooled to below 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 600g of 80% acetone for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two additional times.

15 The wetcake obtained from the previous three washes was slurried in 600g of 100% acetone water using an air driven stirrer and a grounded stainless steel beaker for 15 minutes and then aspirator vacuum filtered with a sintered glass funnel and rubber dam.

20 The final wetcake was dried in the fluidized bed dryer for 35 minutes (air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes). The product was ground using the Retsch mill with a 1mm screen.

Table 15:HEC Recipes

(all weights in grams)

| Sample # | Cellulose | TBA | IPA | Acetone | H ₂ O | 50% NaOH | EO | 70% Nitric Acid | MS |
|----------|-----------|-------|-----|---------|------------------|----------|------|-----------------|-----|
| 1 | 46.0 | 517.8 | 8.6 | 7.9 | 63.5 | 13.0 | 16.1 | 14.6 | 0.7 |
| 2 | 49.77 | 517.8 | 8.6 | 7.9 | 59.73 | 12.7 | 10.6 | 14.6 | 0.8 |
| 3 | 49.77 | 517.8 | 8.6 | 7.9 | 59.73 | 13.0 | 19.5 | 14.6 | 1.3 |

Slurry preparation and homogenizer processing were performed as in example 2, except that fewer passes were required to process to a gel.

5

Table 16: Rheology of Microfibrillated HEC

| Sample | MS of HEC | Yield Stress (Pa) | G' @ 5.75 Pa (Pa) |
|--------|-----------|-------------------|-------------------|
| 1 | 0.7 | 1.66 | 43.6 |
| 2 | 0.8 | 3.65 | 10.3 |
| 3 | 1.3 | 2.98 | 2.96 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Samples 1 though 3 are given in Figures 20 through 22.

10 **Drainage Aids in Paper Manufacture:** the following examples demonstrate the effectiveness of derivatized microfibrillar polysaccharide as a drainage-improvement aid.

15 Drainage measurements were performed on a Canadian Standard Freeness (CSF) tester, using a bleached kraft pulp consisting of 70% hardwood and 30% softwood. All freeness testing was performed in hard water having a pH of 7.95-8.05, alkalinity of 50 ppm (as calcium carbonate), and hardness of 100 ppm (as calcium carbonate) using TAPPI method T 227 om-92. A pulp consistency of 0.3% was used. Higher CSF values indicate better (faster) drainage.

20 The following results were obtained using RTG microfibrillated CMC prepared in example 7, which has a degree of substitution of about 0.17 charge group per anhydroglucosamine unit. All loadings are calculated as percent of additive (dry basis) relative to pulp.

Example 14: RTG CMC Sample Material Alone.

| | % RTG CMC Material <u>(based on pulp)</u> | % RTG | |
|---|---|--------------|------------|
| | | CMC Material | |
| | | | <u>CSF</u> |
| 5 | 0 | | 210 |
| | 0.025 | | 274 |
| | 0.050 | | 285 |
| | 0.100 | | 315 |
| | 0.200 | | 317 |

10 **Example 15: RTG CMC Sample Material and Hercules Reten® 1232 (R-1232).**

| | % RTG Material <u>(based on pulp)</u> | CSF VALUES | |
|----|--|---------------|---------------|
| | | 0.1% | 0.2% |
| | | <u>R-1232</u> | <u>R-1232</u> |
| 15 | 0 | 380 | 462 |
| | 0.1 | 485 | 591 |
| | 0.2 | 526 | 608 |
| | 0.4 | 587 | 637 |
| | 0.6 | 572 | 671 |

16 **Example 16: RTG CMC Sample Material and Hercules Kymene® 557H resin (K-557H).**

A constant 2:1 ratio of K-557H to material was employed. (Kymene is a registered trademark of Hercules Incorporated.) Two different starting pulps were used, one with a relatively high freeness, and one relatively low.

| | % RTG Material <u>(based on pulp)</u> | % | Pulp 1 | Pulp 2 |
|----|--|---------------|------------|------------|
| | | <u>K-557H</u> | <u>CSF</u> | <u>CSF</u> |
| | | | | |
| 25 | 0 | 0 | 184 | 413 |
| | 0.1 | 0.2 | 281 | 531 |
| | 0.2 | 0.4 | 321 | 565 |
| | 0.4 | 0.8 | 382 | 574 |

30 **Example 17: RTG CMC Material and Hercules Kymene 450 resin (K-450).**

A constant 2:1 ratio of K-450 to sample material was employed. Two different starting pulps were used, one with a relatively high freeness, and one relatively low.

| | % RTG Material <u>(based on pulp)</u> | % <u>K-450</u> | Pulp 1 <u>CSF</u> | Pulp 2 <u>CSF</u> |
|---|--|-------------------|----------------------|----------------------|
| 5 | 0 | 0 | 184 | 413 |
| | 0.1 | 0.2 | 285 | 536 |
| | 0.2 | 0.4 | 335 | 546 |
| | 0.4 | 0.8 | 357 | 562 |

As with ordinary CMC, the sample material extends the wet and dry strength activity of additives such as Hercules Kymene 557H or Kymene 450 resin. Thus an advantage of the use of the sample material is the provision of a combined wet strength/dry strength/drainage/retention aid.

10 **Use in paper sizing compositions:** the following examples relate to use CMC II as made in example 3 having a DS of about 0.15 in connection with compositions used in paper sizing.

15 **Example 18.** A 600 ml beaker was used to combine 66.0 grams of Precis® 787 ketene dimer (available from Hercules Incorporated, Wilmington, Delaware; Precis is a registered trademark of Hercules Incorporated), 1.5g of CMC II (as made in example 3, DS about 0.15), and 232.5 grams of DI water. The pre-mix was dispersed by stirring for two minutes using a Tekmar Ultra-turax SD45 rotor-stator high shear mixer (Tekmar Company, Cincinnati, Ohio) at a power setting of 50. This pre-mix was then quickly poured into the feed chamber of the impingement mixer. With mechanical stirring at about 250 RPM, premix was passed through the impingement mixer with its pressure set at 5000 psi. The emulsion was collected and a second pass was made. The second pass product was collected in a clean jar, a stir bar was added, the jar was capped, and then cooled in a 5 to 15°C water bath.

20 **Example 19.** Same as Example 18, using 66.0 g Precis ketene dimer, 1.5g of the sample material, 66.0g of 50% aluminum sulfate ($18\text{H}_2\text{O}$) solution in water, and 166.5 g DI water.

Example 20.

Same as Example 18, using 66.0 g Precis ketene dimer; 1.5g of the sample material; 132.0g of a solution containing 25% (wt) aluminum sulfate ($18\text{H}_2\text{O}$), deionized water, and sufficient alkalinity to raise the pH to 4.0; and 100.5 g DI water.

5 **Example 21.**

Same as Example 18, using 66.0 g Precis ketene dimer; 75.0g of a 2% solution of CMC 7M (DS of 0.7) (Hercules Incorporated, Wilmington DE) in deionized water; and 132.0g of a solution containing 25% (wt) aluminum sulfate ($18\text{H}_2\text{O}$), deionized water, and sufficient alkalinity to raise the pH to 4.0; and 27.0 g DI water.

10 **Example 22.**

3.0g of CMC II (as made in example 3, DS about 0.15) were dispersed in 465g DI water for 5 minutes using the high shear mixer at a power setting of 50, then given three passes through the impingement mixer at 5000 psi. As in Example 18, 66.0 g Precis ketene dimer were combined with 234.0 g of the sample material in DI water gel, 15 stirred using the high shear mixer at a power setting of 50, then given two passes through the impingement mixer at 5000 psi and cooled.

Example 23.

4.0g of CMC II (as made in example 3, DS about 0.15) was dispersed in 400g DI water for 5 minutes using the high shear mixer at a power setting of 50, then given 20 three passes through the Microfluidizer at 5000 psi to give a gel.

In an 8 ounce wide mouth jar, 176.0 grams of Precis 787 ketene dimer and 224.0 grams of DI water were combined. The pre-mix was sheared in the high shear mixer for 5 minutes at a power setting of 50, then quickly poured into the feed chamber of the impingement mixer. With mechanical stirring at about 250 RPM, the premix was 25 passed twice through the impingement mixer set at 5000 psi

150.0 g of the gel made above was combined with 150.0 g Precis ketene dimer 44% emulsion, and stirred 5 minutes using the high shear mixer at a power setting of 50.

Example 24.

In an 8 ounce wide mouth jar, 66.0 grams of Precis 787 ketene dimer, 1.5g of 30 pre-sheared, solvent exchange dried material as made in Example 7 (DS of about 0.16), and 232.5 grams of DI water were combined. The pre-mix was sheared in the high shear mixer for 5 minutes at a power setting of 50, then quickly poured into the feed

chamber of the impingement mixer. With mechanical stirring at about 250 RPM, the premix was passed through the impingement mixer at 5000 psi. The emulsion was collected and a second pass was made. The second pass product was collected in a clean jar, a stir bar was added, and the jar was capped and cooled in a 5 to 15°C water

5 bath.

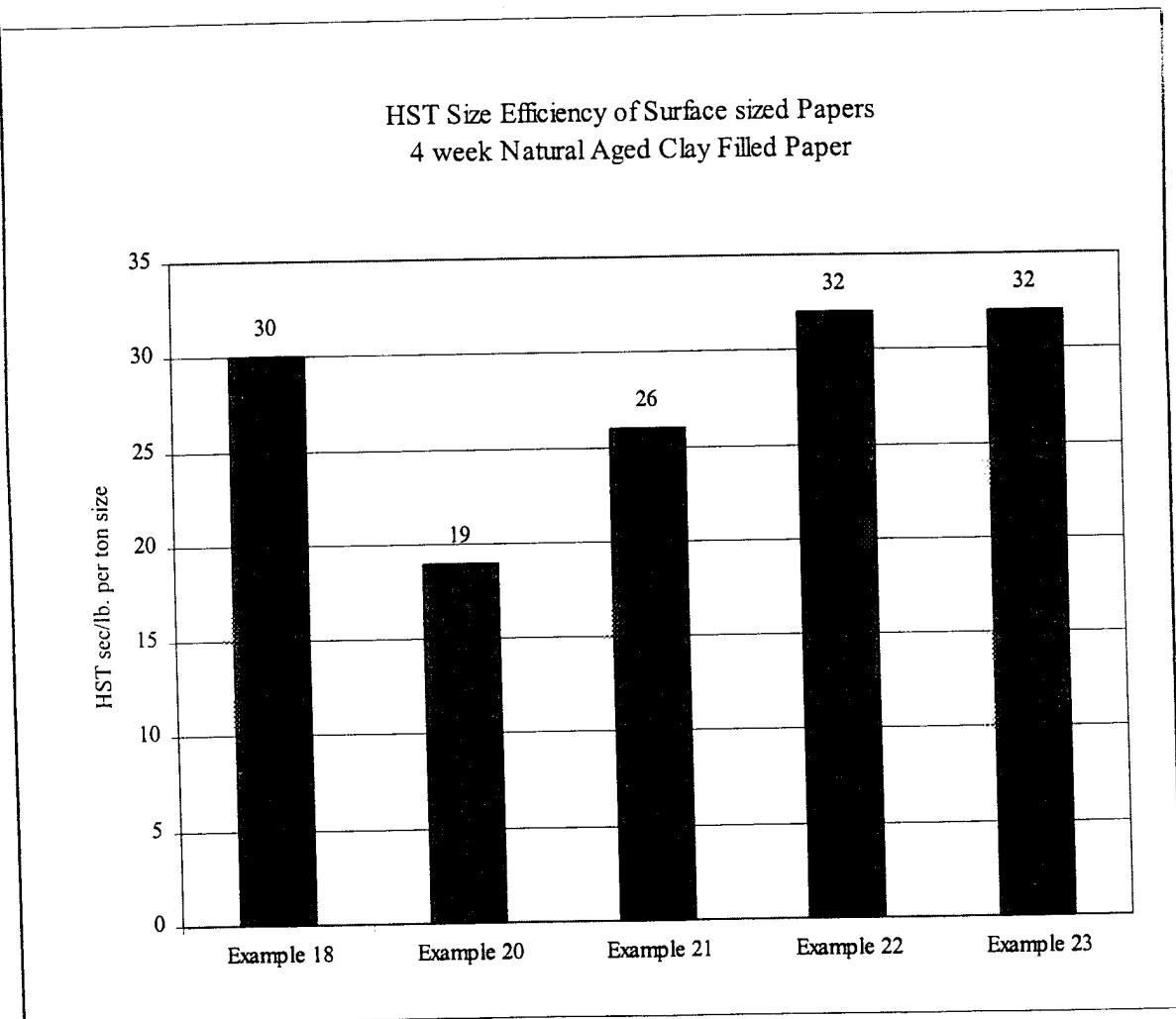
The following pages provide testing results for the sample emulsions using TAPPI Standard Method T560:

Table 17: Surface Sizing of Example 18 through Example 24 Size Emulsions
 (formulation weight in grams)

¹Examples 19 and 23 gave emulsions which broke overnight and were not suitable for surface sizing the next day. The failure of Example 19 is
most likely due to low pH resulting from the presence of the 50% alum, and can be corrected by raising the pH of the alum. Without being
5 bound by any particular theory, it is known that aluminum can appear in a polymeric form, and so may form a co-acervate, at higher pH. In
general, the pH of the alum, poly-aluminum chloride, or other aluminum salts should preferably be as near as possible to the pKa of the
derivatized microfibrillar cellulose. Thus, in Example 18 the addition of low pH 50% alum solution gave an emulsion with poor stability, while
similar recipes in Examples 18 and 20, made without alum or with alum whose pH had been raised to pH 4.0, gave good emulsions. In Example
23, adding the microfibrillated gel without a second impingement mixer shearing as in Example 22 gave an emulsion which was not stable
10 overnight, and thus could not be size tested the next day.

The emulsions from Examples 18, 20, 21, 23, and 24 were then tested in sizing compositions, and the results are shown in Chart 1. The procedure used to obtain this data was as follows: all samples were made with 5% (wt.) D-150 starch (Grain Processing Corp., Muscatine, IA). Five pieces of paper and a wet pick-up sheet for each run were size pressed using a wet nip size press. Each sheet was dry pressed with a drum dryer at 220 °F ± 5 °F for 20 seconds. The weight of wet the pick-up sheet was determined before and after the size press to give wet pick-up percent. Hercules Size Testing (HST) was performed on each paper sheet (5 per run) utilizing TAPPI procedure T560.

Chart 1



10

Examples 25 - 27.

A series of emulsions was made using Aquapel® 364 sizing agent rather than Precis ketene dimer as the size, with the formulations shown in Table 18. In each case the

sample was sonicated on a Branson 350 Ultrasonicator at a power setting of 6. Samples of fine paper were made on a continuous Fourdrinier-type machine, using the emulsions and sizing tested after 100 hours natural aging using a standard HST ink resistance test (TAPPI Method T-530) using a 1% formic acid ink. Chart 2 shows the HST sizing results, which show the samples to be at least as good as or better than three commercial controls using Hercon® paper sizing agent.

Table 18

| | Example 25 | Example 26 | Example 27 |
|---|------------|------------|------------|
| Aquapel 364 (1) | 10 | 10 | 10 |
| Carrageenan 2% (2) | 50 | | |
| CMC II (prepared in Example 3, DS about 0.15) | | 1 | |
| Ambergum® CMC 2% (3) | | | 50 |
| pH 4 Alum | 20 | 20 | 20 |
| Reten® 203 20% (4) | 5 | 5 | 5 |
| Biocide AMA 415 | 0.02 | 0.02 | 0.02 |
| Water | 14.98 | 63.98 | 14.98 |

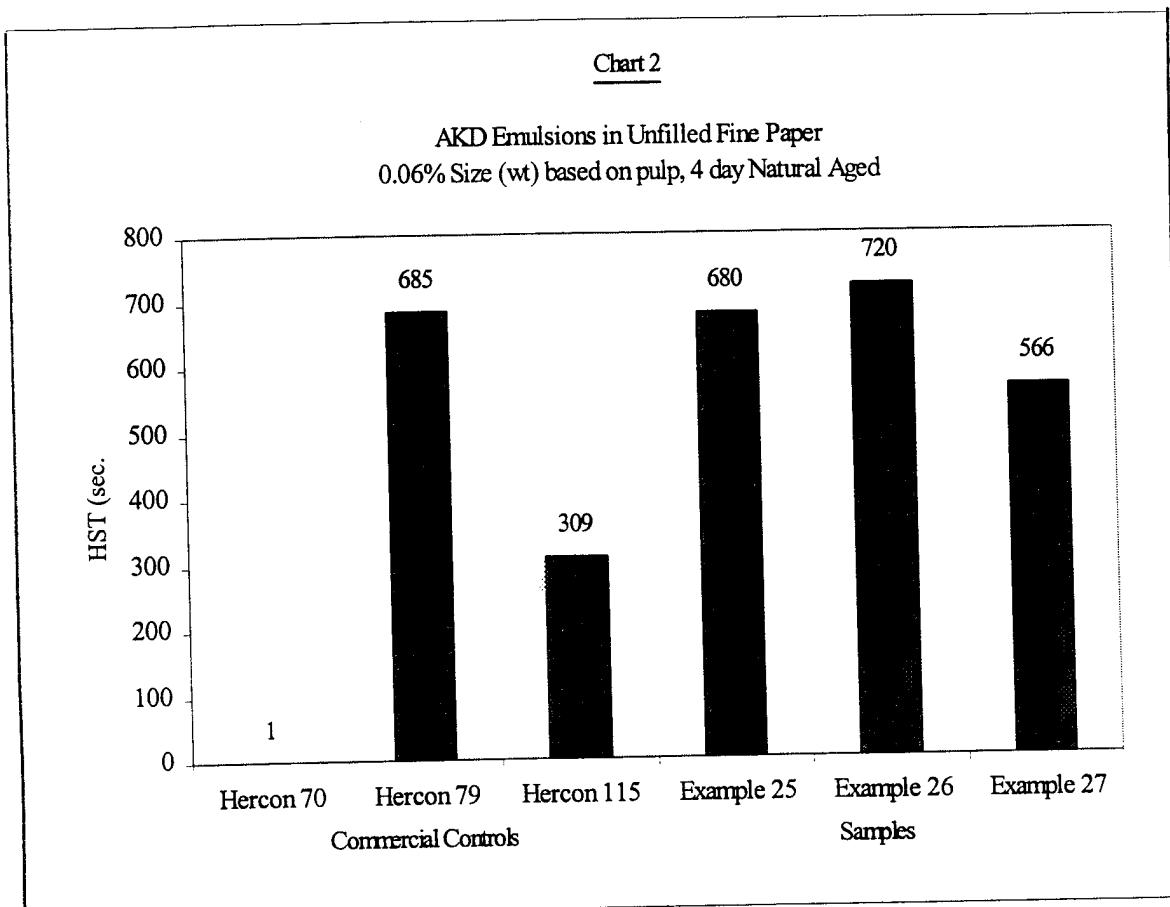
(1) Aquapel 364 Ketene Dimer sizing agent - Hercules Incorporated

(2) Carrageenan - GenuGel® Carrageenan Type LC-5, Hercules Incorporated

10 (3) Ambergum - Type 99-3021, Hercules Incorporated

(4) Reten 203 - Cationic resin, Hercules Incorporated

(Ambergum, Aquapel, Hercon, Genugel, and Reten are registered trademarks of Hercules Incorporated)



Papermaking

The paper used in the sizing examples was made at pH 7 from a 75:25 blend of hardwood and softwood pulps beaten to a Canadian standard freeness of 525 and formed into sheets having a basis weight of 65.1 g/m². Hercon 70, Hercon 79, and Hercon 115 sizing agents were all added at 0.06%, based on the pulp (corresponding to 1.2 pounds per ton). Laboratory water was used, having a hardness of 50 ppm, an alkalinity of 25 ppm, and a pH of 8.1 - 8.4.

Use in food and personal care compositions: the following examples relate to the use or derivatized microfibrillar polysaccharides in food and personal care products.

Example 28: use as fat replacer, viscosifier in food applications.

Fat Free Mayonnaise Model System

| Ingredients (wt. %) | 1 | 2 | 3 |
|--------------------------|------|------|------|
| RTG Microfibrillated CMC | 0.8 | | |
| Microfibrillated CMC | | 0.8 | |
| water | 76.2 | 76.2 | 77.0 |
| starch (Pureflo)* | 4.0 | 4.0 | 4.0 |
| maltodextrin | 10.0 | 10.0 | 10.0 |

Fat Free Mayonnaise Model System (con't)

| <u>Ingredients (wt. %)</u> | 1 | 2 | 3 |
|----------------------------|-------|-------|------|
| salt | 2.0 | 2.0 | 2.0 |
| vinegar (12% acetic acid) | 4.0 | 4.0 | 4.0 |
| 5 egg yolk | 3.0 | 3.0 | 3.0 |
| viscosity (cps) | 42000 | 45000 | 6000 |

*marketed by National Starch and Chemical Co.

Procedure 1: RTG Microfibrillated CMC prepared in example 7 above (DS about 0.16) was dispersed in water with agitation. Starch and maltodextrin were added with agitation. The mixture was heated to 80° - 90° C followed by cooling to 15° - 20° C. Egg yolk then vinegar were added. The product was then mixed by means of a colloid mill. This mixing consists of one pass through a Greerco colloid mill model W250V-B (Greerco Corp., Hudson, NH) with an emulsion rotor and stator at a 0.001 inch gap setting. The texture of this product is then evaluated after 24 hours.

Procedure 2: to a 1% microfibrillated CMC gel as made in example 3 above (DS about 0.16) the balance of the water was added. Starch and maltodextrin were then added with agitation. The mixture was heated to 80° - 90° C followed by cooling to 15° - 20° C. Egg yolk then vinegar were added. The product was then mixed by means of a colloid mill. The texture of this product is then evaluated after 24 hours.

Procedure 3: starch and maltodextrin were added to water with agitation. The mixture was heated to 80° - 90° C followed by cooling to 15° - 20° C. Egg yolk then vinegar were added. The product is then mixed by means of a colloid mill. The texture of this product is then evaluated after 24 hours.

Evaluation: viscosity was measured with a Brookfield (Model DV-II+), 20° C, helipath, 5 rpm spindle C, program S93.

The appearance of the product containing either RTG Microfibrillated CMC or Microfibrillated CMC is that of a gel that holds its shape for a period of time when cut and does not synerese. When a portion of the product is lifted with a spoon or spatula, it does not appear to have stringiness or excessive tackiness; the texture is described as short. These are subjective textural features similar to that of reduced fat spoonable dressings and mayonnaises.

Example 29: use in personal care products.Moisturizing Lotion

| Phase | Ingredient | Wt % |
|-------|--|-------|
| A | DI water | 81.85 |
| | Hydrophobe Modified Hydroxyethyl Cellulose (Natrosol® Plus 330, Hercules Incorporated) | 0.24 |
| | Glycerin | 2.00 |
| | Disodium ethylene diamine tetraacetic acid | 0.05 |
| B | Petrolatum | 5.00 |
| | Mineral Oil | 3.00 |
| | Glycol Stearate | 2.00 |
| | Isostearyl Benzoate | 2.00 |
| | Parraffin | 2.00 |
| | Dimethicone | 0.50 |
| | RTG microfibrillar CMC as in example 7 (DS about 0.16) | 0.36 |
| C | Germaben® II (preservative) | 1.00 |

Procedure: the Part A ingredients were combined, mixed until the water-soluble

- 5 polymer dissolved, and heated to 60-65 °C. All Part B ingredients were combined except the microfibrillar CMC, and heated to 60-65 °C until homogeneous. The RTG microfibrillar CMC was then dispersed into part B, and part B was added to part A with vigorous agitation, which was continued until the mixture was smooth and homogeneous. It was then cooled to 30 °C, and part C was added.

10

Properties

pH.....5.7

Viscosity* (cP) at 25 °C.....16,600

Appearance.....Milky-white emulsion

Stability.....> 5 weeks at 50 °C

- 15 *Complex viscosity in the linear viscoelastic regime was measured with a Bohlin controlled stress rheometer.

This example demonstrates the ability of the RTG CMC material to stabilize an oil in water emulsion, performing a role typically performed by surfactant/cosurfactant network forming systems.

Night Cream

| Phase | Ingredient | Wt % |
|-------|---|------|
| A | DI water | 78.3 |
| | Glycerin | 2.00 |
| | Germaben® II (preservative) | 0.50 |
| | Hydrophobically Modified Hydroxyethyl Cellulose (Natrosol® Plus 330, Hercules Incorporated) | 0.72 |
| B | Avocado Oil | 4.00 |
| | Isostearyl Isostearate | 4.00 |
| | Octyl Stearate | 3.00 |
| | Isopropyl Myristate | 3.00 |
| | Propylene Glycol Isostearate | 4.00 |
| | RTG Microfibrillar CMC as in example 7 (DS about 0.16) | 0.48 |

5

Procedure: the ingredients for part A were combined and mixed until the water-soluble polymer dissolved. The ingredients for part B were then combined, and part B was added to part A with vigorous agitation, which was continued until the mixture was smooth and homogeneous.

10

Properties

pH.....6.0

Viscosity* (cP) at 25 °C.....30,200

Appearance.....Creamy white emulsion

Stability.....> 5 weeks at 50 °C

15 *Complex viscosity in the linear viscoelastic regime was measured with the Bohlin rheometer.

This example demonstrates the ability of the RTG CMC material to stabilize an oil in water emulsion, performing a role typically performed by surfactant/cosurfactant network-

forming systems. The RTG CMC also is processed at room temperature, while typical surfactant/cosurfactant systems require heat.

Alpha-Hydroxy Acid Anti-Age Cream

| Phase | Ingredient | Wt % |
|-------|---|------|
| A | DI water | 71.9 |
| | Glycerin | 5.4 |
| B | Cetyl Alcohol | 3.2 |
| | Glyceryl Stearate and PEG-100 Stearate (Arlacel 165, ICI) | 4.8 |
| | Stearic Acid | 1.6 |
| | Isopropyl Palmitate | 4.8 |
| | Mineral Oil and Lanolin Alcohol (Amerchol L-101, Amerchol) | 4.8 |
| | Dimethicone | 1.6 |
| | RTG Microfibrillar CMC as made in example 7 (DS about 0.16) | 0.6 |
| C | Lactic Acid (88%) | 0.3 |
| | Germaben® II (preservative) | 1.0 |

(As used herein, "anti-age" refers to that category of epidermal lotions and creams intended

- 5 to contribute to a more youthful appearance by the user, such as by the reduction or removal of wrinkles.) Procedure: The ingredients for part A were combined and heated to 75 °C. The part B ingredients, except RTG microfibrillar CMC, were then combined and heated to 75 °C until homogeneous. The RTG microfibrillar CMC was then dispersed into part B. Part B was next added to part A until the mixture became smooth and
10 homogeneous. The mixture was then cooled to 40 °C, and part C was added. This composition was formulated at pH 3.5-4.0, and stabilized with microfibrillar CMC rather than with typical xanthan, clay mixtures.

Properties

pH.....3.7

15 Viscosity* (cP) at 25 °C.....932,000

Appearance.....Glossy white, stiff cream

Stability.....> 5 weeks at 50 °C

*Complex viscosity in the linear viscoelastic regime was measured with the Bohlin rheometer.

This example demonstrates the ability of the RTG CMC material to stabilize an oil in water emulsion at low pH.

5

High SPF Organic Sunscreen Cream

| Phase | Ingredient | Wt % |
|-------|---|------|
| A | DI water | 63.9 |
| B | Cetearyl Alcohol and Cetearyl Phosphate (Crodafos CES, Croda) | 6.6 |
| C | Benzophenone-3 | 5.0 |
| | Octyl methoxycinnamate | 7.5 |
| C | Octyl Salicylate | 5.0 |
| | Menthyl Anthranilate | 5.0 |
| D | Octyl Stearate | 5.0 |
| | RTG Microfibrillar CMC as in example 7 (DS about 0.16) | 0.3 |
| E | NaOH, 18% | 0.6 |
| F | Butylated hydroxytoluene | 0.1 |
| | Germaben® II (preservative) | 1.0 |

10

Procedure: The ingredients for part A and part B were combined and heated to 70 °C. Part C was then added separately, mixing after addition of each part C ingredient. Part D was then added with vigorous agitation, which was continued until the mixture became smooth and homogeneous. Part E was then added, the mixture was cooled to 45 °C, and part F was added.

Properties

pH.....5.9

Viscosity* (cP) at 25 °C.....613,000

Appearance.....Light, off-white cream

Stability.....> 5 weeks at 50 °C

15

*Complex viscosity in the linear viscoelastic regime was measured with the Bohlin rheometer.

This example demonstrates use of microfibrillated CMC with organic sunscreen.

Formulation of a TiO₂ Based Sunscreen Lotion

| Phase | Ingredient | Wt % |
|-------|--|------|
| A | DI water | 67.2 |
| | Disodium ethylene diamine tetraacetic acid | 0.1 |
| | Propylene Glycol | 5.0 |
| B | C ₁₂₋₁₅ Alkyl Benzoate | 3.0 |
| B | Butyl Stearate | 3.0 |
| | Myristyl Myristate | 4.0 |
| | Sorbitan Oleate | 0.1 |
| | RTG Microfibrillar CMC as in example 7 (DS about 0.16) | 0.6 |
| C | Germaben® II (preservative) | 1.0 |
| D | Titanium Dioxide | 6.0 |
| | Octyl Palmitate | 9.0 |
| | Polyglyceryl-10 decanoate | 1.0 |

Procedure: the ingredients for part A were combined and heated to 50 °C. All of the part B ingredients, except microfibrillar CMC, were combined and heated to 60-65 °C until homogeneous. The microfibrillar CMC was then dispersed into part B, which was then added to part A with vigorous agitation, and agitation was continued until the mixture was smooth and homogeneous. The ingredients for part D were combined and mixed well. Part C was added to the AB emulsion; then, with moderate agitation, part D was slowly added to the emulsion and cooled to 30 °C.

Properties

10 pH.....7.1

Viscosity* (cP) at 25 °C.....33,900

Appearance.....Glossy, white emulsion gel

Stability.....> 5 weeks at 50 °C

*Complex viscosity in the linear viscoelastic regime was measured with the Bohlin 15 rheometer.

This example demonstrates use of microfibrillated CMC with inorganic sunscreen. The present invention has of necessity been discussed herein by reference to certain specific methods and materials. The enumeration of these methods and materials was

merely illustrative, and in no way constitutes any limitation on the scope of the present invention. It is to be expected that those skilled in the art may discern and practice variations of or alternatives to the specific teachings provided herein, without departing from the scope of the present invention.

5 The present invention has of necessity been discussed herein by reference to certain specific methods and materials. The enumeration of these methods and materials was merely illustrative, and in no way constitutes any limitation on the scope of the present invention. It is to be expected that those skilled in the art may discern and practice variations of or alternatives to the specific teachings provided herein, without departing
10 from the scope of the present invention.

WHAT I/WE CLAIM IS:

1. A derivatized microfibrillar polysaccharide, derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality comprises anionic charge.

5 2. The derivatized microfibrillar polysaccharide of claim 1, wherein the polysaccharide in said derivatized microfibrillar polysaccharide comprises at least one of cellulose, hemicellulose, chitin, chitosan, guar gum, pectin, alginate, agar, xanthan, starch, amylose, amylopectin, alternan, gellan, mutan, dextran, pullulan, fructan, locust bean gum, 10 carrageenan, glycogen, glycosaminoglycans, murein, bacterial capsular polysaccharides, and derivatives thereof.

3. The derivatized microfibrillar polysaccharide of claim 2, wherein said polysaccharide is at least one of cellulose, chitin, chitosan, pectin, agar, starch, 15 carrageenan, and derivatives thereof.

4. The derivatized microfibrillar polysaccharide of claim 3, comprising derivatized microfibrillar cellulose.

5. The derivatized microfibrillar polysaccharide of claim 4, wherein said cellulose is obtained from at least one of chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal 20 hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.

6. The derivatized microfibrillar polysaccharide of claim 5, wherein said cellulose is obtained from at least one of purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton 25 linters; fruits; and vegetables.

7. The derivatized microfibrillar cellulose of claim 4, comprising at least one of hydroxyethyl cellulose, ethylhydroxyethyl cellulose, carboxymethylcellulose, carboxymethylhydroxyethyl cellulose, hydroxypropylhydroxyethyl cellulose, methyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose, 30 carboxymethylmethyl cellulose, hydrophobically modified carboxymethylcellulose, hydrophobically modified hydroxyethyl cellulose, hydrophobically modified hydroxypropyl cellulose, hydrophobically modified ethylhydroxyethyl cellulose,

hydrophobically modified carboxymethylhydroxyethyl cellulose, hydrophobically modified hydroxypropylhydroxyethyl cellulose, hydrophobically modified methyl cellulose, hydrophobically modified methylhydroxypropyl cellulose, hydrophobically modified methylhydroxyethyl cellulose, hydrophobically modified carboxymethylmethyl cellulose, nitrocellulose, cellulose acetate, cellulose sulfate, cellulose vinyl sulfate, cellulose phosphate, and cellulose phosphonate.

5 8. The derivatized microfibrillar cellulose of claim 4, wherein said derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 100% in water.

10 9. The derivatized microfibrillar cellulose of claim 8, wherein said derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 50 % in water.

15 10. The derivatized microfibrillar cellulose of claim 4, wherein said derivatized microfibrillar cellulose forms a gel at at least one point in the concentration range of from about 0.05 % up to about 0.99% in water.

11. The derivatized microfibrillar polysaccharide of claim 1, further comprising a solvent, wherein said derivatized microfibrillar polysaccharide is substantially insoluble in said solvent.

20 12. The derivatized microfibrillar polysaccharide of claim 11, wherein said solvent is water, alcohol, or oil.

13. The derivatized microfibrillar polysaccharide of claim 12, wherein said solvent is water.

25 14. The derivatized microfibrillar polysaccharide of claim 13, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic functionality.

15. The derivatized microfibrillar polysaccharide of claim 1, wherein said derivatized microfibrillar polysaccharide is derivatized microfibrillar cellulose having a degree of substitution of less than about 0.5.

30 16. The derivatized microfibrillar polysaccharide of claim 15, wherein said degree of substitution is less than about 0.35.

17. The derivatized microfibrillar polysaccharide of claim 16, wherein said degree of substitution is less than about 0.2.

18. The derivatized microfibrillar polysaccharide of claim 17, wherein said degree of substitution is less than about 0.18.

19. The derivatized microfibrillar polysaccharide of claim 18, wherein said degree of substitution is less than about 0.1.

5 20. The derivatized microfibrillar polysaccharide of claim 15, wherein said degree of substitution is between about 0.02 and about 0.5.

21. The derivatized microfibrillar polysaccharide of claim 20, wherein said degree of substitution is between about 0.05 and about 0.2.

10 22. The derivatized microfibrillar polysaccharide of claim 1, derivatized to comprise substituents that provide electrostatic functionality in the form of anionic charge, wherein the degree of substitution representing substituents that provide electrostatic functionality in the form of anionic charge is at least about 0.02.

15 23. The derivatized microfibrillar polysaccharide of claim 1, wherein said anionic charge is provided by carboxyl, sulfate, sulfonate, phosphonate, or phosphate groups, or combinations thereof.

24. The derivatized microfibrillar polysaccharide of claim 14, wherein said electrostatic functionality is provided by both anionic and cationic charge.

20 25. The derivatized microfibrillar cellulose of claim 24, wherein said electrostatic functionality is provided by substituents that contain both anionic and cationic charge in the same substituent.

26. The derivatized microfibrillar cellulose of claim 24, wherein said electrostatic functionality is provided both by substituents having anionic charge and by substituents having cationic charge.

27. The derivatized microfibrillar polysaccharide of claim 13, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide steric functionality.

28. The derivatized microfibrillar polysaccharide of claim 27, having a molar substitution of less than about 3.0.

29. The derivatized microfibrillar polysaccharide of claim 28, wherein said molar substitution is less than about 1.5.

30 30. The derivatized microfibrillar polysaccharide of claim 29, wherein said molar substitution is less than about 1.0.

31. The derivatized microfibrillar polysaccharide of claim 30, wherein said molar substitution is less than about 0.5.

32. The derivatized microfibrillar polysaccharide of claim 28, wherein said molar substitution is between about 0.5 and 3.0.

5 33. The derivatized microfibrillar polysaccharide of claim 27, wherein said substituents comprise at least one of hydroxyethyl groups; hydroxypropyl groups; methyl groups; ethyl groups; straight- or branched-chain alkyl, alkenyl, or alkynyl groups having from about 4 to about 30 carbons; aryl, arylalkyl, arylalkenyl, cyclic, and heterocyclic hydrocarbons having from about 4 to about 30 carbons; or combinations thereof.

10 34. The derivatized microfibrillar polysaccharide of claim 33, further wherein said derivatized microfibrillar polysaccharide is a derivatized microfibrillar cellulose.

35. The derivatized microfibrillar cellulose of claim 4, comprising carboxymethylcellulose.

15 36. The derivatized microfibrillar cellulose of claim 34, having a degree of substitution of less than about 0.35.

37. The derivatized microfibrillar cellulose of claim 36, wherein said degree of substitution is less than about 2.0.

38. The derivatized microfibrillar cellulose of claim 37, wherein said degree of substitution is between about 0.02 and about 0.2.

20 39. The derivatized microfibrillar cellulose of claim 38, wherein said degree of substitution is between about 0.10 and about 0.2.

40. The derivatized microfibrillar polysaccharide of claim 4, wherein said derivatized microfibrillar cellulose forms a gel at a concentration of less than about 1% in water.

25 41. Microfibrillar carboxymethylcellulose having a degree of substitution of between about 0.10 and about 0.20.

42. A comestible composition of matter comprising derivatized microfibrillar polysaccharide derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality is provided by anionic charge.

30 43. The comestible composition of matter of claim 42, in the form of a low fat, reduced fat, or fat-free mayonnaise.

44. The comestible composition of matter of claim 42, in the form of a salad dressing.

45. The comestible composition of matter of claim 42, further comprising a pharmaceutically active ingredient.

5 46. The comestible composition of claim 45, wherein said derivatized microfibrillar polysaccharide at least partially provides controlled, sustained, or delayed release of said pharmaceutically active ingredient.

10 47. A non-comestible composition of matter comprising derivatized microfibrillar polysaccharide derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality is provided by anionic charge.

48. The non-comestible composition of matter of claim 47, in the form of a wound care product.

15 49. The non-comestible composition of matter of claim 48, wherein said wound care product is a wound dressing.

50. The non-comestible composition of matter of claim 48, wherein said wound care product is an ostomy ring.

51. The non-comestible composition of matter of claim 47, in the form of a skin care lotion or cream.

20 52. The non-comestible composition of matter of claim 47, in the form of a sunscreen lotion or cream.

53. The non-comestible composition of matter of claim 47, in the form of an oral care composition.

25 54. The non-comestible composition of matter of claim 53, wherein said oral care product is a toothpaste.

55. The non-comestible composition of matter of claim 47, further comprising a fertilizer, herbicide, fungicide, or pesticide.

30 56. The non-comestible composition of matter of claim 55, wherein said derivatized microfibrillar polysaccharide at least partially provides controlled, sustained, or delayed release of said fertilizer, herbicide, or pesticide.

57. The non-comestible composition of matter of claim 47, in the form of a drilling fluid.

58. A paper composition comprising derivatized microfibrillar cellulose derivatized to comprise groups that provide electrostatic and/or steric functionality, further wherein said electrostatic functionality comprises the presence of anionic charge.

59. The paper composition of claim 58, wherein said derivatized microfibrillar cellulose is microfibrillar carboxymethylcellulose.

60. A method for producing derivatized microfibrillar polysaccharide, said method comprising at least one of the following:

a) a derivatizing step of treating a microfibrillar polysaccharide to obtain a derivatized microfibrillar polysaccharide;

10 b) a microfibrillizing step of treating a derivatized non-microfibrillar polysaccharide to produce a derivatized microfibrillar polysaccharide; or,

c) microfibrillizing and derivatizing a non-microfibrillar polysaccharide substantially simultaneously,

15 wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic and/or steric functionality, further wherein said electrostatic functionality is provided by anionic charge.

61. The method of claim 60, wherein the polysaccharide is at least one of cellulose, hemicellulose, chitin, chitosan, guar gum, pectin, alginate, agar, xanthan, starch, amylose, amylopectin, alternan, gellan, mutan, dextran, pullulan, fructan, locust bean gum, 20 carrageenan, glycogen, glycosaminoglycans, murein, bacterial capsular polysaccharides, and derivatives thereof.

62. The method of claim 61, wherein said polysaccharide is at least one of cellulose, chitin, chitosan, pectin, agar, starch, carrageenan, and derivatives thereof.

63. The method of claim 62, wherein the polysaccharide is cellulose and said 25 derivatized microfibrillar polysaccharide is derivatized microfibrillar cellulose.

64. The method of claim 63, wherein said cellulose is obtained from at least one of chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, 30 velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.

65. The method of claim 64, wherein said cellulose is obtained from at least one of purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.

66. The method of claim 60, comprising the steps of:

5 a) derivatizing cellulose with monochloroacetic acid or a salt thereof under alkaline conditions to produce carboxymethylcellulose;

b) suspending the carboxymethylcellulose in water to form a suspension; and

c) homogenizing said suspension to produce microfibrillated carboxymethylcellulose.

10 67. The method of claim 60, wherein said derivatizing step comprises contacting a non-microfibrillar polysaccharide with a swelling agent.

68. The method of claim 67, further wherein said contacting takes place under alkaline conditions.

69. The method of claim 68, wherein said swelling agent is an anionic reagent.

15 70. The method of claim 69, wherein the polysaccharide is cellulose.

71. The method of claim 70, further wherein said alkaline conditions comprise contacting the cellulose with said anionic reagent in the presence of an alkaline reagent which is at least one of sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an alkali silicate, an alkali aluminate, an alkali carbonate, an amine, 20 ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof.

72. The method of claim 60, wherein said derivatizing step takes place at high solids.

73. The method of claim 60, wherein said anionic charge comprises the presence of carboxyl, sulfate, sulfonate, phosphonate, or phosphate groups, or 25 combinations thereof.

74. The method of claim 73, wherein said derivatizing step comprises carboxymethylation of the cellulose.

75. The method of claim 63, wherein said derivatized microfibrillar cellulose comprises at least one of hydroxyethyl cellulose, ethylhydroxyethyl cellulose, 30 carboxymethylcellulose, carboxymethylhydroxyethyl cellulose, hydroxypropylhydroxyethyl cellulose, methyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose, carboxymethylmethyl cellulose, hydrophobically modified

carboxymethylcellulose, hydrophobically modified hydroxyethyl cellulose, hydrophobically modified hydroxypropyl cellulose, hydrophobically modified ethylhydroxyethyl cellulose, hydrophobically modified carboxymethylhydroxyethyl cellulose, hydrophobically modified hydroxypropylhydroxyethyl cellulose, hydrophobically modified methyl cellulose, hydrophobically modified methylhydroxypropyl cellulose, hydrophobically modified methylhydroxyethyl cellulose, hydrophobically modified carboxymethylmethyl cellulose, nitrocellulose, cellulose acetate, cellulose sulfate, cellulose vinyl sulfate, cellulose phosphate, and cellulose phosphonate.

5 76. The method of claim 60, wherein said microfibrillizing step comprises
10 applying energy to said polysaccharide under conditions sufficient to produce
microfibrillar polysaccharide.

77. The method of claim 76, further comprising enzyme-treating said non-microfibrillar polysaccharide prior to said microfibrillizing step

15 78. The method of claim 76, comprising applying at least one of
homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, and milling to said non-microfibrillar polysaccharide.

20 79. The method of claim 78, comprising passing said non-microfibrillar polysaccharide through a homogenizer under conditions sufficient to produce
microfibrillar polysaccharide.

80. The method of claim 79, wherein said conditions comprise passing said non-microfibrillar polysaccharide through a pressure differential of at least about 3,000 psi.

81. The method of claim 80, further comprising passing said non-microfibrillar polysaccharide through said homogenizer at least three times.

25 82. The method of claim 60, wherein said derivatized microfibrillar polysaccharide forms a gel throughout a concentration range of from about 0.01 % to about 100% in water.

30 83. The method of claim 82, wherein said derivatized microfibrillar polysaccharide forms a gel throughout a concentration range of between about 0.01 % and about 50 % in water.

84. The method of claim 60, wherein said derivatized microfibrillar polysaccharide forms a gel at at least one point in the concentration range of from about 0.05 % to about 0.99% in water.

5 85. The method of claim 84, wherein said derivatized microfibrillar polysaccharide forms a gel at a concentration of about 0.9% in water.

86. The method of claim 60, wherein said derivatized microfibrillar polysaccharide is substantially insoluble in the solvent of use.

87. The method of claim 86, wherein the solvent of use is water.

10 88. The method of claim 87, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic functionality.

89. The method of claim 88, wherein said derivatized microfibrillar polysaccharide is derivatized microfibrillar cellulose having a degree of substitution of less than about 0.5.

15 90. The method of claim 89, wherein said degree of substitution is less than about 0.35.

91. The method of claim 90, wherein said degree of substitution is less than about 0.2.

20 92. The method of claim 91, wherein said degree of substitution is less than about 0.18.

93. The method of claim 92, wherein said degree of substitution is less than about 0.1.

94. The method of claim 89, wherein said derivatized microfibrillar cellulose has a degree of substitution of between about 0.02 and about 0.5.

25 95. The method of claim 94, wherein said degree of substitution is between about 0.05 and about 0.2.

96. The method of claim 86, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise a steric substituent.

30 97. The method of claim 96, further wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic functionality.

98. The method of claim 96, wherein said derivatized microfibrillar polysaccharide has a molar substitution of less than about 3.0.

99. The method of claim 98, wherein said molar substitution is less than about 1.5.

5 100. The method of claim 99, wherein said molar substitution is less than about 1.0.

101. The method of claim 100, wherein said molar substitution is less than about 0.5.

102. The method of claim 98, wherein said molar substitution is between about 10 0.5 and 3.0.

103. The method of claim 63, wherein said derivatized microfibrillar cellulose is a carboxymethylcellulose.

104. The method of claim 103, wherein said carboxymethylcellulose has a degree of substitution of less than about 0.35.

15 105. The method of claim 104, wherein said degree of substitution is less than about 2.0.

106. The method of claim 105, wherein said degree of substitution is between about 0.02 and about 2.0.

20 107. The method of claim 106, wherein said degree of substitution is between about 0.1 and about 0.2.

108. Derivatized microfibrillar polysaccharide produced by the method of claim 60.

109. Derivatized microfibrillar cellulose produced by the method of claim 63.

25 110. The derivatized microfibrillar cellulose of claim 63, derivatized to comprise substituents that provide steric functionality.

111. The derivatized microfibrillar cellulose of claim 110, wherein said substituents comprise at least one of hydroxyethyl groups; hydroxypropyl groups; methyl groups; ethyl groups; straight- or branched-chain aliphatic groups having from about 4 to about 30 carbons; or combinations thereof.

30 112. The derivatized microfibrillar cellulose of claim 109, derivatized to comprise substituents that provide electrostatic functionality by anionic charge.

113. The derivatized microfibrillar cellulose of claim 112, wherein said anionic charge comprises the presence of carboxyl, sulfate, sulfonate, phosphonate, or phosphate groups, or combinations thereof.

114. The derivatized microfibrillar cellulose of claim 113, wherein said anionic charge comprises the presence of carboxyl groups.

115. The derivatized microfibrillar cellulose of claim 112, wherein said electrostatic functionality is provided by both anionic and cationic charge.

116. The derivatized microfibrillar cellulose of claim 115, wherein said electrostatic functionality is provided by substituents that contain both anionic and cationic charge in the same substituent.

117. The derivatized microfibrillar cellulose of claim 115, wherein said electrostatic functionality is provided both by substituents having anionic charge and by substituents having cationic charge.

118. A method of modifying the rheological properties of a composition of matter, said method comprising the step of incorporating, into said composition of matter, derivatized microfibrillar polysaccharide that is derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality is provided by anionic charge.

119. The method of claim 118, wherein said composition comprises a liquid.

120. The method of claim 119, wherein said liquid is water.

121. The method of claim 120, comprising using said derivatized microfibrillar polysaccharide in an amount effective to provide scale control and/or corrosion control.

122. The method of claim 118, wherein said derivatized microfibrillar polysaccharide is derivatized microfibrillar cellulose.

123. The method of claim 119, wherein said rheological properties are at least one of viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention.

124. The method of claim 118, wherein said composition of matter is a food, pharmaceutical, neutraceutical, personal care, fiber, paper, paint, coating, or construction composition.

125. The method of claim 124, wherein said composition of matter is an oral care product.

126. The method of claim 124, wherein said composition of matter is a cream or lotion for epidermal application.

127. The method of claim 124, wherein said composition of matter is moisturizing, night, anti-age, or sunscreen cream or lotion.

5 128. The method of claim 124, wherein said composition of matter is a food spread.

129. The method of claim 128, wherein said food spread is a reduced fat, low fat, or fat free food spread.

10 130. The method of claim 129, wherein said food spread is a reduced fat, low fat, or fat free mayonnaise.

131. The method of claim 124, wherein said composition of matter is a drilling fluid.

15 132. A method of improving the physical and/or mechanical properties of a coating composition by incorporating, into said coating composition, an effective amount of a derivatized microfibrillar polysaccharide derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality is provided by anionic charge.

20 133. The method of claim 132, wherein said physical and/or mechanical properties include at least one of film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

25 134. A method of improving at least one of sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, adsorbency, film formation, membrane formation, and polyelectrolyte complexation during paper manufacture, said method comprising the step of using a derivatized microfibrillar cellulose during said manufacture, wherein said derivatized microfibrillar cellulose is derivatized by electrostatic and/or steric substituents, further wherein said electrostatic substituents comprise the presence of either anionic charge or both anionic and cationic charge.

135. The method of claim 134, wherein said derivatized microfibrillar cellulose is used as a drainage aid and/or as a sizing agent.

30 136. The method of claim 134, wherein said derivatized microfibrillar cellulose is microfibrillated carboxymethylcellulose.

137. The method of claim136, comprising using said microfibrillated carboxymethylcellulose in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture.

138. The method of claim137, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; and combinations thereof.

139. The method of claim137, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

140. The method of claim137, further wherein said microfibrillated carboxymethylcellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

141. The method of claim136, comprising using said microfibrillated carboxymethylcellulose in a papermaking machine for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture

142. The method of claim141, wherein said dispersed particles comprise at least one of pulp fines, fillers, sizing agents, pigments, clays, detrimental organic particulate materials, detrimental inorganic particulate materials, and combinations thereof.

143. The method of claim141, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; and combinations thereof.

144. The method of claim141, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

5 145. The method of claim141, further wherein said microfibrillated carboxymethylcellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

10 146. The method of claim136, comprising using said microfibrillated carboxymethylcellulose in a papermaking machine to improve the uniformity of formation of a sheet of paper during its manufacture.

147. The method of claim146, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose 15 containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; and combinations thereof.

148. The method of claim146, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

149. The method of claim146, further wherein said microfibrillated carboxymethylcellulose is used in the presence of: at least one polymer of ethylene oxide, 25 ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

150. The method of claim136, comprising using said microfibrillated carboxymethylcellulose in a papermaking machine to improve the strength of a sheet of paper produced on a papermachine.

30 151. The method of claim150, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose

containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; and combinations thereof.

5 152. The method of claim 150, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

10 153. The method of claim 150, further wherein said microfibrillated carboxymethylcellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

15 154. A method for improving the stability of an emulsion, dispersion, or foam system, said method comprising the step of including, in the system, a derivatized microfibrillar polysaccharide derivatized by electrostatic and/or steric substituents, further wherein said electrostatic substituents comprise the presence of anionic charge.

155. The method of claim 154, wherein said derivatized microfibrillar polysaccharide is added to the system.

156. The method of claim 155, wherein said system comprises an emulsion, further wherein said emulsion is produced by processing of an emulsion formulation.

157. The method of claim 156, further wherein said derivatized microfibrillar polysaccharide is added prior to completion of processing of said emulsion formulation.

158. The method of claim 156, wherein a non-microfibrillated polysaccharide is added prior to completion of processing of said emulsion formulation, and said emulsion formulation is processed under conditions sufficient to microfibrillate said non-microfibrillated polysaccharide.

159. The method of claim 158, further wherein said non-microfibrillated or only partially microfibrillated polysaccharide is non-derivatized or only partially derivatized, and said emulsion formulation is further processed under conditions sufficient to derivatized said non-derivatized polysaccharide, or to complete derivatization of said only partially derivatized polysaccharide, respectively.

160. The method of claim 156, wherein a non-derivatized or only partially derivatized polysaccharide is added prior to completion of processing of said emulsion formulation, and the emulsion formulation is processed under conditions sufficient to derivatize said non-derivatized polysaccharide, or to complete derivatization of said only partially derivatized polysaccharide, respectively.

161. The method of claim 160, further wherein said non-derivatized or only partially derivatized polysaccharide is non-microfibrillated or only partially microfibrillated, and said emulsion formulation is further processed under conditions sufficient to microfibrillate said non-derivatized polysaccharide, or to complete microfibrillation of said only partially derivatized polysaccharide, respectively.

162. The method of claim 155, wherein said system is a water-in-oil or oil-in-water emulsion.

163. The system produced by the method of claim 154.

164. A system comprising an emulsion, dispersion, or foam containing a derivatized microfibrillar polysaccharide, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic and/or steric functionality, further wherein said electrostatic functionality is provided by anionic charge.

165. A polyelectrolyte complex comprising a derivatized microfibrillar polysaccharide comprising substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality comprises anionic charge.

Figure 1

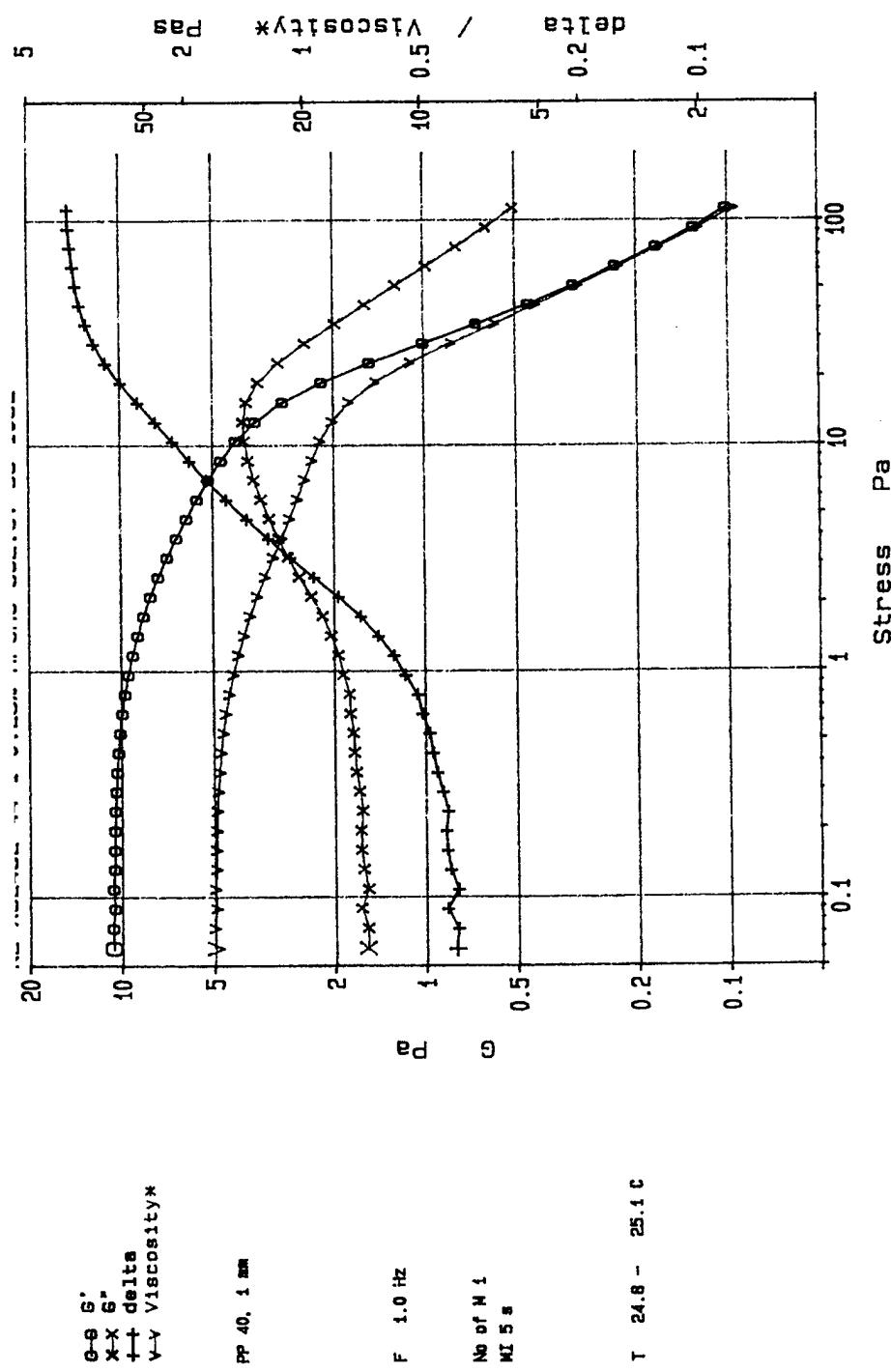


Figure 2

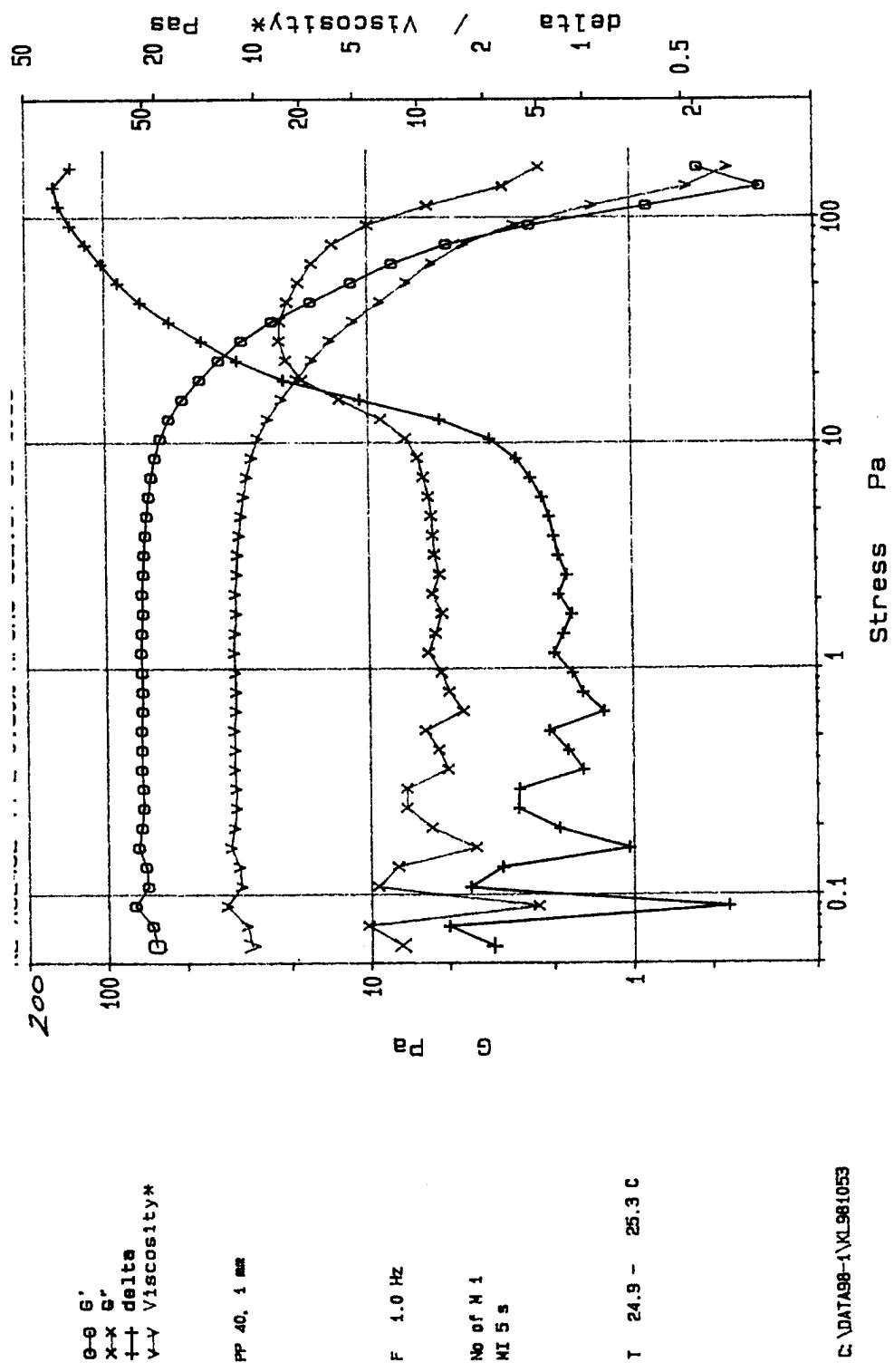


Figure 3

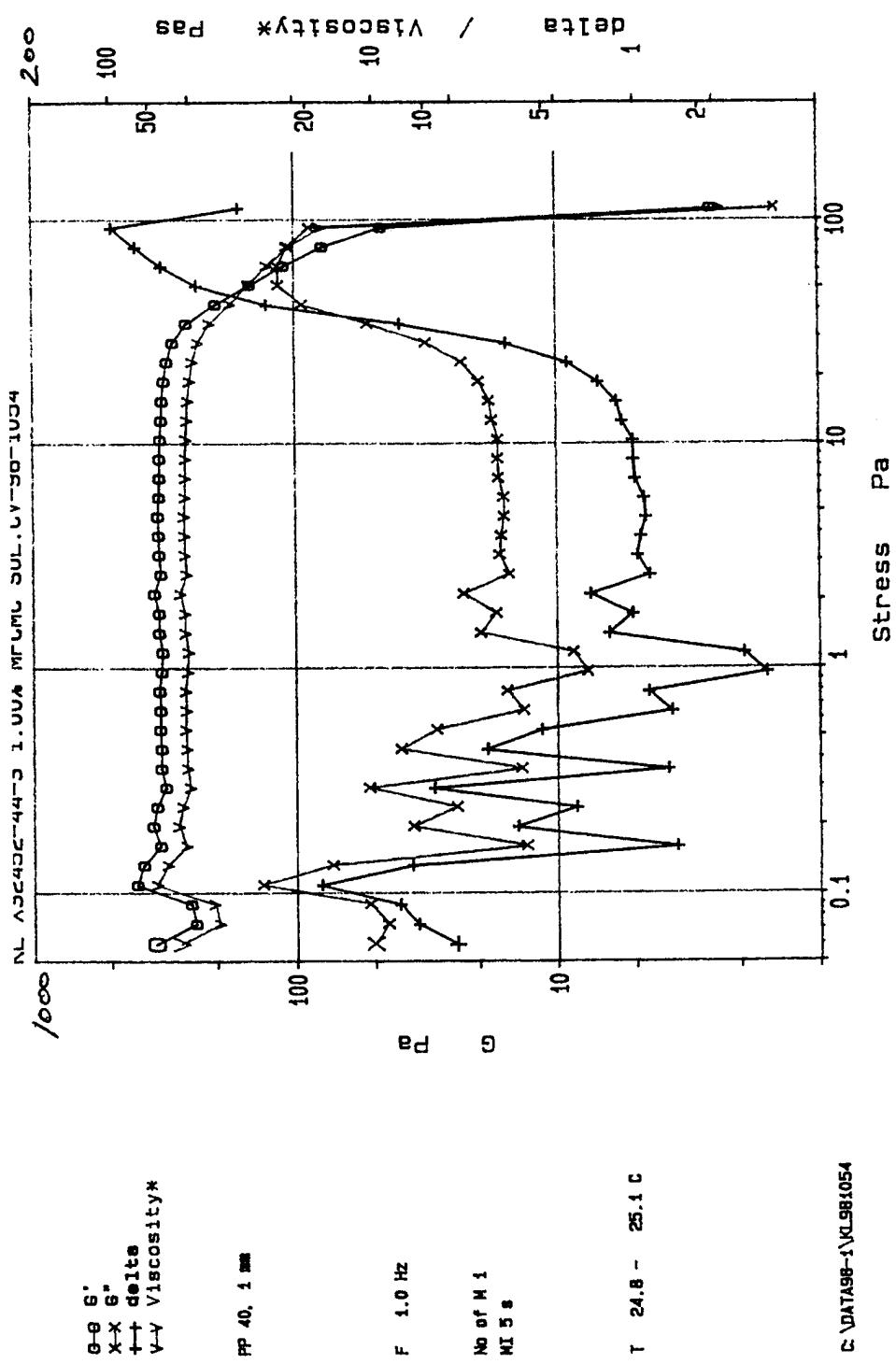


Figure 4

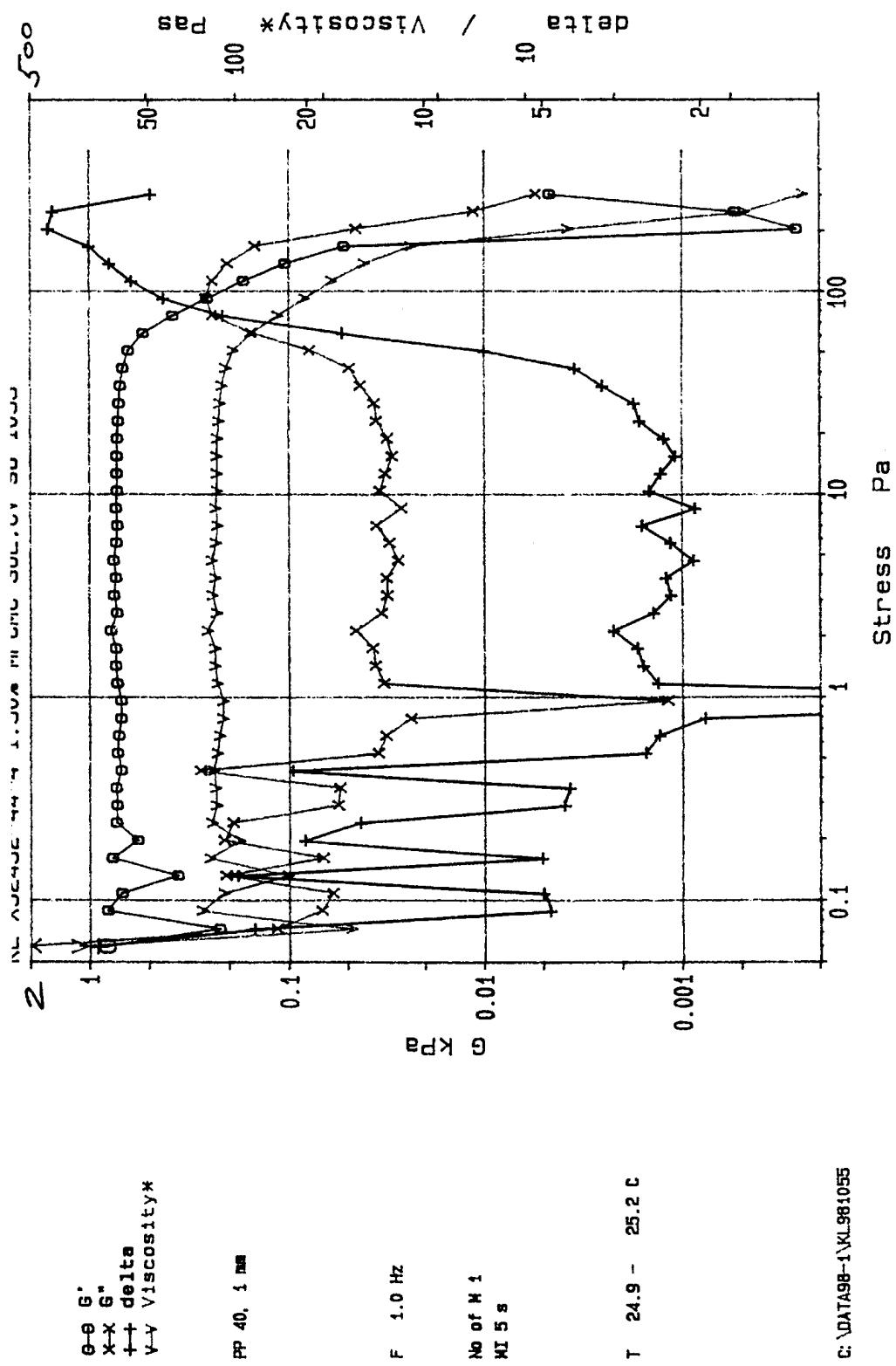


Figure 5

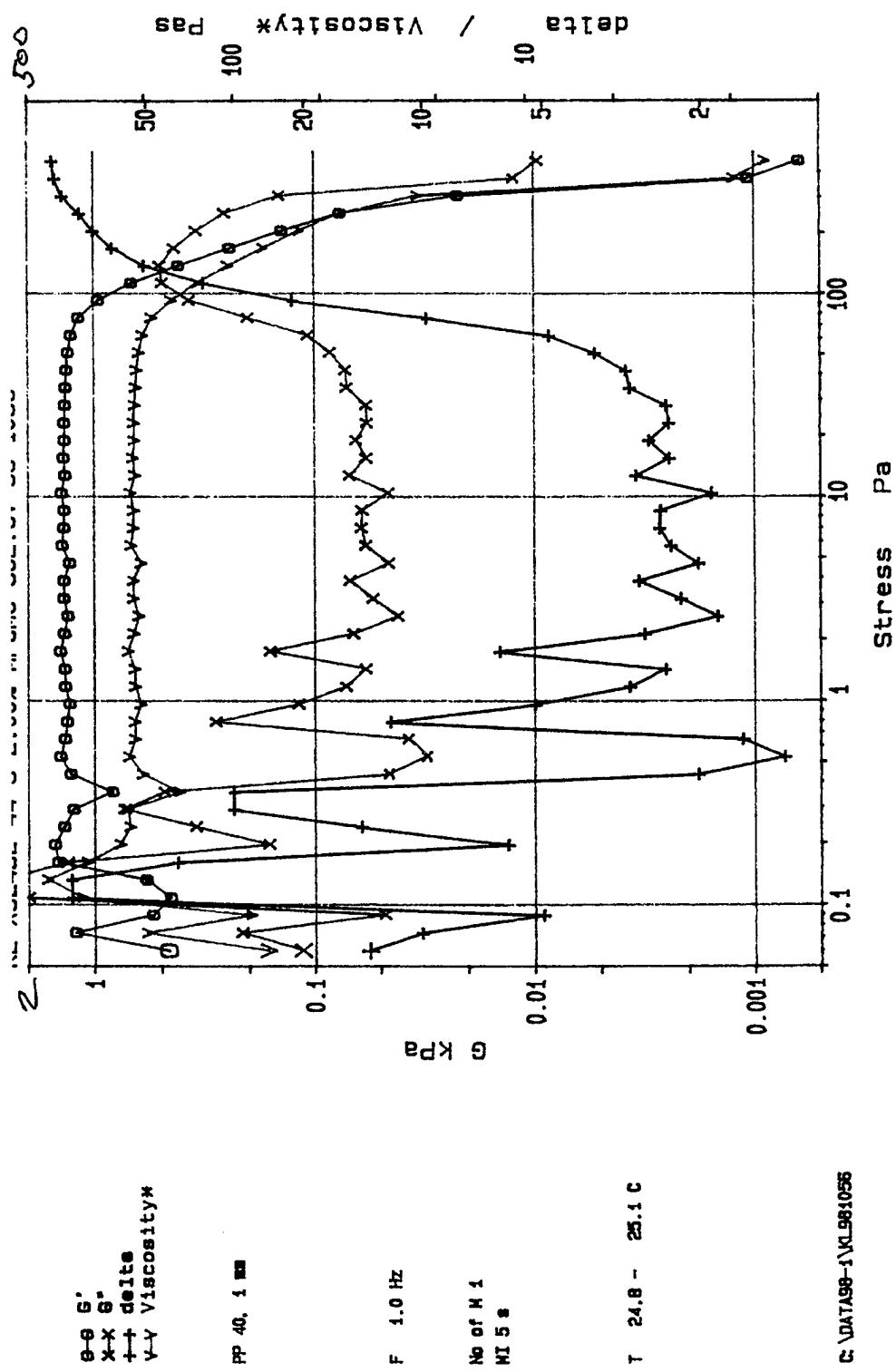


Figure 6

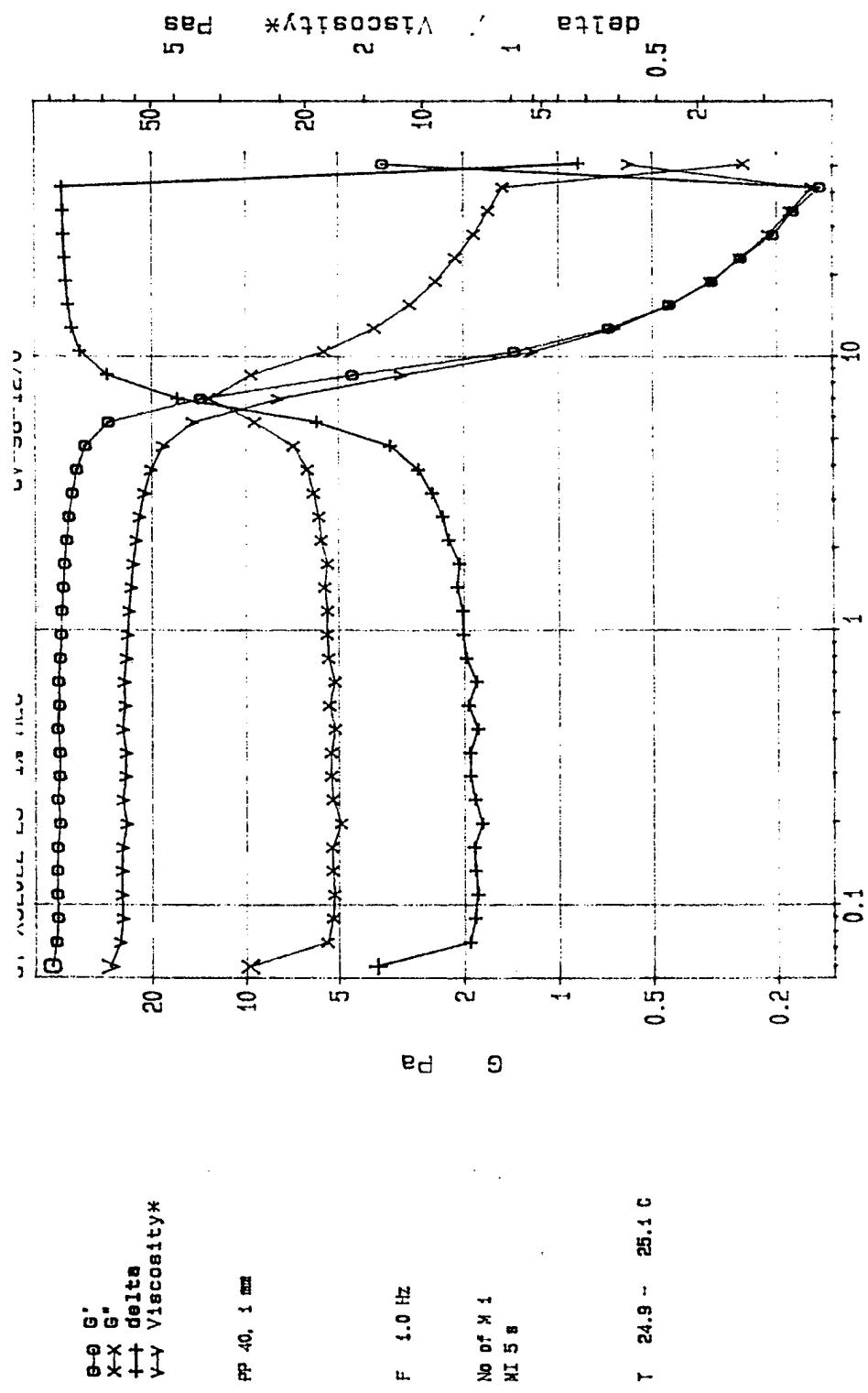


Figure 7

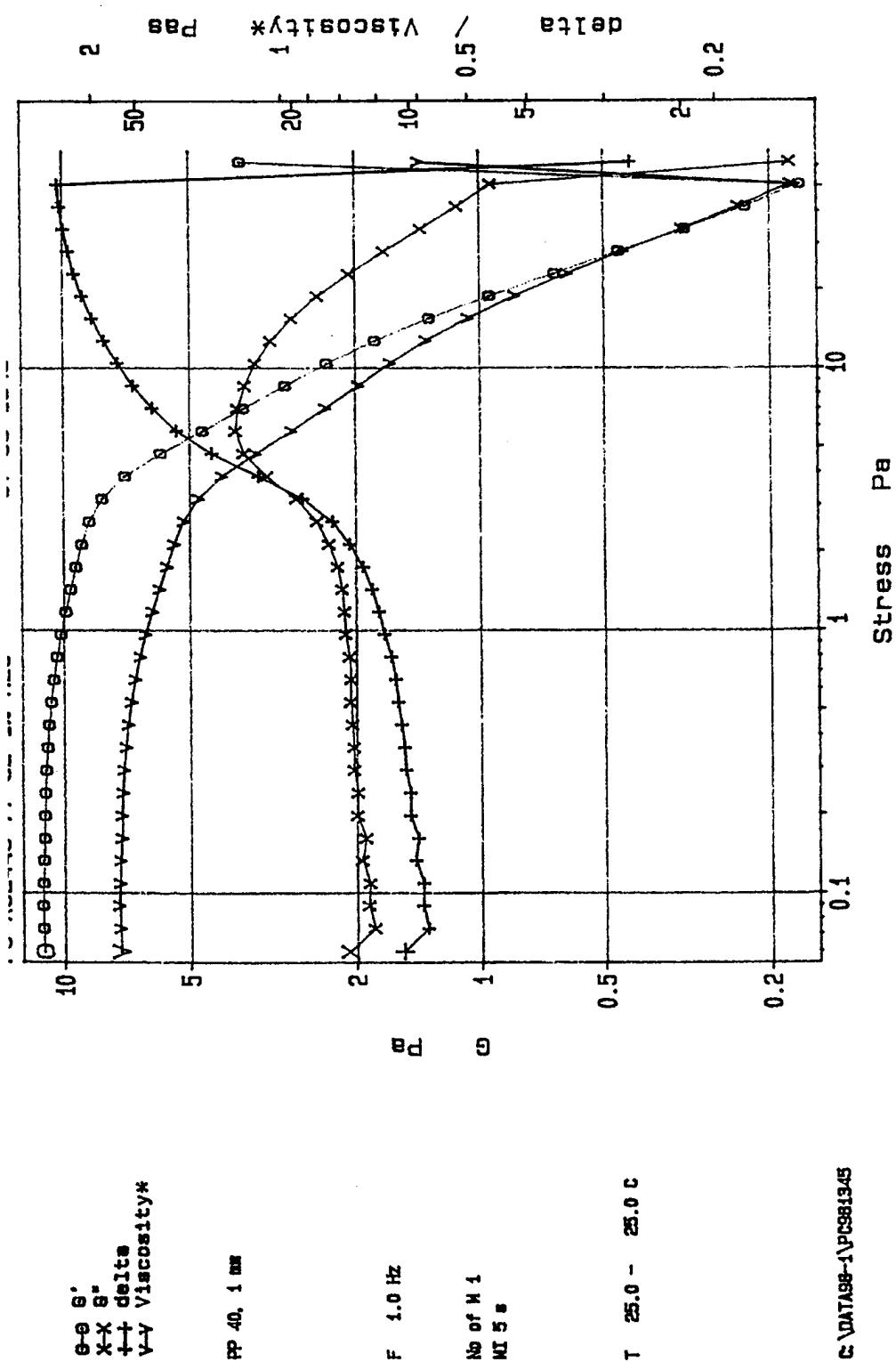


Figure 8

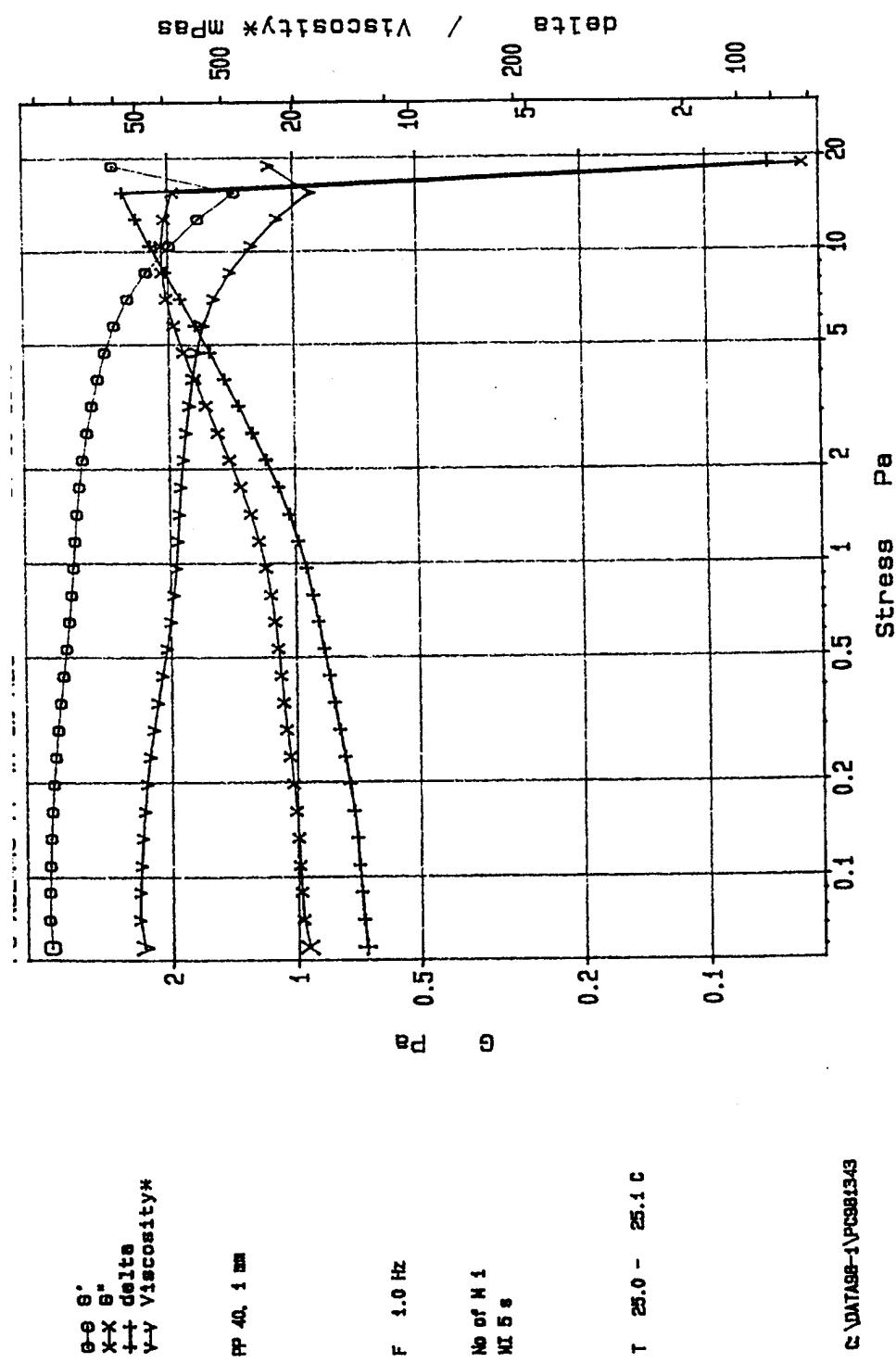
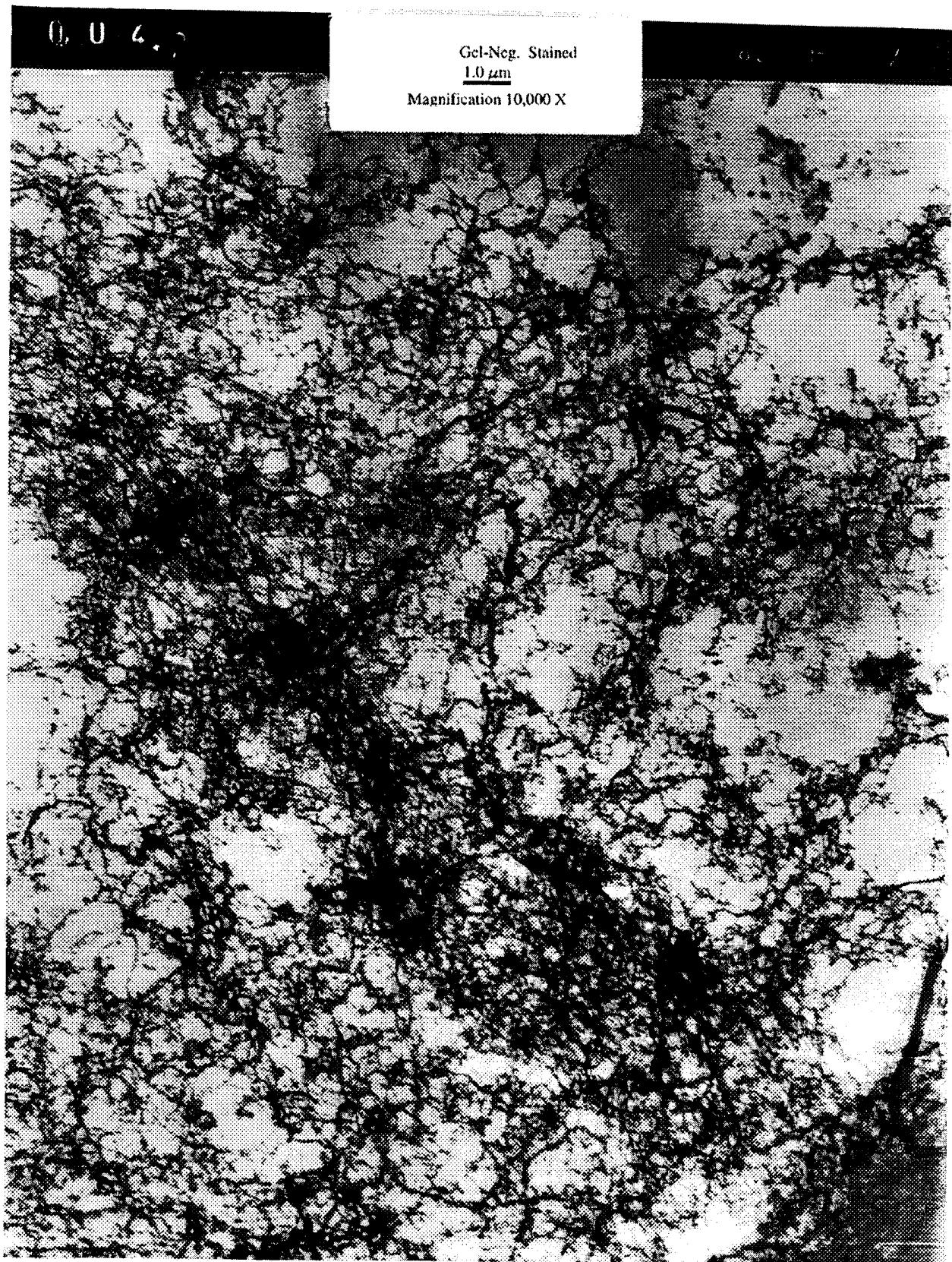


Figure 9



US007967904B2

(12) **United States Patent**
Bowden et al.

(10) **Patent No.:** US 7,967,904 B2
(45) **Date of Patent:** *Jun. 28, 2011

(54) **BIODEGRADABLE OR COMPOSTABLE CONTAINERS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **12/367,628**

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Related U.S. Application Data

(60) Continuation of application No. 11/486,722, filed on Jul. 14, 2006, now abandoned, which is a continuation of application No. 10/977,082, filed on Oct. 29, 2004, now Pat. No. 7,083,673, which is a division of application No. 10/341,288, filed on Jan. 13, 2003, now Pat. No. 6,878,199.

(60) Provisional application No. 60/348,003, filed on Jan. 11, 2002.

(51) **Int. Cl.**

B32B 21/02 (2006.01)
C08L 3/02 (2006.01)

(52) **U.S. Cl.** **106/162.51**; 264/109; 264/112;
428/535

(58) **Field of Classification Search** None
See application file for complete search history.

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(57) **ABSTRACT**

The present invention provides an improved method and materials for forming biodegradable containers that can hold food products in dry, damp or wet conditions and provides the biodegradable containers prepared according to the disclosed process. The containers are produced through the use of a pre-gelled starch suspension that is unique in its ability to form hydrated gels and to maintain this gel structure in the presence of many other types of materials and at low temperatures.

30 Claims, No Drawings

BIODEGRADABLE OR COMPOSTABLE CONTAINERS

This application is a continuation of U.S. patent application Ser. No. 11/486,722, filed Jul. 14, 2006, now abandoned, which is a continuation of U.S. patent application Ser. No. 10/977,082, filed Oct. 29, 2004, now U.S. Pat. No. 7,083,673, which is a divisional of U.S. patent application Ser. No. 10/341,288, filed Jan. 13, 2003, now U.S. Pat. No. 6,878,199, which claims the benefit of U.S. Provisional Application No. 60/348,003, filed Jan. 11, 2002.

FIELD OF THE INVENTION

This application is in the field of biodegradable and in particular compostable containers that can hold items in a dry, damp or wet condition. The products are based on novel starch compositions that can form and maintain a hydrated gel at low temperatures.

BACKGROUND OF THE INVENTION

Materials such as paper, paperboard, plastic, polystyrene, and even metals are presently used in enormous quantity in the manufacture of articles such as containers, separators, dividers, lids, tops, cans, and other packaging materials. Modern processing and packaging technology allows a wide range of liquid and solid goods to be stored, packaged, and shipped in packaging materials while being protected from harmful elements, such as gases, moisture, light, microorganisms, vermin, physical shock, crushing forces, vibration, leaking, or spilling. Many of these materials are characterized as being disposable, but actually have little, if any, functional biodegradability. For many of these products, the time for degradation in the environment can span decades or even centuries.

Each year, over 100 billion aluminum cans, billions of glass bottles, and thousands of tons of paper and plastic are used in storing and dispensing soft drinks, juices, processed foods, grains, beer and other products. In the United States alone, approximately 5.5 million tons of paper are consumed each year in packaging materials, which represents only about 15% of the total annual domestic paper production.

Packaging materials (e.g., paper, paperboard, plastic, polystyrene, glass, or metal) are all, to varying extents, damaging to the environment. For example, the manufacture of polystyrene products involves the use of a variety of hazardous chemicals and starting materials, such as benzene (a known mutagen and a probable carcinogen). Chlorofluorocarbons (or "CFCs") have also been used in the manufacture of "blown" or "expanded" polystyrene products. CFCs have been linked to the destruction of the ozone layer.

Due to widespread environmental concerns, there has been significant pressure on companies to discontinue the use of polystyrene products in favor of more environmentally safe materials. Some groups have favored the use of products such as paper or other products made from wood pulp. However, there remain drawbacks to the sole use of paper due to the tremendous amount of energy that is required to produce it. A strong need to find new, easily degradable materials that meet necessary performance standards remains.

Degradability is a relative term. Some products which appear to be degraded merely break apart into very small pieces. These pieces are hard to see, but can still take decades or centuries to actually break down. Other products are made from materials which undergo a more rapid breakdown than non-biodegradable products. If the speed of this degradation

is such that the product will degrade within a period of less than approximately 24 days under normal environmental conditions, the product is said to be compostable. Achievement of products made of compostable materials which also meet a variety of needs, such as containers for products in a damp or wet condition, has posed a significant challenge.

One solution has been to make packaging materials out of baked, edible sheets, e.g., waffles or pancakes made from a mixture of water, flour and a rising agent. Although edible sheets can be made into trays, cones, and cups which are easily decomposed, they pose a number of limitations. For example, since fats or oils are added to the mixture to permit removal of the sheet from the baking mold, oxidation of these fats cause the edible sheets to go rancid. In general, edible sheets are very brittle and far too fragile to replace most articles made from conventional materials. They are also overly sensitive to moisture and can easily mold or decompose prior to or during their intended use.

Starch is a plentiful, inexpensive and renewable material that is found in a large variety of plant sources, such as grains, tubers, and fruits. In many cases, starch is discarded as an unwanted byproduct of food processing. Starch is readily biodegradable and does not persist in the environment for a significant period after disposal. Starch is also a nutrient, which facilitates its breakdown and elimination from the environment.

Due to the biodegradable nature of starch, there have been many attempts to incorporate it into a variety of materials. Starch has been incorporated into multi-component compositions in various forms, including as filler and binder, as has been used as a constituent within thermoplastic polymer blends.

Starch can be used as a binder or glue to adhere solid constituents together to form a heterogenous mixture of different components. At some point before or during the molding phase, the starch is typically dissolved or gelatinized in an appropriate solvent, such as water, so that the starch becomes a flowable material into which the other components can be dispersed. Since native starch has a melting point that approaches its decomposition temperature, it is necessary to add polar liquids or solvents to allow the starch to become molten, solvated or otherwise liquified into a plastic state at a temperature that is safely below its decomposition temperature. Upon resolidification of the gelatinized starch, typically by removing enough of the water by evaporation so that the starch recrystallizes or otherwise dries out, the starch forms a solid or semi-solid binding matrix that can bind the remaining components together. Although many have attempted for years to perfect a starch blend that would yield an environmentally sound material while, at the same time, being economical to make, such a combination has not yet been achieved.

There remains a need in the art to provide a fully compostable product that is strong, not prone to mold or pests, and can be readily and inexpensively made. Furthermore, there is a need to develop a robust method to develop compostable products that can be used to hold dry, wet or damp material at a range of temperatures.

PCT Publication No. WO 99/02598, filed by Business Promotions, Inc., describes a method for making a biodegradable product for use as a container for foodstuffs, including hot and cold liquids. The product is manufactured under pressure and heat in a mold, based on a basic material made of amylose-comprising flour derived from an edible crop plant, wood flour, natural wax and water. The basic material consists substantially of a moist granulate comprising 50-250 parts by

weight flour, 10-85 parts by weight wood flour, 2-30 parts by weight natural wax and 50-250 parts by weight water.

European Patent 0773721B1 to Coöperatieve Verkoop discloses compounds made of a starch suspension and a wax coating, which is baked into a base mold. The coating is made of a wax composition comprising at least 50% wax and having a melting temperature of at least 40° C. The starch composition is preferably made by a process that includes 5-75% of a starch derivative which has a reduced swelling capacity at increased temperatures when compared to native starch.

PCT Publication No. WO 01/60898, filed by Novamont describes products such as sheets of different thicknesses and profile based on destructured or complexed starch, which are biodegradable. In particular, the patent claims partly-finished products, for example a foam sheet material, comprising destructured or complexed starch foamed as a continuous phase, having a density between 20 and 150 kg/m³, cell dimensions in a range between 25 and 700 μm with a cell distribution such that 80% of them have a dimension between 20 and 400 μm.

U.S. Pat. No. 6,451,170 to Cargill, Inc. describes improved starch compositions of cross-linked cationic starch, used in the papermaking process. The '170 patent claims the following papermaking process: 1) providing a cationized cross-linked starch component having a hot paste viscosity in the range of from about 200 cps to about 3000 cps as measured in a Brookfield viscometer at about 95° C. using a No. 21 spindle; 2) cooking a first portion of the starch component to generate a cooked starch component at an average cooking temperature below 330° F. for a period of time; 3) dewatering a paper furnish (the paper furnish including: (i) cellulosic fibers in an aqueous slurry, (ii) inorganic particles comprising at least 50 percent by weight particles having an average particle size of no greater than 1 micron, and (iii) the cooked starch component); and 4) adjusting the dewatering rate by cooking a second portion of the starch component at an average temperature at least 10° F. different than the first cooking temperature. The fourth step in the papermaking process can also include adjusting the first pass retention during dewatering by cooking a second portion of the starch composition at an average temperature at least 10° F. different than the first cooking temperature.

U.S. Pat. No. 5,122,231 to Cargill, Inc. describes a new cationic cross-linked starch for use in papermaking in the wet end system of a paper machine using a neutral or alkaline finish. The '231 patent claims methods to increase starch loading capacity in a papermaking process in which the papermaking process has a pH of about 6 or greater. One method is directed to adding the cationized cross-linked starch to a paper furnish of the process prior to the conversion of the furnish to a dry web wherein the starch is cationized to a degree of substitution on the hydroxyl groups of the starch between about 0.005 and about 0.050 and wherein after the cationization the starch is cross-linked to a hot paste viscosity in the range of from about 500 cps to about 3000 cps as measured on a Brookfield viscometer at about 95° C. using a No. 21 spindle. Another method is directed to adding cationized cross-linked starch to a paper furnish of the process in an amount effective for making Zeta potential of the furnish about zero and wherein the starch is cationized with monovalent cations and has a degree of substitution of monovalent cations on the hydroxyl groups of the starch between about 0.005 and about 0.050 and wherein after cationization the starch is cross-linked to a hot paste viscosity in the range of from about 500 cps to about 3000 cps as measured on a Brookfield viscometer at about 95° C. using a No. 21 spindle.

U.S. Pat. Nos. 5,569,692 and 5,462,982, both assigned to Novanont, disclose a composition for a biodegradable material which can be used at high temperatures comprising destructured starch, a thermoplastic polymer, and a plasticizer having a boiling point higher than 150° C. in an amount from 20 to 100% based on the weight of starch, said destructured-starch being obtained by destructuring starch as it is, without the addition of water. The inventors found that if a starch is destructured as it is, with the addition of a high-boiling plasticizer (such as glycerine) and a destructuring agent (such as urea), in an extruder heated to a temperature below the boiling point of the plasticizer (but between 120 and 170° C.), destructured starch compositions are obtained which can be mixed with polymers having relatively high melting points and are suitable for extrusion at temperatures higher than 120° C. at low pressure. The compositions thus obtained are particularly suitable for subsequent operations such as thermoforming and blowing.

U.S. Pat. No. 5,252,271 to Bio-Products International discloses a material that is based on a dry starch composition, having no greater than 30% water content; which is mixed with a mild acid in dry, powdered form (preferably malic acid, tartaric acid, citric acid, maleic acid and succinic acid) at a percentage of 0.2 to 7% of the total starch composition. Adding a dry, powdered carbonate composition capable of reacting with acid to generate CO₂ gas at a composition percentage of 0.1 to 2% of the total starch composition and mixing and advancing the product with water within an extrusion barrel of the extrusion means to generate elevated heat and pressure for converting the material to a gelatinous state that can be dried and remain pliable.

U.S. Pat. No. 4,863,655 to National Starch and Chemical Corp. discloses a biodegradable packaging material comprising an expanded, high amylose starch product having at least 45% (by weight of the final material) amylose content and a low density, closed cell structure with good resilience and compressibility. Another embodiment provides a method of preparing the packaging material with a total moisture content of 21% or less by weight, at a temperature of from 150 to 250° C.

U.S. Pat. No. 5,428,150 to Cerestar Holdings discloses a method for making a starch-containing composition to produce a material suitable for the production of molded articles in which the composition contains in addition to the starch a starch degradation product selected from starch hydrolysis products having dextrose equivalent's of 1 to 40, particularly a maltodextrin, oxidized starches and pyrodext.

U.S. Pat. Nos. 5,660,900, 5,868,824, and PCT Publication No. WO 96/05254 filed by Khashoggi disclose compositions for manufacturing biodegradable articles from highly inorganically filled materials having a starch-based binder. These documents describe articles of manufacture that have high levels of the inorganic filler in a polymer matrix without adverse affects on the properties of the binding system. The articles contain a matrix of starch and at least one inorganic aggregate, present as at least about 20% by weight (or 5% by volume) of the final mixture. The matrix is prepared from about 10% to 80% of a starch-based binder that has been substantially gelatinized by water and then hardened through the removal of a substantial quantity of the water by evaporation with an inorganic aggregate dispersed throughout the starch-bound cellular matrix. The mixture is designed with the primary considerations of maximizing the inorganic components, minimizing the starch component and solvent, and selectively modifying the viscosity to produce articles that have the desired properties for their intended use.

U.S. Pat. Nos. 5,736,209 and 5,810,961, and PC Publication No. WO 97/37842, also assigned to Khashoggi Industries, disclose methods to develop biodegradable paper and products which include a binding matrix of starch and cellulosic ether, and fibers substantially homogeneously dispersed throughout the matrix. The '209 patent discloses a concentration range for the starch of about 5% to about 90% by weight of solids in the sheet, for the cellulosic ether a range from about 0.5% to about 10% by weight of solids, and for fibers a concentration range from about 3% to about 40%. Optionally, an inorganic mineral filler can be added. Sheets produced using this biodegradable material having a thickness less than about 1 cm and a density greater than about 0.5 g/cm³ are described.

PCT Publication No. WO 01/51557, also filed by Khashoggi, is directed to compositions and methods for manufacturing thermoplastic starch compositions having a particulate filler (present in an amount greater than about 15% by weight of the thermoplastic starch) and, optionally, fiber reinforcement. Native starch granules are made thermoplastic by mixing and heating in the presence of an appropriate plasticizer (including somewhat polar solvents such as water or glycerin) to form a starch melt. The starch melt is then blended with one or more non-starch materials in order to improve the properties and reduce the cost of the resulting thermoplastic starch composition. A particulate filler component is thereafter blended with the starch melt, preferably an inexpensive, naturally occurring mineral particulate filler ("inorganic filler"), included in an amount greater than about 15% by weight of the thermoplastic starch composition. In addition, this reference discloses a composition comprising a thermoplastic starch melt having a water content of less than about 5% by weight while in a melted state, wherein at least one plasticizer has a vapor pressure of less than about 1 bar when in a melted state and in which a solid particulate filler phase is dispersed and included in an amount from about 5% to about 95% by weight. An additional embodiment discloses dispersion of a solid particulate filler phase in an amount from about 5% to about 95% by weight of the thermoplastic starch composition and a fibrous phase in a concentration of from about 3% to about 70% by weight.

U.S. Pat. No. 6,168,857 to Khashoggi Industries discloses a starch-bound sheet having a thickness less than about 1 cm and a density greater than about 0.5 g/cm³ comprising: (a) a binding matrix including starch and an auxiliary water-dispersible organic polymer, wherein the starch has a concentration greater than about 5% by weight of total solids in the sheet; and (b) fibers substantially homogeneously dispersed throughout the starch-bound sheet; and optionally an inorganic mineral filler.

U.S. Pat. Nos. 5,618,341, 5,683,772, 5,709,827, and 5,679,145 and PCT publication No. WO 97/2333, assigned to Khashoggi Industries, disclose starch-based compositions that can be used in making containers. U.S. Pat. Nos. '341 and '145 teach methods for dispersing fibers within a fibrous composition comprising the steps of: (a) combining together water, fibers, and a thickening agent such that the thickening agent (such as a pregelatinized starch) and water interact together to form a fluid fraction that is characterized by a yield stress and viscosity that enables the fibers to be substantially uniformly dispersed throughout the fibrous composition as the fibers and fluid fraction are mixed together, the fibers having an average length greater than about 2 mm and an average aspect ratio greater than about 25:1; and (b) mixing together the combined thickening agent, water, and fibers in order to substantially uniformly disperse the fibers throughout the fibrous composition. The thickening agent is included

in an amount in a range from about 5% to about 40% by weight of the fluid fraction. The inventive method involves a fluid system that is able to impart shear from a mechanical mixing apparatus down to the fiber level in order to obtain a starch-based composition having substantially uniformly dispersed fibers. U.S. Pat. No. '772 additionally discloses an inorganic filler to enhance the strength and flexibility of the articles. '827 additionally discloses methods to make the article of manufacture that is developed from mixtures including fibers having an average aspect ratio greater than about 25:1. The '341, '772, '827, and '145 patents and WO 97/2333 application, disclose high aspect ratios (i.e., about 25:1 or greater) and long-length (i.e., at least about 2 mm) fibers to reinforce the structure. PCT publication No. WO 97/2333 discloses articles that contain high starch contents (from about 50% to about 88% by weight ungelatinized and about 12% to about 50% by weight of gelatinized starch).

U.S. Pat. No. 6,303,000 to Omnova Solutions discloses a method to improve the strength of paper by adding an aqueous cationic starch dispersion modified with a blocked glyoxal resin to a paper pulp slurry. The starch dispersion is prepared by gelatinizing an aqueous suspension of starch granules (including potato, corn, waxy corn, red and white milo, wheat and tapioca, thin-boiling starches, and starches that have been additionally chemically modified) and reacting the starch with a blocked glyoxal resin at temperatures of at least 70° C., preferably 85 to 95° C. Suitable blocked glyoxal resins which can be used with the invention include cyclic urea/glyoxal/polyol condensates, polyol/glyoxal condensates, urea or cyclic urea/glyoxal condensates and glycol/glyoxal condensates in an amount from about 3% to about 30%, preferably 9 to 20%, of the total dry weight of starch. The resulting gelatinized starch composition can be cooled and stored, or directly added to a dilute paper pulp slurry to increase the tensile strength and elasticity of the resulting paper product.

PCT Publication No. WO 01/05892 filed by Kim & Kim describes methods for manufacturing plastic-substitute goods by using natural materials by preparing a glue made by mixing 20% by weight of a starch and 80% by weight of water together, heating this mixture; washing and drying rice husks to a drying extent of 98%; mixing the glue and the rice husks together so as to form a mixture of the glue and the rice husks, drying them to a drying extent of 98%, and crushing them to a size range of 0.1-0.1 mm. Then, mixing 80% by final weight of the mixture of the glue and the rice husks, 5% by final weight water, and 15% by final weight of rosin to form a final mixture; and molding the final mixture using a molding machine at a temperature of 100-350° C. under a pressure of 5 kg/cm at a production frequency of 30-80 seconds per product.

PCT Publication No. WO 02/083386 also filed by Kim & Kim describes methods for manufacturing plastic-substitute goods by using natural materials using a starch-based glue and melamine-resin. Melamine or urea resin is a thermosetting resin which is formed by reaction of melamine or urea acting upon formaldehyde. The products are manufactured by first preparing a mixture of 20% by weight of a starch and 80% by weight of water, heating this mixture; washing and drying rice husks to a drying extent of 98%; mixing the glue and the rice husks together so as to form a mixture of the glue and the rice husks, drying them to a drying extent of 98%, and crushing them to a size range of 0.01-0.1 mm. Melamine resin is obtained by a process of first, mixing 30% by weight of formaldehyde solution and 70% by weight of water, 30% by weight of melamine or urea and heating the mixture at a temperature of 350° C. A mixture is then made of 70% by final

weight of the mixture of the glue and the rice husks, 15% by weight of water, and 15% by weight of melamine resin to form a final mixture. The final mixture is molded by a molding machine at a temperature of 100-350° C. under a pressure of 5 kg/cm at a product ion frequency of 30-80 seconds per product.

U.S. Publication No. US 2002/0108532 and PCT Publication No. WO 00/39213 filed by Apack AG disclose methods to produce a shaped body made of biodegradable material that shows good expansion behavior during thermoforming from 7.6 to 8.5% by weight of cellulosic fibers, from 16.1 to 17.6% by weight of native starch, from 5.4 to 6% by weight of pregelatinized starch and from 68.0 to 70.6% by weight of water. First, the pregelatinized starch is produced by mixing between 5.4-6% starch and 94-94.6% water, heating the mixture to 68-70° C., holding the mixture constant at 68-70° C. for 10 minutes, and cooling the pregelatinized starch to 50° C. Then, adding the 16.1 to 17.6% by weight of native starch, 7.6 to 8.5% by weight of cellulosic fibers, and 68.0 to 70.6% by weight of water to the pregelatinized solution at a temperature of 50° C.; mixing for 5 minutes to achieve a homogeneous mixture at 40° C., not allowing the mixture to substantially cool, and placing the mixture in a baking mold, and baking the mixture at 100-200° C. for 10-100 seconds to form the shaped body.

German patent DE 19,706,642 to Apack Verpackungen GmbH discloses the production of a biodegradable article from 25-75% fibers, 13-38% starch and 13-38% water. First, the 25-75% fibers, 13-38% starch are mixed in a dry state in a continuous process; then water is admixed continuously. The mixture is then subjected to a baking process to obtain the finished molded article, and then the molded article is coated with a biologically degradable film that is impermeable to humidity.

Although numerous attempts have been made to provide suitable biodegradable and compostable materials for packaging, the resulting substances are not ideal. The currently available materials either cannot successfully be used to package materials, particularly those that are wet, or do not effectively degrade under normal environmental conditions. A need exists to develop materials that will reduce the build up of disposed, slowly degrading materials, and to limit the environmental damage caused by toxic chemicals used in the production of packaging materials.

It is therefore an object of the present invention to provide a robust process and materials for the production of an efficiently biodegradable container.

It is a further object of the present invention to provide a materials and a process for producing a biodegradable container that can hold products in dry, wet or damp conditions.

It is another object of the present invention to provide a material and a process to produce biodegradable containers through the use of a pregelatinized starch solution that is stable at a wide range of temperatures.

It is a further object of the present invention to provide a process and material to produce biodegradable containers through the use of a pregelatinized paper starch solution that is stable at a wide range of temperatures.

It is another object of the present invention to provide a process and material to produce biodegradable containers from a wide range of materials.

It is yet another object of the present invention to provide a process and material to produce biodegradable containers under a wide range of environmental conditions.

It is still another object of the present invention to provide biodegradable and compostable products.

SUMMARY OF THE INVENTION

The present invention provides an improved method and materials, for forming biodegradable containers that can hold food products in dry, damp or wet conditions. The containers are produced through the use of a pre-gelled starch suspension that is unique in its ability to form hydrated gels and to maintain this gel structure in the presence of many other types of materials and at low temperatures. In addition, this pre-gelled starch has the ability to melt into plastic like materials at relatively low temperatures in the presence of a wide range of materials under varying environmental conditions. Further, this pre-gelled material allows for the development of containers with high binding strengths and open cell structures to provide insulation and cross-linking of components.

One aspect of the present invention is a process for forming a biodegradable container by:

(a) forming a pre-gelled starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) adding to the pre-gelled starch suspension a dry or damp, homogeneous mixture containing at least wood fibers having an aspect ratio between approximately 1:2 and 1:8 (width:length) to form a homogenous moldable composition; and

(c) molding the homogenous moldable composition with heat to form a biodegradable container.

In another embodiment, the present invention is a process for forming a biodegradable container by:

(a) forming a first pre-gelled starch suspension that is maintained at a low temperature, for example, preferably 0-60° C., most preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), a second pre-gelled starch suspension, and/or a native starch to form a homogenous mixture;

(c) adding to the pre-gelled starch suspension the dry or damp, homogeneous mixture to form a homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

In a specific embodiment, the present invention is a process for forming a biodegradable container by:

(a) forming a pre-gelled starch suspension (the pre-gel) produced from approximately 3-10% potato starch by weight of the pre-gel and approximately 90-97% water by weight of the pre-gel such that the pre-gelled suspension is maintained at low temperatures, for example, preferably 0-60° C., most preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), a pre-gelled starch suspension produced from approximately 15% corn starch (by weight of the pre-gel) and approximately 85% water by weight of the pre-gel, and a native starch (for example approximately 50-70%, or, more specifically, 57-65.8%, corn starch (by weight of the homogenous moldable composition) or approximately 2-15% or, more specifically, 3-5% potato starch (by weight of the homogenous moldable composition)) to form a homogeneous mixture;

(c) adding to the pre-gelled potato starch suspension the homogeneous mixture to form a final homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

Another aspect of the present invention is a process for forming a biodegradable container by:

(a) forming a pre-gelled paper starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) adding to the pre-gelled paper starch suspension a dry or damp, homogeneous mixture containing at least wood fibers having an aspect ratio between approximately 1:2 and 1:8 (width:length) to form a homogeneous moldable composition; and

(c) molding the homogeneous moldable composition with heat to form a biodegradable container.

In other embodiments, the present invention is directed to a process for forming a biodegradable container by:

(a) forming a first pre-gelled paper starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), and a native starch(s) to form a homogeneous mixture;

(c) adding to the first pre-gelled starch suspension the homogenous mixture to form a homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

In a specific embodiment, the present invention is directed to a process for forming a biodegradable container by:

(a) forming a pre-gelled starch suspension produced from approximately 2-15% potato starch (by weight of the pre-gel), preferably about 2.5, 5, 10, or 15%; approximately 5-10% paper pulp (by weight of the pre-gel), preferably about 5.9-8%; and approximately 75-95% water (by weight of the pre-gel) such that the pre-gelled suspension is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8, preferably between 1:2 and 1:4), native corn starch and native potato starch to form a homogeneous mixture;

(c) adding to the pre-gelled potato starch suspension the homogeneous mixture to form a homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

In other embodiments, the following materials can be added to the wood fibers to form a homogeneous mixture:

(i) waxes, fatty alcohols, phospholipids or other high molecular weight biochemicals, such as glycerol, for example between approximately 1-5% or, more specifically, 2.6-3.7% glycerol (by weight of the homogenous moldable composition);

(ii) approximately 0.5-20% water (by weight of the homogenous moldable composition), preferably about 0.5-10%, 0.5-11% 0.5-12%, 10 or 20%;

(iii) baking powder, for example between approximately 0.1-15% by weight of the homogenous moldable composition, preferably about 0.42, 1 or 12%; and/or

(iv) additional materials, such as up to approximately 5% by weight of the homogenous moldable composition of natural earth fillers, for example, clays such as bentonite, amorphous raw products such as gypsum and calcium sulfate, minerals such as limestone, or man made materials such as fly-ash.

In still other embodiments, the process comprises the steps of:

(a) forming a pre-gelled starch suspension or paper starch suspension that is maintained at a low temperature, for example, preferably from about 0-60° C., most preferably from about 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8) and (i) dry or damp starch, such as corn starch; (ii) pre-gelled starch, such as a

10 pre-gelled corn starch produced from approximately 15% corn starch (by weight of the pre-gel) and 85% water; (iii)

waxes, fatty alcohols, phospholipids and other high molecular weight biochemicals, such as glycerol, for example between approximately 1-5% glycerol (by weight of the

15 homogenous moldable composition); (iv) approximately 0.5-20% water, preferably about 0.5-10%, 0.5-11% 0.5-12%, 10 or 20% (by weight of the homogenous moldable composition); (v) baking powder, for example between approximately

15 0.1-15% (by weight of the homogenous moldable composition), preferably 0.42, 1 or 12%; and/or (vi) additional mate-

rials, such as up to approximately 5%, 0-4%, 0-13%, 2-13%, or 0-15% by weight of the homogenous moldable composi-

20 tion of natural earth fillers, for example, clays such as bentonite, amorphous raw products such as gypsum and calcium sulfate, minerals such as limestone, and man made materials such as fly-ash to form a homogeneous mixture;

(c) adding to the pre-gelled starch suspension the dry or damp, homogeneous mixture to form a homogenous moldable composition; and

25 (d) molding the homogenous moldable composition with heat to form a biodegradable container.

In one embodiment, the pre-gelled starch suspension is produced from approximately 2.5-15% starch (by weight of the pre-gel), such as potato or corn starch, and from approxi-

30 mately 85-97.5% of water by weight of the homogenous moldable composition. In another embodiment, the pre-

35 gelled starch suspension is produced from approximately 2.5-5.5% starch and from approximately 94.5-97.5% water (by weight of the pre-gel). In preferred embodiments, the

40 pre-gelled starch suspension is produced from approximately 2.5-10% potato starch, more preferably 3%, 5%, 7.5% or 10%

potato starch, and 90, 92.5, 95 or 97% water (by weight of the pre-gel). In another preferred embodiment, the pre-gelled

45 starch suspension is produced from approximately 15% corn starch (by weight of the pre-gel).

In another embodiment, the pregelled paper starch solution is produced from approximately 5-10% paper pulp (by

50 weight of the pre-gel), preferably 5.9-8%, more preferably, 7.3-7.5, 6.5-6.7, or 5.9-6.1%; approximately 5-15%, prefer-

ably 10% potato or other natural starch (such as corn starch), and approximately 75-90% water (by weight of the pre-gel).

In one embodiment, the native starch can be corn starch or

55 potato starch. In another embodiment potato starch and corn starch can be used together. In a further embodiment, the corn

starch can comprise approximately 4-18%, preferably from 4.45-17.9%, or from about 5-35%, preferably 5.9-34.4% by

weight of the homogenous moldable composition, preferably, 4, 5, 6, 13, 15, 16, 17, 18, 20, 21, 22, 26, 28, 29, 30, 31 or 34%.

In a still further embodiment, the wood fibers or flour can

60 comprise approximately 11-24%, preferably 11, 12, 13, 14, 16, 17, 18, 19, 20, 21, 22, 23, or 23.3% by weight of the

homogenous moldable composition that contains the pregelled starch solution. In an alternate embodiment, the

65 wood fibers or flour can comprise approximately 7-11%, preferably 7, 8, 9, 10 or 11%, by weight of the homogenous moldable composition that contains the pregelled paper starch solution. The wood fibers or flour can have an aspect

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ratio, width to length of between approximately 1:2 and 1:10, 1:2 and 1:9, 1:2 and 1:8, 1:2 and 1:7, 1:2 and 1:6, 1:2 and 1:5, 1:2 and 1:4, 1:2 and 1:3, or a fraction thereof, for example a ratio of between 1:2 and 1:9.9.

In another embodiment, the containers which are formed using the method of the invention are efficiently biodegradable, preferably disintegrating to component parts in less than one year. In another embodiment, the containers are compostable, disintegrating to component molecules in less than six months, preferably in less than approximately 24 days.

In further embodiments, pressure can also be used in combination or alternation with heat to mold the biodegradable container. Any amount of pressure can be used that achieves the desired product, for example, pressure between approximately 2-3 psi may be appropriate. Likewise, any amount of heat may be used that achieves the desired result. For example, in one embodiment, the heat used to mold the biodegradable containers is between approximately 150-250° C.; preferably 195-225° C., most preferably 215° C.

In another embodiment, the container can be coated with any suitable liquid-resistant coating. Examples include, but are not limited to, coatings such as PROTECOAT® (from New Coat, Inc.), ZEIN® (a biodegradable material isolated from corn); polylactic acid (PLA, a polymer of lactic acid from fermentation feed stock); poly hydroxyalkanoates (PHA, from microbial fermentation); bacterial cellulose; chitosan based polymers (for example from shell fish wastes); or waxes and oil based coatings. These materials can be applied either as a thin film or can be sprayed/dipped onto the product. Bonding processes for application of thin films of water-resistant material are known in the art.

In one embodiment, a method is provided for creating a waterproof container by:

(a) forming a first pre-gelled starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), and wax, fatty alcohol, phospholipids or other high molecular weight biochemicals, such as glycerol;

(c) adding to the first pre-gelled starch suspension the homogeneous mixture containing the wood fiber and other material;

(d) molding the homogeneous composition with heat to form a biodegradable container; and

(e) coating the container with a liquid-resistant coating, such as PROTECOAT® (from, New Coat, Inc.), ZEIN® (a biodegradable material isolated from corn); poly lactic acid (PLA, a polymer of lactic acid from fermentation feed stock); poly hydroxyalkanoates (PHA, from microbial fermentation); bacterial cellulose; chitosan based polymers (for example from shell fish wastes); or waxes and oil based coatings.

In another embodiment, it is recognized that to facilitate the coating of the molded article, as well as for other specific indications, such as decreasing the residual odor of wood in the final product, the amount of paper pulp can be increased to 50%, or 30-50%, by weight of the final mixture, and the amount of wood flour or fiber can be decreased to 0%.

In a further embodiment, a vacuum can be used to form a film around the molded article. When using a vacuum to form a film around the molded article, it is recognized that increasing the levels of wood flour/fiber and/or paper pulp can facilitate the vacuuming process. In one embodiment, the wood flour/fiber and/or paper pulp levels can be increased to 30, 40 or 50% by weight of the final mixture.

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Thus, in an alternate aspect of the present invention, a process is provided for forming a biodegradable container by:

(a) forming a paper starch suspension, wherein the paper pulp that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.; and

(b) molding the homogeneous moldable composition with heat to form a biodegradable container.

In one embodiment, a process is provided for forming a biodegradable container by:

(a) forming a paper starch suspension, wherein the pregelled paper starch solution is produced from up to approximately 50, 60, 75, 85 or 90% paper pulp (by weight of the pre-gel) and approximately 5-15%, preferably 10% potato or other natural starch (such as corn starch), and approximately 5.90% water (by weight of the pre-gel), and wherein the paper pulp that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.; and

(b) molding the homogeneous moldable composition with heat to form a biodegradable container.

Another embodiment of the present invention provides a process for forming a biodegradable container by:

(a) forming a pre-gelled paper starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together (i) 0-24% wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8) by weight of the homogenous moldable composition; (ii) dry or damp starch, such as corn starch; (iii) pre-gelled starch, such as a pre-gelled corn starch produced from approximately 15% corn starch (by weight of the pre-gel) and 85% water; (iv) waxes, fatty alcohols, phospholipids and other high molecular weight biochemicals, such as glycerol, for example between approximately 1-5% glycerol (by weight of the homogenous moldable composition); (v) approximately 0.5-20% water, preferably about 0.5-10%, 0.5-11%, 0.5-12%, 10 or 20% (by weight of the homogenous moldable composition); (vi) baking powder, for example between approximately 0.1-15% (by weight of the homogenous moldable composition), preferably 0.42, 1 or 12%; and/or (vii) additional materials, such as up to approximately 5%, 0-4%, 0-13%, 2-13%, or 0-15% by weight of the homogenous moldable composition of natural earth fillers, for example, clays such as bentonite, amorphous raw products such as gypsum and calcium sulfate, minerals such as limestone, and man made materials such as fly-ash to form a homogeneous mixture;

(c) adding to the pre-gelled starch suspension the dry or damp, homogeneous mixture to form a homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

In a further embodiment, a process is provided for forming a biodegradable container by:

(a) forming a pre-gelled paper starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together (i) 0-24% wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8) by weight of the homogenous moldable composition; (ii) dry or damp starch, such as corn starch; (iii) pre-gelled starch, such as a pre-gelled corn starch produced from approximately 15% corn starch (by weight of the pre-gel) and 85% water; (iv) waxes, fatty alcohols, phospholipids and other high molecular weight biochemicals, such as glycerol, for example between approximately 1-5% glycerol (by weight of the homogenous moldable composition); (v) approximately 0.5-

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20% water, preferably about 0.5-10%, 0.5-11% 0.5-12%, 10 or 20% (by weight of the homogenous moldable composition); (vi) baking powder, for example between approximately 0.1-15% (by weight of the homogenous moldable composition), preferably 0.42, 1 or 12%; and/or (vii) additional materials, such as up to approximately 5%, 0-4%, 0-13%, 2-13%, or 0-15% by weight of the homogenous moldable composition of natural earth fillers, for example, clays such as bentonite, amorphous raw products such as gypsum and calcium sulfate, minerals such as limestone, and man made materials such as fly-ash to form a homogeneous mixture;

(c) adding to the pre-gelled starch suspension the dry or damp, homogeneous mixture to form a homogenous moldable composition;

(d) molding the homogenous moldable composition with heat to form a biodegradable container; and

(e) coating the container with a liquid-resistant coating, such as PROTECOAT® (from New Coat, Inc.), ZEIN® (a biodegradable material isolated from corn); poly lactic acid (PLA, a polymer of lactic acid from fermentation feed stock); poly hydroxyalkanoates (PHA, from microbial fermentation); bacterial cellulose; chitosan based polymers (for example from shell fish wastes); or waxes and oil based coatings.

It is recognized that in any embodiment of the present invention, paper pulp can be substituted for wood fibers/flour.

In another embodiment, a process is provided for creating an open cell foam container by:

(a) forming a first pre-gelled starch suspension that is maintained at a low temperature, for example, preferably from 0-60° C., most preferably from 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), a second pre-gelled starch suspension to form a homogeneous composition, and a source of gas, such as a source of carbon dioxide gas;

(c) adding to the first pre-gelled starch suspension a dry or damp, homogeneous mixture containing the wood fibers and second pre-gelled starch; and

(d) molding the homogeneous composition with heat to form a biodegradable container.

In a specific embodiment, the present invention is directed to a process for forming an open cell foam container by:

(a) forming a pre-gelled starch suspension produced from approximately 3-5% potato starch (by weight of the pre-gel) and approximately 95-97% water (by weight of the pre-gel) such that the pre-gelled suspension is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), a second pre-gelled starch suspension (the second pre-gel) produced from approximately 15% corn starch (by weight of the second pre-gel) and approximately 85% water (by weight of the second pre-gel), and baking powder, for example between 0.42-12% baking powder (by weight of the homogeneous moldable composition) to form a homogeneous mixture;

(c) adding to the pre-gelled potato starch suspension a homogeneous mixture containing the wood fibers and pre-gelled corn starch to form a homogeneous moldable composition; and

(d) molding the homogeneous moldable composition with heat to form a biodegradable container.

The processes described herein will produce biodegradable containers that are formed from different combinations of materials by weight. For example, containers can be formed from approximately 16-61% pre-gelled potato starch

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suspension (by weight of the homogenous moldable composition) and approximately 11-37% (or 11-15%) wood fibers or flour (by weight of the homogenous moldable composition). In addition, various combinations of other materials can be added to the wood fibers or flour to produce a homogenous mixture before mixing it with the pre-gelled starch suspension, including, but not limited to:

(i) approximately 57-66% pre-gelled corn starch suspension (by weight of the homogenous moldable composition) (suspension formed from approximately 5-15% corn starch (by weight of the pre-gel) and approximately 85-95% water by weight of the pre-gel);

(ii) approximately 4-35% native starch (by weight of the homogenous moldable composition), for example 3-5% (preferably 3.7% or 4.2%) native potato starch, and/or 15.4-34.4% native corn starch;

(iii) approximately 1-5% glycerol (by weight of the homogenous moldable composition);

(iv) up to approximately 10 or 20% water (by weight of the homogenous moldable composition);

(v) approximately 0.1-15% baking powder (by weight of the homogenous moldable composition);

(vi) less than approximately 5% natural materials (by weight of the homogenous moldable composition), such as bentonite clay.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

The term "sheet" as used herein refers to any substantially flat, corrugated, curved, bent, or textured sheet made using the methods described herein. The sheets can also include organic coatings, printing, other sheets laminated thereto. The sheets within the scope of the present invention can have greatly varying thicknesses depending on the particular applications for which the sheets are intended. The sheets can be as thin as about 0.001 mm or as thick as 1 cm or greater where strength, durability, and/or bulk are important considerations.

The term "film" is not inherently different from the term "sheet" except that "film" normally denotes a very thin sheet. Films are often formed by processes that are different from how sheets are normally formed, such as by film blowing rather than sheet calendering. In general, films will be defined as sheet-like articles having thicknesses as low as about 1 micron and up to about 1 mm.

The term "molded article" shall refer to articles that are shaped directly or indirectly from starch compositions using any molding method known in the art.

The term "container" as used in this specification and the appended claims is intended to include any article, receptacle, or vessel utilized for storing, dispensing packaging portioning, or shipping various types of products or objects (including, but not limited to, food and beverage products). Specific examples of such containers include, among others, boxes, cups, "clam shells," jars, bottles, plates, bowls, trays, cartons, cases, crates, cereal boxes, frozen food boxes, milk cartons, bags, sacks, carriers for beverage containers, dishes, egg cartons, lids, straws, envelopes, or other types of holders. In addition to integrally formed containers, containment products used in conjunction with containers are also intended to be included within the definition "container". Such articles include, for example, lids, liners, straws, partitions, wrappers, cushioning materials, utensils, and any other product used in packaging, storing, shipping, portioning, serving, or dispensing an object within a container.

As used herein, the term "dry or damp" refers to a solid composition that can be dry, or can be moist or wetted, gen-

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erally with water, although other solvents may be used. The amount of liquid in the composition is not sufficient to act as a carrier between particles in the composition.

As used herein, the term "homogeneous mixture" refers to mixtures of solid particulates or of solids in a liquid carrier which are substantially uniform in composition on a macroscopic scale. It will be appreciated that mixtures of different types of solid particles or of solids in a liquid carrier are not homogeneous when viewed on a microscopic scale, i.e., as the particle size level.

Pre-Gelled Starch Suspensions

The starch component can include any known starch material, including one or more unmodified starches, modified starches, and starch derivatives. Preferred starches can include most any unmodified starch that is initially in a native state as a granular solid and which will form a thermoplastic melt by mixing and heating. Starch is typically considered a natural carbohydrate chain comprising polymerized glucose molecules in an alpha-(1,4) linkage and is found in nature in the form of granules. Such granules are easily liberated from the plant materials by known processes. Starches used in forming the pre-gelled starch suspension used in the method of the invention desirably possess the following properties: the ability to form hydrated gels and to maintain this gel structure in the presence of many types of other materials; and the ability to melt into plastic-like materials at low temperatures, for example, between 0-75° C., preferably between 0-65° C., and in the presence of a wide range of materials and in moist environments and to exhibit high binding strengths and produce an open cell structure for both insulation and cross linking of components. The preferred sources of starch for pregels are cereal grains (e.g., corn, waxy corn, wheat, sorghum, rice, and waxy rice, which can also be used in the flour and cracked state), tubers (potato), roots (tapioca (i.e., cassava and maniac), sweet potato, and arrowroot), modified corn starch, and the pith of the sago palm.

While not intending to be bound to any specific mechanistic explanation for the desirable properties observed when the method of the invention is employed, it is believed that the gel property holds other components in suspension until the product can be molded and to hold the moisture levels constant within the mixture until and during molding. The second property is evident in the transition in the mold of the gel structure into a drier and dried form that will then melt into the binding plastic-like product within the confines of the mold. This complex three dimensional cross linked structure is the backbone for the product, exhibiting both strength and insulation properties. The pre-gelled starch is prepared by mixing the starch with water (for example at levels of approximately 2% to 15% by weight of the pre-gel, preferably at least 2.5%, 3%, 5%, 10%, or 15%) at about ambient temperature (approximately 25° C.). The gel is formed by slowly heating the water-starch mixture with constant agitation until a gel forms. Continued heating will slowly degrade the gel, so the process should be stopped as soon as an appropriate level of gelation is achieved. Gels can be used cold. The gel is stable for a few days if refrigerated. For storage a biocide can be added, preferably at a concentration of about 10 to about 500 ppm.

Preferred starch-based binders are those that gelate and produce a high viscosity at a relatively low temperature. For example, potato starch quickly gelates and reaches a maximum viscosity at about 65° C. The viscosity then decreases, reaching a minimum at about 95° C. Wheat starch acts in a similar fashion and can also be used. Such starch-based binders are valuable in producing thin-walled articles having a smooth surface and a skin with sufficient thickness and density to impart the desired mechanical properties.

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In general, starch granules are insoluble in cold water; however, if the outer membrane has been broken by, e.g., by grinding, the granules can swell in cold water to form a gel. When the intact granules are treated with warm water, the granules swell and a portion of the soluble starch diffuses through the granule wall to form a paste. In hot water, the granules swell to such an extent that they burst, resulting in gelation of the mixture. The exact temperature at which a starch swells and gelates depends on the type of starch. Gelation is a result of the linear amylose polymers, which are initially compressed within the granules, stretching out and cross-linking with each other and with the amylopectin. After the water is removed, the resulting mesh of inter-connected polymer chains forms a solid material that can have a tensile strength up to about 40-50 MPa. The amylose polymers can also be used to bind individual aggregate particles and fibers within the moldable mixture.

It is possible to reduce the amount of water in starch melts by replacing the water inherently found in starch with an appropriate low volatile plasticizer capable of causing starch to melt below its decomposition temperature, such as glycerin, polyalkylene oxides, mono- and diacetates of glycerin, sorbitol, other sugar alcohols, and citrates. This can allow for improved processability, greater mechanical strength, better dimensional stability over time, and greater ease in blending the starch melt with other polymers.

Water can be removed before processing by using starch that has been pre-dried so as to remove at least a portion of the natural water content. Alternatively, water can be removed during processing by degassing or venting the molten mixture, such as by means of an extruder equipped with venting or degassing means. Native starch can also initially be blended with a small quantity of water and glycerin in order to form starch melts that are subjected to a degassing procedure prior to cooling and solidification in order to remove substantially all of the water therefrom.

In one aspect of the present invention, the pre-gelled starch suspension is produced from approximately 3-10%, preferably, 3, 5, 7.5 or 10%, starch by weight of the pre-gel, preferably, potato starch, and 90-97% water by weight of the pre-gel such that the pre-gelled suspension is maintained at low temperatures. In one embodiment, the pregeled starch solution can be maintained at all temperatures above freezing, 0° C. In another embodiment, the pregelled starch solution can be maintained for greater than 24 hours, up to a few days, if stored refrigerated, for example, between 3-15° C.

In another aspect of the present invention, a pre-gelled paper starch suspension is produced from approximately 5-15%, preferably 10%, starch (by weight of the pre-gel), preferably potato starch; 5-10% paper pulp (by weight of the pre-gel), preferably 5.9-8%, more preferably, 7.3-7.5, 6.5-6.7, or 5.9-6.1%; and 75-92.5% water (by weight of the pre-gel), such that the pre-gelled suspension is maintained at low temperatures. In one embodiment, the pregelled paper starch solution can be maintained at all temperatures above freezing, 0° C. In another embodiment, the pregelled paper starch solution can be maintained for greater than 24 hours, up to a few days, if stored refrigerated, for example, between 3-15° C.

Paper Pulp

In one aspect of this invention, prepulped paper is mixed with the pregel. The preferred amount of paper pulp added is in the range of 5-10% by weight of the pre-gel, preferably 5.9-8%, more preferably, 7.3-7.5, 6.5-6.7, or 5.9-6.1%. The prepulped paper can be mixed with 5-15%, preferably 10% potato or other natural starch (such as corn starch), and 75-90% water, for example, 580 gm water, 57.5 gm dry potato

starch, and 42.31 gm paper pulp. The mixture is stirred at slow rpm while increasing the temperature to 60-70° C., after which premixed dry ingredients (wood flour (preferably 5-10% (w/w) with an aspect ratio of 1:8; 1:9.9; 1:9 or 1:5), native potato starch (preferably 10-15% (by weight)) and/or native corn starch (preferably 10-20% (by weight)) can be added.

Paper pulp for this invention can be produced by any method known in the art. Paper pulp is a fibrous material produced by mechanically or chemically reducing woody plants into their component parts from which, pulp, paper and paperboard sheets are formed after proper slushing and treatment, or used for dissolving purposes (Lavigne, J R "Pulp & Paper Dictionary" 1993: Miller Freeman Books, San Francisco). Cellulose pulp production is a process that utilizes mainly arboreal species from specialized cultivations. To produce the paper pulp, wood, typically reduced to dimensions of about 30-40 mm and a thickness of about 5-7 mm, is treated at high temperature and pressure with suitable mixes of chemical reagents that selectively attack lignin and hemicellulose macromolecules, rendering them soluble. Pulps coming from this first treatment, commonly called "cooking", are called "raw pulps"; they still contain partly modified lignin and are more or less Havana-brown colored. Raw pulps can be submitted to further chemical-physical treatments suitable to eliminate almost entire lignin molecules and colored molecules in general; this second operation is commonly referred to as "bleaching". For this process, rapid growth ligneous plants are mainly used, which, with the help of chemical substances (alkali or acids), in condition of high pressure and temperature, are selectively delignified to obtain pulps containing cellulose and other components of lignocellulose. These pulps are then submitted to mechanical and chemical-physical treatments, in order to complete the removal of lignin and hemicellulose residual components, and utilized thereafter for paper production. Any form of paper pulp can be used in the packaging materials described herein.

Dry or Damp Starch

After formation of a pregel, dry or damp materials can be added (such as fibers, flour, pulp, or dry starches) to produce the final moldable mixture. The dry or damp materials can be pre-mixed before addition to the pregel, to increase the homogeneity of the final product and increase the structural integrity of the final molded product. Preferably, the amount of pregel added to the final mixture is in the range of about 7-60% by weight of the homogenous moldable composition. Preferably, the pregel is about at least 7%, 8%, 9%, 10%, 11%, 12%, 16.3%, 25%, 33%, 42%, 47%, 54%, 50%, 52%, 55%, 56%, 60% or 60.4% by weight of the homogenous moldable composition.

One component in the dry/damp material that can be added to the pre-gelled starch is a dry or damp starch binder component. This starch can be corn or other dry starch (for example potato, rice or wheat starch). Pre-gelatinized starch-based binders can also be added to the moldable mixture. Pregelatinized starch-based binders are starches that have previously been gelated, dried, and ground back into a powder. Since pre-gelatinized starch-based binders gelate in cold water, such starch-based binders can be added to the moldable mixture to increase the mixture viscosity prior to being heated. The increased viscosity prevents settling and helps produce thicker cell walls. This starch component can be pre-gelled in a manner similar to that describes above. For example, the second starch component can be pregelled in a mixture of between about 1 and 15% starch (for example 15% corn starch) and 85-99% water. In these cases additional dry starch can be added as necessary to the homogeneous mixture

to adsorb excess water. If the pregelled second starch is still damp, the preferred amount to be added is in the range of 55-65% by weight of the homogenous moldable composition, most preferably about 57% or about 65%.

The concentration of the native starch binder within the moldable mixtures of the present invention are preferably in a range from about 5% to about 60% by weight of the homogenous moldable composition, more preferably in a range from about 15% to about 30%, and most preferably about at least 6%, 20%, 21%, 25%, 26%, 27%, 28%, 29%, 30%, 31%, or 34% by weight of the homogenous moldable composition. Furthermore, combinations of different starches can be employed to more carefully control the viscosity of the mixture throughout a range of temperatures, as well as to affect the structural properties of the final hardened article. For example, the mixture can consist of a mixture of dry or damp corn and potato starch (16-44% of corn and potato starch by weight of the homogenous moldable composition), such that the corn starch comprises between about 13-30%, preferably between about 13-18% or 28-30%, and the potato starch comprises between about 3-14%, preferably approximately 1-14% or 3-5% of the final homogenous moldable composition.

Starch is produced in many plants, and many starches can be suitable, however, as with the starch used in the pre-gel, preferred sources of starches are seeds of cereal grains (e.g., corn, waxy corn, wheat, sorghum, rice, and waxy rice), which can be used in the flour and cracked state. Other sources of starch include tubers (potato), roots (tapioca (i.e., cassava and maniac), sweet potato, and arrowroot), and the pith of the sago palm. The starch can be selected from natural starch, chemically and/or physically modified starch, biotechnologically produced and/or genetically modified starch and mixtures thereof.

Suitable starches can also be selected from the following: ahipa, aipo (arracacha), arrowhead (arrowroot, Chinese potato, jicama), baddo, bitter casava, Brazilian arrowroot, casava (yucca), Chinese artichoke (crosne), Japanese artichoke (chorogi), Chinese water chestnut, coco, cocoyam, dasheen, eddo, elephant's ear, girasole, goo, Japanese potato, Jerusalem artichoke (sunroot, girasole), lily root, ling gaw, malanga (tanier), plantain, sweet potato, mandioca, manioc, Mexican potato, Mexican yam bean, old cocoyam, saa got, sato-imo, seegoo, sunchoke, sunroot, sweet casava, tanier, tannia, tannier, tapioca root, taro, topinambour, water chestnut, water lily root, yam bean, yam, yautia, barley, corn, sorghum, rice, wheat, oats, buckwheat, rye, kamut brand wheat, triticale, spelt, amaranth, black quinoa, hie, millet, plantago seed husks, psyllium seed husks, quinoa flakes, quinoa, teff.

Starches that can be used for the present invention include unmodified starches (amylose and amylopectin) and modified starches. By modified, it is meant that the starch can be derivatized or modified by typical processes known in the art such as, e.g. esterification, etherification, oxidation, acid hydrolysis, cross-linking, and enzyme conversion. Typical modified starches include esters, such as the acetate and, the half-esters of dicarboxylic acids/anhydrides, particularly the alkenylsuccinic acids/anhydrides; ethers, such as the hydroxyethyl and hydroxypropyl starches; oxidized starches, such as those oxidized with hypochlorite; starches reacted with cross-linking agents, such as phosphorus oxychloride, epichlorohydrin, hydrophobic cationic epoxides, and phosphate derivatives prepared by reaction with sodium or potassium orthophosphate or tripolyphosphate, and combinations thereof. Modified starches also include seagel, long-chain alkylstarches, dextrins, amine starches, and dialdehyde

starches. Unmodified starch-based binders are generally preferred over modified starch-based binders because they are significantly less expensive and produce comparable articles.

The dry ingredients, such as corn starch and wood flour are preferably pre-mixed into a homogeneous mixture before being added to the pregel. The dry/damp starch and the wood flour or fibers can be mixed to form a homogeneous mixture using any suitable means, such as, for example, a Kitchen Aid® Commercial Mixer.

Wood Flour or Fibers

In the present invention, additional fibers can be employed as part of the dry/damp material added to the pre-gelled starch. The fibers used are preferably organic, and most preferably cellulose-based materials, which are chemically similar to starches in that they comprise polymerized glucose molecules. "Cellulosic fibers" refers to fibers of any type which contain cellulose or consist of cellulose. Plant fibers preferred here are those of differing lengths typically in the range from 600 micron to 3000 micron, principally from hemp, cotton, plant leaves, sisal, abaca, bagasse, wood (both hard wood or soft wood, examples of which include southern hardwood and southern pine, respectively), or stems, or inorganic fibers made from glass, graphite, silica, ceramic, or metal materials. The cellulosic fibers include wood fibers and wood flour. In one embodiment, 11-24% by weight of wood fibers or flour are added to the final mixture. In the preferred embodiments, wood fibers or flour comprise about at least 11%, 12%, 13%, 14%, 16%, 17%, and 23.3% by weight of the homogenous moldable composition.

Wood flour and fibers are very much like rough tooth picks that have small barb like structures coming out from the main fiber to participate in the cross linkage process with the cooling starch melt. This property adds both strength and water resistance to the surface produced within the mold. The rapid grinding process to produce flour or short fibers by-passes the expensive and polluting processes that are used to manufacture pulp and paper. The wood flour can be a resinous wood flour. Preferably, the wood flour is softwood flour, which contains relatively large amounts of resin. Moreover, softwood is used industrially on a large scale, such as in the building trade, with the consequence that an abundance of wood flour from, for instance, saw mills, is available at a low price. Wood flours can be graded based on the mesh size the flour. In general, wood flour having a mesh size of 20-100 is suitable, and an aspect ratio or 1:8 or 1:9, or 1:10 or less.

Larger particles are considered to be fibers. The expression "fibers" refers to fine, thin objects restricted in their length, the length being greater than the width. They can be present as individual fibers or as fiber bundles. Such fibers can be produced in a manner known to those skilled in the art. Preferred fibers have a low length to diameter ratio and produce materials of excellent strength and light weight. In general, the fibers used in the invention will have an aspect ration of about between 1:2 and 1:10; 1:2 and 1:9; 1:2 and 1:8; 1:2 and 1:7; 1:2 and 1:6; 1:2 and 1:5; 1:2 and 1:4; 1:2 and 1:3; 1:2 and 1:2; or 1:2 and 1:9.9.

It should also be understood that some fibers, such as southern pine and abaca, have high tear and burst strengths, while others, such as cotton, have lower strength but greater flexibility. In the case where better placement, higher flexibility, and higher tear and burst strength are desired, a combination of fibers having varying aspect ratios and strength properties can be added to the mixture.

In a additional aspect of the present invention, it is recognized that to decrease the residual odor of the wood in the final product, the amount of paper pulp can be increased to 50%, or

30-50%, by weight of the final mixture, and the amount of wood flour or fiber can be decreased to 0%.

Additional Materials

In addition to the dry/damp starch and the wood flour, the homogenous mixture can also include one or more additional materials depending on desired characteristics of the final product. Natural earth fillers can be included for a stronger product. Suitable fillers include but are not limited to clays such as bentonite, amorphous raw products such as gypsum (calcium sulfate dehydrate) and calcium sulfate, minerals such as limestone and man made materials such as fly ash. These natural earth fillers are able to take part in the cross linking and binding that occurs during the molding process. Other examples of useful fillers include perlite, vermiculite, sand, gravel, rock, limestone, sandstone, glass beads, aerogel, xerogels, seagel, mica, clay, synthetic clay, alumina, silica, fused silica, tabular alumina, kaolin, microspheres, hollow glass spheres, porous ceramic spheres, calcium carbonate, calcium aluminate, lightweight polymers, xonotlite (a crystalline calcium silicate gel), lightweight expanded clays, hydrated or unhydrated hydraulic cement particles, pumice, exfoliated rock, and other geologic materials. Partially hydrated and hydrated cement, as well as silica fume, have a high surface area and give excellent benefits such as high initial cohesiveness of the freshly formed article. Even discarded inorganically filled materials, such as discarded containers or other articles of the present invention can be employed as aggregate fillers and strengtheners. It will also be appreciated that the containers and other articles of the present invention can be easily and effectively recycled by simply adding them to fresh moldable mixtures as an aggregate filler. Hydraulic cement can also be added in either its hydrated or unhydrated form. Both clay and gypsum can be important aggregate materials because they are readily available, relatively inexpensive, workable, form easily, and can also provide a degree of binding and strength if added in high enough amounts (for example in the case of gypsum hemihydrate). Because gypsum hemihydrate can react with the water within the moldable mixture, it can be employed as a means for holding water internally within the molded article. Preferably, the inorganic materials are added in an amount from up to approximately 5%, 0-4%, 0-13%, 2-13% or 0-15% by weight of the weight of the final composition.

Because of the wide variety of agents that can be used as fillers, preferred concentration ranges are difficult to calculate. For bentonite clay a preferred range is from about 2.5-4% of the weight of the final mixture. The additional agents can be predissolved or can be added dry. A preferred clay slurry is 20% bentonite clay in water.

In addition, further cellulose-based thickening agents can be added, which can include a wide variety of cellulosic ethers, such as methylhydroxyethylcellulose, hydroxyethylethylethylcellulose, carboxymethylcellulose, methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxyethylpropylcellulose, hydroxypropylmethylcellulose, and the like. Other natural polysaccharide-based thickening agents include, for example, alginic acid; phycocolloids, agar, gum arabic, guar gum, locust bean gum, gum karaya, xanthan gum, and gum tragacanth. Suitable protein-based thickening agents include, for example, ZEIN® (a prolamine derived from corn), collagen (derivatives extracted from animal connective tissue such as gelatin and glue), and casein (derived from cow's milk). Suitable synthetic organic thickening agents include, for example, polyvinyl pyrrolidone, polyethylene glycol, polyvinyl alcohol, polyvinylmethyl ether, polyacrylic acids, polyacrylic acid salts, polyvinyl acrylic acids, polyvinyl acrylic acid salts, polyacrylamides, ethylene oxide polymers,

polylactic acid, and latex. Latex is a broad category that includes a variety of polymerizable substances formed in a water emulsion. An example is styrene-butadiene copolymer. Additional copolymers include: vinyl acetate, acrylate copolymers, butadiene copolymers with styrene and acetonitrile, methylacrylates, vinyl chloride, acrylamide, fluorinated ethylenes. Hydrophilic monomers can be selected from the following group: N-(2-hydroxypropyl)methacrylamide, N-isopropyl acrylamide, N,N-diethylacryl-amide, N-ethylmethacrylamide, 2-hydroxyethyl methacrylate, acrylic acid 10 2-(2-hydroxyethoxy)ethyl methacrylate, methacrylic acid, and others, and can be used for the preparation of hydrolytically degradable polymeric gels. Suitable hydrophobic monomers can be selected from the 2-acetoxyethyl methacrylate group of monomers comprising dimethylaminoethyl methacrylate, n-butyl methacrylate, tert-butylacrylamide, n-butyl acrylate, methyl methacrylate, and hexyl acrylate. The polymerization can be carried out in solvents, e.g. in dimethylsulfoxide, dimethylformamide, water, alcohols as methanol and ethanol, using common initiators of the radical polymerization. The hydrophilic gels are stable in an acidic environment at pH 1-5. Under neutral or weak alkaline conditions at pH above 6.5, the gels degrade. The gels mentioned above are nontoxic as well as the products of their biodegradation.

Other copolymers include: aliphatic polyester, polycaprolactone, poly-3-hydroxybutyric acid, poly-3-hydroxyvaleric acid, polyglycolic acid, copolymers of glycolic acid and lactic acid, and polylactide, PVS, SAN, ABS, phenoxy, polycarbonate, nitrocellulose, polyvinylidene chloride, a styrene/alyl alcohol copolymer, polyethylene, polypropylene, natural rubber, a styrene/butadiene elastomer and block copolymer, polyvinylacetate, polybutadiene, ethylene/propylene rubber, starch, and thermoplastic segmented polyurethane, homopolymers on copolymers of polyesters, polyorthoesters, polylactides, polyglycolides, polycaprolactones, polyhydroxybutyrate, polyhydroxyvalerate, poro acids, pseudopolyamino acids, polyamides and polyanhydrides, homopolymers and copolymers of polylactic acid, polyglycolic acid, polycaprolactone (PCL), polyanhydrides, polyorthoesters, polyaminoacids, pseudopolyaminoacids, polyhydroxybutyrate, polyhydroxyvalerate, polyphosphazenes, and polyalkylecyanoacrylates.

Additional polymers that can be added include: citrates, diethyl citrate (DEC), triethyl citrate (TEC), acetyl triethyl citrate (ATEC), tributyl citrate (TBC), acetyl tributyl citrate (ATBC), phthalates such as dimethyl phthalate (DMP), diethyl phthalate (DEP), triethyl phthalate (TEP), dibutyl phthalate (DBP), dioctyl phthalate, glycol ethers such as ethylene glycol diethyl ether, propylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether (Transcutol™), propylene glycol monotertiary butyl ether, dipropylene glycol monomethyl ether, n-methylpyrrolidone, 2 pyrrolidone (2-Pyrrol™), propylene glycol, glycerol, glyceryl dioleate, ethyl oleate, benzylbenzoate, glycofuran sorbitol sucrose acetate isobutyrate, butyryltri-n-hexyl-citrate, acetyltri-n-hexyl citrate, sebacates such as dibutyl sebacate, tributyl sebacate, dipropylene glycol methyl ether acetate (DPM acetate), propylene carbonate, propylene glycol laurate, propylene glycol caprylate/caprate, caprylic/capric triglyceride, gamma butyrolactone, polyethylene glycols (PEG), glycerol and PEG esters of acids and fatty acids (Gelucires™, Labrafils™ and Labrasol™) such as PEG-6 glycerol mono oleate, PEG-6 glycerol linoleate, PEG-8 glycerol linoleate, PEG-4 glyceryl caprylate/caprate, PEG-8 glyceryl caprylate/caprate, polyglyceryl-3-oleate, polyglyceryl-6-dioleate, polyglyceryl-3-isostearate, PEG-32

glyceryl laurate (Gelucire 44/1™), PEG-32 glyceryl palmitostearate (Gelucire 50/13™), PEG-32 glyceryl stearate (Gelucire 53/10™), glyceryl behenate, cetyl palmitate, glyceryl di and tri stearate, glyceryl palmitostearate, and glyceryl triacetate (Triacetin™), vegetable oils obtained from seeds, flowers, fruits, leaves, stem or any part of a plant or tree including cotton seed oil, soy bean oil almond oil, sunflower oil, peanut oil, sesame oil. The use of two or more plasticizers in a combination or blend of varying ratios and hydrophilicity or hydrophobicity is also encompassed by the present invention. Plasticizers also include: phthalates, glycol ethers, n-methylpyrrolidone, 2 pyrrolidone, propylene glycol, glycerol, glyceryl dioleate, ethyl oleate, benzylbenzoate, glycofuran sorbitol, sucrose acetate isobutyrate, butyryltri-n-hexylcitrate, acetyltri-n-hexyl citrate, sebacates, dipropylene glycol methyl ether acetate (DPM acetate), propylene, carbonate, propylene glycol laurate, propylene glycol caprylate/caprate, caprylic/capric triglyceride, gamma butyrolactone, polyethylene glycols (PECs), vegetable oils obtained from seeds, flowers, fruits leaves, stem or any part of a plant or tree including cotton seed oil, soy bean oil, almond oil, sunflower oil peanut oil, sesame oil, glycerol and PEG esters of acids and fatty acids, polyglyceryl-3-oleate, polyglyceryl-6-dioleate, polyglyceryl-3-isostearate, PEG-32 glyceryl laurate, PEG-32 glyceryl palmitostearate, PEG-32 glyceryl stearate, glyceryl behenate, cetyl palmitate, glyceryl di and tri stearate, glyceryl palmitostearate, and glyceryl triacetate. These materials can also be added in combination with other polymers to improve flexibility.

The addition of these items will increase the efficiency of production of the product on an item basis. Baking powder and other materials, such as leavening agents, which release gases, (e.g., sodium or calcium bicarbonates or carbonates) 35 can be included in the compositions of the invention to elevate the number of open cells in the final structure by introducing a source of carbon dioxide gas which is released in the mold.

Glycerol, microcrystalline wax, fatty alcohols and other similar organic molecules can be added as a mold release agent, and to produce a smoother surface on the finished product Examples of agents that can be added, either as plasticizers or as mold releasing agents are ethylene glycol, propylene glycol, glycerin, 1,3-propanediol, 1,2-butandiol, 1,3-butandiol, 1,4-butanediol, 1,5-pentandiol, 1,5-bexandiol, 45 1,6-hexandiol, 1,2,6-hexantriol, 1,3,5-hexantriol, neopenetylglycol, sorbitol acetate, sorbitol diacetate, sorbitol monoethoxylate, sorbitol diethoxylate, sorbitol hexaethoxylate, sorbitol dipropoxylate, arrunosorbitol, trihydroxymethylaminomethane, glucose/PEG, the reaction product of ethylene oxidewith glucose, trimethylolpropane monoethoxylate, mannitol monoacetate, mannitol monoethoxylate, butyl glucoside, glucose monoethoxylate, a-methyl glucoside, the sodium salt of carboxymethylsorbitol, polyglycerol monoethoxylate, erythritol, pentaerythritol, arabitol, adonitol, xylitol, mannitol, iditol, galactitol, aitol, sorbitol, polyhydric alcohols generally, esters of glycerin, formamide, N-methylformamide, DMSO, mono- and diglycerides, alkylarriuides, polyols, trimethylolpropane, polyvinylalcohol with from 3 to 20 repeating units, polyglycerols with from 2 to 10 repeating units, and derivatives of the foregoing. Examples of derivatives include ethers, thiethers, inorganic and organic esters, acetals, oxidation products, amides, and amines. These agents can be added from 0-10%, preferably 3-4% (w/w). A consideration of the inventive mixture should be that the composition preferably contains at least 75%, more preferably at least 95% of natural or organic-derived materials by weight of the homogenous moldable composition,

Preparation of Molded Articles

The starch-wood flour mixture, with any included additives, is added to the pre-gelled starch and mixed (for example with a Kitchen Aid Commercial Mixer) until a homogeneous mixture is generated. The mixture can be as thick as peanut butter or as thin as a pancake batter. Varying amounts of additional water can be added to facilitate different types of molding, since the form of the pre-molded [green] product is dependent on the mold, heating rate and drying/melt time. If the product is to be molded by classic injection methods the material is thinner, if the material is molded on the equipment described below the mixture is thicker. The material can also be rolled into green sheets and molded, extruded and made into dry pellets for other processes. The means of production for the product could be created from any of several possible process approaches. One specific methodology is described below, but this description is intended only to describe one possible means of production, and shall not be construed in any way to represent a limitation to the outlined approach. While the compression molding process detailed herein is useful, other types of compression molding, injection molding, extrusion, casting, pneumatic shaping, vacuum molding, etc can be used. One embodiment involves a means of production incorporating moving upper and lower continuous track assemblies each with an upper and lower substantially elongated horizontal section, and with a curved portion of track joining the upper and lower horizontal section for each of the upper and lower tracks. Riding in each of the track assemblies is a linked belt made from any material or combination of materials that allows the belt or belt assembly to be in constant or intermittent motion about the tracks. The track assemblies are located vertically such that the upper portion of the lower track and the lower portion of the upper track are in close proximity such that the belts of each track move at a synchronized speed and in a common direction, in this embodiment, the male mold portion is mounted to the belt following the upper track, and the female portion of the mold is mounted to the belt following the lower track, with the tracks synchronized in a fashion that causes the mold halves to join and close as they merge between the upper and lower tracks. In this embodiment, the material to be processed is deposited into the female mold half prior to the mold halves closing, or is injected into the mold after it has been closed. The track and belt assemblies hold the mold halves together during drying by any of a number of, or combination of, methods including without limitation spring force, pneumatic force, or mechanical compression. Other forcing methods are possible. One possible arrangement of the curved end of the tracks aligns them such that the lower tracks' upper horizontal section are located to start before the upper tracks' lower horizontal section to allow the female mold half on the upper section of the lower track to assume a substantially horizontal orientation prior to the male mold half attached to upper track, thereby allowing the female mold half to receive deposited material before it engages the corresponding male mold half merging from the upper track and belt assembly. Other aspects that can be incorporated in this embodiment include, removable cavity inserts and/or multiple cavities in the molds: heating of the molds or product to speed drying by electric, microwave, hot gas, friction, ultrasonic, or any other means; on the fly cleaning of the molds, on the fly coating of product with any of a number of coating agents.

In another embodiment, once the moldable mixture has been prepared, it is positioned within a heated mold cavity. The heated mold cavity can comprise many different embodiments, including molds typically used in conventional injection molding processes and die-press molds brought together

after placing the inorganically filled mixture into the female mold. In one preferred embodiment, for example, the moldable mixture is placed inside a heated female mold. Thereafter, a heated male mold is complementarily mated with the heated female mold, thereby positioning the mixture between the molds. As the mixture is heated, the starch-based binder gelates, increasing the viscosity of the mixture. Simultaneously, the mixture increases in volume within the heated molds cavity as a result of the formation of gas bubbles from the evaporating solvent, which are initially trapped within the viscous matrix. By selectively controlling the thermodynamic parameters applied to the mixture (e.g., pressure, temperature, and time), as well as the viscosity and solvent content, the mixture can be formed into a form-stable article having a selectively designed cellular structural matrix.

In a non-limiting embodiment, a temperature between 195-225° C., preferably 200° C. is used for baking for a time period of 60-90 seconds, preferably 75 seconds. Temperatures can vary based on the article being manufactured, for example, 200° C. is preferred for the rapid production of thin-walled articles, such as cups. Thicker articles require a longer time to remove the solvent and are preferably heated at lower temperatures to reduce the propensity of burning the starch-based binder and fiber. Leaving the articles within the locked molds too long can also result in cracking or deformation of the articles.

The temperature of the mold can also effect the surface texture of the molds. Once the outside skin is formed, the solvent remaining within the interior section of the mixture escapes by passing through minute openings in the outside skin and then traveling between the skin and the mold surface to the vent holes. If one mold is hotter than the other, the laws of thermodynamics would predict, and it has been empirically found, that the steam will tend to travel to the cooler mold. As a result, the surface of the article against the hotter mold will have a smoother and more uniform surface than the surface against the cooler mold.

A variety of articles can be produced from the processes and compositions of the present invention. The terms "article" and "article of manufacture" as used herein are intended to include all goods that can be formed using the disclosed process.

Coating of Molded Article

Before, during, or after any of the molding processes, coatings can be applied to the surface of a substantially dried article for any desired purpose, such as to make the article more waterproof, grease and food product proof, more flexible, or to give it a glossier surface. Coatings can be used to alter the surface characteristics including sealing and protecting the article made therefrom. Coatings can provide protection against moisture, base, acid, grease, and organic solvents. They can provide a smoother, glossier, or scuff-resistant surface, they can help reinforce the article and coatings can also provide reflective, electrically conductive or insulative properties.

Water resistance can be achieved through the use of a water resistant layer applied on one or both sides of the product. There are many currently available coatings that can be used to coat this product. Some of these are: PROTECOAT® 6616B by New Coat, Inc.; ZEIN® a biodegradable material isolated from corn; poly lactic acid [PLA]—a polymer of lactic acid from fermentation feed stock; polyhydroxyl-kanoates [PHA] from microbial fermentation; bacterial cellulose; chitosan based polymers—from shell fish wastes; natural waxes and oil based coatings.

Appropriate organic coatings include edible oils, melamine, polyvinyl chloride, polyvinyl alcohol, polyvinyl

acetate, polyacrylates, polyamides, hydroxypropylmethylcellulose, polyethylene glycol, acrylics, polyurethane, polyethylene, polylactic acid, Biopol™ (a polyhydroxybutyrate-hydroxyvalerate copolymer), starches, soybean protein, polyethylene, and synthetic polymers including biodegradable polymers, waxes (such as beeswax or petroleum based wax), elastomers, edible oils, fatty alcohols, phospholipids and other high molecular weight biochemicals, and mixtures or derivatives thereof. Biopol® is manufactured by ICI in the United Kingdom. Elastomer, plastic, or paper coatings can aid in preserving the integrity of the article. Appropriate inorganic coatings include sodium silicate, calcium carbonate, aluminum oxide, silicon oxide, kaolin, clay, ceramic and mixtures thereof. The inorganic coatings can also be mixed with one or more of the organic coatings set forth above. Coatings based upon materials such as soybean oil or Methocel® (available from Dow Chemical), either alone or in combination with polyethylene glycol, can be applied to the surface in order to permanently soften the article or a hinge area within the article.

The coating can be applied either during the forming process or after the article is formed. The coating can be formed during the forming process by adding a coating material that has approximately the same melting temperature as the peak temperature of the mixture. As the mixture is heated, the coating material melts and moves with the vaporized solvent to the surface of the article where it coats the surface.

The coatings can be applied to the shaped articles using any coating means known in the art of manufacturing paper, paperboard plastic, polystyrene, sheet metal, or other packaging materials, including blade, puddle, air-knife, printing, Dahlgren, gravure, and powder coating. Coatings can also be applied by spraying the article with any of the coating materials listed below or by dipping the article into a vat containing an appropriate coating material. These materials can be applied either as a thin film or can be sprayed/dipped onto the product. The apparatus used for coating will depend on the shape of the article. For example, cups will usually be coated differently than flat plates. Bonding processes for application of thin films of water-resistant material are known in the art. Each of these coatings are biodegradable and should not significantly impact the compostability of the product. The second method of improving the water resistance of the product is to add one or more biodegradable materials to the material either before molding or as part of the molding process. In each of these cases the basic composition of the product will remain fairly constant.

A waterproof coating is desirable for articles intended to be in contact with water. As the articles having a starch-based binder have a high affinity for water, the preferred coatings are non-aqueous and have a low polarity. Appropriate coatings include paraffin (synthetic wax); shellac; xylene-formaldehyde resins condensed with 4,4'-isopropylidenediphenolepichlorohydrin epoxy resins; drying oils; reconstituted oils from triglycerides or fatty acids from the drying oils to form esters with various glycols (butylene glycol, ethylene glycol), sorbitol, and trimethylol ethane or propane; synthetic drying oils including polybutadiene resin; natural fossil resins including copal (tropical tree resins, fossil and modern), damar, elemi, gilsonite (a black, shiny asphaltite, soluble in turpentine), glycol ester of damar, copal, elemi, and sandarac (a brittle, faintly aromatic translucent resin derived from the sandarac pine of Africa), shellac, Utah coal resin; rosins and rosin derivatives including rosin (gum rosin, tall oil rosin, and wood rosin), rosin esters formed by reaction with specific glycols or alcohols, rosin esters formed by reaction formaldehydes, and rosin salts (calcium resinate and zinc resinate);

phenolic resins formed by reaction of phenols with formaldehyde; polyester resins; epoxy resins, catalysts, and adjuncts; coumarone-indene resin; petroleum hydrocarbon resin (cyclopentadiene type); terpene resins; urea-formaldehyde resins and their curing catalyst; triazine-formaldehyde resins and their curing catalyst; modifiers (for oils and alkyls, including polyesters); vinyl resinous substances (polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, etc.); cellulosic materials (carboxymethylcellulose, cellulose acetate, ethylhydroxyethylcellulose, etc.); styrene polymers; polyethylene and its copolymers; acrylics and their copolymers; methyl methacrylate; ethyl methacrylate; waxes (paraffin type I, paraffin type II, polyethylene, sperm oil, bees, and spermaceti); melamine; polyamides; polylactic acid; Biopol® (a polyhydroxybutyrate-hydroxyvalerate copolymer); soybean protein; other synthetic polymers including biodegradable polymers; and elastomers and mixtures thereof. Biopol® is manufactured by ICI in the United Kingdom. Appropriate inorganic coatings include sodium silicate, calcium carbonate, aluminum oxide, silicon oxide, kaolin, clay, ceramic and mixtures thereof. The inorganic coatings can also be mixed with one or more of the organic coatings set forth above.

If the articles are used as containers or for other products intended to come into contact with foodstuffs, the coating material will preferably include an FDA-approved coating. An example of a particularly useful coating is sodium silicate, which is acid resistant. Resistance to acidity is important, for example, where the article is a container exposed to foods or drinks having a high acid content, such as soft drinks or juices. It is generally unnecessary to protect the article from basic substances, but increased resistance to basic substances can be provided by an appropriate polymer or wax coating, such as those used to coat paper containers.

Polymeric coatings, such as polyethylene, are useful in forming generally thin layers having low density. Low density polyethylene is especially useful in creating containers which are liquid-tight and even pressure-tight to a certain extent. Polymeric coatings can also be utilized as an adhesive when heat sealed.

Aluminum oxide and silicon oxide are useful coatings, particularly as a barrier to oxygen and moisture. The coatings can be applied to the article by any means known in the art, including the use of a high energy electron beam evaporation process, chemical plasma deposition and sputtering. Another method of forming an aluminum oxide or silicon oxide coating involves treating article with an aqueous solution having an appropriate pH level to cause the formation of aluminum oxide or silicon oxide on the article due to the composition of the article.

Waxes and wax blends, particularly petroleum and synthetic waxes, provide a barrier to moisture, oxygen, and some organic liquids, such as grease or oils. They also allow an article such as a container to be heat sealed. Petroleum waxes are a particularly useful group of waxes in food and beverage packaging and include paraffin waxes and microcrystalline waxes.

In some cases, it can be preferable for the coating to be elastomeric or deformable. Some coatings can also be used to strengthen places where the articles are severely bent. In such cases, a pliable, possibly elastomeric, coating can be preferred.

Of course, it should be understood that the starch compositions of the present invention can themselves be used as coating materials in order to form a synergistic composite with, or otherwise improve the properties of, any number of other materials. Such disparate materials such as paper,

paperboard, molded starch-bound articles such as starch-based foams, metals, plastics, concrete, plaster, ceramics, and the like can be coated with starch composition.

It can be desirable to apply print or other indicia, such as trademarks, product information, container specifications, or logos, on the surface of the article. This can be accomplished using any conventional printing means or processes known in the art of printing paper or cardboard products, including planographic, relief, intaglio, porous, and impactless printing. Conventional printers include offset, Van Dam, laser, direct transfer contact, and therrographic printers. However, essentially any manual or mechanical means can be used.

In a further aspect of the present invention, it is recognized that to facilitate the coating of the molded article, as well as for other specific indications, the amount of paper pulp can be increased to 50%, or 30-50%, by weight of the final mixture, and the amount of wood flour or fiber can be decreased to 0%.

When using a vacuum to form a film around the molded article, increasing the levels of wood flour/fiber and/or paper pulp can facilitate the vacuuming process. For example, wood flour/fiber and/or paper pulp levels can be increased to 30, 40 or 50% by weight of the final mixture.

Types of Articles Produced

Materials capable of holding dry, damp and wet products have diverse uses. Containers suitable for holding dry materials can be used to hold dried fruit, or raw nuts such as almonds. Containers suitable for holding damp materials can be used to hold fresh mushrooms or tomatoes (for example in groups of 4 or 6) and should be able to perform this function for a period of at least about two to three weeks since normal packing to use time is about 14 days. Damp food packing can also be used with a hot fast food item such as french fries or hamburger, in which case the container needs to last for only a short time, for example about one hour after addition of the damp food. Damp food packing could also be used, in combination with an adsorbent pad, to package raw meat. In this case, the container needs to withstand exposure to the meat for a period of seven days or longer and desirably can stand at least one cycle of freeze and thaw. If possible this package should be able to withstand a microwave signal. When formulated for holding wet foods, the containers of the invention will suitably have the ability to hold a hot liquid, such as a bowl of soup, a cup of coffee or other food item for a period of time sufficient to allow consumption before cooling, for example within one hour of purchase. Such containers can also be used to hold a dry product that will be re-hydrated with hot water such as the soup-in-a-cup products.

Articles made from the present invention can be manufactured into a wide variety of finished articles that can presently be made plastics, paper, paperboard, polystyrene, metals, ceramics, and other materials. Merely by way of example, it is possible to manufacture the following exemplary articles: films, bags, containers, including disposable and nondisposable food or beverage containers, cereal boxes, sandwich containers, "clam shell" containers (including, but not limited to, hinged containers used with fast-food sandwiches such as hamburgers), drinking straws, baggies, golf tees, buttons, pens, pencils, rulers, business cards, toys, tools, Halloween masks, building products, frozen food boxes, milk cartons, fruit juice containers, yoghurt containers, beverage carriers (including, but not limited to, wraparound basket-style carriers, and "six pack" ring-style carriers), ice cream cartons, cups, french fry containers, fast food carryout boxes, packaging materials such as wrapping paper, spacing material, flexible packaging such as bags for snack foods, bags with an open end such as grocery bags, bags within cartons such as a dry cereal box, multiwell bags, sacks, wraparound casing,

support cards for products which are displayed with a cover (particularly plastic covers disposed over food products such as lunch meats, office products, cosmetics, hardware items, and toys), computer chip boards, support trays for supporting products (such as cookies and candybars), cans, tape, and wraps (including, but not limited to, freezer wraps, tire wraps, butcher wraps, meat wraps, and sausage wraps); a variety of cartons and boxes such as corrugated boxes, cigar boxes, confectionery boxes, and boxes for cosmetics, convoluted or spiral would containers for various products (such as frozen juice concentrate, oatmeal, potato chips, ice cream, salt, detergent, and motor oil), mailing tubes, sheet tubes for rolling materials (such as wrapping paper, cloth materials, paper towels and toilet paper), and sleeves; printed materials and office supplies such as books, magazines, brochures, envelopes, gummed tape, postcards, three-ring binders, book covers, folders, and pencils-, various eating utensils and storage containers such as dishes, lids, straws, cutlery, knives, forks, spoons, bottles, jars, cases, crates, trays, baking trays, bowls, microwavable dinner trays, "TV" dinner trays, egg cartons, meat packaging platters, disposable plates, vending plates, pie plates, and breakfast plates, emergency emesis receptacles (i.e., "barf bags"), substantially spherical objects, toys, medicine vials, ampules, animal cages, firework shells, model rocket engine shells, model rockets, coatings, laminates, and an endless variety of other objects.

The container should be capable of holding its contents, whether stationary or in movement or handling, while maintaining its structural integrity and that of the materials contained therein or thereon. This does not mean that the container is required to withstand strong or even minimal external forces. In fact, it can be desirable in some cases for a particular container to be extremely fragile or perishable. The container should, however, be capable of performing the function for which it was intended. The necessary properties can always be designed into the material and structure of the container beforehand.

The container should also be capable of containing its goods and maintaining its integrity for a sufficient period of time to satisfy its intended use. It will be appreciated that, under certain circumstances, the container can seal the contents from the external environments, and in other circumstances can merely hold or retain the contents.

The terms "container" or "containers" as used herein, are intended to include any receptacle or vessel utilized for, e.g., packaging, storing, shipping, serving, portioning, or dispensing various types of products or objects (including both solids and liquids), whether such use is intended to be for a short-term or a long-term duration of time.

Containment products used in conjunction with the containers are also intended to be included within the term "containers." Such products include, for example, lids, straws, interior packaging, such as partitions, liners, anchor pads, corner braces, corner protectors, clearance pads, hinged sheets, trays, funnels, cushioning materials, and other object used in packaging, storing, shipping, portioning, serving, or dispensing an object within a container.

The containers within the purview of the present invention can or can not be classified as being disposable. In some cases, where a stronger, more durable construction is required, the container might be capable of repeated use. On the other hand, the container might be manufactured in such a way so as to be economical for it to be used only once and then discarded. The present containers have a composition such that they can be readily discarded or thrown away in conventional waste landfill areas as an environmentally neutral material.

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The articles within the scope of the present invention can have greatly varying thicknesses depending on the particular application for which the article is intended. They can be as thin as about 1 mm for uses such as in a cup. In contrast, they can be as thick as needed where strength, durability, and/or bulk are important considerations. For example, the article can be up to about 10 cm thick or more to act as a specialized packing container or cooler. The preferred thickness for most articles is in a range from about 1.5 mm to about 1 cm, with about 2 mm to about 6 mm preferred.

Using a microstructural engineering approach, the present invention can produce a variety of articles, including plates, cups, cartons, and other types of containers and articles having mechanical properties substantially similar or even superior to their counterparts made from conventional materials, such as paper, polystyrene foam, plastic, metal and glass. The inventive articles can also be made at a fraction of the cost of their conventional counterparts. The minimal cost is a result of the relatively inexpensive aggregate which typically comprises a large percentage of the mixture and the minimum processing energy required.

The method of the present invention provides basic methodologies which can be utilized with little modification and a basic material from which product items can be produced by tailoring of the additives and additional processing steps employed. The composition preferably contains at least 75%, at least 85% or at least 95% or more of natural or organic-derived materials by weight of the homogenous moldable composition.

EXAMPLES

The following examples are presented in order to more specifically teach compositions and process conditions for forming the thermoplastic starch compositions according to the present invention, as well as articles therefrom. The examples include various mix designs, as well as various processes for manufacturing thermoplastic starch compositions, including sheets, films, pellets, containers, and other articles of manufacture.

Examples of Articles Formed from Pregelled Starch Suspensions

Example Mixture A

31.5 gm of 5% potato starch gel
18 gm of dry corn starch
6 gm of dry wood flour [60 mesh soft wood]

Test characteristics—the thick stiff mixture was flat molded in a 4"x4" flat mold at a low pressure (between 2 and 3 psi) to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 9 (on a scale of 10, with 1=breaks with little resistance and 10=breaks with significant resistance. A styrofoam tray for meat=8 on this scale and a styrofoam burger clamshell box=5). This mixture was to test a thick mixture and was determined that for a complete molded test item the mixture had to be pre shaped into a flat rolled sheet about 2" square.

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Example Mixture B

5 gm 5% potato starch gel
19.5 gm of 15% corn starch gel
0.125 gm of 80 mesh softwood flour
0.125 gm baking powder—[added to elevate the number of open cells in the final structure by introducing a source of carbon dioxide released by heat and water.]

10 The flat test [2-3 psi and 250° C. mold] item was dry and had a large number of air cells in the cross linked test pad. The strength test was 2 indicating that items molded from this mixture would be used for low breakage packaging, such as shock spacers.

Example Mixture C

15 16.3% 3% potato starch gel
5.9% dry corn starch
14% 80 mesh softwood flour
1% dry baking powder
1% glycerol-[added to produce a product that would release from the mold and to produce a smoother surface on the finished product.]

20 25 The flat test [2-3 psi and 250 deg C. mold] item has a stronger strength index of 4, greater than mixture C with the same open cell structure. This mixture will allow for a stronger product, while still retaining the open cell structure for items such as spacers in packing boxes, e.g., dimpled trays to separate layers of apples in a packing box. This item would, as mixture C, provide good shock protection [crush strength].

Example Mixture D

35 25% of a 3% potato starch gel
57% of a 15% corn starch gel
17% 80 mesh softwood flour
1% baking powder
40 To this mixture was added various amounts of natural material fillers in an effort to reduce the cost per item. In this test group powdered calcium carbonate or bentonite clay was added to the potato starch gel before mixing with the corn starch/wood flour mix. At low levels [up to 5% there is no effect on the strength or amount of entrapped air pockets, suggesting that low levels of these two fillers are appropriate]. At higher levels the basic formulation had to be changed to accommodate the chemical and physical changes that the fillers produced.

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Example Mixture E

10 gms of a gel mix of 5% potato starch & 20% bentonite clay
55 6 gms of dry corn starch
7 gms of 80 mesh softwood flour
1 gm glycerol
6 grams of water

60 Test characteristics—the thick stiff mixture was flat molded in a 4"x4" flat mold at a low pressure [between 2 and 3 psi] to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 7 with a high level of entrained air pockets. This type of product is hard and has a high degree of strength for use as a primary package. The inclusion of the clay produces a product with higher strength, in addition to reducing the unit cost.

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Example F

16.3 gms of a 5% potato starch gel
5.9 gms of dry corn starch
3.8 gms of 80 mesh softwood flour
1 gm of glycerol

Test characteristics—the thick mixture was flat molded in a 4"×4" flat mold at a low pressure [between 2 and 3 psi] to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 8 with a very high level of entrained air pockets.

Example G

15.1 gms of a 5% potato starch gel
9.1 gms of dry corn starch
4.3 gms of 80 mesh softwood flour
1 gm of glycerol

Test characteristics—the somewhat thick mixture was flat molded in a 4"×4" flat mold at a low pressure (between 2 and 3 psi) to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 9 with a high level of entrained air pockets. This mixture is the strongest of the basic formula tests using a mixture that was thick. The next test was to use the same basic formula but with additional water to allow the mixture to be injected as a thinner mix.

Example H

15.1 gms of a 5% potato starch gel
9.1 gms of dry corn starch
4.3 gms of 80 mesh softwood flour
1 gm glycerol
4 gms of water

Test characteristics—the thinner mixture was flat molded in a 4"×4" flat mold at a low pressure (between 2 and 3 psi) to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 9 with a high level of entrained air pockets. The addition of more water allowed the product to fill the mold more quickly thereby producing a product with strength similar to styrofoam (2 mm thickness standard production). Three millimeter thick trays were made by molding for various times between 3 and 5 minutes at temperatures between 300 and 375° F. using the following formulations. Satisfactory products were obtained.

Example I

10.8 gm wood flour [6020 grade]
23.2 gm corn starch
41.8 gm 5% pre-gelled potato starch in water
12 gm 20% bentonite clay slurry in water

Example J

10.8 gm of wood flour [6020 grade]
23.2 gm corn starch
41.8 gm of 7.5% pre-gelled potato starch in water
2 mm thick tray were molded at various times between 45 seconds and 2 minutes at temperatures between 350 and 450° F. using the following formulations. Satisfactory products were obtained.

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Example K

10.8 gm wood flour [4025 grade]
23.2 gm corn starch
3.3 gm potato starch
41.8 gm 10% pre-gelled potato starch in water

Example L

10.8 gm wood flour [4025 grade]
23.2 gm corn starch
3.1 gm potato starch
3.3 gm bentonite clay
41.8 gm of 10% pre-gelled potato starch in water

These trays (in the above examples) have also been coated with a thin film of food grade polymer and/or food grade paraffin wax A specific aspect of this product is the observation that the addition of components is very important. When the dry ingredients, such as corn starch and wood flour are added to the potato starch gel, without premixing into a homogenous mixture, the product suffers a dramatic reduction in strength and will not spread evenly in the mold, producing open voids and unfilled corners. The observation of specific addition was seen in a dozen or more trial mixtures that used a different order of mixing of components. In addition the surface of the molded product can be rough vs the smooth surface of sequentially mixed products. More recently the product was tested in a three dimensional mold, using classic compression molding techniques, i.e., heated mold with a constant pressure applied during the process. In these test the requirement for a specific order of mixing was also observed and when this order was not observed the finished product suffered significant problems, including incomplete product spread during the molding process, reduction in smoothness of the molded product and a reduction in strength, as measured by classic penetrometer methods.

Example M

1. Form pregelled paper potato starch suspension:

57.5 g potato starch: 8.5%
43.2 g recycled paper pulp: 6.3%
575 g water: 85%

Add components, heat to 60-70° C. (ideal) 65° C. with mixing on high speed with a wire whisk to form gel. Once gelled, it is a stable gel that can be cooled, refrigerated, etc, but not frozen.

2. Premix the following materials:

92.3 g wood flour (aspect ratio 1:4)
132.7 g potato starch
159 g corn starch

to from homogeneous mixture

3. Add homogenous mixture of wood and starches with the pregelled paper potato starch, mix with a dough hook mixer on low speed

This mixture is stable and can be cooled, refrigerated, etc, but not frozen.

4. Place mixture into mold (50-55 g) and bake at 195-225.degree. C. (ideal 215.degree. C.) for 60-90 seconds (ideal 75)

5. Coating: Especially like PROTECOAT® 6616B by New Coat, Inc, commercial, biodegradable, acrylic based, FDA approved for food.

Examples of Articles Formed from Pregelled Paper
Starch Suspensions

Example N

10 1. Form pregelled paper potato starch suspension:

57.5 g dry potato starch: 8.5%

42.31 g recycled paper pulp: 6.2%

580 g water: 85.3%

Add components in a mixer, heat to 60-70° C. (ideal temp 65° C.) with mixing on low RPM with a wire whisk to form gel. When the paper pulp is dispersed, and as the temperature begins to rise (above 30° C.), the RPM of the mixer is increased until the maximum RPM is reached.

The heating continues until the temp reaches 65.degree. C. At this time, the mixture is a homogeneous gel suspension. The heat is turned off and beater heads changed to classic dough hook and speed is lowered to 10% of maximum KITCHENAID®. Alternatively, for smaller batches, see for example, step #2 below, the mixing is done by hand. Once gelled, it is a stable gel that can be cooled, refrigerated, etc, but not frozen.

2. Premix the following materials:

4.8 g wood flour (aspect ratio 1:4 or less)

6.9 g potato starch

8.3 g corn starch

to form homogeneous mixture

3. Add homogenous mixture of wood and starches to 29.9 g of the pregelled paper potato starch, mix with a dough hook mixer on low speed. This mixture is stable and can be cooled or refrigerated, but not frozen.

4. Place mixture into mold (50-55 g) and bake at 195-225° C. (ideal 215° C.) for 60-90 seconds (ideal 75° C.)

5. Coating: Especially like PROTECOAT® 6616B by New Coat, Inc, commercial, biodegradable, acrylic based, FDA approved for food.

The following examples and formulas work with both the compression molding process and injection molding processes to produce strong products as measured by pentrometers. In addition, these examples and formulas produce products with thicknesses between 1.5 and 3.0 mm, for example, thicknesses of 1.5 mm, 1.75 mm, 2.0 mm or 3.0 mm.

| List of | Weight in grams mixed by Formula ID # | | | |
|-----------------------|---------------------------------------|------|------|------|
| Ingredients | O | P | Q | R |
| 4025 wood flour | 4.8 | 4.8 | 4.5 | 5.0 |
| Potato starch | 6.9 | 5.9 | 6.5 | 7.2 |
| Corn starch | 8.3 | 9.3 | 7.8 | 8.6 |
| paper pulp | 2.2 | 2.2 | 2.1 | 2.3 |
| 10% Potato starch gel | 29.9 | 29.9 | 31 | 28.9 |
| Total wt. Molded | 52.1 | 52.1 | 51.9 | 52.0 |

Each modification listed in the above table is based on what works best for a specific flexibility and/or method of molding. For example, as you change the concentration of potato starch, the flexibility will change.

| List of | Weight in grams mixed by Formula ID # | |
|-----------------------|---------------------------------------|------|
| Ingredients | S | T |
| 4025 wood flour | 6.7 | 4.8 |
| Potato starch | 9.6 | 6.9 |
| Corn starch | 11.6 | 8.3 |
| paper pulp | 3.1 | 2.2 |
| 10% Potato starch gel | 41.8 | 29.9 |

| | | |
|---------------------|---------------------------------|-------|
| 10 Total wt. Molded | 72.8 | 52.0 |
| Thickness of Mold | 3 mm. (deeper sides than #T) | 2 mm. |

| List of | Weight in grams mixed by Formula ID # | | |
|-----------------------|---------------------------------------|------|------|
| Ingredients | U-1 | U-2 | U-3 |
| 4025 wood flour | 3.3 | 5.6 | 3.5 |
| Potato starch | 6.2 | 10.5 | 6.6 |
| Corn starch | 6.1 | 10.3 | 6.5 |
| paper pulp | 1.8 | 3.0 | 1.9 |
| 10% Potato starch gel | 27.6 | 46.6 | 29.4 |

| | | | |
|---------------------|-------|-------|-------|
| 20 Total wt. Molded | 45 | 76.0 | 48 |
| Thickness of Mold | 2 mm. | 3 mm. | 2 mm. |

| List of | Weight in grams mixed by Formula ID # | | |
|-----------------------|---------------------------------------|------|------|
| Ingredients | V-1 | V-2 | V-3 |
| 4025 wood flour | 4.8 | 8.2 | 5.4 |
| Potato starch | 6.9 | 11.8 | 7.8 |
| Corn starch | | | |
| paper pulp | 1.8 | 3.1 | 2.0 |
| 10% Potato starch gel | 29.9 | 51.0 | 33.8 |

| | | | |
|---------------------|-------|-------|-------|
| 25 Total wt. Molded | 43.4 | 74.0 | 49 |
| Thickness of Mold | 2 mm. | 3 mm. | 2 mm. |

| List of | Weight in grams mixed by Formula ID # | |
|-----------------------|---------------------------------------|------|
| Ingredients | W-1 | W-2 |
| 4025 wood flour | 3.8 | 6.3 |
| Potato starch | 6.9 | 11.5 |
| Corn starch | 2 | 3.3 |
| paper pulp | 1.8 | 3.0 |
| 10% Potato starch gel | 29.8 | 49.8 |

| | | |
|---------------------|-------|-------|
| 45 Total wt. Molded | 44.4 | 74.0 |
| Thickness of Mold | 2 mm. | 3 mm. |

The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications will be obvious to those skilled in the art from the foregoing detailed description of the invention and may be made while remaining within the spirit and scope of the invention.

We claim:

1. A process for forming a biodegradable material by:
 - forming a pre-gelled starch suspension that is maintained between approximately 0 and 60° C.;
 - adding to the pre-gelled starch suspension a dry or damp, homogeneous mixture containing at least wood fibers having an aspect ratio between approximately 1:2 and 1:8 width:length to form a homogenous moldable composition; and
 - molding the homogenous moldable composition with heat to form a biodegradable material.
2. The process of claim 1, wherein the homogenous mixture further comprises a second pre-gelled starch suspension, and/or a native starch.

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3. The process of claim 1 wherein the pre-gelled starch suspension is a pre-gelled paper starch suspension.

4. The process of claim 3, wherein the pre-gelled starch suspension comprises approximately 2-15% potato starch by weight of the pre-gel; approximately 5-10% paper pulp by weight of the pre-gel; and approximately 75-95% water by weight of the pre-gel such that the pre-gelled suspension is maintained at low temperatures; and wherein the homogenous mixture comprises wood fibers or flour having an aspect ratio between approximately 1:2 and 1:8, native corn starch and native potato starch.

5. The process of claim 1 further comprising adding a material selected from the following list to the wood fibers to form a homogeneous mixture: (i) waxes, fatty alcohols, phospholipids or other high molecular weight biochemicals; (ii) approximately 0.5-20% water by weight of the homogenous moldable composition; (iii) baking powder; and/or (iv) natural earth fillers, clays, bentonite, amorphous raw products, gypsum or calcium sulfate, minerals or man made inert fillers.

6. The process of claim 1, wherein the pregelled starch suspension is produced from approximately 2.5-15% starch by weight of the pre-gel, and from approximately 85-97.5% of water by weight of the homogenous moldable composition.

7. The process of claim 1, wherein the pre-gelled starch suspension is produced from approximately 2.5-5.5% starch and from approximately 94.5-97.5% water.

8. The process of claim 1, wherein the pre-gelled starch suspension is produced from approximately 2.5-10% potato starch, and 90 to 97.5% water by weight of the pre-gel.

9. The process of claim 1, wherein the pre-gelled starch suspension is produced from approximately 15% corn starch by weight of the pre-gel.

10. The process of claim 1, wherein the pregelled paper starch solution is produced from approximately 5-10% paper pulp by weight of the pre-gel, approximately 5-15%, natural starch, and approximately 75-90% water by weight of the pre-gel.

11. The process of claim 1, wherein the starch is corn starch or potato starch.

12. The process of claim 1, wherein the starch is a mixture of potato starch and corn starch.

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13. The process of claim 1, wherein corn starch comprises approximately 4-18%, by weight of the homogenous moldable composition.

14. The process of claim 1, wherein wood fibers or flour comprise approximately 11-24% of the homogenous moldable composition that contains the pregelled starch solution.

15. The process of claim 1, wherein the wood fibers or flour comprise approximately 7-11% by weight of the homogenous moldable composition that contains the pregelled paper starch solution.

16. A biodegradable, compostable material made according to a process of claim 1.

17. The process of claim 1 further comprising using pressure in combination or alternation with heat to mold the biodegradable material.

18. The process of claim 17, wherein the heat used to mold the biodegradable materials is between approximately 150-250° C. and the pressure is between 2-3 psi.

19. The material of claim 16 coated with a suitable liquid-resistant coating.

20. The material of claim 16, wherein the material is in the form of a cup, a tray, a bowl, a plate, or a utensil.

21. The process of claim 4, wherein the potato starch is about 2.5% by weight of the pre-gel.

22. The process of claim 4, wherein the potato starch is about 5% by weight of the pre-gel.

23. The process of claim 4, wherein the potato starch is about 10% by weight of the pre-gel.

24. The process of claim 4, wherein the potato starch is about 15% by weight of the pre-gel.

25. The process of claim 4, wherein the paper pulp is about 5.9% by weight of the pre-gel.

26. The process of claim 4, wherein the paper pulp is about 7.3% by weight of the pre-gel.

27. The process of claim 4, wherein the paper pulp is about 8% by weight of the pre-gel.

28. The process of claim 4, wherein wood fibers or flour have an aspect ratio between about 1:2 and 1:4.

29. The process of claim 5, wherein the high molecular weight biochemical is glycerol.

30. The process of claim 5, wherein the mineral is limestone.

* * * * *



US006303000B1

(12) **United States Patent**
Floyd et al.(10) **Patent No.:** US 6,303,000 B1
(45) **Date of Patent:** Oct. 16, 2001(54) **PAPER MAKING PROCESS UTILIZING A REACTIVE CATIONIC STARCH COMPOSITION**(75) Inventors: **William C. Floyd**, Chester; **Nolan Thompson**; **Louis R. Dragner**, both of Rock Hill, all of SC (US)(73) Assignee: **Omnova Solutions Inc.**, Fairlawn, OH (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/143,556**(22) Filed: **Aug. 31, 1998**(51) Int. Cl.⁷ **D21H 21/18**(52) U.S. Cl. **162/175**; 106/206.1

(58) Field of Search 162/175, 158; 106/162.51, 206.1

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(57) **ABSTRACT**

A method for manufacturing paper with improved strength by introducing into the paper pulp in the wet end of a paper making process an aqueous starch dispersion of a gelatinized cationic starch and a blocked glyoxal resin.

12 Claims, No Drawings

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**PAPER MAKING PROCESS UTILIZING A
REACTIVE CATIONIC STARCH
COMPOSITION**

BACKGROUND OF THE INVENTION

The present invention relates to a process for manufacturing paper and more particularly to adding to a dilute paper pulp slurry prior to sheet formation a modified starch dispersion of a cationic starch which has been gelatinized and reacted with a blocked glyoxal resin.

Industrial starch may be utilized in a wide variety of applications including as coatings for paper or paper board and as a bonding wet end additive in papermaking. Starch compositions may desirably be prepared in the form of aqueous dispersions capable of being added to the pulp slurry.

For many commercial applications starch is gelatinized by the end user prior to being used. Gelatinization occurs after starch granules are dispersed as a slurry in water with the resultant aqueous slurry being heated to over 50° C. and usually over about 65° C. Under such conditions starch grains tend to absorb water, swell, and eventually rupture to allow starch fragments and molecules to disperse in water. This rupturing and dispersion is generally referred to as "gelatinization" and is an irreversible reaction resulting in a relatively thick starch dispersion.

The cross-linking of starches with multi functional reagents which are reactive with starch hydroxyl groups is well known. Glyoxals and polyaldehyde compounds and resins have been previously utilized as cross-inkers. The simple mixing of glyoxal with a starch dispersion will provide a gel. U.S. Pat. No. 4,455,416 describes a paper coating containing starch binder and a cyclic urea/glyoxal/polyol condensate as an insolubilizer for the binder. As an insolubilizer the glyoxal condensate is inactive until the coating is applied and cured upon drying whereupon the glyoxal crosslinks the starch to impart water resistance. U.S. Pat. No. 4,021,260 describes ethoxylated fatty alcohols as starch viscosity control agents. U.S. Pat. No. 3,324,057 discloses the use of dialdehyde starch in the preparation of paper coatings. U.S. Pat. No. 3,740,391 describes the production of aqueous dispersions of a starch first reacted with an acrylamide and, subsequently, with glyoxal. U.S. Pat. No. 4,013,629 discloses a glyoxal binder system. U.S. Pat. No. 4,425,452 discloses coating paper material via an enzymatically converted starch. British Patent No. 2017124 discloses polysaccharides cross-linked with glyoxal.

A stable fluid aqueous modified starch dispersion is prepared in U.S. Pat. No. 5,032,683, the disclosure of this patent being incorporated herein by reference. This starch dispersion is prepared by gelatinizing an aqueous slurry of a starch and reacting with a glyoxal compound. The present invention has found that a cationic starch dispersion modified with blocked glyoxal resin when added in the wet end of a papermaking process provides significant improvements in strength to the resultant paper.

BRIEF DESCRIPTION OF THE INVENTION

It is an object of this invention to provide a process of manufacturing paper having improved strength.

This and other objects are achieved by introducing into the paper pulp in the wet end of a papermaking process an aqueous starch dispersion of a gelatinized cationic starch and a blocked glyoxal resin.

**DETAILED DESCRIPTION OF THE
INVENTION**

An aqueous cationic starch dispersion modified with a blocked glyoxal resin is prepared which is readily flowable

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and wherein gelation and viscosity increases over time are inhibited. The starch dispersion is prepared by gelatinizing an aqueous suspension or slurry of starch granules and adding, preferably reacting the starch with a blocked glyoxal resin at temperatures of at least 70° C., preferably 85 to 95° C. Preferably gelatinization and the reaction with the blocked glyoxal resin are carried out simultaneously, although the starch can be pre-gelatinized and then reacted with the glyoxal compound with heating.

It is theorized that by reacting gelatinized starch at the higher temperatures with the blocked glyoxal resin the amylose is derivatized with the glyoxal so that retrogradation of the amylose and the formation of amylose fatty acid complexes upon cooling is inhibited, resulting in aqueous dispersions having a flowable viscosity and in which gelation and viscosity increases over time are inhibited. Without intending to be bound by theory it is believed that the glyoxals react with amylose to make highly labile hemiacetals which disrupt the crystallinity of amylose, thus significantly inhibiting retrogradation. Further, it is believed that glyoxal added after gelatinization and cool-down does not form hemi-acetals with the same efficiency as those added during heating because after gelatinization and cool-down crystallization occurs which limits the sites of reaction with glyoxal. Further, the use of a blocked glyoxal resins provides improved starch rheology reducing the tendency for gelling and is less prone to retrogradation and precipitation.

The starch dispersion prepared according to this invention will generally have a viscosity of less than 1000 cps, preferably less than 350 cps. Except where otherwise indicated, viscosity readings set forth herein are taken in aqueous solution at 35% solids content (by weight), are Brookfield viscosities (RV, #3 spindle at 100 rpm), and viscosity readings are taken at room temperature.

Suitable blocked glyoxal resins which may be used in accordance with the invention are described in U.S. Pat. No. 4,695,606 and include but are not limited to cyclic urea/glyoxal/polyol condensates, polyol/glyoxal condensates, urea or cyclic urea/glyoxal condensates and glycol/glyoxal condensates. The amount of glyoxal compound may be adjusted within broad limits, but is generally from about 3% to about 30%, preferably 9 to 20%, of the total dry weight of starch (and/or derivatives thereof) present.

In accordance with the invention, an aqueous slurry of cationic starch is prepared. Preferably the starch is an amylose containing starch. The starch may be obtained from any conventional source, including potato, corn, waxy corn, red milo, white milo, wheat and tapioca and may be pearl or lightly thinned and may have been oxidized, hydroxyalkylated, acid modified, enzyme converted or various combinations thereof. Also, suitable to this invention are thin-boiling starches that have been additionally chemically modified to reduce the setback or retrogradation tendencies of the starch. The prior art describes methods for making a wide variety of starch derivatives that display reduced setback. Higher molecular weight starches are preferred because of greater strength than low molecular weight starches. In certain preferred embodiments a blend of hydroxyethylated starch and an acid and/or enzyme-converted starch may be utilized with cationic starch. For example, cationic corn or potato starch may be utilized together with an acid modified or an oxidized hydroxyethylated starch such as a hydroxyethylated potato starch.

It is important for the starch to contain cationic functionality to enhance retention on the anionic paper fibers. Such

functionality is commonly introduced via tertiary or quaternary amino groups appended to the starch.

Preferably, the blocked glyoxal resin is added to the aqueous starch slurry and the slurry is heated to about 90° C. for at least about 30 minutes to gelatinize the starch. The starch slurry and blocked glyoxal resin may be heated briefly to higher temperatures such as those obtained with a steam injection cooker. The heat beneficially drives the reaction of the blocked glyoxal resin and starch simultaneously with starch gelatinization. The resulting gelatinized starch composition is then preferably treated with a biocide if it will be stored, preferably after it has been allowed to cool to about 40° C. Biocide is preferably added at a concentration by weight, of about 10 ppm to about 500 ppm. Suitable biocides include Kathon® LX from Rohm & Haas which is a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one and Proxel® GXL from ICI which is 1,2 benzothiazolin-3-one. Gelatinization in the presence of the glyoxal resin preferably takes place in an aqueous slurry at a solids content between about 15% and about 50% by weight, preferably between about 25% and about 35%. In alternative methods, dry starch and dry glyoxal resin may be intermixed prior to introduction into an aqueous slurry for the gelatinization and/or reaction steps.

Typically, an aqueous slurry of the granular cationic starch is prepared, and the blocked glyoxal resin is added to the agitated slurry. The starch is then gelatinized, or cooked out, either in a batch process or by a jet cooker. The cationic starch glyoxal resin condensate dispersion is then added to the dilute pulp slurry prior to sheet formation and thoroughly fixed. Generally the starch dispersion is added to the pulp slurry at a level of 2 to 50 lbs. dry starch, preferably 5 to 20 lbs. dry starch, per ton of dry pulp. The resin is attached to the cationic starch, which is attracted to the anionic pulp fibers thereby introducing the resin to the fiber. The sheet of paper is then formed, containing both the cationic starch and the resin. Upon drying the sheet, the resin reacts further with the cationic starch and/or cellulosic fiber, resulting in improved sheet properties such as wet tensile.

Polyacrylamide and acrylamide copolymers can also be added to improve tensile strength of the starch films drawn down from these compositions. These polymers also react with glyoxal to form a polymer-reinforced starch film upon drying. Generally the acrylamide polymer or acrylamide copolymer is added at a level of up to 50% by weight of the blocked glyoxal resin. The acrylamide is preferably a copolymer of acrylamide and is water soluble.

The invention is further illustrated by the following examples which are set forth only as illustrations of the invention and not as limitations thereof.

EXAMPLE I

An acid-modified corn starch (Keofilm® 90, available from Hubinger Corporation) was selected for film studies. As a control, a 20% solution of Keofilm® 90 was prepared, heated to 90° C. for 30 minutes, then cooled. A film, Sample A, was drawn down on Mylar, then dried and cured for 2 minutes at 250° F.

A second batch of Keofilm® 90, identical to the first, was prepared. Upon cooling, 10% by dry weight of a blocked glyoxal resin (Sequex®R) was added and thoroughly mixed. A film, Sample B was drawn down on Mylar, then dried and cured for 2 minutes at 250° F.

A third batch of Keofilm® 90 was prepared, identical to the first, except that the 10% of blocked glyoxal resin (Sequex®R) was added before the starch was heated. After cooking at 90° C. for 30 minutes, the starch dispersion was cooled, and a film drawn down on Mylar. This film, Sample C, was then dried and cured for 2 minutes at 250° F. All 3 films were tested for tensile and elongation on an Instron Model 1110 Tensile Tester (films where 2 inches^{7/16} inches and 12–13 mil. thick) with the results as shown in Table 1.

TABLE 1

| Sample | Dry Tensile (Kg) | Dry Elongation (%) | Wet Tensile (Kg) | Wet Elongation (%) |
|--------|------------------|--------------------|------------------|--------------------|
| A | 7.19 | 5.6 | 0.11 | 3.72 |
| B | 8.82 | 5.6 | 1.81 | 8.26 |
| C | 9.42 | 6.1 | 1.98 | 8.94 |

Table 1 shows the benefits of this invention in that Sample C showed greater wet and dry tensile strength and elongation. The improved strength performance obtained by this invention for the starch films has also been observed in waxy starches which do not contain amylose.

EXAMPLE II

The presence of the blocked glyoxal resin in the paper sheet may be determined by the improved sheet properties or calorimetrically. A dilute solution of N-methyl benzo thiazolinone hydrazone hydrochloride (MBTH) when spotted on the paper and warmed will evolve a yellow coloration if glyoxal or glyoxal based resins are present. If the glyoxal compound and cationic starch are merely mixed together, or added separately to the pulp slurry, inferior results are obtained.

The following examples are provided to illustrate this invention. Hand sheets were made using a 50/50 hardwood/softwood fiber blend. The freeness was held at approximately 370–350 at 1.5% consistency and adjusted to pH 4.5 with sulfuric acid. The hand sheet were made using 250 g of cellulose paper pulp to produce a 3.5 g hand sheet. Test samples were selected based on sample weight.

An aqueous slurry of Sta-lok® 400 (a cationic potato starch from A. E. Staley Mfg. Co.) was prepared at 4% solids. To this was added 9% (dry on dry) Sequex®R (a cyclic urea/glyoxal condensate, 45% solids, from Sequa Chemicals, Inc.). This was agitated and heated to 90° C. for 30 minutes to afford a clear amber solution which thickened upon cooling. Sufficient quantities of this were added to pulp slurries so as to achieve the equivalent of 40, 60 and 80 pounds of cationic starch per ton of pulp. Sheets of each dosage were prepared in triplicate. For controls, handsheets were prepared with no additives, and with cationic starch only at the equivalent of 40, 60 and 80 pounds of cationic starch per ton of pulp.

The results show that this invention provides an improvement in dry tensile, a substantial improvement in wet tensile and superior Mullen burst strength compared to the controls. Testing was done on 1×4 inch strips of paper on an Instrum Model 1100 Tensile Tester.

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| Additive Dosage | Cationic Starch | | | | Cationic Starch/Resin | | |
|-------------------------|-----------------|------|------|------|-----------------------|------|------|
| | None | 40 | 60 | 80 | 40 | 60 | 80 |
| Sheet wt, g | 3.2 | 3.6 | 3.6 | 3.6 | 3.3 | 3.7 | 3.7 |
| Tensile, Dry, kg | 15.4 | 17.8 | 17.5 | 17.4 | 13.9 | 18.5 | 22.4 |
| % stretch | 4.9 | 4.7 | 5.0 | 5.4 | 4.9 | 5.3 | 5.6 |
| Wet, kg | 0.36 | 0.54 | 0.76 | 0.90 | 0.8 | 1.1 | 1.4 |
| % stretch | 2.3 | 2.7 | 3.4 | 3.7 | 3.6 | 3.7 | 4.4 |
| Tabor Stiffness | 3.7 | 4.4 | 8.2 | 2.8 | 2.8 | 3.7 | 4.1 |
| Mullen Burst | 60.4 | 82.6 | 72.4 | 66.6 | 65.4 | 82.8 | 80.2 |
| Hercules Size Test, sec | 1.0 | 0.8 | 0.7 | 0.8 | 0.2 | 0.4 | 0.3 |

EXAMPLE III

A series similar to that described in Example II was prepared consisting of a base sheet with no additives, (A) a set with cationic starch applied at a rate equivalent to 40, 60 and 80 pounds per ton, (B) a set with 9% blocked glyoxal resin (Sequez®R, dry resin on starch) reacted with the cationic starch and applied at a rate of 40, 60 and 80 pounds of cationic starch per ton of pulp, (C) a set similar to B except that the amount of blocked glyoxal reacted with the cationic starch was 12% (dry on dry), and (D) a set similar to B except that the amount of blocked glyoxal resin reacted with the cationic starch was 20% (dry on dry). The appropriate amount of starch was added to the pulp slurry and mixed, then handsheets were formed and dried on a rotary drier. Three handsheets for each formulation were tested and average results are reported on attached sheets.

These results show that higher levels of resin may not be beneficial and that the system may be overdosed. The 9% level of resin gives the best overall performance, particularly at the 60 and 80 pound per ton levels. It should be noted that as the level of cationic starch increased in A, wet tensile increases while Mullen Burst strength decreases, and dry tensile is level. With the B set of samples, as the level cationic starch increases, dry tensile increases, wet tensile increases and Mullen Burst Strength rises and stays high.

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EXAMPLE IV

This example sought to examine the effect of different modes of combining the blocked glyoxal resin with the cationic starch and their introduction to the pulp slurry. A set of control base sheets was made having no additives followed by (A) a series in which cationic starch was added to the pulp slurry at the equivalent dosages of 40, 60 and 80 pounds per ton. A similar series (B) followed in which 9% of the blocked glyoxal resin was cooked out with the starch at 90° C. for 30 minutes. This was followed by a series, (C) in which the starch was cooked out then cooled to 50° C., whereupon the blocked glyoxal resin was stirred in. A final series (D) was prepared in which the cationic starch was cooked out then added to the pulp slurry. The blocked glyoxal resin was then added to the pulp slurry. Handsheets were formed from these slurries and dried on a rotary drier. Sheets were tested as before with results shown as follows.

These results show that reacting the resin with the cationic starch during the gelatinization is the preferred process. Some reaction apparently does take place when the starch is first cooked out and cooled prior to introducing the resin. This procedure is less efficient in that it requires a dosage of 80 pounds per ton to achieve performance equivalent to 60 pounds per ton prepared by the preferred procedure. The 80 pound per ton samples of set B are lower than expected, which may indicate poor mixing. Set D gives inferior results similar to set A with cationic starch only. This indicates that very little resin was retained on the fiber.

| Addition | A | | | | B | | | |
|----------|------------|------|-------|-------|------|-------|-------|------|
| | Conditions | Base | 40 | 60 | 80 | 40 | 60 | 80 |
| Dry | | 12.3 | 13.75 | 14.84 | 14.3 | 16.64 | 18.01 | 16.1 |
| Tensile | | 4.05 | 4.2 | 4.1 | 4.1 | 4.8 | 7.84 | 4.8 |
| % Dry | | | | | | | | |
| Stain | | | | | | | | |
| West | | .244 | .57 | .21 | .234 | .79 | .965 | .792 |
| Tensile | | 3.04 | 3.41 | 3.2 | 3.2 | 3.83 | 4.03 | 3.68 |
| % Wet | | | | | | | | |
| Strain | | | | | | | | |
| Mullens | | 38.4 | 53.4 | 54 | 56 | 58.8 | 62 | 58.2 |
| Burst | | | | | | | | |

| Addition | C | | | | D | | |
|----------|---|--|--|--|---|--|--|
| | | | | | | | |
| | | | | | | | |

| | A | | | | B | | | | C | | | | D | | | |
|---------|------|------|-------|-------|------|------|-------|------|------|------|-------|-------|------|----|----|----|
| | Base | 40 | 60 | 80 | 40 | 60 | 80 | 40 | 60 | 80 | 40 | 60 | 80 | 40 | 60 | 80 |
| Dry | 15.4 | 17.6 | 17.48 | 17.41 | 13.9 | 18.5 | 22.36 | 15.7 | 17.0 | 16.6 | 18.58 | 16.74 | 19.7 | | | |
| Tensile | | | | | | | | | | | | | | | | |
| % Dry | 4.89 | 4.7 | 4.98 | 5.4 | 4.9 | 5.26 | 5.65 | 4.3 | 4.53 | 5.06 | 4.98 | 4.36 | 4.47 | | | |
| Strain | | | | | | | | | | | | | | | | |
| Wet | .36 | .543 | .76 | .905 | .82 | 1.1 | 1.39 | .95 | .93 | 1.01 | .757 | 1.14 | 1.4 | | | |
| Tensile | | | | | | | | | | | | | | | | |
| % Wet | 2.3 | 2.68 | 3.42 | 3.67 | 3.6 | 3.67 | 4.4 | 4.04 | 4.1 | 4.3 | 3.72 | 4.6 | 3.9 | | | |
| Strain | | | | | | | | | | | | | | | | |
| Mullen | 60.4 | 82.6 | 72.4 | 66.6 | 65.4 | 82.8 | 80.2 | 6.7 | 78.4 | 70.6 | 78.6 | 66.8 | 73.2 | | | |
| Burst | | | | | | | | | | | | | | | | |

Base Sheet-No Additives

A. STA-LOK 400 only

B. STA-LOK 400 plus 9% Sequez® R (Converted 210° F.)

C. STA-LOK 400 plus 12% Sequez® R (Converted 210° F.)

D. STA-LOK 400 plus 20% Sequez® R (Converted 210° F.)

| -continued | | | | | | | | |
|-------------------------|------|-------|-------|-------|-------|-------|-------|--|
| Conditions | Base | 40 | 60 | 80 | 40 | 60 | 80 | |
| Dry Tensile % Dry Stain | 12.3 | 13.75 | 14.94 | 18.21 | 15.05 | 13.63 | 13.10 | |
| West | 4.05 | 4.7 | 4.6 | 4.7 | 4.77 | 4.88 | 4.45 | |
| Tensile % Wet Strain | .244 | .669 | .49 | .977 | .662 | .687 | .525 | |
| Mullens | 3.04 | 3.5 | 3.74 | 4.11 | 3.43 | 3.58 | 3.51 | |
| Burst | 38.4 | 51.6 | 63.4 | * | 51.4 | 46.6 | 47.1 | |

The terms and descriptions used herein are preferred embodiments set forth by way of illustration only, and are not intended as limitations on the many variations which those of skill in the art will recognize to be possible in practicing the present invention as defined by the following claims.

What is claimed is:

1. A method for manufacturing paper sheet comprising: adding to a paper pulp slurry in the wet end of a paper making machine an aqueous reaction product of a cationic starch and a blocked glyoxal compound, wherein said reaction occurs during the gelatinization of said starch and prior to said addition; forming the paper sheet; and drying the paper sheet.
2. Method of claim 1 wherein the cationic starch is selected from the group consisting of potato starch, corn-starch and wheat starch.
3. Method of claim 1 wherein the amount of glyoxal resin is within the range of 3 to 30% of the dry weight of the starch.

4. Method of claim 3 wherein the amount of glyoxal resin is within the range of 9 to 20% of the dry weight of the starch.
5. Method of claim 1 wherein the glyoxal resin is selected from the group consisting of polyol/glyoxal condensate and cyclic urea/glyoxal condensate.
6. Method of claim 1 wherein the said reaction product is added to the paper slurry at a level of 2 to 50 pounds dry starch per ton of dry pulp.
7. A method for manufacturing paper comprising: adding an aqueous reaction product of a cationic starch and a blocked glyoxal compound to a paper pulp slurry in a wet end of a paper making machine, wherein said reaction occurs during gelatinization of said starch and prior to said addition; forming paper; and drying the paper.
8. A method according to claim 7, wherein the cationic starch is selected from the group consisting of potato starch, cornstarch and wheat starch.
9. A method according to claim 7, wherein the amount of glyoxal resin is within the range of 3 to 30% of the dry weight of the starch.
10. A method according to claim 9, wherein the amount of glyoxal resin is within the range of 9 to 20% of the dry weight of the starch.
11. A method according to claim 10, wherein the glyoxal resin is selected from the group consisting of polyol/glyoxal condensate and cyclic urea/glyoxal condensate.
12. A method according to claim 11, wherein the said reaction product is added to the paper slurry at a level of 2 to 50 pounds dry starch per ton on dry pulp.

* * * * *

United States Patent [19]

Floyd et al.

[11] Patent Number: 4,695,606

[45] Date of Patent: Sep. 22, 1987

[54] COATING BINDER ADDITIVE

[75] Inventors: William C. Floyd, Chester; Sai H. Hui, Rock Hill, both of S.C.

[73] Assignee: Sun Chemical Corporation, New York, N.Y.

[21] Appl. No.: 909,621

[22] Filed: Sep. 22, 1986

[51] Int. Cl.⁴ C08F 8/28; C08L 61/00

[52] U.S. Cl. 525/160; 525/154; 525/157; 525/161; 525/162; 525/163; 525/383

[58] Field of Search 525/154, 383, 326.9, 525/515, 162, 160, 161, 163; 528/245; 162/168.3

[56]

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Primary Examiner—Theodore E. Pertilla

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[57]

ABSTRACT

A coating binder additive is prepared comprising a blocked glyoxal resin mixed with a vinyl or acrylic water soluble polymer which is reactive with free glyoxal.

11 Claims, No Drawings

COATING BINDER ADDITIVE

This invention relates to paper coating compositions. More particularly it relates to an additive which insolubilizes the binders in coatings for paper.

BACKGROUND OF THE INVENTION

Paper coating compositions are generally a fluid suspension of pigment, such as clay with or without titanium dioxide, calcium carbonate, or the like, in an aqueous medium which includes a binder such as starch, modified starch, styrene-butadiene copolymer, acrylic polymer, or protein to adhere the pigment to paper.

The hydrophilic nature of the binder requires the presence of an insolubilizing material which crosslinks the binder making it hydrophobic and thus improving the off-set characteristics of the surface of the coated paper. The most widely-used crosslinking materials are glyoxal resins and formaldehyde-donor agents such as melamine-formaldehyde, urea-melamine-formaldehyde, and partially or wholly methylated derivatives thereof.

Glyoxal is a highly reactive monomer which cures quickly and has excellent insolubilizing properties. As a result of this rapid crosslinking of glyoxal and binder, however, the viscosity of the coating composition increases so rapidly and is so great that the composition cannot be used. Frequently glyoxal-insolubilized coatings gel completely, particularly in high solids formulations. Gelling can also occur in moderate or low solids formulations if they are not used promptly. Thus in situations where it is required that the viscosity remain stable for many hours, for example when high-solids coatings are to be applied by blade coating techniques, a glyoxal system is unsuitable.

Melamine-formaldehyde resins do not build viscosity in the coating compositions, but they have the disadvantage of having an unpleasant odor and of releasing free formaldehyde. Curing with such resins involves the crosslinking of the binder molecule with the methylol or methylated methylol group of the melamine resin, usually in an acid or neutral coating, and full insolubilization of the binder takes place slowly over a period of several days. Free formaldehyde can be released either directly from the coating mixture or when the coating is cured on the drying machine. The presence of even less than one percent of free formaldehyde, based on the total weight of the product, is undesirable, not only because of its objectionable odor, but because it is an allergen and an irritant, causing severe reactions in the operators who manufacture the coatings and who treat and handle the coated paper.

Various compositions have been disclosed in the art as useful as insolubilizers. The use of the reaction product of urea and glyoxal as an insolubilizer is disclosed in U.S. Pat. No. 3,869,296. Treating agents formed by the reaction of ethylene urea with glyoxal are disclosed in Japanese publication No. 5 3044-567, but they too do not have satisfactory properties. The use of an acrylamide/glyoxal adduct was disclosed in U.S. Pat. No. 3,549,568 to improve the wet rub of paper coating compositions. U.S. Pat. No. 4,343,655 teaches the use of the alkylated products of the reaction of glyoxal and cyclic ureas as crosslinking resins for binders for paper coating compositions. U.S. Pat. No. Re. 30,259 disclosed paper strengthening resins in which water soluble thermosetting polyvinylamide resins are reacted with glyoxal.

In particular, U.S. Pat. No. 4544609 discloses an insolubilizer which is useful as a binder for a paper coating composition comprising the reaction product of polyacrylamide, glyoxal and cyclic urea. While this insolubilizer has been effective, due to its high viscosity gelling can occur in concentrates of the insolubilizer containing greater than 20-25% solids.

SUMMARY OF THE INVENTION

10 Briefly, the coating binder additive comprises a blocked glyoxal resin mixed with a vinyl or acrylic water soluble polymer which is reactive with free glyoxal. This additive is an excellent crosslinking resin for binders for paper coating compositions. It does not build viscosity as does free glyoxal; it does not contain or evolve free formaldehyde; it has insolubilizing effects similar to those of the previously known agents; and imparts strength to the binder and enhances various printing properties of the coated substrate.

20 DETAILED DESCRIPTION OF THE INVENTION

25 In accordance with the present invention a binder additive is prepared which is useful for insolubilizing and strengthening starch, protein and polyvinyl alcohol binders for paper coating compositions. The binder additive is prepared as follows: (1) an acrylic or vinyl polymer which is water soluble and which reacts with free (unblocked) glyoxal or glyoxal resin is prepared; and 30 (2) the polymer is mixed with a blocked glyoxal resin, preferably the reaction product of glyoxal and a urea or a cyclic urea, to give the product of this invention.

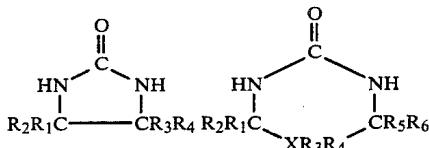
35 The glyoxal resin component of this mixture is blocked to inhibit it from reacting with the other components of the paper coating composition prior to curing. Inhibiting the reactivity of the glyoxal resin allows a product to be formulated at higher solids and/or lower viscosity than otherwise possible with unblocked glyoxal resin. Further, by blocking the glyoxal resin, the reaction is delayed until the paper is cured. The 40 curing process unblocks the glyoxal and resin allowing them to react with the binder and polymer resulting in a cross-linked binder with superior strength and improved printing properties. Using this invention, it is possible to prepare a paper coating with a high level of natural binder that performs as well as a coating with a high level of synthetic (latex) binder. With free (unblocked) glyoxal, the coating additive can be unstable 45 resulting in thickening or gelling of the additive, or the coating may show unacceptably high viscosity or gelling over time.

50 Glyoxal readily reacts with binders such as starch, protein and polyvinyl alcohol and with polyacrylamide and other polymeric agents in a crosslinking reaction. Crosslinking causes the mixture of glyoxal resin and the binders and/or polymeric agents to thicken or gel. By suitably blocking the glyoxal resin, it may be mixed with these binders and polymeric agents without reacting to 55 any great degree. The reactivity can be controlled so that it occurs in a paper coating as it is being dried and cured. Furthermore, judicious choice of polymeric agent allows coating properties to be enhanced as the glyoxal resin reacts with binder and the polymer. Mixing a suitable polymeric agent with free (unblocked) glyoxal, or adding free glyoxal to a coating containing a suitable polymeric agent generally causes thickening or 60 gelling due to premature reaction.

The glyoxal may be blocked by reaction with a blocking component becoming a blocked glyoxal resin. Suitable blocking components include urea, substituted ureas (such as dimethyl urea), various cyclic ureas such as ethylene urea, substituted ethylene ureas (such as 4,5-dihydroxyethylene urea), propylene urea, substituted propylene ureas (such as 4-hydroxy-5-methylpropylene urea), carbamates (such as isopropyl or methyl carbamate), glycols (such as ethylene glycol to make 2,3-dihydrodioxane, or dipropylene glycol to make an oligomeric condensation product), polyols (i.e. containing at least three hydroxy groups such as glycerin, to make 2,3-dihydroxy-5-hydroxymethyl dioxane) as well as unalkylated or partially alkylated polymeric glyoxal derived glycols such as poly (N-1',2-dihydroxyethyl-ethylene urea). Preferably, the blocking component is a urea or cyclic urea because the blocked glyoxal resins formed are very stable providing long shelf life.

The reaction of the glyoxal and the blocking component, preferably a urea or cyclic urea, generally takes place within the temperature range of about 25° to 100° C., and preferably about 40° to 80° C. In general the pH of the reactants and resultant binder additive is about 2.5 to 8.0 and preferably is about 4 to 6.5

The urea reactant may be urea, monourein or the like. If a cyclic urea is selected it may have one of the following general formulas:



wherein R₁, R₂, R₃, R₄, R₅ and R₆ may be the same or different and each may be H, OH, COOH, R, OR, or COOR wherein R is an alkyl or a substituted alkyl group having 1 to 4 carbon atoms and X may be C, O, or N; when X is O, R₃ and R₄ are each zero; when X is N, R₃ or R₄ is zero.

Typical examples of such urea reactant compounds include, but are not limited to ethylene urea, propylene urea, uron, tetrahydro-5(2 hydroxyethyl)-1,3,5-triazin-2-one, 4,5-dihydroxy-2-imidazolidinone, 4,5-dimethoxy-2-imidazolidinone, 4-methyl ethylene urea, 4-ethyl ethylene urea, 4-hydroxyethyl ethylene urea, 4,5-dimethyl ethylene urea, 4-hydroxy-5-methyl propylene urea, 4-methoxy-5-methyl propylene urea, 4-hydroxy-5,5-dimethyl propylene urea, 4-methoxy-5,5-dimethyl propylene urea, tetrahydro-5-(ethyl)-1,3,5-triazin-2-one, tetrahydro-5-(propyl)-1,3,5-triazin-2-one, tetrahydro-5-(butyl)-1,3,5-triazin-2-one, 4-hydroxy-5,5-dimethyl pyrimid-2-one, and the like, and mixtures thereof.

A polymer is chosen which is water soluble and which will react with free (unblocked) glyoxal and glyoxal resin. Since the polymer is mixed with a blocked glyoxal resin in the binder additive, the polymer will react under curing conditions with the released glyoxal and resin resulting in crosslinking between the polymer, glyoxal, resin and binder (e.g. starch) which will strengthen the binder considerably. Since the polymer does not react with the crosslinker until curing of the coating composition, the binder additive and coating composition can maintain a low viscosity without gelling over time (i.e. storage stable). In addition, since the polymer has not been reacted with the glyoxal resin, the reactivity of the glyoxal resin can be maintained for

subsequent curing with the binder. Further, the hydrophilic nature of the polymer results in a coating which can hold moisture and can benefit subsequent printing of the coated substrate.

Preferably a low molecular weight polymer is prepared with the molecular weight being controlled by, for example, using an alcohol such as isopropanol as a chain terminator, using a low concentration of acrylamide monomer, or using a low monomer concentration per unit time (using monomer feed instead of bulk). The preferred molecular weight is less than 100,000 daltons, optimally less than 30,000 daltons, which helps provide a binder additive and coating composition with a low viscosity and which does not gel.

Suitable polymers include polymers of monomers such as acrylamide, 2-hydroxyethyl acrylate, methacrylamide, N-(hydroxymethyl) acrylamide, N-substituted acrylamides and N-substituted methacrylamides, as well as co- or ter polymers of the above with monomers such as acrylic acid, acrylonitrile, crotonic acid, fumaric acid, itaconic acid, maleic acid, methacrylic acid, monoethyl maleate, vinyl pyrrolidone, or vinyl sulfonic acid. The monomers may also be with small amounts of vinyl acetate or C-1 to C-4 alkyl esters of acrylic or methacrylic acid. One preferred embodiment is a copolymer of acrylamide and methacrylic acid. Another preferred embodiment is a polymer containing acrylamide reacted with either formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde or isobutyraldehyde. The polymer may also be partially hydrolyzed polyvinyl acetate.

In the binder additive the ingredients are generally present in a ratio of 25:1 to 1:2, preferably 10:1 to 1:1, parts by dry weight of the blocked glyoxal resin to polymer. The blocked glyoxal resin generally comprises a mole ratio of about 4:1 to 1:2, preferably 2:1 to 1:1, of glyoxal to blocking component.

The binder additive of this invention has reactive sites capable of reacting with the cellulosic hydroxyl group, thus binding the starch or protein molecules in the coating composition. Because of its polymeric nature, the additive is capable of reacting with several binder molecules, leading to greater insolubilizing efficiency and so requiring less of the additive of this invention than of glyoxal or of a melamine-formaldehyde resin to accomplish the same degree of insolubilization. The additive is not excessively reactive, as is glyoxal, so no viscosity build-up takes place in the coating composition. Since there is no formaldehyde in the system, the problems found with free formaldehyde are avoided.

The binder additive of this invention is useful as an insolubilizer for natural binders. The binders used in the paper coating compositions of this invention include, but are not limited to, unmodified starch; oxidized starch; enzyme-converted starch; starches having functional groups such as hydroxyl, carboxyl, amido, and amino groups; proteins, such as casein; polyvinyl alcohol; and the like, and their mixtures. Through use of the binder additive, the coating composition containing natural binders are able to impart properties, such as gloss, strength, etc. which are closer to those imparted by latex binders, but at a fraction of the cost of latex binders.

The coating composition will generally contain pigments which may be clay with or without titanium dioxide and/or calcium carbonate, and the like, and mixtures thereof. In addition to the binder, the pigment

material, and the additive described above, the paper coating composition may also include materials such as dispersants (e.g. sodium hexametaphosphate), lubricants (e.g. calcium stearate), defoamers (e.g. oil based emulsions or ethyl alcohol), preservatives, colored pigments, viscosity modifiers (e.g. carboxymethylcellulose), and the like, in conventional amounts, as well as a latex (e.g. a polymer such as a styrene-butadiene copolymer or acrylic polymer) which may be used as a binder in addition to the natural binders.

In the paper coating compositions described herein the amount of binder is based upon the amount of pigment with the ratio varying with the amount of bonding desired and with the adhesive characteristics of the particular binder employed. In general, the amount of binder is about 5 to 25 percent and preferably about 12 to 18 percent, based on the weight of the pigment. The amount of additive varies with the amount and properties of the binder and the amount of insolubilization desired. In general, the additive is added at about 1 to 10 percent, and preferably about 3 to 7 percent, based on the weight of the binder (solids or dry basis). The total solids content of the paper coating composition generally is within the range of about 40 to 70 percent, depending upon the method of application and the product requirements.

The coating composition of this invention can be applied to paper or paper-like substrates by any known and convenient means.

EXAMPLE I

A blocked glyoxal resin, identified herein as Resin A, was prepared by reacting glyoxal with cyclic urea (4-hydroxy-5-methylpyrimidone) as follows. A two-liter flask was equipped with a mechanical stirrer, thermometer and condenser. To the flask was charged propionaldehyde (95.5 g, 1.64 moles) and 50% aqueous formaldehyde (98.7 g, 1.64 moles). As this mixture was stirred, a solution of 98.7 g (1.64 moles) of urea in 86.6 g of water was added. The reaction exothermed to 55° C. and was held there for 3 hours, becoming milky white. Sulfuric acid (40%, 19.5 g) was added causing the reaction to exotherm to 85° C., passing through a thickened state before thinning out again. After 2 hours, the reaction was clear amber. The temperature was held at 85° C. for another two hours. The reaction was cooled to 45° C. and 456 g (3.1 moles) of 40% glyoxal was added. This was heated to 65°-70° C. for 1 hour and vacuum stripped to 50% solids. The pH was adjusted to 5.0 with caustic soda and solids adjusted to 45%. A clear, amber solution was obtained.

EXAMPLE II

A blocked glyoxal resin, identified herein as Resin B, was obtained by reacting glyoxal with ethylene urea as follows. A one-liter flask was fitted with a mechanical stirrer, thermometer and condenser. To this was charged 290 g (2.0 moles) of 40% glyoxal and 90 g (1.05 moles) of ethylene urea. This was stirred as the pH was adjusted to 4.0 to 5.0 with sodium bicarbonate. The reaction was heated to 50°-60° C. for 2 hours. The pH was then adjusted to 2.5 with 40% sulfuric acid and held at 50°-60° C. for 3 more hours. After cooling to 35° C., the pH was adjusted to 5.0 with 25% caustic soda. Solids were adjusted to 45% with 110 g of water. This was filtered to afford a clear, light yellow solution.

EXAMPLE III

A polymer, identified herein as Polymer A, was prepared by copolymerizing acrylamide and methacrylic acid as follows. A two-liter resin kettle was equipped with a mechanical stirrer, N₂ sparge, condenser, thermometer and two addition funnels. To the kettle was charged 280 g of water and 114 g of isopropanol. This mixture was heated to 70° C. and sparged with nitrogen. As the mixture was heating, 261 g of 50% acrylamide (1.84 moles), 10 g (0.11 moles) of methacrylic acid, and 279 g of deionized water were mixed together and charged to one funnel. To the other funnel was charged a mixture of 54 g of deionized water and 1.34 g of ammonium persulfate. The contents of the two funnels were added simultaneously over a 1.5 hour period. During this addition and for two hours thereafter the temperature was held as 70° C. The reaction mixture was then cooled to 30° C. and the pH adjusted from 4.2 to 5.5 with caustic soda. The polymer had a Brookfield viscosity of 60 cps with a #2 spindle at 50 rpm and 200 cps with #2 spindle at 100 rpm and had a solids level of 17.6% by weight.

EXAMPLE IV

A N-hydroxy propyl acrylamide polymer, identified herein as Polymer B, was prepared by reacting propionaldehyde with polyacrylamide as follows. A one-liter flask was fitted with a nitrogen sparge, mechanical stirrer, condenser and 2 addition funnels. To the flask was charged 599 g of deionized water and 12 g of isopropanol. This was sparged with nitrogen and heated to 70° C. To one addition funnel was charged 160 g of 50% acrylamide. To the other was charged a solution of 0.8 g of ammonium persulfate in 32 g of deionized water. The contents of the two funnels were added simultaneously over 1 hour. The reaction was held at 70° C. for another two hours, then cooled. The finished product had a Brookfield viscosity of 70 cps with a #2 spindle at 50 rpm and a solids level of 12% by weight.

A portion of this product (185.1 g) was placed in a 250 ml flask with a magnetic stirrer, pH probe and thermometer, then cooled to 15° C. The pH was adjusted to 10.0 with caustic soda solution. To this was added 3 g (approx. 20 mole % with respect to acrylamide) of propionaldehyde over a 10 minute period. The pH was maintained at 10.0 and held there for 1 hour. The pH was then adjusted to 6.0 with acetic acid.

EXAMPLE V

A mixture was made of 3 parts by weight of Resin A and 1 part by weight of Polymer A. Liquid chromatography showed that the product was a mixture and that the components had not reacted. A similar mixture was made of Resin B and Polymer A, and was also found to be a mixture.

EXAMPLE VI

Binder additives were prepared containing as a blocked glyoxal resin either Resin A or Resin B, mixed with one of the following polymers: a 1:1 copolymer of acrylamide and N-methylol acrylamide; and poly(N-methylol acrylamide). These binder additives when added to a coating composition all gave coatings that were superior (better wet rub, higher pick strength, better smoothness, more porosity, better gloss and brightness) to a control coating composition containing

a conventional insolubilizer which comprised a cyclic urea-glyoxal reaction product.

EXAMPLE VII

One part Polymer B was blended with 3 parts Resin B to give a binder additive with superior coating properties. Dry pick results were particularly impressive.

EXAMPLE VIII

Paper coatings compositions were prepared either as a high latex coating containing 4 parts starch (Penford Gum 280, hydroxyethylated corn starch) and 8 parts latex (Dow 620, styrene-butadiene copolymer) or as a high starch coating containing 9 parts starch (Penford Gum 280) and 3 parts latex (Dow 620). Each coating composition also contained 50 parts No. 1 clay, 50 parts No. 2 clay and 0.15% Dispex N-40 (sodium polyacrylate dispersant). A binder additive was added where indicated at a level of 4% by weight of the starch. For comparison, certain coating samples used a commercial starch insolubilizer (Sunrez 700C, a cyclic urea-glyoxal reaction product blended with glyoxal and propylene glycol) as the additive. Paper was coated with a blade coater and tested as indicated below. The object was to produce a high starch coating that had properties similar to the high latex coating. The following coating samples 1-8 were high starch or high latex coatings containing the identified additive.

| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|------------------|----|----|----|----|----|----|----|----|
| Gloss | 64 | 63 | 56 | 58 | 57 | 54 | 68 | 55 |
| Smoothness | 26 | 22 | 31 | 23 | 24 | 20 | 18 | 30 |
| IGT Dry Pick | 84 | 84 | 62 | 66 | 72 | 68 | 77 | 65 |
| Wet rub, spec 20 | 85 | 90 | 51 | 55 | 68 | 76 | 83 | 55 |
| Brightness | 82 | 81 | 81 | 81 | 82 | 82 | 82 | 82 |
| Porosity | 15 | 20 | 35 | 33 | 38 | 25 | 23 | 38 |
| Crock (Rank) | 3 | 2 | 4 | 5 | 1 | 7 | 6 | 8 |
| Printed Gloss | 87 | 86 | 80 | 77 | 80 | 82 | 86 | 80 |

- 1 high latex, no additive;
- 2 high latex, with Sunrez 700C;
- 3 high starch, no additive;
- 4 high starch, with Sunrez 700C;
- 5 high starch, with Resin A;
- 6 high starch, with Resin B;
- 7 high starch, with Polymer A/Resin B mixture (1:6.75 by dry weight ratio); and
- 8 high starch, with Polymer A

These results show that the binder additive of this invention containing a mixture of blocked glyoxal resin and polymer (Sample 7) gave a high starch paper coating with performance that closely matches that of the more expensive high latex coatings of Samples 1 and 2. It further shows that the addition to a high starch coating of the blocked glyoxal resin alone (Samples 4, 5 and 6) or polymer alone (Sample 8) does not give the performance of either a high starch coating containing the binder additive of this invention (Sample 7) or a high latex coating (Samples 1 and 2). The enhanced synergistic performance of the binder additive of this invention is an unexpected benefit. A coating product formulated with a binder additive containing a mixture of Resin A and Polymer A showed similar results to the binder additive containing the mixture of Polymer A and Resin B above.

EXAMPLE IX

A reaction product of polyacrylamide, glyoxal and urea was prepared as follows. To a 400 ml beaker was charged 121.5 g (0.84 moles) of 40% glyoxal and 18.0 g (0.21 moles) of ethylene urea. The pH was adjusted to 6.0 and allowed to stir one hour. The pH was then adjusted to 7.9, and 150 g of polyacrylamide (11% solids, RV viscosity, #1 spindle at 50 rpm is 66 cps) was

added. This stirred one hour with pH dropping to 6.1. Propylene glycol (15.9 g) was added with 98g of water, reducing the solids to 32%. This reaction product compared with the Resin A/Polymer A blend of Example V (32% solids). The reaction product performed reasonably well when tested shortly after preparation; however, it gelled in less than one month. In contrast, the Resin A/Polymer A blend was still fluid after 6 weeks. The short shelf life of the reaction product is probably due to insufficiently blocked glyoxal.

EXAMPLE X

A reaction product, similar to those produced in U.S. Pat. No. 4,544,609, of polyacrylamide, glyoxal and urea was produced as follows. Polyacrylamide (150 g, 14% solids, 0.29 moles, RV viscosity #2 spindle at 50 rpm is 40 cps) and 17.7 g urea (0.29 moles) were mixed together and heated to 60° C. The pH was 4.7. Over a one hour period, 128 g (0.88 moles) of 40% glyoxal was added, maintaining 60° C. After the glyoxal was added, the pH was adjusted to 4.0 and held at 60° C. for 3 hours. Solids were 30.6%. This reaction product also gelled in about 1 month.

What is claimed is:

1. An additive for binders for paper coating compositions which comprises:
a blocked glyoxal resin, which is the reaction product of a glyoxal and a blocking component, mixed with a vinyl or acrylic water soluble polymer which is reactive with free glyoxal, the amounts being within the ratio of 25:1 to 1:2 parts by dry weight of the blocked glyoxal resin to the polymer.
2. Additive of claim 1 wherein the blocking component is selected from the group consisting of urea, cyclic urea, carbamate, glycol, polyol containing at least three hydroxy groups and unalkylated or partially alkylated polymeric glyoxal derived glycol.
3. Additive of claim 2 wherein the blocking component is a urea or cyclic urea.
4. Additive of claim 3 wherein the polymer has a molecular weight of less than 100,000 daltons.
5. Additive of claim 1 wherein the polymer is made from a monomer selected from the group consisting of acrylamide, 2-hydroxyethyl acrylate, methacrylamide, N-substituted acrylamide and N-substituted methacrylamide and co- and ter- polymers thereof.
6. Additive of claim 5 wherein the polymer is a copolymer of the monomer of claim 5 with a monomer selected from the group consisting of acrylic acid, acrylonitrile, crotonic acid, fumaric acid, itaconic acid, maleic acid, methacrylic acid, monoethyl maleate, vinyl pyrrolidone, vinyl sulfonic acid, vinyl acetate, and C-1 to C-4 alkyl esters of acrylic or methacrylic acid.
7. Additive of claim 4 wherein the polymer is a copolymer of acrylamide and methacrylic acid.
8. Additive of claim 4 wherein the polymer contains acrylamide reacted with an aldehyde selected from the group consisting of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and isobutyraldehyde.
9. Additive of claim 5 wherein the ratio of blocked glyoxal resin to polymer is within the range of 10:1 to 1:1 parts by dry weight.
10. Additive of claim 1 wherein mole ratio of glyoxal to blocking component is within the range of 4:1 to 1:2.
11. Additive of claim 3 wherein the mole ratio of glyoxal to blocking component is within the range of 2:1 to 1:1.

* * * * *

ФЕДЕРАЛЬНАЯ СЛУЖБА
ПО ИНТЕЛЛЕКТУАЛЬНОЙ СОБСТВЕННОСТИ

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(54) СПОСОБ ВОССТАНОВЛЕНИЯ НЕДОСТАЮЩИХ ЧАСТЕЙ ЛИСТОВ БУМАГИ

(57) Реферат:

Изобретение относится к бумажной промышленности. Для реставрации листов проводят их подготовку, подготовку волокнистой массы со связующим, отлив волокнистой массы со связующим на недостающие части листа и сушку листа. При этом в качестве связующего используют бактериальную целлюлозу, культивированную штаммом Acetobacter xylinum BKM B-880 в

количестве 2-6% от массы абсолютно сухой сульфатной хвойной беленой целлюлозы. После отлива листы подвергают сушке при температуре 80°C. Способ позволяет повысить прочность шва между восполняющей частью и реставрируемым документом. Прочность шва сохраняется на высоком уровне после 12 суток искусственного тепло-влажного старения при температуре 80°C и влажности 65%. 2 з.п. ф-лы, 2 табл., 8 пр.

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(54) METHOD TO RESTORE MISSING PARTS OF PAPER SHEETS

(57) Abstract:

FIELD: textiles, paper.

SUBSTANCE: for restoration paper sheets they are prepared, pulp with a binder is prepared, pouring of the pulp with the binder on the missing parts of the sheet, and drying the sheet. At that, as a binder, bacterial cellulose is used cultured by strain Acetobacter xylinum B-880 of All-Russian collection of microorganisms, in the amount of 2-6%

by weight of oven-dry softwood sulfate bleached pulp. After pouring the sheets are dried at a temperature of 80°C. Seam strength remains at high level after 12 days of artificial thermo-humid at a temperature of 80°C and humidity 65%.

EFFECT: method enables to improve the seam strength between the compensative part and the restored document.

3 cl, 2 tbl, 8 ex

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Изобретение относится к способам восстановления недостающих частей листов бумаги при механизированной реставрации книг, карт, гравюр, газет, рукописных и архивных материалов методом восполнения утраченных частей листа и предназначено для использования в практике работы крупных книгохранилищ, архивов и в целлюлозно-бумажной промышленности.

В настоящее время большинство крупных реставрационных подразделений в мире располагают аппаратурой для механизированной реставрации методом долива утраченных частей листов документов. Одним из недостатков метода является невысокая прочность шва между старой и восполняемой частью листа. Для упрочнения шва в бумажную массу можно вводить различные связующие.

В патенте СА №1.279.450 описан способ использования бактериальной целлюлозы в качестве связующего для получения нетканых и бумагоподобных материалов из различных волокон, в том числе из волокон растительного происхождения.

15 Определено оптимальное количество вводимой в массу бактериальной целлюлозы - 20%. Также заявлен способ культивирования бактериальной целлюлозы в динамических условиях. Однако в данном патенте не исследовалось влияние добавок бактериальной целлюлозы на прочность шва между старой и восполняемой частью

20 листа при механизированной реставрации документов и влияние на прочность шва ускоренного тепло-влажного старения.

В настоящей заявке бактериальную целлюлозу, предлагаемую к использованию в качестве связующего в бумажную массу для механизированной реставрации документов, получают путем поверхностного культивирования

25 штамма *Gluconacetobacter xylinus* ВКМ В 880. Наногель-пленка бактериальной целлюлозы (НГПЦ GX) получена на питательных средах, содержащих в качестве источника углерода отходы или полуотходы производств, имеющих моносахара, например гидролизат древесины или щелока целлюлозно-бумажного производства

30 (патент RU №2189394, опубл. 20.09.2002). Способ реализован на модельной установке для производства НГПЦ GX.

Наиболее близким по технической сущности и техническому результату является способ восстановления недостающих частей листов бумаги (А.С. №1151635, Опубл. 23.04.85, Бюл. №15), включающий подготовку реставрируемых листов, отлив

35 волокнистой массы со связующим на недостающие части листа, прессование и сушку с одновременным растворением связующего, при этом в качестве связующего используют поливинилспиртовые волокна. Известная добавка обеспечивает повышение производительности реставрационных работ при сохранении

40 качественных показателей листов. Однако известный способ требует особого режима прессования и сушки бумаги для набухания и растворения поливинилспиртовых волокон. Кроме того, поливинилспиртовые волокна как связующее хорошо зарекомендовали себя при введении в бумажную массу только из хлопковой целлюлозы в количестве не более 10% к массе целлюлозного волокна (Бланк М.Г.

45 Поливинилспиртовые волокна как связующее при механизированной реставрации бумаги // Теория и практика сохранения книг в библиотеке, вып.6, Л, ГПБ, 1974, с 87-105.)

Технической задачей и положительным результатом данного способа являются

50 повышение механической прочности шва между документом и восполняющей частью при использовании бумажной массы из сульфатной беленой хвойной целлюлозы, стабильность прочности шва в процессе искусственного тепло-влажного старения, а также исключение процесса прессования и упрощение процесса сушки бумаги.

Указанная задача и положительный результат достигаются за счет того, что способ восстановления недостающих частей листов бумаги включает подготовку реставрируемых листов, подготовку волокнистой массы со связующим, отлив волокнистой массы со связующим на недостающие части листа и сушку листа, отличающийся тем, что для повышения прочности шва между восполняющей частью и реставрируемым листом документа в качестве связующего используют бактериальную целлюлозу, культивированную штаммом *Gluconacetobacter xylinus* ВКМ

В 880 в количестве 2-6% от массы абсолютно сухой сульфатной хвойной беленой целлюлозы. Способ характеризуется тем, что НГПЦ ГХ предварительно подвергают распуску в течение 100-120 мин с последующим размолом: рафинирующий размол 20-30 мин, рубка 1-3 мин при концентрации 0,2%.

Реализация предлагаемого способа восстановления недостающих частей листов бумаги, иллюстрируется следующими примерами его осуществления.

Пример 1-8. Подготовку бумажной массы проводят следующим способом: сульфатную беленую хвойную целлюлозу распускают и размалывают до 35 и 45° ШР, затем в размолотую массу добавляют подготовленную ЦГХ в количестве 2-6% к массе абсолютно сухого волокна, перемешивают в течение 10-15 минут и используют для долива недостающих частей на реставрационной машине РОМ-4. ЦГХ подвергают распуску в течение 100-120 минут с последующим размолом (рафинирующий размол в течение 20-30 минут и рубка в течение 1-3 минут). Распуск и размол проводят при концентрации 0,2%. В качестве модельных образцов документов для реставрации использовали листы книги начала XX в. из сульфитной целлюлозы и листы документа первой половины XIX в. из тряпичной полумассы. Предварительно обработанные реставрируемые листы укладывают на сетку, подают массу с волокнистым связующим и производят отлив под вакуумом. При этом, в результате фильтрации воды сквозь сетку волокна заполняют незанятые листами участки сетки. Затем отлитый лист подвергают сушке при температуре 80°C (щадящий режим для документов).

Результаты определения прочности шва между реставрируемым документом и восполняющей частью представлены в таблице 1.

Таблица 1

| Прочность шва между реставрируемым документом и восполняющей частью | | | | | | | | |
|---|--|------|------|------|------|------|--|------|
| Показатели | Примеры | | | | | | | |
| | №1 | №2 | №3 | №4 | №5 | №6 | №7 | №8 |
| Основа композиции | Сульфатная беленая хвойная целлюлоза (35°ШР) | | | | | | Сульфатная беленая хвойная целлюлоза (45°ШР) | |
| Вид добавки | ЦГХ | | | | | | ЦГХ | |
| Количество добавки | 0 | 2 | 4 | 6 | 0 | 2 | 4 | 6 |
| Разрушающее усилие шва с листами документа начала ХХ в., Н | 1,5 | 3,7 | 4,0 | 4,0 | 3,5 | 6,0 | 6,2 | 6,2 |
| Разрушающее усилие шва с листами документа начала первой половины XIX в., Н | 9,5 | 15,5 | 16,0 | 16,0 | 11,0 | 18,7 | 19,5 | 20,5 |

Анализ экспериментальных результатов, представленных в таблице 1, показывает, что введение ЦГХ в композицию бумажной массы для механизированной реставрации документов (примеры 1-8) способствует повышению прочности шва между восполняемой и восполняющей частями листа документа. Так, при содержания ЦГХ в количестве 2-4% в композиции бумажной массы прочность шва при реставрации документа начала ХХ в. увеличивается в 2,5-2,7 раза (примеры 2, 3) и в 1,7-1,8 раза

(примеры 6, 7), при реставрации документа начала первой половины XIX в. - в 1,6-1,8 раза (примеры 2, 3, 6, 7).

Для исследования стабильности прочности шва в процессе хранения образцы подвергали искусственному тепло-влажному старению в камере «ТАВАИ». Режим старения соответствовал стандарту ISO 56-30: 1986 «Бумага. Картон. Ускоренное старение (4.3). Обработка влажным теплом при температуре 80°C и относительной влажности 65%». Искусственное старение проводили в течение 12 суток. Результаты испытаний представлены в таблице 2.

Из таблицы 2 видно, что прочность шва между восполняющей частью, содержащей добавки, ЦГХ и документом после 12 суток тепло-влажного старения остается выше (примеры 2-4, 6-8), чем с восполняющей частью, не содержащей добавки ЦГХ (примеры 1, 5).

| Таблица 2 Прочность шва между реставрируемым документом и восполняющей частью после 12 суток искусственного тепло-влажного старения | | | | | | | | |
|--|--|------|------|------|--|------|------|------|
| Показатели | Примеры | | | | | | | |
| | №1 | №2 | №3 | №4 | №5 | №6 | №7 | №8 |
| Основа композиции | Сульфатная беленая хвойная целлюлоза (35°ШР) | | | | Сульфатная беленая хвойная целлюлоза (45°ШР) | | | |
| Вид добавки | ЦГХ | | | | | | ЦГХ | |
| Количество добавки | 0 | 2 | 4 | 6 | 0 | 2 | 4 | 6 |
| Разрушающее усилие шва с листами документа начала ХХ в., Н | 1,0 | 2,0 | 2,0 | 2,2 | 2,5 | 3,5 | 3,5 | 3,5 |
| Разрушающее усилие шва с листами документа начала первой половины XIX в., Н | 7,5 | 11,0 | 12,5 | 12,5 | 8,5 | 15,0 | 15,0 | 16,0 |

Формула изобретения

1. Способ восстановления недостающих частей листов бумаги, включающий подготовку реставрируемых листов, подготовку волокнистой массы со связующим, отлив волокнистой массы со связующим на недостающие части листа и сушку, отличающийся тем, что для повышения прочности шва между восполняющей частью и реставрируемым листом документа в качестве связующего используют бактериальную целлюлозу, культивированную штаммом *Gluconacetobacter xylinus* ВКМ В-880 в количестве 2-6% от массы абсолютно сухой сульфатной беленой хвойной целлюлозы.

2. Способ по п.1, отличающийся тем, что бактериальную целлюлозу предварительно подвергают роспуску в течение 100-120 мин с последующим размолом: рафинирующий размол 20-30 мин, рубка 1-3 мин при концентрации массы 0,2%.

3. Способ по п.1, отличающийся тем, что комплекс: реставрируемый лист плюс восполняющая часть подвергают искусственному тепло-влажному старению при температуре 80°C и влажности 65% в течение 12 суток, после этого проверяют прочность шва.



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DESCRIPTION RU2472891

METHOD FOR RESTORING MISSING PARTS OF PAPER SHEETS

The invention relates to methods for recovering the missing parts of paper sheets during the mechanized restoration of books, maps, prints, newspapers, manuscripts and archival materials by the method of replenishing the lost parts of the sheet and is intended for use in the practice of large book depositories, archives and in the pulp and paper industry.

Currently, most major restoration divisions in the world have equipment for mechanized restoration by adding to the lost parts of sheets of documents. One of the disadvantages of the method is the low strength of the seam between the old and the replenished part of the sheet. To strengthen the seam in the paper pulp, you can enter various binders.

CA patent No. 1,279,450 describes a method for using bacterial cellulose as a binder for the production of non-woven and paper-like materials from various fibers, including from fibers of plant origin. The optimal amount of bacterial cellulose introduced into the mass was determined - 20%. A method for cultivating bacterial cellulose under dynamic conditions is also claimed. However, this patent did not investigate the effect of bacterial cellulose additives on the strength of the joint between the old and the replenished part of the sheet during mechanized restoration of documents and the effect on the strength of the joint of accelerated warm-wet aging.

In this application, bacterial cellulose, proposed for use as a binder in a paper pulp for mechanized restoration of documents, is obtained by surface cultivation of a strain of *Gluconacetobacter xylinus* BKM B 880. Nanogel-film of bacterial cellulose (НГПЦ GX) was obtained on nutrient media containing waste or semi-waste from monosugar production as a carbon source, for example, wood hydrolyzate or pulp and paper liquor production (patent RU No. 2189394, publ. 20.09.2002). The method is implemented on a model plant for the production of NGPTs GX.

The closest in technical essence and technical result is a method of restoring the missing parts of sheets of paper (A.S. No. 1151635, Publ. 23.04.85, Bull. No. 15), including the preparation of restored sheets, the casting of the pulp with a binder onto the missing parts of the sheet, pressing and drying with the simultaneous dissolution of the binder, while polyvinyl alcohol fibers are used as the binder. Known additive provides increased productivity of restoration work while maintaining the quality indicators of the sheets. However, the known method requires a special mode of pressing and drying paper for swelling and dissolving polyvinyl alcohol fibers. In addition, polyvinyl alcohol fibers as a binder have proven themselves when introduced into paper pulp only from cotton pulp in an amount of not more than 10% by weight of cellulose fiber (Blank M.G. Polyvinyl alcohol fibers as a binder in mechanized paper restoration // Theory and Practice of Book Preservation in the library, issue 6, L, GPB, 1974, pp. 87-105.

)

The technical task and the positive result of this method is to increase the mechanical strength of the seam between the document and the replenishing part when using pulp of sulphate bleached softwood pulp, stability of the strength of the seam during artificial heat-wet aging, as well as the elimination of the pressing process and simplification of the drying process of paper.

This task and a positive result are achieved due to the fact that the method of restoring the missing parts of the paper sheets includes preparing the restored sheets, preparing the pulp with a binder, casting the pulp with a binder to the missing parts of the sheet and drying the sheet, characterized in that to increase the strength of the seam between the bacterial cellulose cultured with the *Gluconacetobacter xylinus* BKM B 880 strain in an amount of 2-6% by weight of abs understood softwood kraft dry bleached pulp. The method is characterized in that NGPC GX is preliminarily dissolved for 100-120 minutes, followed by grinding: refining grinding 20-30 minutes, chopping 1-3 minutes at a concentration of 0.2%.

The implementation of the proposed method for recovering the missing parts of sheets of paper is illustrated by the following examples of its implementation.

Example 1-8. The paper pulp is prepared in the following way: sulfate bleached softwood pulp is dissolved and milled to 35 and 45 ° C, then the prepared CGX is added to the ground pulp in an amount of 2-6% by weight of absolutely dry fiber, mixed for 10-15 minutes and used for topping up the missing parts on the ROM-4 restoration machine. CGX is subjected to dissolution for 100-120 minutes, followed by grinding (refining grinding for 20-30 minutes and chopping for 1-3 minutes). Dissolution and grinding is carried out at a concentration of 0.2%. As model samples of documents for restoration, sheets of a book from the beginning of the 20th century were used. from sulphite pulp and sheets of the document of the first half of the XIX century. from rag half mass. The pre-treated restoration sheets are laid on a grid, the mass is fed with a fibrous binder, and vacuum casting is performed. At the same time, as a result of filtering water through the grid, the fibers fill unoccupied sheets of the grid. Then the cast sheet is dried at a temperature of 80 ° C (sparing mode for documents).

The results of determining the strength of the seam between the restored document and the replenishing part are presented in table 1.

Table 1 Strength of the seam between the restored document and the replenishing part Indicators Examples No. 1 No. 2 No. 3 No. 4 No. 5 < SEP> No. 6 No. 7 No. 8 Basis of composition Sulfated bleached softwood pulp (35 ° SR) Sulfated bleached softwood pulp (45 ° SR) Type of additive < SEP > TSGX TSGX Additive amount 0 2 4 6 0 2 4 6 Destructive seam force with sheets of a document from the beginning of the 20th century, N 1,5 3,7 4,0 4,0 3,5 6,0 6,2 6,2 Destructive force of a seam with sheets of a document from the beginning of the first half of the 19th century, H 9,5 15,5 16,0 16,0 11,0 18,7 19,5 20,5

Analysis of the experimental results presented in table 1 shows that the introduction of UGX in the composition of the paper pulp for mechanized restoration of documents (examples 1-8) helps to increase the strength of the seam between the filled and filling parts of the sheet of the document. So, when the content of CGX in the amount of 2-4% in the composition of the paper pulp, the strength of the seam during restoration of the document of the beginning of XX century. increases by 2.5-2.7 times (examples 2, 3) and 1.7-1.8 times (examples 6, 7), with the restoration of the document beginning of the first half of the XIX century. - 1.6-1.8 times (examples 2, 3, 6, 7).

To study the stability of the weld strength during storage, the samples were subjected to artificial warm-wet aging in a TABAI chamber. The aging regime was in accordance with ISO 56-30: 1986 "Paper. Cardboard. Accelerated Aging (4.3). "Wet heat treatment at a temperature of 80 ° C and a relative humidity of 65%." Artificial aging was carried out for 12 days. The test results are presented in table 2.

From table 2 it is seen that the strength of the seam between the replenishing part containing additives, CGX and the document after 12 days of warm-wet aging remains higher (examples 2-4, 6-8) than with the replenishing part, not containing additives CGX (examples 1 , 5).

Table 2 Strength of the seam between the restored document and the replenishing part after 12 days of artificial warm-wet aging Indicators Examples No. 1 No. 2 No. 3 No. 4 No. 5 No. 6 No. 7 No. 8 Basis of composition Sulfated bleached softwood pulp (35 ° SR) Sulfated bleached softwood pulp (45 ° SR) Type of additive ЦГХ ЦГХ Amount of additive 0 2 4 6 0 2 4 6 Destructive force of a seam with sheets of a document from the beginning of the 20th century, H 1,0 2,0 2,0 2,2 2,5 < SEP> 3,5 3,5 3,5 Destructive force of a seam with sheets of a document of the beginning of the first half of the 19th century, N 7,5 11,0 12,5 12,5 8,5 15,0 15,0 <SEP> 16,0



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CLAIMS RU2472891

1.

A method of recovering missing parts of paper sheets, including preparing restored sheets, preparing pulp with a binder, casting the pulp with a binder into the missing parts of the sheet and drying, characterized in that bacterial cellulose is used as a binder to increase the strength of the seam between the filling part and the restored sheet of the document cellulose cultivated with a strain of *Gluconacetobacter xylinus* VKM B-880 in an amount of 2-6% by weight of absolutely dry sulphate bleached softwood pulp.

2.

The method according to claim 1, characterized in that the bacterial cellulose is first subjected to dissolution for 100-120 minutes, followed by grinding: refining grinding 20-30 minutes, chopping 1-3 minutes at a mass concentration of 0.2%.

3.

The method according to claim 1, characterized in that the complex: the restored sheet plus the replenishing part is subjected to artificial warm-wet aging at a temperature of 80 ° C and a humidity of 65% for 12 days, after which the strength of the seam is checked.



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О П И С А Н И Е ИЗОБРЕТЕНИЯ

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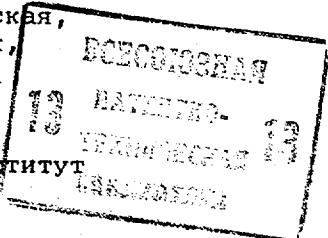
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(54) ВОЛОКНИСТАЯ МАССА ДЛЯ ИЗГОТОВЛЕНИЯ РЕСТАВРАЦИОННОЙ БУМАГИ

1

Изобретение относится к получению волокнистой массы для изготовления реставрационной бумаги, которая предназначена для восстановления недостающих частей листа книг, рукописей, произведений искусства, выполненных на бумажной основе.

В настоящее время для реставрации документов используют бумаги из различных полуфабрикатов, например из сульфатной беленой целлюлозы, хлопковой беленой целлюлозы [1].

Известные бумаги имеют высокую степень белизны, однако при использовании для реставрации документов их необходимо оттенять под цвет реставрируемого материала, например, обрабатывать с поверхности синтетическими красителями или экстрактами растительного происхождения, содержащими окрашенные вещества, например водными экстрактами чая или кофе. Таким образом, удается получить бумагу от светло-желтого до интенсивно коричневого цвета.

Наиболее близкой к изобретению по технической сущности и достигаемому положительному эффекту является волокнистая масса для изготовления реставрационной бумаги, содержащая

сульфатную хвойную беленую целлюлозу и облагороженную низкозольную хвойную целлюлозу [2].

В качестве облагороженной низкозольной целлюлозы волокнистая масса содержит сульфитную беленую облагороженную целлюлозу с зольностью 0,5-1,5% при следующем соотношении компонентов, мас.%: сульфатная беленая целлюлоза 75; сульфитная беленая облагороженная целлюлоза 25.

Недостатком известной волокнистой массы является то, что полученная из нее бумага требует дополнительной обработки красителями. Готовую бумагу необходимо выдерживать в течение 30 с в ванне с красителем, затем сушить таким образом, чтобы предотвратить коробление. Кроме того, указанная бумага сравнительно легко поддается старению.

Целью изобретения является повышение долговечности бумаги.

Поставленная цель достигается тем, что согласно изобретению волокнистая масса для изготовления реставрационной бумаги, содержащая сульфатную хвойную беленую целлюлозу и облагороженную низкозольную хвойную целлюлозу, согласно изобретению в качестве

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облагороженной низкозольной хвойной целлюлозы содержит сульфатную небеленую хвойную целлюлозу с зольностью 0,05-0,8% при следующем соотношении компонентов, мас.%: сульфатная беленая хвойная целлюлоза 50-95 и сульфатная небеленая хвойная целлюлоза с зольностью 0,05-0,8% 5-50.

Границные значения содержания введенной в композицию бумаги сульфатной небеленой целлюлозы определены пределами колористических свойств бумаги, подверженной естественному старению. Введение в композицию бумажной массы менее 5% сульфатной небеленой целлюлозы практически не меняет белизны и желтизны бумаги, а содержание в композиции бумажной массы более 50% указанной целлюлозы снижает белизну бумаги до 45%, что практически не характерно для старинных бумаг.

В качестве облагороженной низкозольной целлюлозы предлагаемая бумажная масса содержит целлюлозу, подвергнутую кислотному облагораживанию. Содержание минеральных примесей в целлюлозе в пределах 0,05-0,8% обусловлено невозможностью получения в производственных условиях зольности менее 0,05%, а зольность более 0,8% отрицательно влияет на долговечность бумаги. pH водной вытяжки хвойной сульфатной целлюлозы должна находиться в пределах 7,2-8,5. Указанные границы являются оптимальными с точки зрения достижения минимальной скорости старения.

Для придания бумаге необходимых физико-механических свойств в композицию бумажной массы вводят химические добавки: различного рода наполнители, проклеивающие вещества и коагулирующие вещества. Обязательным условием изготовления реставрационных видов бумаги является проведение процесса отлива в нейтральной или слабо-щелочной среде.

Пример 1. В волокнистую массу, содержащую, мас.%: сульфатная небеленая целлюлоза ГОСТ 5186-74 (марки ЭК-2) 20 с зольностью 0,45% и pH водной вытяжки 8,1 и сульфатная беленая целлюлоза ГОСТ 3914-60 (марки АС-1) 80, размолотые раздельно до 46°ШР, вводят минеральный наполнитель - мел в количестве 10% от массы волокна, канифольный клей в количестве 1% от массы волокна. Величину pH до 7,2 регулируют введением алюмината натрия и сульфата алюминия. На экспериментальной машине отливают бумагу массой 80 г/м². Бумагу в исходном состоянии и после ускоренного термического старения (72 ч при 105°C) подвергают испытаниям на оптические и физико-механические свойства.

Пример 2. В волокнистую массу, содержащую, мас.%: сульфатная небеленая целлюлоза с зольностью 0,05-5 (pH водной вытяжки 7,2) и сульфатная беленая целлюлоза 95, размолотые раздельно до 43°ШР, вводят минеральный наполнитель - каолин в количестве 20% от массы волокна и канифольный клей в количестве 2% от массы волокна. В качестве коагулянта используют уксуснокислую соль продукта конденсации дициандиамида и формальдегида в количестве 1% от массы волокна. Величину pH регулируют введением сульфата алюминия. Из подготовленной бумажной массы получают бумагу массой 60 г/м² и испытывают ее, как в примере 1.

Пример 3. В волокнистую массу, содержащую, мас.%: сульфатная небеленая целлюлоза с содержанием золы 0,8% 50 (pH водной вытяжки 8,5); сульфатная беленая целлюлоза 50, размолотые отдельно до 50°ШР, вводят мел в количестве 5% от массы волокна и канифольный клей в количестве 2% от массы волокна. Величину pH регулируют до 8,0. В качестве коагулянта используют алюминат натрия. Из приготовленной бумажной массы получают бумагу массой 60 г/м² и испытывают, как в примере 1.

Пример 4 (контрольный). В волокнистую массу, содержащую, мас.%: сульфатная небеленая целлюлоза (марки НС-1) с содержанием золы 1,5% 30 (pH водной вытяжки 7,0) и сульфатная беленая целлюлоза (марки АС-1) 70, размолотые раздельно до 48°ШР, вводят минеральный наполнитель - каолин в количестве 10% от массы волокна и канифольный клей в количестве 1%. Величину pH регулируют при помощи сернокислого алюминия до значения 7,0. В качестве коагулянта используют алюминат натрия. Из приготовленной бумажной массы получают бумагу массой 80 г/м² и испытывают, как в примере 1.

Пример 5 (прототип). Составляют композицию, содержащую, мас.%: сульфатная беленая целлюлоза 75 и сульфитная беленая облагороженная целлюлоза 25. На бумагоделательной машине изготавливают бумагу аналогично примеру 1. Полученную бумагу подвергают тонированию в ванне, содержащей 40 мл прямого красителя, коричневого светопрочного концентраций 1 г/л, 100 мл NaCl, концентраций 10 г/л, 12 мл Na₂CO₃ (10 г/л) и 848 мл дистиллированной воды. Тонирование проводят при температуре 50°C в течение 30 с. Бумагу высушивают на воздухе и затем подвергают старению.

Результаты испытаний бумаги по примерам 1-5 приведены в таблице.

Волокнистая масса для изготовления реставрационной бумаги обеспечивает получение бумаги с широким спектром белизны и оттенков желтизны. Полученная бумага хорошо сопротивляется старению, о чем свидетельствует показатель излома, который практически не меняется в период искусственного старения, в то время как из приведенных ранее работ и результатов испытаний бумаги по прототипу следует, что этот показатель уменьшается значительно (в прототипе в 2-3 раза). Повышение долговечности бумаги подтверждается также меньшим снижением белизны после искусственного старения. Так белизна тонированного реставрационного материала по прототипу снижается от 49 до 45,4% (на 3,6%), тогда как у реставрационного материала при близкой белизне по прототипу 49,5 имеет место снижение белизны после старения на 0,8% (пример 3).

| Состав волокна по примерам | Белизна бумаги, % | | Желтизна бумаги, % | | Излом бумаги, число двойных перегибов | |
|-------------------------------|----------------------|-------------------|-----------------------|-------------------|---|-------------------|
| | исход- ной | после старения | исходной | после старения | исходной | после старения |
| 1 | 58,0 | 56,7 | 10,2 | 12,8 | 67,0 | 65,0 |
| 2 | 74,0 | 70,3 | 9,0 | 12,6 | 37,0 | 36,0 |
| 3 | 49,5 | 48,7 | 10,6 | 12,6 | 147,0 | 143,0 |
| 4 | 76,3 | 69,8 | 11,6 | 14,5 | 46,0 | 20,0 |
| Прототип | | | | | | |
| а) исходная | 81,3 | 78,8 | 8,3 | 11,8 | 83,0 | 42,0 |
| б) тонированная | 49,0 | 45,4 | 12,4 | 16,8 | 61,0 | 23,0 |

Формула изобретения

Волокнистая масса для изготовления реставрационной бумаги, содержащая сульфатную хвойную беленую целлюлозу и облагороженную низкозольную хвойную целлюлозу, отличающаяся тем, что, с целью повышения долговечности бумаги, она содержит в качестве облагороженной низкозольной хвойной целлюлозы сульфатную небеленую хвойную целлюлозу с зольностью 0,05-0,8% при следующем соот-

5 Из примера 4 видно, что использование небеленой сульфатной целлюлозы с зольностью выше 0,8% не приводит к желаемому результату, т.е. падение показателей белизны, желтизны и излома при хранении бумаги более интенсивное, чем при использовании сульфатной небеленой целлюлозы с содержанием золы в пределах от 0,05 - до 0,8%.

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Падение желтизны реставрационного материала по прототипу составляет 4,4%, тогда как у материала из предлагаемой бумажной массы желтизна 15 после старения падает на 2-2,9%, что свидетельствует о долговечности предлагаемого реставрационного материала.

20 Кроме того, предлагаемая композиция позволяет упростить технологию получения реставрационного материала, так как исключается операция тонирования при сохранении колористических свойств материала.

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ношении компонентов мас.%: сульфатная беленая хвойная целлюлоза 50-95 и сульфатная небеленая хвойная целлюлоза с зольностью 0,05-0,8% 5-50.

55 Источники информации, принятые во внимание при экспертизе

1. Фляте Д.М. Свойства бумаги. М., "Лесная промышленность", 1956, с. 539.

2. Новые реставрационные материалы и методы реставрации. Сб. № 1, Л., 60 1977, с. 79-82 (прототип).



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DESCRIPTION SU979564

Pulp for making restoration paper

The enriched low-ash softwood pulp contains sulfate unbleached softwood pulp with an ash content of 0.05-0.8% in the following ratio of components, wt.-%: Sulfated bleached softwood pulp 50-95 and sulfate unbleached softwood pulp with ash, 8% 5-50. The boundary values of the content of sulfate and unbleached pulp introduced into the paper composition are determined by the limits of coloristic properties, paper subject to natural aging. The introduction of less than 5% sulfate unbleached pulp into the paper pulp composition does not practically change the whiteness and yellowness of the paper, and the content of more than 50% of the pulp in the paper pulp composition reduces the whiteness of the paper to 45%, which is practically not typical for old papers. As an enriched low-ash pulp, the proposed paper pulp contains cellulose subjected to acid treatment. The content of mineral impurities in the cellulose in the range of 0.05-0.8% is due to the impossibility of obtaining an ash content of less than 0.05% under industrial conditions, and an ash content of more than 0.8% . negatively affects paper trading. The pH of the aqueous extract of softwood sulphate pulp should be in the range of 7.2-8.5. these boundaries are optimal from the point of view of achieving a minimum aging rate.

To give the paper the necessary physical and mechanical properties, chemical additives of various kinds, fillers, sizing agents and coagulating substances are introduced into the paper pulp composition. A prerequisite for the manufacture of restoration types of paper is the process of ebb in a neutral or semi-alkaline environment. , Example 1. In fiber pulp, May su, containing, wt.-%: GOST .5186-74 sulfate unbleached pulp GOST .5186-74 (grade EK-2) 20 with an ash content of 0.45% and 8.1 aqueous extract pH and GOST 3914-60 bleached bleached pulp (mark AC-1) 80, grinded separately to .46ShR, a mineral filler is introduced - chalk in the amount of 10% by weight of the fiber, rosin glue in the amount of 1% by weight of the fiber. The pH value to 7.2 is regulated by the introduction of sodium aluminate and aluminum sulfate. On an experimental machine, paper 6 was cast with a weight of 80 g / m. The paper in its original state and after accelerated thermal aging (72 h at) is subjected to tests for optical and physico-mechanical properties.

6 Example 2 Into the pulp, containing, wt.-%: Sulfate unbleached pulp with an ash content of 0.05-5 (water extract 7.2) and sulfate bleached pulp 95, milled separately to, a mineral filler is introduced - kaolin in an amount of 20% by weight of fiber and rosin glue in an amount of 2% by weight of fiber. The coagulant used is the acetic acid salt of the condensation product of dicyandiamide and formaldehyde in an amount of 1% by weight of fiber. The pH value is regulated by the introduction of aluminum sulfate. From the prepared pulp, paper is obtained with a mass of 60 g / m and it is tested, as in example 1. PRI me R 3, In the pulp containing, wt.% Sulfate and bleached pulp with an ox content of 0.8% 50 (pH of an aqueous extract of 8.5). bleached sulphate pulp 50, ground separately, is added chalk in an amount of 5% by weight of fiber. a and rosin glue in an amount of 2% by weight of fiber. The pH is adjusted to 8.0. Sodium aluminate is used as a coagulite. From the prepared pulp, a paper of mass 6 O g / m is obtained and tested as in Example 1.

Example 4 (control). Into pulp containing May. %: sulfate unbleached pulp (grade NS-1) with an ash content of 1.5% 30 (pH of aqueous extract 7.0) and sulfate bleached pulp (grade AC-1) 70, milled separately to 48, introduce a mineral filler - kaolin in an amount of 10% by weight of fiber and rosin glue in an amount of 1%. The value of pR is regulated using aluminum sulfate to a value of 7.0. Sodium aluminate is used as a coagulant. From the prepared pulp get paper mass of 80 test, as in example 1. Example 5 (prototype). A composition is prepared containing, in wt.-%: Sulfate bleached pulp 75 and sulfite bleached enriched jcellulose 25. Paper is made on papermaking MaBmHe in the same manner as in Example 1. The resulting paper is subjected to thinning in a bath containing 40 MP of direct dye, brown lightfast concentration of 1 g / l, 100 ml of NaCl, concentration of 10 g / l, 12 ml (10 g / l) and 848 ml of distilled water. Toning is carried out at a temperature for 30 s.

The paper is dried in air and then aged.

The test results of the paper according to examples 1-5 are shown in the table.

The pulp for the manufacture of restoration paper provides paper with a wide range of whiteness and shades of yellowness. The resulting paper resists aging well, as evidenced by the kink index, which practically does not change during artificial aging, while from the previous works and the results of testing the paper on the prototype it follows that this figure decreases significantly (in the prototype by 2-3 times) The increased durability of the paper is also confirmed by a lower decrease in whiteness after artificial aging. So the whiteness of the tinted restoration material according to the prototype decreases from 49 to 45.4% (by 3.6%), while the restoration material with a close whiteness according to the prototype 49.5 has a decrease in whiteness after aging by 0.8% (example 3)

From example 4 it is seen that the use of unbleached sulfate pulp with an ash content above 0.8% does not lead to KejriaeMOMy result, that is, the decrease in whiteness, yellowness and kink during paper storage is more intense than when using sulfate unbleached pulp with ash content in ranging from 0.05 to 0.8%.

The fall in the yellowness of the restoration material according to the prototype is 4.4%, while in the case of material from the proposed paper pulp, the yellowness 15 after aging drops by 2-2, (indicates the durability of the proposed restoration material).

20 In addition, the proposed composition allows to simplify the technology of obtaining restoration material, as the operation of tinting while maintaining color

25 material properties.

Patents

(restoration) ((paper) OR (work art)) (pulp) before:publication:2014-03-27

1 of 53967 < >

[← Back to results](#) restoration; paper, work art; pulp; After: publication 1900-01-01; Before: publication 2014-03-27;

Fibrous mass for making restoration paper

SU979564A1

USSR - Soviet Union

[Download PDF](#)[Find Prior Art](#)[Similar](#)**Other languages:** Russian

Inventor: Виктор Александрович Волков, Георгий Федорович Ширянов, Наталья Владимировна Преображенская, Зинаида Петровна Дворяшина, Евгения Александровна Арсеньева, Тамерлан Станиславович Тимошук, Александр Александрович Иванов, Лариса Дмитриевна Сапиро

Worldwide applications1981 [SU](#)[Application SU813313991A events](#)

- 1981-07-09 Application filed by Центральный научно-исследовательский институт бумаги
- 1981-07-09 Priority to SU813313991A
- 1982-12-07 Application granted
- 1982-12-07 Publication of SU979564A1

Info: Cited by (1), Similar documents, Priority and Related Applications

External links: Espacenet, Global Dossier, Discuss

Claims (1)

[Hide Dependent](#) ^

1. Claim

Fibrous pulp for the manufacture of restoration paper, containing sulphate softwood bleached pulp and enriched low-ash softwood pulp, characterized in that, in order to increase the durability of paper, it contains, as an enriched low-ash softwood pulp, sulphated unbleached softwood pulp 0-0-0 ash , 8% in the following ratio of components, wt%: sulfate bleached softwood pulp _50-95 \$ 0. And sulfate unbleached softwood pulp with an ashes of 0.05-0.8% 5-50.

Description

Refined low-ash softwood pulp contains, unbleached softwood softwood pulp with an ash content of 0.05-0.8% in the following ratio, wt%: Sulfate bleached softwood pulp 50-95 and sulfate unbleached softwood pulp with ash, 8% 5-50. The boundary values of the content of unbleached pulp introduced into the paper sulphate composition are determined by the limits of color properties. paper, subject to natural aging. Introduction to the composition of paper pulp less than 5% sulfate unbleached pulp practically does not change the whiteness and yellowness of the paper, and the content in the composition of paper pulp more than 50% of the specified pulp reduces the whiteness of paper to 45%, which is practically not typical of old-fashioned papers. As a refined low-ash pulp, the proposed paper pulp contains cellulose, which is suitable for acid refining. The content of mineral impurities in cellulose in the range of 0.05-0.8% is due to the inability to produce ash less than 0.05% under production conditions, and ash more than 0.8% has a negative effect on paper trade. The pH of the aqueous extract of softwood sulphate pulp should be in the range of 7.2-8.5. The indicated limits are optimal from the point of view of achieving the minimum aging rate. In order to impart the necessary physical and mechanical properties to the paper, chemical additives of various kinds, fillers, sizing agents and coagulating agents are introduced into the composition of the pulp. An essential condition for the production of restoration types of paper is to carry out the casting process in a neutral or slightly alkaline environment. Example 1. In fiber conveyor, May Su containing, in wt%: Sulphate unbleached cellulose GOST .5186-74 (grade EK-2) 20 with ash of 0.45% and pH of the aqueous extract 8.1, and sulphate henbane pulp GOST 3914-60 (mark AC-1) 80, ground separately to. 46SR, mineral filler is introduced - chalk in the amount of 10% by weight of the fiber, rosin glue in the amount of 1% by weight of the fiber. The pH value is adjusted to 7.2 by the introduction of sodium aluminate and aluminum sulphate. On the experimental machine, paper 6 of 80. g / m is cast. The paper in its initial state and after accelerated thermal aging (72 hours at) is subjected to optical and physico-mechanical properties. 6 Example 2. In the pulp content, in wt%: Sulphate non-bleached pulp with an ash content of 0.05-5 (aqueous extract 7.2) and sulphate bleached pulp 95, milled separately until the mineral filler is added - kaolin in the amount 20% by weight of the fiber and rosin glue in the amount of 2% by weight of the fiber. As a coagulant, acetic acid salt of the condensation product of dicyandiamide and formaldehyde is used in an amount of 1% by weight of the fiber. The pH is controlled by the introduction of aluminum sulfate. Paper prepared with a mass of 60 g / m is obtained from the prepared paper pulp and tested as in Example 1. EXAMPLE 3, B pulp containing, in wt%, Sulphate paper, cellulose with an ox content of 0.8% 50 (pH water extract 8.5). sulphate henbane cellulose 50, milled separately before, introduced chalk in the amount of 5% by weight of the fiber. and rosin glue in the amount of 2% by weight of the fiber. The pH is adjusted to 8.0. Sodium aluminate is used as a coagulant. From the prepared paper pulp, paper of 6 0g / m is obtained and tested as in Example 1. Example 4 (control). In the pulp, containing, May. %: sulphate non-bleached cellulose (grade NS-1) with an ash content of 1.5% 30 (pH of the aqueous extract 7.0) and sulfate bleached cellulose (grade AC-1) 70, milled separately to 48, injected with mineral filler - kaolin in the amount of 10% by weight of the fiber and rosin glue in the amount of 1%. The RP value is adjusted with aluminum sulphate to a value of 7.0. Alumine sodium schnate is used as a

coagulant. From the prepared paper pulp, a paper weighing 80 is obtained is tested as in Example 1. Example 5 (prototype). A composition containing, in wt.-%: Sulphate henbane, cellulose 75 and sulphite henbenerated j cellulose 25, is compiled. Papermaking MaBmHe is made into paper as in Example 1, the resulting paper is subjected to toning in a bath containing 40 MP of direct dye, brown with a light-resistant concentration of 1 g / l, 100 ml of NaCl, with a concentration of 10 g / l, 12 ml (Yu g / l) and 848 ml of distilled water. Tinting is carried out at a temperature of 30 seconds. The paper is dried in air and then aged.

The test results of paper in examples 1-5 are shown in the table.

Fiber pulp for the manufacture of restoration paper provides paper with a wide range of whiteness and shades of yellow. The resulting paper is well resistant to aging, as evidenced by the fracture index, which practically does not change during the period of artificial aging, while from the earlier works and the results of testing the paper of the prototype it follows that this index decreases significantly (in the prototype in 3 times). Increased paper durability is also confirmed by a lower decrease in whiteness after artificial aging. So, the whiteness of the tinted restoration material of the prototype is reduced from 49 to 45.4% (by 3.6%), whereas for the restoration material with the close whiteness of the prototype 49.5, there is a decrease in whiteness after aging by 0.8% (Example 3).

From example 4 it can be seen that the use of unbleached sulphate pulp with an ash content above 0.8% does not lead to KejriaeMOMy result, that is, "the decrease of whiteness, yellowness and kink during storage of paper is more intense than when using sulphate unbleached pulp with ash content in ranges from 0.05 to 0.8%.

The yellowness of the restoration of the material of the prototype is 4.4%, while the material from the proposed paper pulp yellowness 15 drops by 2-2 after aging (indicating the durability of the proposed restoration material).

20 In addition, the proposed composition makes it possible to simplify the technology for obtaining a restoration material, since the operation of toning is eliminated while maintaining the color

25 material properties.

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* Cited by examiner, † Cited by third party, ‡ Family to family citation

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Priority And Related Applications

Priority Applications (1)

| Application | Priority date | Filing date | Title |
|--------------|---------------|-------------|---|
| SU813313991A | 1981-07-09 | 1981-07-09 | Fibrous mass for making restoration paper |

Applications Claiming Priority (1)

| Application | Filing date | Title |
|--------------|-------------|---|
| SU813313991A | 1981-07-09 | Fibrous mass for making restoration paper |

Concepts

machine-extracted

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|-------------------------|---|--------------------|-------|-------------|
| ■ sulfate |  | claims,description | 19 | 0 |
| ■ ash | | claims,description | 15 | 0 |
| ■ softwood | | claims,description | 12 | 0 |
| ■ manufacturing process | | claims,description | 2 | 0 |

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특허법인태평양

전체 청구항 수 : 총 19 항

심사관 : 장기완

(54) 발명의 명칭 복합체 조성물 및 복합체

(57) 요약

본 발명의 복합체 조성물은 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하는 복합체 조성물로서, 상기 섬유상 필러의 평균 섬유 지름이 4~1000nm인 것을 특징으로 한다. 상기 섬유상 필러는 셀룰로오스 섬유인 것이 바람직하다. 또, 셀룰로오스 섬유는 셀룰로오스 원료를 화학 처리 및 기계적 처리 중 적어도 한쪽에 의해 미세하여 얇어진 섬유인 것이 바람직하고, 포함되는 셀룰로오스 문자 중의 수산기의 일부가 알데히드기 및 카르복실기 중 적어도 한쪽으로 산화되어 있는 것이 바람직하다. 본 발명의 복합체는 이와 같은 복합체 조성물을 성형해서 이루어진 것이다.

(30) 우선권주장

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특허청 구의 범위

청구항 1

평균 섬유 지름이 4~1000nm인 셀룰로오스 섬유와,

상기 셀룰로오스 섬유와 혼합된, 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하는 복합체 조성물로서,

상기 셀룰로오스 섬유는 셀룰로오스 원료에 대하여 공산화제를 작용시킴으로써 미세화시키고, 셀룰로오스 분자 중의 수산기의 일부를 알데히드기 및 카르복실기 중 적어도 한쪽으로 산화하여 이루어진 것임을 특징으로 하는 복합체 조성물.

청구항 2

청구항 1에 있어서,

상기 알데히드기 및 상기 카르복실기 양의 총합은 상기 셀룰로오스 섬유의 중량에 대해 0.2~2.2mmol/g인 복합체 조성물.

청구항 3

청구항 1에 있어서,

상기 셀룰로오스 섬유는 추가로 셀룰로오스 원료를 기계적 처리함으로써 미세화시킨 것인 복합체 조성물.

청구항 4

청구항 1에 있어서,

상기 셀룰로오스 섬유는 천연 셀룰로오스를 상기 셀룰로오스 원료로서 준비하고, N-옥실 화합물을 산화 촉매로서 이용함과 함께, 수중에서 상기 천연 셀룰로오스에 대하여 상기 공산화제를 작용시킴으로써 상기 천연 셀룰로오스를 산화하여 얻어진 것인 복합체 조성물.

청구항 5

청구항 1에 있어서,

상기 셀룰로오스 섬유는 I형 결정 구조를 가지는 복합체 조성물.

청구항 6

청구항 1에 있어서,

상기 수지는 가소성 수지 및 경화성 수지 중 적어도 한쪽인 복합체 조성물.

청구항 7

청구항 1에 있어서,

상기 수지는 에폭시 수지를 포함하는 것인 복합체 조성물.

청구항 8

청구항 1에 있어서,

상기 수지는 폐놀 수지를 포함하는 것인 복합체 조성물.

청구항 9

청구항 1에 있어서,

상기 수지는 커플링제 및 이 커플링제의 가수분해물 중 적어도 한쪽을 포함하는 것인 복합체 조성물.

청구항 10

청구항 9에 있어서,

상기 커플링제는 알록시실란 또는 알록시티탄인 복합체 조성물.

청구항 11

청구항 1에 있어서,

상기 금속 산화물의 평균 입경이 1~1000nm인 복합체 조성물.

청구항 12

청구항 1에 있어서,

상기 금속 산화물은 이산화규소인 복합체 조성물.

청구항 13

청구항 1에 있어서,

상기 박편상 무기 재료는 운모, 베미큘라이트, 몬모릴로나이트, 철 몬모릴로나이트, 바이델라이트, 사포나이트, 헥토라이트, 스티븐사이트, 논트로나이트, 마가디아이트, 일러라이트, 카네마이트, 스멕타이트 및 충상 티탄산 중에서 선택되는 1종 이상인 복합체 조성물.

청구항 14

청구항 1에 있어서,

상기 복합체 조성물에서의 상기 셀룰로오스 섬유의 함유율은 0.1~99.9중량%인 복합체 조성물.

청구항 15

청구항 1에 있어서,

두께 30μm에서의 전광선 투과율이 80% 이상인 복합체 조성물.

청구항 16

청구항 1에 있어서,

30°C 내지 180°C에서의 열팽창 계수가 50ppm/°C 이하인 복합체 조성물.

청구항 17

청구항 1 내지 청구항 16 중 어느 한 항에 기재된 복합체 조성물을 성형해서 이루어지며, 두께가 10~2000μm인 것을 특징으로 하는 복합체.

청구항 18

청구항 17에 있어서,

30°C 내지 150°C에서의 열팽창 계수가 0.4~50ppm/°C인 복합체.

청구항 19

청구항 17에 있어서,

습도 팽창 계수가 100ppm/습도% 이하인 복합체.

영 세 시

기 술 문 앙

[0001] 본 발명은 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하는 복합체 조성물 및 복합체에 관한 것이다.

제 1 기술

[0002] 수지의 열선행착 계수의 저감, 또는 탄성률, 휨 강도 등의 기계적 강도를 올리기 위해서 구상 필러나 섬유상 필러를 배합하는 것이 널리 행해지고 있다. 근래, 종래의 마크로필러를 대신하는 재료로서 실리카 미립자나 금속 미립자 등의 구상의 미립자나, 막대 모양의 워스커 타입의 나노사이즈 필러에 관한 연구가 한창이다. 그렇지만 이들 필러에 대하여 섬유상의 나노 재료에 대한 연구는 보고가 적다.

[0003] 근래, 셀룰로오스를 이용한 플라스틱 대체품이 많이 보고되고 있다. 예를 들면, 고압 호모지나이저로 불리는 극히 높은 압력을 부여할 수 있는 장치를 이용하여 셀룰로오스의 피브릴상 물질을 고도로 미세화해 얻어진 셀룰로오스의 마이크로피브릴을 충전재로서 이용한 복합체, 그 외 마이크로플루이저법, 글라인더법, 동결 건조법, 강선 탄력 혼련법, 볼밀 분쇄법에 의해 다운사이징한 셀룰로오스의 마이크로피브릴을 충전재로서 이용한 복합체를 들 수 있다. 이를 충전재를 이용하면 비교적 강도가 높은 성형체가 얻어진다는 보고가 되고 있다(예를 들면, 특허문헌 1 참조).

[0004] 그렇지만, 종래의 마이크로피브릴화 방법에서는 다운사이징 처리에 다대한 에너지를 필요로 하여 비용적으로 불리한 동시에, 얻어지는 미세화 섬유의 섬유 지름에도 비교적 넓은 분포가 존재해 미세화의 정도도 불완전하다. 경우에 따라서는 $1\mu\text{m}$ 이상의 굽은 섬유도 약간 남는 경우가 있기 때문에, 마이크로피브릴 섬유 지름이나 밀도에서 특히 넓은 분포가 존재해 성형품의 강도에서 절대값의 저하나 격차가 생기는 경우가 있다.

[0005] 또, 특허문헌 2에 기재되어 있듯이 균이 생성되는 박테리아 셀룰로오스를 이용하여 투명하고 저선행착률을 가지는 섬유 강화 복합 재료가 얻어지는 것이 알려져 있다. 그렇지만, 전술한 기계적으로 셀룰로오스 마이크로피브릴을 얻는 경우와 마찬가지로, 생산 속도가 늦고 공업적 관점으로부터 생각하면 반드시 유리하다고는 말할 수 없다.

[0006] 또, 셀룰로오스는 섬유 표면에 수산기를 다수 가지기 때문에 친수성이 높고, 흡수시에 치수나 물성이 크게 변화된다. 이 때문에, 흡수시에는 복합 재료의 치수나 물성도 크게 변화해 복합 재료의 용도가 한정된다는 문제가 존재하고 있다.

성형기술 분야

특허문헌

[0007] (특허문헌 0001) 일본 공개특허 2003-201695호 공보

(특허문헌 0002) 일본 공개특허 2005-60680호 공보

발명의 내용

제 1 개혁하는 과제

[0008] 본 발명의 목적은 저열행착 계수, 고강도, 고투명성, 저습도 행착 계수(고내수성)를 가지는 복합체 조성물 및 그 성형체인 복합체를 생산 효율적으로 제공하는 것에 있다.

과제의 해결 수단

[0009] 상기 목적을 달성하기 위해서, 본 발명은

섬유상 필러와,

- [0011] 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하는 복합체 조성물로서,
- [0012] 상기 섬유상 필러의 평균 섬유 지름이 4~1000nm인 것을 특징으로 하는 복합체 조성물이다.
- [0013] 또, 본 발명의 복합체 조성물에서는 상기 섬유상 필러는 셀룰로오스 섬유인 것이 바람직하다.
- [0014] 또, 본 발명의 복합체 조성물에서는 상기 셀룰로오스 섬유는 셀룰로오스 원료를 화학 처리 및 기계적 처리 중 적어도 한쪽에 의해 미세화하여 얻어진 섬유인 것이 바람직하다.
- [0015] 또, 본 발명의 복합체 조성물에서는 상기 셀룰로오스 섬유는 포함되는 셀룰로오스 분자 중의 수산기의 일부가 알데히드기 및 카르복실기 중 적어도 한쪽으로 산화되어 있는 것이 바람직하다.
- [0016] 또, 본 발명의 복합체 조성물에서는 상기 셀룰로오스 섬유는 천연 셀룰로오스를 원료로 하고, N-옥실 화합물을 산화 촉매로서 이용하는 동시에, 수중에서 상기 원료에 공산화제를 작용시킴으로써 상기 원료를 산화하여 얻어진 것이 바람직하다.
- [0017] 또, 본 발명의 복합체 조성물에서는 상기 수지는 가소성 수지 및 경화성 수지 중 적어도 한쪽인 것이 바람직하다.
- [0018] 또, 본 발명의 복합체 조성물에서는 상기 수지는 에폭시 수지를 포함하는 것이 바람직하다.
- [0019] 또, 본 발명의 복합체 조성물에서는 상기 수지는 폐놀 수지를 포함하는 것이 바람직하다.
- [0020] 또, 본 발명의 복합체 조성물에서는 상기 수지는 커플링제 및 이 커플링제의 가수분해물 중 적어도 한쪽을 포함하는 것이 바람직하다.
- [0021] 또, 본 발명의 복합체 조성물에서는 상기 커플링제는 알콕시실란 또는 알콕시티탄인 것이 바람직하다.
- [0022] 또, 본 발명의 복합체 조성물에서는 상기 금속 산화물의 평균 입경이 1~1000nm인 것이 바람직하다.
- [0023] 또, 본 발명의 복합체 조성물에서는 상기 금속 산화물은 이산화규소인 것이 바람직하다.
- [0024] 또, 본 발명의 복합체 조성물에서는 상기 박편상 무기 재료는 운모, 베미큘라이트, 몬모릴로나이트, 철 몬모릴로나이트, 바이엘라이트, 사포나이트, 헥토라이트, 스티븐사이트, 녹트로나이트, 마가디아이트, 일러라이트, 카네마이트, 스黠타이트 및 층상 티탄산 중에서 선택되는 1종 이상인 것이 바람직하다.
- [0025] 또, 본 발명의 복합체 조성물에서는 상기 복합체 조성물에서의 상기 섬유상 필러의 함유율은 0.1~99.9중량%인 것이 바람직하다.
- [0026] 또, 본 발명의 복합체 조성물에서는 두께 30μm에서의 전광선 투과율이 80% 이상인 것이 바람직하다.
- [0027] 또, 본 발명의 복합체 조성물에서는 30°C 내지 180°C에서의 열팽창 계수가 50ppm/°C 이하인 것이 바람직하다.
- [0028] 상기 목적을 달성하기 위해서, 본 발명은 상기 복합체 조성물을 성형해서 이루어지며, 두께가 10~2000μm인 것을 특징으로 하는 복합체이다.
- [0029] 또, 본 발명의 복합체에서는 30°C 내지 150°C에서의 열팽창 계수가 0.4~50ppm/°C인 것이 바람직하다.
- [0030] 또, 본 발명의 복합체에서는 습도 팽창 계수가 100ppm/습도% 이하인 것이 바람직하다.

발명을 실시하기 위한 구체적인 내용

- [0031] 이하, 본 발명의 복합체 조성물 및 복합체의 바람직한 실시형태에 대해서 상세하게 설명한다.
- [0032] 본 발명의 복합체 조성물은 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함한다. 그리고, 본 발명의 복합체는 이 복합체 조성물을 소정의 형상으로 성형함으로써 제조된 것이다.
- [0033] <복합체 조성물>
- [0034] (섬유상 필러)
- [0035] 우선, 섬유상 필러에 대해서 설명한다.
- [0036] 본 발명에 이용되는 섬유상 필러의 평균 섬유 지름은 4~1000nm이고, 4~300nm인 것이 바람직하며, 4~200nm인 것

이 보다 바람직하다. 또한, 평균 섬유 지름이 상기 상한값을 웃돌면 투명성이 악화되는 동시에 기계적인 강도의 향상이 보여지지 않는다. 한편, 평균 섬유 지름이 상기 하한값을 밀돌아도 상관없지만, 그러한 섬유상 필러를 얻는 것은 곤란하다.

[0037] 본 발명에 이용되는 섬유상 필러의 길이에 대해서는 특별히 한정되지 않지만, 섬유상 필러의 평균 길이가 100nm 이상이면 보강 효과가 얻어지기 쉬워 강도의 향상이 도모된다.

[0038] 여기서, 섬유상 필러의 평균 섬유 지름의 측정은 이하와 같이 하여 실시할 수 있다.

[0039] 우선, 고형분율로 0.05~0.1중량%인 섬유상 필러의 분산체를 조제하고, 이 분산체를 카본막 피복 그리드 상에 캐스트하여 TEM 관찰용 시료로 한다. 또, 큰 섬유 지름의 섬유상 필러를 포함하는 경우에는 유리 상에 캐스트하여 SEM 관찰용 시료로 해도 된다.

[0040] 현미경 관찰시에는 구성하는 섬유상 필러의 크기(섬유 지름)에 따라 5000배, 10000배 혹은 50000배 중 어느 하나의 배율로 전자 현미경 화상을 취득한다. 이때에 얻어진 화상 내에 종횡 임의의 화상 폭의 축을 상정했을 경우에 적어도 축에 대해 20개 이상의 섬유상 필러가 축과 교차하도록 시료 조건 및 관찰 조건(배율 등)을 설정한다.

[0041] 그리고, 이 조건을 만족하는 관찰 화상에 대해 1매의 화상당 종횡 2개씩의 무작위인 축을 끌어 각 축에 교차하는 섬유상 필러의 섬유 지름을 눈으로 봐서 읽어낸다. 또한, 시료 표면에 대해서 서로 중복하지 않도록 관찰 위치를 옮기면서 최저 3매의 관찰 화상을 취득해 각 화상에 대해서 각각 상기와 같이 하여 섬유 지름을 읽어낸다. 이에 의해, 최저 20개×2×3=120개의 섬유상 필러에 대해서 섬유 지름의 정보가 얻어진다. 이와 같이 하여 얻어진 섬유 지름의 데이터에 기초하여 평균 섬유 지름을 산출한다.

[0042] 본 발명에 이용되는 섬유상 필러는 어떠한 섬유여도 되지만, 바람직하게는 셀룰로오스 섬유로 구성된 것이다.

[0043] 셀룰로오스 섬유로는 천연 셀룰로오스 섬유, 재생 셀룰로오스 섬유 등을 들 수 있다. 한편, 셀룰로오스 섬유 이외의 섬유로는 예를 들면, 키친 섬유, 키토산 섬유 등을 들 수 있다.

[0044] 이 중, 천연 셀룰로오스 섬유로는 침엽수나 광엽수로부터 얻어지는 정제 펄프, 코튼 런터나 코튼 런트로부터 얻어지는 셀룰로오스 섬유, 바로니아나 시오그사 등의 해초로부터 얻어지는 셀룰로오스 섬유, 호야로부터 얻어지는 셀룰로오스 섬유, 박테리아를 생산하는 셀룰로오스 섬유 등을 들 수 있다. 한편, 재생 셀룰로오스 섬유로는 천연 셀룰로오스 섬유를 일단 용해한 후, 셀룰로오스 조성인 채로 섬유상으로 재생한 것을 들 수 있다.

[0045] 또, 본 발명에 이용되는 셀룰로오스 섬유는 고결정성인 것이 바람직하게 이용된다. 이와 같은 셀룰로오스 섬유는 특히 선행창률이 작고, 기계적 강도가 높아지기 때문에 섬유상 필러로서 바람직하게 이용된다. 또한, 이러한 관점으로부터 본 발명에 이용되는 셀룰로오스 섬유로는 재생 셀룰로오스 섬유보다도 천연 셀룰로오스 섬유가 바람직하다.

[0046] 또, 본 발명에 이용되는 셀룰로오스 섬유로는 공지의 어떠한 방법으로 얻어진 것이어도 되고, 그 제법은 특별히 한정되지 않지만, 일례로서 셀룰로오스 원료(천연 셀룰로오스 또는 재생 셀룰로오스)를 매체 교반 밀 처리장치, 진동 밀 처리 장치, 고압 호모지나이저 처리 장치, 초고압 호모지나이저 처리 장치 등의 각종 미세화 장치에 의해 기계적으로 미세화한 것이 이용된다. 또, 다른 방법으로서 일렉트로스피닝법, 스팀제트법, APEX(등록 상표) 기술(Polymer Group. Inc.)법 등에 의해 얻어진 셀룰로오스 섬유를 이용할 수도 있다. 그렇지만, 에너지 효율 등을 고려하면, 셀룰로오스 원료로는 이하에 나타내는 화학적인 처리를 수반하는 방법에 의해 얻어진 셀룰로오스 섬유가 가장 바람직하다.

[0047] 이하에서 설명하는 셀룰로오스 섬유의 제작 방법은 셀룰로오스 원료에 화학적 처리를 실시한 후, 기계적 처리에 제공함으로써 분산매 중에 분산시켜 셀룰로오스 섬유(나노 셀룰로오스 섬유)를 제작하는 방법이다.

[0048] 구체적으로는 [1] 천연 셀룰로오스를 원료로 하고, 수중에서 N-옥실 화합물을 산화 촉매로 하여 공산화제를 작용시킴으로써 천연 셀룰로오스를 산화하여 반응물 섬유를 얻는 산화 반응 공정과, [2] 불순물을 제거하고 물을 함침시킨 반응물 섬유를 얻는 정제 공정과, [3] 물을 함침시킨 반응물 섬유를 분산매에 분산시키는 분산 공정을 가진다. 이하에 각 공정에 대해서 상세하게 설명한다.

[1] 산화 반응 공정

[0050] 우선, 산화 반응 공정에서는 수중에 셀룰로오스 원료를 분산시킨 분산액을 조제한다. 여기서, 이용되는 셀룰로오스 원료에는 미리 고해(叩解) 등의 표면적을 높이는 처리를 실시한 것이 바람직하게 이용된다. 이에 의해 반

응 효율을 높일 수 있어 생산성을 높일 수 있기 때문이다. 또, 셀룰로오스 원료로는 단리, 정제 후 네바드라이로 보존하고 있던 것을 사용하는 것이 바람직하다. 이에 의해, 셀룰로오스 원료를 구성하는 마이크로피브릴의 수렴체가 팽윤하기 쉬운 상태가 되기 때문에 역시 반응 효율을 높여 미세화 처리 후의 수 평균 섬유 지름을 작게 할 수 있다.

[0051] 또한, 본 공정에서의 셀룰로오스 원료의 분산매로서 물을 이용했을 경우, 분산액(반응 수용액) 중의 셀룰로오스 농도는 시약의 충분한 확산이 가능한 농도이면 임의이지만, 통상 분산액의 중량에 대해서 5중량% 이하이다.

[0052] 또, 셀룰로오스의 산화 촉매로서 사용 가능한 N-옥실 화합물은 다수 보고되고 있다. 예를 들면, 「Cellulose」 Vol. 10, 2003년, 제335~341페이지에서의 I.Shibata 및 A.Isoyai에 의한 「TEMPO 유도체를 이용한 셀룰로오스의 촉매 산화: 산화 생성물의 HPSEC 및 NMR 분석」이라는 제목의 기사에 기재된 TEMPO(2,2,6,6-테트라메틸-1-페페리딘-N-옥실), 4-아세트아미드-TEMPO, 4-카르복시-TEMPO 및 4-포스포노옥시-TEMPO의 각종 N-옥실계 화합물 촉매는 수중에서의 상온에서의 반응 속도에서 바람직하게 이용된다. 또한, 이들 N-옥실 화합물의 첨가는 촉매량으로 충분하고, 바람직하게는 0.1~4mmol/l, 보다 바람직하게는 0.2~2mmol/l의 범위에서 반응 수용액에 첨가된다.

[0053] 또, 공산화제로는 예를 들면, 차아할로겐산 또는 그의 염, 아할로겐산 또는 그의 염, 과할로겐산 또는 그의 염, 과산화수소 및 과유기산 등을 들 수 있지만, 특히 알칼리 금속 차아할로겐산염, 구체적으로는 차아염소산 나트륨이나 차아브롬산 나트륨 등이 바람직하게 이용된다. 차아염소산 나트륨을 사용하는 경우 브롬화 알칼리 금속, 예를 들어 브롬화 나트륨의 존재 하에서 반응을 진행시키는 것이 반응 속도에 있어서 바람직하다. 이 브롬화 알칼리 금속의 첨가량은 N-옥실 화합물에 대해서 바람직하게는 약 1~40배 몰량, 보다 바람직하게는 약 10~20배 몰량이 된다.

[0054] 또, 반응 수용액의 pH는 약 8~11의 범위에서 유지되는 것이 바람직하다. 수용액의 온도는 약 4~40°C의 범위에서 임의이지만, 반응은 실온에서 실시하는 것이 가능하고, 특히 온도 제어는 필요로 하지 않는다.

[0055] 공산화제에 의해 셀룰로오스 분자에는 수산기를 치환하도록 카르복실기가 도입되지만, 본 발명에 사용되는 미세 셀룰로오스 섬유를 얻음에 있어서는 셀룰로오스 원료의 종류에 따라 필요하게 되는 카르복실기 양이 상이하기 때문에 그것에 따라 공산화제의 첨가량이나 공산화제를 작용시키는 시간을 설정하면 된다. 구체적으로는 카르복실기 양이 많을수록 최종적으로 얻어지는 셀룰로오스 섬유의 최대 섬유 지름 및 수 평균 섬유 지름은 작아지므로, 그것을 고려해 설정하면 된다.

[0056] 예를 들면, 셀룰로오스 원료로서 목재 펄프 및 면계 펄프를 이용하는 경우, 필요하게 되는 카르복실기 양은 셀룰로오스 원료에 대해서 0.2~2.2mmol/g이며, 셀룰로오스 원료로서 박테리아 셀룰로오스(BC)나 호야로부터의 추출 셀룰로오스를 이용하는 경우, 필요하게 되는 카르복실기 양은 0.1~0.8mmol/g가 된다. 이와 같이 셀룰로오스 원료의 종류에 따라서 공산화제의 첨가량과 반응 시간을 제어함으로써 각 셀룰로오스 원료에 최적인 카르복실기 양을 도입할 수 있다.

[0057] 또한, 이상과 같은 카르복실기의 도입량에 근거하면, 공산화제의 첨가량을 유도할 수 있고, 일례로서 셀룰로오스 원료 1g에 대해서 약 0.5~8mmol의 공산화제를 첨가하는 것이 바람직하고, 반응 시간은 약 5~120분, 길어도 240분 이내로 하는 것이 바람직하다.

[0058] 또, 본 산화 반응 공정을 거친으로써, 셀룰로오스 분자에는 카르복실기가 도입되지만, 산화 처리의 진행 정도에 따라서는 알데히드기가 도입되는 경우도 있다. 따라서, 본 산화 반응 공정 종료 후 셀룰로오스 분자의 수산기는 알데히드기 및 카르복실기 중 적어도 한쪽으로 치환되어 있게 된다.

[2] 정제 공정

[0060] 정제 공정에 있어서는 반응 슬러리 중에 포함되는 반응물 섬유와 물 이외의 화합물, 구체적으로는 미반응 차아염소산이나 각종 부생성물 등과 같은 화합물을 계외로 제거하는 것을 목적으로 한다. 반응물 섬유는 통상 이 단계에서는 나노 섬유(nanofiber) 단위까지 뿐만 아니라 흩어지게 분산되어 있는 것은 아니기 때문에, 통상의 정제법, 즉 세정과 여과를 반복함으로써 고순도(99중량% 이상)화를 도모할 수 있다.

[0061] 본 정제 공정에서의 정제 방법은 원심 탈수를 이용하는 방법과 같이 상술한 목적을 달성할 수 있는 장치(예를 들면, 연속식 디켄더)이면 어떠한 장치를 이용해도 상관없다. 이렇게 하여 얻어지는 반응물 섬유는 쥐어짠 상태의 고형분(셀룰로오스) 농도로서 대략 10~50중량%의 범위에 있다. 또한, 이후의 공정에서 나노 섬유 단위로 분산시키는 것을 고려하면, 50중량%보다 높은 고형분 농도로 하는 것은 분산에 극히 높은 에너지가 필요해지기 때문에 바람직하지 않다.

- [0062] [3] 분산 공정
- [0063] 상술한 공정에 있어서는 물을 함침시킨 반응물 섬유가 얻어지지만, 이것을 용매 중에 분산시켜 분산 처리를 실시함으로써 본 발명에 이용되는 미세 셀룰로오스 섬유가 분산체 상태로 얻어진다.
- [0064] 여기서, 분산매로서의 용매는 통상은 물이 바람직하지만, 물 이외에도 목적에 따라 물에 가용되는 알코올류(메탄올, 에탄올, 이소프로판올, 이소부탄올, sec-부탄올, tert-부탄올, 메틸셀로솔브, 에틸셀로솔브, 에틸렌글리콜, 글리세린 등), 에테르류(에틸렌글리콜 디메틸에테르, 1,4-디옥산, 테트라히드로푸란 등), 켐톤류(아세톤, 메틸에틸케톤), N,N-디메틸포름아미드, N,N-디메틸아세트아미드, 디메틸설폭시드 등이어도 된다. 또, 이들 혼합물도 바람직하게 사용할 수 있다.
- [0065] 또, 상술한 반응물 섬유 용매에 의해 회석, 분산시킬 때에는 조금씩 용매를 가해 분산시켜 나간다는 단계적인 분산을 실시함으로써, 효율적으로 나노 섬유 레벨의 섬유의 분산체를 얻을 수 있다. 또한, 조작상 문제로부터 분산 공정 후에는 분산체가 접성이 있는 상태 혹은 겔상이 되도록 분산 조건을 선택하면 된다.
- [0066] 여기서, 분산 공정에서 사용되는 분산기로는 다양한 것을 사용할 수 있다. 구체예를 나타내면, 반응물 섬유에서의 반응의 진행도(알데히드기나 카르복실기로의 변환량)에도 의존하지만, 바람직하게 반응이 진행되는 조건 하에서는 스크류형 믹서, 페들 믹서, 디스퍼터형 믹서, 터빈형 믹서 등의 공업 생산기로서의 범용 분산기로 충분히 미세 셀룰로오스 섬유의 분산체를 얻을 수 있다.
- [0067] 또, 호모 믹서, 고압 호모지나이저, 초고압 호모지나이저, 초음파 분산 처리, 비터, 디스크형 리파이너, 코니칼형 리파이너, 더블 디스크형 리파이너, 그라인더와 같은 고속 회전 하에서 강력한 고해 능력을 가지는 장치를 사용함으로써, 보다 효율적이면서 고도의 다운사이징이 가능해진다. 나아가, 이를 장치를 사용함으로써 알데히드기나 카르복실기의 도입량이 비교적 작은 경우(예를 들면, 알데히드기나 카르복실기의 셀룰로오스에 대한 총 합량으로서 0.1~0.5mmol/g)에도, 고도로 미세화된 미세 셀룰로오스 섬유의 분산체를 제공할 수 있다.
- [0068] 다음에, 미세 셀룰로오스 섬유를 분산매 중에 분산시킨 분산체로부터 미세 셀룰로오스 섬유를 회수하는 방법에 대해서 설명한다.
- [0069] 구체적으로는 상술한 미세 셀룰로오스 섬유의 분산체를 건조시킴으로써 미세 셀룰로오스 섬유를 회수할 수 있다.
- [0070] 여기서 건조에는 예를 들면, 분산매가 물인 경우에는 동결 건조법, 분산매가 물과 유기용매의 혼합액인 경우에는 드럼 드라이어에 의한 건조나 경우에 따라서는 스프레이 드라이어에 의한 분무 건조를 바람직하게 사용할 수 있다.
- [0071] 또, 상술한 미세 셀룰로오스 섬유의 분산체 중에는 바인더로서 수용성 고분자(폴리에틸렌옥사이드, 폴리비닐알코올, 폴리아크릴아미드, 카르복시메틸 셀룰로오스, 히드록시에틸 셀룰로오스, 히드록시프로필 셀룰로오스, 메틸 셀룰로오스, 전분, 천연 검류 등), 당류(글루코오스, 프룩토오스, 만노오스, 갈락토오스, 트레할로오스 등)를 첨가하도록 해도 된다. 이를 바인더 성분은 극히 비점이 높고 게다가 셀룰로오스에 대해서 친화성을 가지기 때문에 이를 성분을 분산체 중에 첨가함으로써, 드럼 드라이어나 스프레이 드라이어와 같은 범용의 건조법으로 건조시켰을 경우에도, 재차 분산매 중에 분산시켰을 때의 응집이 방지되어 나노 섬유로서 분산된 미세 셀룰로오스 섬유의 분산체를 확실히 얻을 수 있다. 이 경우에는 분산체 중에 첨가되는 바인더의 양은 반응물 섬유에 대해서 10~80중량%의 범위에 있는 것이 바람직하다.
- [0072] 또한, 회수된 미세 셀룰로오스 섬유는 다시 분산매(물이나 유기용매 혹은 이들 혼합액) 중에 혼입하고 적당한 분산력을 가함으로써(예를 들면, 상술한 분산 공정에서 사용되는 각종 분산기를 이용한 분산을 실시함), 미세 셀룰로오스 섬유의 분산체로 할 수 있다.
- [0073] 본 발명에 사용되는 미세 셀룰로오스 섬유는 셀룰로오스의 수산기의 일부가 카르복실기 또는 알데히드기로 산화되어 있고, 또한 셀룰로오스 I형 결정 구조를 가지는 것이 바람직하다. 또한, 미세 셀룰로오스 섬유가 I형 결정 구조를 가지는 것은 천연 유래의 셀룰로오스 고체 원료를 표면 산화하여 미세화시킨 섬유인 것을 의미한다.
- [0074] 또, 미세 셀룰로오스 섬유가 I형 결정 구조를 가지는 것은 그 광각 X선 회절상 측정에 의해 얻어지는 회절 프로파일에 있어서, $2\theta=14\sim17^\circ$ 부근과 $2\theta=22\sim23^\circ$ 부근의 두 개의 위치에 전형적인 피크를 가지는 것에 기초하여 동정(同定)할 수 있다. 또한 미세 셀룰로오스 섬유의 셀룰로오스에 알데히드기 혹은 카르복실기가 도입되어 있는 것은 수분을 완전히 제거한 샘플에 대한 전반사식 적외 분광 스펙트럼(ATR)에서 카르보닐기에 기인하는 흡수

(1608cm⁻¹ 부근)가 존재함으로써 확인할 수 있다. 특히, 셀룰로오스에 산 형의 카르복실기(-COOH)가 도입되어 있는 경우에는 상기 측정에서 1730cm⁻¹에 흡수가 존재한다.

[0075] 미세한 셀룰로오스 섬유는 상술한 이유에 의해 셀룰로오스에 존재하는 카르복실기와 알데히드기 양의 총합이 많으면 많을수록, 보다 미소한 섬유 지름으로서 안정하게 존재할 수 있다. 예를 들면 목재 펄프나 면 펄프의 경우, 미세한 셀룰로오스 섬유에 존재하는 카르복실기와 알데히드기 양의 총합(이하, 생략해서 「총합량」이라고 함)이 셀룰로오스 섬유의 중량에 대해 0.2~2.2mmol/g, 바람직하게는 0.5~2.2mmol/g, 더욱 바람직하게는 0.8~2.2mmol/g이면, 나노 섬유로서의 안정성이 뛰어난 셀룰로오스 섬유가 얻어진다. 또, BC나 호야로부터의 추출 셀룰로오스와 같은 마이크로피브릴의 섬유 지름이 비교적 굵은 셀룰로오스의 경우(평균 섬유 지름이 수 10nm 수준)에는 총합량은 0.1~0.8mmol/g, 바람직하게는 0.2~0.8mmol/g이면, 나노 섬유로서의 안정성이 뛰어난 셀룰로오스 섬유가 얻어진다. 또한, 총합량이 상기 하한값보다도 작은 경우에는 종래 알려져 있는 미세화된 셀룰로오스 섬유와의 물성상 차이(예를 들면, 분산체에서의 분산 안정화 효과)도 작아지는 동시에 미소한 섬유 지름의 섬유로서 얻어지기 어려워지기 때문에 바람직하지 않다.

[0076] 또한, 비이온성 치환기인 알데히드기에 대해 카르복실기가 도입됨으로써 전기적인 반발력이 생겨난다. 이에 의해, 마이크로피브릴이 응집을 유지하지 않고 뿐뿐이 흩어지려고 하는 경향이 증대하기 때문에 나노 섬유의 분산체로서의 안정성은 보다 증대한다. 예를 들면 목재 펄프나 면 펄프의 경우, 미세한 셀룰로오스 섬유에 존재하는 카르복실기의 양이 셀룰로오스 섬유의 중량에 대해 0.2~2.2mmol/g, 바람직하게는 0.4~2.2mmol/g, 더욱 바람직하게는 0.6~2.2mmol/g이면, 나노 섬유로서의 안정성이 극히 뛰어난 셀룰로오스 섬유가 얻어진다. 또, BC나 호야로부터의 추출 셀룰로오스와 같은 마이크로피브릴의 섬유 지름이 비교적 굵은 셀룰로오스의 경우에는 카르복실기의 양은 0.1~0.8mmol/g, 바람직하게는 0.2~0.8mmol/g이면 나노 섬유로서의 안정성이 뛰어난 셀룰로오스 섬유가 얻어진다.

[0077] 여기서, 셀룰로오스 섬유의 중량에 대한 셀룰로오스의 알데히드기 및 카르복실기의 양(mmol/g)은 이하의 수법에 의해 평가한다.

[0078] 건조 중량을 정칭한 셀룰로오스 시료를 이용해 농도가 0.5~1중량%인 슬러리를 60ml 조제하고 0.1M의 염산 수용액에 의해 pH를 약 2.5로 한 후, 0.05M의 수산화나트륨 수용액을 적하하여 슬러리의 전기 전도도 측정을 실시한다. 이 측정은 pH가 약 11이 될 때까지 계속한다. 전기 전도도의 변화가 완만한 약산의 중화 단계에서 소비된 수산화나트륨 양(V)으로부터 아래 식을 이용해 관능기량을 산출한다. 여기서 산출된 관능기량을 「관능기량 1」이라고 한다. 이 관능기량 1이 카르복실기의 양을 나타낸다.

$$\text{관능기량}(\text{mmol/g}) = V(\text{ml}) \times 0.05 / \text{셀룰로오스의 중량(g)}$$

[0080] 다음에, 셀룰로오스 시료를 아세트산에 의해 pH 4~5로 조제한 2% 아염소산 나트륨 수용액 중에서 추가로 48시간 상온에서 산화하여, 상기 수법에 의해 다시 관능기량을 산출한다. 여기서 산출된 관능기량을 「관능기량 2」라고 한다. 그리고, 이 산화에 의해 추가된 관능기량(= 관능기량 2 - 관능기량 1)을 산출한다. 이 관능기량이 알데히드기의 양을 나타낸다.

[0081] (수지)

[0082] 본 발명에서 이용되는 수지로는 공지의 것을 이용할 수 있고, 특별히 한정되지는 않지만 각종 경화성 수지, 각종 가소성 수지, 각종 수용성 수지 등을 포함하는 것을 들 수 있다.

[0083] 수용성 수지로는 물에 용해되는 것이면 특별히 한정되지 않고, 열가소성 수지, 경화성 수지, 천연 고분자 등을 들 수 있지만, 바람직하게는 폴리비닐알코올, 폴리에틸렌옥시드, 폴리아크릴아미드, 폴리비닐피롤리돈과 같은 합성 고분자, 전분류, 알긴산류와 같은 다당류, 목재의 구성 성분인 헤미셀룰로오스, 젤라틴, 니카와, 카제인을 비롯한 단백질과 같은 천연 고분자 등을 들 수 있다.

[0084] 또, 열가소성 수지로는 특별히 한정되는 것은 아니지만, 예를 들면 염화비닐 수지, 아세트산비닐 수지, 폴리스티렌, ABS 수지, 아크릴 수지, 폴리에틸렌, 폴리에틸렌 테레프탈레이트, 폴리에틸렌 나프탈레이트, 폴리프로필렌, 불소 수지, 폴리아미드 수지, 열가소성 폴리아미드 수지, 폴리아세탈 수지, 폴리카보네이트, 폴리젖산, 폴리글리콜산, 폴리-3-히드록시 부티레이트, 폴리히드록시 발리레이트, 폴리에틸렌 아디페이트, 폴리카프로락톤, 폴리프로필락톤 등의 폴리에스테르, 폴리에틸렌글리콜 등의 폴리에테르, 폴리글루타민산, 폴리리진 등의 폴리아미드 등을 들 수 있다.

- [0085] 한편, 경화성 수지로는 예를 들면, 폐놀 수지, 우레아 수지, 멜라민 수지, 불포화 폴리에스테르 수지, 에폭시 수지, 아크릴 수지, 옥세탄 수지, 디알릴 프탈레이트 수지, 폴리우레탄 수지, 규소 수지, 말레이미드 수지, 열경화성 폴리이미드 수지 등을 들 수 있다.
- [0086] 이 중, 아크릴 수지로는 아크릴산, 메타크릴산, 메틸 아크릴레이트, 메틸 메타크릴레이트와 같은 알킬 아크릴레이트 또는 알킬 메타크릴레이트 외, 환상 아크릴레이트 또는 메타크릴레이트, 히드록시에틸 아크릴레이트 등을 1종 이상 포함하는 수지를 들 수 있다.
- [0087] 또, 폐놀 수지는 분자 내에 폐놀성 수산기를 1개 이상 가지는 유기 화합물이다. 예를 들면, 노볼락이나 비스페놀류, 나프톨이나 나프톨을 분자 내에 가지는 수지, 파라크실릴렌 변성 폐놀 수지, 디메틸렌에테르형 레졸, 메틸올형 폐놀 등의 레졸 수지를 들 수 있다. 또, 이를 수지를 추가로 메틸올화시킨 화합물, 폐놀성 수산기를 1개 이상 포함하는 리그닌이나 리그닌 유도체, 리그닌 분해물, 또한 리그닌이나 리그닌 유도체, 리그닌 분해물을 변성한 것 혹은 이것들을 석유 자원으로부터 제조된 폐놀 수지와 혼합한 것을 포함하는 수지를 들 수 있다.
- [0088] 또, 에폭시 수지는 적어도 1개의 에폭시기를 가지는 유기 화합물이다. 예를 들면, 비스페놀 A형 에폭시 수지, 비스페놀 F형 에폭시 수지, 비스페놀 S형 에폭시 수지 등의 비스페놀형 에폭시 수지, 이를 비스페놀형 에폭시 수지의 수첨화물(水添化物), 디시클로펜타디엔 골격을 가지는 에폭시 수지, 트리글리시딜 이소시아누레이트 골격을 가지는 에폭시 수지, 카르드 골격을 가지는 에폭시 수지, 폴리실록산 구조를 가지는 에폭시 수지, 지환식 다관능 에폭시 수지, 수첨 비페닐 골격을 가지는 지환식 에폭시 수지, 수첨 비스페놀 A 골격을 가지는 지환식 에폭시 수지 등을 들 수 있다.
- [0089] 또, 본 발명에서 이용되는 수지는 각종 커플링제여도 된다.
- [0090] 커플링제로는 공지의 것을 이용할 수 있지만, 실란계 커플링제, 티탄계 커플링제, 지르코늄계 커플링제, 알루미늄계 커플링제 등을 들 수 있고, 이를 중에서도 실란계 커플링제 또는 티탄계 커플링제가 바람직하게 이용된다. 이것들은 비교적 입수가 용이하고, 무기 재료와 유기 재료의 계면에서의 접착성이 높기 때문에 복합체 조성물에 포함되는 커플링제로서 매우 적합하다.
- [0091] 또, 상기 커플링제 가운데 실란계 커플링제는 적어도 규소 원자를 1개 이상, 관능기로서 알콕시기를 1개 이상 포함하고 있는 것이 바람직하다. 또, 그 이외의 관능기로는 에폭시기 혹은 에폭시 시클로헥실기, 아미노기, 수산기, 아크릴기, 메타크릴기, 비닐기, 폐닐기, 스티릴기, 이소시아네이트기 등을 들 수 있다. 또한, 본 발명에 있어서는 커플링제와 동등한 효과가 얻어지는 것으로부터, 알콕시기를 4개 포함하는 테트라알콕시실란도 실란 커플링제에 포함된다.
- [0092] 실란계 커플링제의 구체예로는 테트라알콕시실란 화합물, 메틸트리알콕시실란, 디메틸디알콕시실란과 같은 알킬기 함유 알콕시실란 화합물, 3-글리시독시프로필 트리알콕시실란, 3-글리시드프로필메틸 디알콕시실란, 2-(3,4-에폭시시클로헥실)에틸 트리알콕시실란 등의 에폭시실란 화합물, 3-아미노프로필 트리알콕시실란, N-페닐-3-아미노프로필 트리알콕시실란과 같은 아미노알콕시실란 화합물, 3-아크릴옥시프로필 트리알콕시실란, 메타크릴옥시프로필 트리알콕시실란, 3-메타크릴옥시프로필메틸 디알콕시실란, 3-메타크릴옥시프로필 트리알콕시실란과 같은 (메타)아크릴알콕시실란 화합물, 비닐트리알콕시실란과 같은 비닐알콕시실란 화합물, 폐닐트리알콕시실란, 디페닐디알콕시실란, 4-히드록시페닐 트리알콕시실란과 같은 폐닐기 함유 트리알콕시실란 화합물, 3-이소시아네이트프로필 트리알콕시실란과 같은 스티릴기 함유 알콕시실란 화합물 등이 예시된다. 이를 중에서도, 테트라알콕시실란 화합물, 알킬기 함유 알콕시실란 화합물, 폐닐기 함유 알콕시실란 화합물이 내수성을 높이는 효과가 높아 바람직하다.
- [0093] 한편, 티탄계 커플링제의 구체예로는 알콕시실란 화합물과 동일한 치환기를 가지는 알콕시티탄 화합물을 들 수 있다. 예를 들면, 이소프로필 트리이소스테아로일 티타네이트, 이소프로필 트리도데실벤젠설헬포닐 티타네이트, 이소프로필 트리스(디옥틸파이로포스페이트) 티타네이트, 테트라이소프로필 비스(디옥틸포스페이트) 티타네이트, 테트라옥틸 비스(디트리테일포스페이트) 티타네이트, 이소프로필 트리옥타노일 티타네이트, 이소프로필 디메타크릴 이소스테아로일 티타네이트, 이소프로필 이소스테아로일 디아크릴티타네이트, 이소프로필 트리(디옥틸포스페이트) 티타네이트, 이소프로필 트리크실페닐 티타네이트, 이소프로필 트리(N-아미노에틸-아미노에틸) 티타네이트, 디쿠밀페닐옥시아세테이트 티타네이트, 디이소스테아로일 에틸렌티타네이트, 비스(디옥틸파이로포스페이트) 에틸렌티타네이트, 비스(디옥틸파이로포스페이트) 옥시아세테이트 티타네이트, 테트라(2,2-디알릴옥시메틸-1-부틸) 비스(디-트리테일) 포스페이트 티타네이트 등을 들 수 있다.
- [0094] 또, 커플링제 대신에 상술한 바와 같이 커플링제의 가수분해물을 이용해도 된다. 커플링제 또는 그 가수분해물

의 선택은 분산매 등과의 상용성, 가수분해물의 안정성 등을 감안해 적당히 실시하면 된다. 또한, 커플링제의 가수분해물은 아세트산 수용액 등의 산성 수용액을 커플링제와 교반 혼합함으로써 용이하게 작성할 수 있다. 또, 커플링제의 가수분해물로는 가수분해성기(알록시드기)를 가수분해한 것이 아니더라도 분자 구조가 커플링제의 가수분해물과 동일하면 어떠한 방법으로 제작된 것이어도 된다.

[0095] 또한, 상술한 수용성 수지, 열가소성 수지, 경화성 수지 및 커플링제는 각각 개별적으로 이용할 수도, 또는 2 이상을 조합해 이용할 수도 있다.

(금속 산화물)

[0097] 본 발명에서 이용되는 금속 산화물은 그 종류가 특별히 한정되는 것은 아니지만, SiO_2 (실리카), Al_2O_3 (알루미나), TiO_2 (티타니아), ZrO_2 (지르코니아) 등의 단일 금속의 산화물을 비롯해 $\text{SiO}_2\text{-Al}_2\text{O}_3$ (무라이트 등), $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-ZrO}_2$, 스페넬 등의 복합 산화물, 티타니아 내포 실리카, 지르코니아 내포 실리카 등을 들 수 있다.

[0098] 이와 같은 금속 산화물은 어떠한 형태를 이루고 있어도 되지만, 바람직하게는 입자상으로 된다. 이 경우, 금속 산화물의 입자를 1종의 산화물 미립자로 구성할 뿐만 아니라, 2종 이상의 산화물을 미립자를 혼합한 혼합물로 구성해도 된다. 이와 같은 산화물 미립자는 졸겔법, 습식법, 기상법, 건식법 등의 방법에 의해 얻을 수 있다.

[0099] 상기 금속 산화물 중에서도 특히 SiO_2 , Al_2O_3 혹은 이들의 복합 산화물을 이용하는 것이 바람직하다. 이것들은 비교적 저렴할 뿐만 아니라, 복합체의 기계적 강도, 내열성, 내마모성의 향상을 도모할 수 있다.

[0100] 특히, 복합체의 내마모성을 향상시키기 위해서는 금속 산화물로서 Al_2O_3 의 미립자를 이용하는 것이 바람직하다. 이 미립자는 가장 저렴하며, 또한 산 및 알칼리에 의한 부식에 강하기 때문에 복합체의 화학적 안정성을 높일 수 있다.

[0101] 또한, 복합체가 전자 부품 등의 용도에 제공되는 경우에는 금속 산화물로서 SiO_2 의 미립자(실리카 미립자)를 이용하는 것이 바람직하다. 이 미립자는 저유전율이기 때문에 복합체의 유전율을 저하시켜 전자 부품에서의 전송 지연 등을 억제할 수 있다.

[0102] 실리카 미립자로는 건조한 분말상의 실리카 미립자, 용매에 분산된 콜로이달 실리카(실리카졸)를 들 수 있다. 분산성의 점에서 물 또는 유기용매, 혹은 이를 혼합 용매에 분산된 콜로이달 실리카(실리카졸)를 이용하는 것이 바람직하다. 용매로는 예를 들면, 물, 메탄올, 에탄올, 이소프로필 알코올, 부틸 알코올, n-프로필 알코올 등의 알코올류, 케톤류, 에스테르류, 글리콜 에테르류를 들 수 있지만, 섬유상 필러의 분산의 용이함으로부터 적당한 용매를 선택할 수 있다.

[0103] 이와 같은 금속 산화물의 평균 입경은 1~1000nm가 바람직하고, 투명성과 작업성의 벨런스의 점에서 보다 바람직하게는 1~50nm, 더욱 바람직하게는 5~50nm, 가장 바람직하게는 5~40nm가 된다. 또한, 상기 하한값 미만에서는 제작된 복합체 조성물의 점도가 극단적으로 증대할 우려가 있다. 한편, 상기 상한값을 넘으면 복합체의 투명성이 현저하게 악화될 우려가 있으므로 바람직하지 않다.

[0104] 또, 금속 산화물로서 실리카 미립자를 이용하는 경우, 파장 400~500nm의 광선 투과율을 저하시키지 않기 위해 1차 입경이 200nm 이상인 실리카 미립자의 비율을 5% 이하로 억제한 실리카 미립자를 이용하는 것이 바람직하고, 그 비율을 0%로 하는 것이 보다 바람직하다. 실리카 미립자의 충전량을 올리기 위해서 평균 입경이 상이한 실리카 미립자를 혼합해 이용해도 된다. 또, 실리카 미립자로서 일본 특개 평7-48117호 공보에 나타내는 바와 같은 다공질 실리카졸이나, 알루미늄, 마그네슘, 아연 등과 규소의 복합 금속 산화물을 이용해도 된다.

(박편상 무기 재료)

[0106] 본 발명에서 이용되는 박편상 무기 재료로는 예를 들면, 천연물 또는 합성물로 이루어진 점토 광물을 들 수 있다. 구체적으로는 운모, 베미큘라이트, 몬모릴로나이트, 철 몬모릴로나이트, 바이델라이트, 사포나이트, 헥토라이트, 스티븐사이트, 논트로나이트, 마가디아이트, 일러라이트, 카네마이트, 층상 티탄산, 스黠타이트 등으로 이루어진 군으로부터 선택되는 적어도 1종을 들 수 있다.

[0107] 박편상 무기 재료는 형상이 비늘 조각상인 것으로서 대표적으로는 입자 1개의 두께가 약 1~10nm, 어스펙트비가 바람직하게는 20~수천, 보다 바람직하게는 20~수백인 비늘 조각상의 입자가 된다. 이와 같은 비늘 조각상의 점토 입자가 복합체 중에 어떠한 층에도 겹침으로써, 가스가 통과하는 경로가 길어져 결과적으로 복합체의 가스

배리어성이 향상된다.

[0108] 또, 복합체 조성물 중의 박편상 무기 재료의 충간에는 필요에 따라 소수성을 가지는 양이온 물질을 포함하도록 해도 된다. 일반적으로 점토 광물은 충간에 친수성의 교환성 양이온을 포함하고 있다. 본 발명에서는 점토 광물인 박편상 무기 재료의 충간에 존재하는 친수성의 교환성 양이온을 소수성의 양이온으로 물질 교환해 유기화시킬 수 있다. 소수성의 양이온 물질로는 예를 들면, 디메틸디스테아릴 암모늄염, 트리메틸스테아릴 암모늄염 등의 제4급 암모늄염이나, 벤질기나 폴리옥시에틸렌기를 가지는 암모늄염을 이용하거나 포스포늄염이나 피리디늄염이나 이미다졸륨염을 사용해 점토의 이온 교환성을 이용하여 유기화할 수도 있다.

[0109] 또한, 본 발명의 복합체 조성물은 전술한 수지, 금속 산화물 및 박편상 무기 재료 가운데 어느 하나를 포함하고 있어도 되고, 2 이상을 포함하고 있어도 된다. 예를 들면, 본 발명의 복합체 조성물은 섬유상 필러와 수지와 금속 산화물과 박편상 무기 재료를 포함하는 것이어야 된다.

[0110] 본 발명의 복합체 조성물에서는 섬유상 필러의 함유율이 0.1~99.9중량%인 것이 바람직하고, 0.1~75중량%인 것이 보다 바람직하다. 또한, 섬유상 필러의 함유율은 특별히 한정되는 것은 아니고, 복합체 조성물을 성형했을 때에 필요해지는 특성에 따라 적절히 조정된다. 복합체 조성물에서 섬유상 필러의 특성을 보다 반영시키고 싶은 경우에는 섬유상 필러의 함유율을 증가시키고, 수지의 특성을 보다 반영시키고 싶은 경우에는 수지의 함유율을 증가시키면 된다.

[0111] 또, 본 발명의 복합체 조성물을 이용하여 광학 용도에 이용되는 복합체를 제조하는 경우에는 복합체 조성물의 30~180°C의 평균 열팽창 계수(평균 선행창 계수)가 50ppm/°C 이하인 것이 바람직하고, 보다 바람직하게는 30ppm/°C 이하, 더욱 바람직하게는 20ppm/°C 이하가 된다.

[0112] 또, 본 발명의 복합체 조성물은 두께 30μm에서의 전광선 투과율이 80% 이상인 것이 바람직하고, 90% 이상인 것이 보다 바람직하다. 이에 의해, 최종적으로 투명성이 높고, 광학 용도에 적절한 복합체가 얻어진다.

<복합체>

[0114] 본 발명의 복합체 조성물을 소정의 형상으로 성형함으로써, 본 발명의 복합체가 얻어진다.

[0115] 본 발명의 복합체는 예를 들면, 태양 전지용 기판, 유기 EL용 기판, 전자 페이퍼용 기판, 액정 표시 소자용 플라스틱 기판으로서 이용되지만, 이 경우 등에 있어서는 전광선 투과율이 70% 이상인 것이 바람직하고, 보다 바람직하게는 80% 이상이며, 더욱 바람직하게는 88% 이상이다.

[0116] 또, 본 발명의 복합체를, 예를 들면 광학 용도, 즉 투명판, 광학 렌즈, 액정 표시 소자용 플라스틱 기판, 컬러 필터용 기판, 유기 EL 표시 소자용 플라스틱 기판, 태양 전지 기판, 터치 패널, 광학 소자, 광도파로, LED 봉지재 등으로서 이용하는 경우 등에 있어서는 30~150°C의 평균 열팽창 계수(평균 선행창 계수)가 50ppm/°C 이하인 것이 바람직하고, 보다 바람직하게는 30ppm/°C 이하이다. 특히 시트상 액티브 매트릭스 표시 소자 기판에 이용하는 경우에는 상기 평균 열팽창 계수가 30ppm/°C 이하인 것이 바람직하고, 보다 바람직하게는 20ppm/°C 이하가 된다. 상기 상한값을 넘으면, 제조 공정에서 흙이나 배선의 단선 등의 문제가 생길 우려가 있기 때문이다. 또한, 하한값은 특별히 설정되지는 않지만, 일례로서 0.4ppm/°C가 된다.

[0117] 또, 본 발명의 복합체를, 예를 들면 액정 표시 소자용 플라스틱 기판, 컬러 필터용 기판, 유기 EL 표시 소자용 플라스틱 기판, 태양 전지 기판, 터치 패널 등으로서 이용하는 경우 등에 있어서는 습도 팽창 계수는 바람직하게는 100ppm/습도% 이하이고, 보다 바람직하게는 50ppm/습도% 이하이며, 더욱 바람직하게는 30ppm/습도% 이하이다. 나아가서는, 본 발명 복합체의 흡수시에서의 팽윤율(팽윤 배율)은 바람직하게는 50배 이하, 보다 바람직하게는 30배 이하, 더욱 바람직하게는 10배 이하가 된다.

[0118] 또, 본 발명의 복합체를 판상으로 성형했을 경우, 그 두께는 10~2000μm인 것이 바람직하고, 10~500μm인 것이 보다 바람직하며, 20~200μm인 것이 더욱 바람직하다. 기판의 두께가 이 범위 내에 있으면, 본 발명의 복합체는 투명 기판으로서 필요하고 또한 충분한 기계적 강도와 광투과성을 겸비한 것이 된다. 또, 기판의 두께를 상기 범위 내로 함으로써, 평탄성이 뛰어나고, 유리 기판과 비교하여 기판의 경량화를 도모할 수 있다.

[0119] 본 발명의 복합체 조성물을 광학 시트로서 이용하는 경우, 평활성 향상을 위해서 양면에 수지의 코트층을 마련해도 된다. 코트하는 수지로는 뛰어난 투명성, 내열성, 내약품성을 가지고 있는 것이 바람직하고, 구체적으로는 다관능 아크릴레이트나 에폭시 수지 등을 들 수 있다. 코트층의 평균 두께는 0.1~50μm인 것이 바람직하고, 0.5~30μm인 것이 보다 바람직하다.

- [0120] 또, 본 발명의 복합체 조성물로부터 얻은 광학 시트를 특히 표시 소자용 플라스틱 기판으로서 이용하는 경우에 필요에 따라 수증기나 산소에 대한 가스 배리어층이나 투명 전극층을 마련해도 된다.
- [0121] 본 발명의 복합체 조성물이 경화성 수지를 포함하는 경우, 경화성 수지의 경화 방법은 특별히 한정되지 않지만, 산 무수물이나 지방족 아민 등의 가교제, 또는 양이온계 경화 촉매, 혹은 음이온계 경화 촉매 등의 경화 촉진제를 이용할 수 있다.
- [0122] 이중, 양이온계 경화 촉매로는 예를 들면 가열에 의해 양이온 중합을 개시시키는 물질을 방출하는 것(예를 들면 오늄염계 양이온 경화 촉매 또는 알루미늄 칼레이트계 양이온 경화 촉매)나, 활성 에너지선에 의해 양이온 중합을 개시시키는 물질을 방출시키는 것(예를 들면 오늄염계 양이온계 경화 촉매 등)을 들 수 있다. 구체적으로는 방향족 설포늄염으로는 삼신화학공업제의 SI-60L, SI-80L, SI-100L, 아사히전화공업제의 SP-66이나 SP-77 등의 헥사플루오로안티모네이트염 등을 들 수 있고, 알루미늄 칼레이트로는 에틸아세트아세테이트 알루미늄디이소프로필레이트, 알루미늄 트리스(에틸아세트아세테이트) 등을 들 수 있고, 3불화붕소아민 착체로는 3불화붕소 모노에틸아민 착체, 3불화붕소 이미다졸 착체, 3불화붕소페리딘 착체 등을 들 수 있다.
- [0123] 한편, 음이온계 경화 촉진제로는 예를 들면 1,8-디아자-비시클로(5,4,0)운데센-7, 트리에틸렌디아민 등의 3급 아민류, 2-에틸-4-메틸이미다졸이나 1-벤질-2-페닐이미다졸 등의 이미다졸류, 트리페닐포스핀, 테트라페닐포스포늄 테트라페닐보레이트 등의 인화합물, 4급 암모늄염, 유기 금속염류 및 이들 유도체 등을 들 수 있고, 이들 중에서도 투명성이 뛰어난 것으로부터 인화합물이나 1-벤질-2-페닐이미다졸 등의 이미다졸류가 바람직하다. 이들 경화 촉진제는 단독으로 이용해도 2종 이상을 병용해도 된다.
- [0124] 본 발명의 복합체 조성물에서는 필요에 따라 열가소성 또는 열경화성 올리고머나 폴리머를 병용할 수 있다. 또, 본 발명의 복합체 조성물 중에는 필요에 따라 특성을 해치지 않는 범위에서 소량의 산화 방지제, 자외선 흡수제, 염안료, 다른 무기 필러 등의 충전제 등을 포함하고 있어도 된다.
- [0125] 본 발명의 복합체 조성물은 임의의 방법에 의해 각 성분을 혼합함으로써 제조된다. 예를 들면, 섭유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 그대로 혼합하는 방법을 들 수 있다. 또, 필요에 따라서 가열하면서 혼합하도록 해도 된다.
- [0126] 또, 용매(분산매)를 이용해 섭유상 필러의 균일 분산액을 조제하고, 후에 탈용매를 실시하는 방법을 이용하면, 섭유상 필러의 분산성 및 금속 산화물이나 박편상 무기 재료의 분산성이 뛰어난 균일한 복합체 조성물을 얻을 수 있다.
- [0127] 이용하는 용매로는, 예를 들면 섭유상 필러의 분산성을 유지할 수 있고, 또한 수지, 금속 산화물 및 박편상 무기 재료를 용해 또는 분산시킬 수 있는 용매가 바람직하다. 이와 같은 용매로는 예를 들면, 물, 메틸알코올, 에틸알코올, 이소프로필알코올, 에틸렌글리콜, 프로필렌글리콜, 디에틸렌글리콜, 디옥산, 아세톤, 메틸에틸케톤, 메틸셀로솔브, 테트라하드로푸란, 펜타에리트리톨, 디메틸설클록시드, 디메틸포름아미드, N-메틸-2-피롤리돈 등을 들 수 있고, 이것들을 단독 혹은 2종류 이상 혼합해 이용할 수도 있다. 또, 원래 분산매의 분극률을 목적으로 하는 분산매의 극성으로 서서히 변화시켜 섭유상 필러를 상이한 극성의 분산매에 분산시키는 것도 가능하다.
- [0128] 나아가 본 발명의 복합체 조성물을 이용하여 태양 전지용 기판, 유기 EL용 기판, 전자 페이퍼용 기판, 액정 표시 소자용 플라스틱 기판 등의 소정의 두께를 가지는 시트를 얻는 방법은 일반적인 시트 형성 방법이면 되고, 특별히 한정되지 않는다. 예를 들면 섭유상 필러와 수지, 금속 산화물 및 박편상 무기 재료를 포함하는 복합체 조성물을 그대로 시트화하는 방법이나, 섭유상 필러의 분산매를 유연(流延)하고 용매를 제거하여 섭유상 필러의 시트를 얻고, 후에 수지를 함침시키는 방법, 또는 섭유상 필러와 수지, 금속 산화물 및 박편상 무기 재료와 용매를 포함하는 용액을 유연한 후, 용매를 제거하여 시트를 얻는 방법 등을 들 수 있다.
- [0129] 그와 같은 프로세스에 있어서 바람직한 태양의 하나로는 섭유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 미리 용매 중에 분산시켜 분산액을 조제한 후, 얻어진 분산액을 여과지, 멤브레인 필터 또는 초망 등에 유연하고, 용매 등의 그 외 성분을 여별 및/또는 건조시켜 복합체 조성물로 이루어진 시트를 얻는 방법이다. 또한, 상기 여별 건조 공정에서는 작업 효율을 높이기 위해 감압 하, 가압 하에서 실시해도 상관없다. 또, 연속적으로 형성하는 경우에는 제지 업계에서 사용되는 초지기를 이용해 박층 시트를 연속적으로 형성하는 방법도 포함된다.
- [0130] 유연하여 시트를 제작하는 경우, 여별 및/또는 건조 후에 형성된 시트가 용이하게 박리될 수 있는 기재 상에 제작되는 것이 바람직하다. 이와 같은 기재로는 금속제 또는 수지제인 것을 들 수 있다. 금속제 기재로는 스테인

레스제 기재, 황동제 기재, 아연제 기재, 구리제 기재, 철제 기재 등을 들 수 있고, 수지제 기재로는 아크릴성 기재, 불소계 기재, 폴리에틸렌테레프탈레이트제 기재, 염화비닐제 기재, 폴리스티렌성 기재, 폴리염화비닐리멘제 기재 등을 들 수 있다.

[0131] 실시예

[0132] 다음에, 본 발명의 구체적 실시예에 대해서 설명한다.

[0133] [미세 셀룰로오스 섬유의 제작 A]

[제작예 A)

[0135] 우선, 주로 1000nm를 넘는 섬유 지름의 셀룰로오스 섬유로 이루어지고, 건조 중량으로 2g 상당분의 미건조 펄프와 0.025g의 TEMPO(2,2,6,6-테트라메틸-1-피페리딘-N-옥실)과 0.25g의 브롬화나트륨을 물 150mℓ에 분산시켜 분산액을 조제했다.

[0136] 다음에, 이 분산액에 대해서 13중량% 차아염소산 나트륨 수용액을 1g의 펄프에 대해서 차아염소산 나트륨의 양이 2.5mmol가 되도록 가해 반응을 개시했다. 반응중에는 분산액 중에 0.5M의 수산화나트륨 수용액을 적하여 pH를 10.5로 유지하도록 했다. 그 후, pH에 변화가 보여지지 않게 된 시점에서 반응 종료라고 보고 반응물을 유리 필터로 여과하고, 여과물을 충분한 양의 물로 세정하는 동시에 여과를 5회 반복했다. 이에 의해, 고형분 농도 25중량%의 물을 포함하는 반응물 섬유를 얻었다.

[0137] 다음에, 얻어진 반응물 섬유에 물을 가해 2중량% 슬러리를 조제했다. 그리고 이 슬러리에 대해서 회전 칼날식 믹서로 약 5분간 처리를 실시했다. 처리에 수반해 현저하게 슬러리의 점도가 상승했기 때문에 조금씩 물을 가해서 가 고형분 농도가 0.2중량%가 될 때까지 믹서에 의한 분산 처리를 계속했다. 이에 의해 셀룰로오스 나노 섬유 분산액을 얻었다.

[0138] 이 셀룰로오스 나노 섬유 분산액을 친수 처리를 완료한 카본막 피복 그리드 상에 캐스트한 후, 2% 우라닐아세테이트로 네가티브 염색했다. 그리고, 캐스트한 셀룰로오스 나노 섬유 분산액을 TEM으로 관찰했는데 최대 섬유 지름이 10nm, 수 평균 섬유 지름이 6nm였다.

[0139] 또, 캐스트한 셀룰로오스 나노 섬유 분산액을 견조시켰는데, 투명한 막상 셀룰로오스가 얻어졌다. 이 막상 셀룰로오스에 대해서 광각 X선 회절상을 얻었는데, 막상 셀룰로오스가 셀룰로오스 I형 결정 구조를 가지는 셀룰로오스 나노 섬유로 이루어진 점이 분명해졌다.

[0140] 또, 동일한 막상 셀룰로오스에 대해서 전반사식 적외 분광 분석을 실시해 ATR 스펙트럼을 얻었다. ATR 스펙트럼의 패턴에서는 카르보닐기의 존재가 확인되어 상술한 방법에 의해 평가한 셀룰로오스 중의 알데히드기의 양 및 카르복실기의 양은 각각 0.31mmol/g 및 0.97mmol/g였다.

[0141] [복합체의 제작 A]

(실시예 1A)

[0143] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 10중량부)을 감압 여과해 물을 제거하고 메탄올로 5회 치환했다. 다음에, 셀룰로오스 나노 섬유 메탄올 분산액을 감압 여과해 메탄올을 제거하고, 추가로 열 양이온 촉매(SI-100L)를 1중량부 함유하는 치환식 에폭시 모노머 90중량부로 치환하는 작업을 5회 반복했다. 그리고, 얻어진 셀룰로오스 나노 섬유 분산 에폭시 수지(셀룰로오스 고형분량 10중량%)를 주형하고 100℃에서 2시간 가열한 후, 추가로 150℃에서 2시간 가열해 경화시켰다. 이에 의해, 두께 1mm의 복합체를 얻었다. 얻어진 복합체를 폭 10mm로 절단하고, 휨 강도 측정용 테스트 피스를 제작했다. 이 테스트 피스에 대해서 휨 강도를 측정하면 48N였다.

(실시예 2A)

[0145] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 15중량부)을 감압 여과해 물을 제거하고 추가로 동결 견조함으로써 셀룰로오스 나노 섬유를 얻었다. 다음에, 페놀 노볼락 수지 85중량부, 헥사메틸렌테트라민 15중량부에 셀룰로오스 나노 섬유를 15중량부 첨가해 얻어진 혼합물을 믹서로 3분간 혼합했다. 또한 혼합물을 100℃의 2개의 가열 룰에 의해 혼련하여 열경화성 수지 성형 재료를 얻었다. 얻어진 성형 재

료를 압축 성형에 의해 125°C에서 2시간 가열한 후, 추가로 150°C에서 2시간 가열해 경화시켰다. 이에 의해, 두께 1mm의 복합체를 얻었다. 얻어진 복합체를 폭 10mm로 절단해 휨 강도 측정용 테스트 피스를 제작했다. 이 테스트 피스에 대해서 휨 강도를 측정하면 60N였다.

[0146] (실시예 3A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)에 테트라에톡시실란을 셀룰로오스 나노 섬유 고형분 중량과 동일한 중량 첨가하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수를 측정했는데, 전광선 투과율은 90%, 열선팽창 계수는 11ppm/°C, 습도 팽창 계수는 26ppm/습도%였다.

[0148] (실시예 4A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)에 페닐트리에톡시실란을 셀룰로오스 나노 섬유 고형분 중량과 동일한 중량 첨가하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수를 측정했는데, 전광선 투과율은 89%, 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 23ppm/습도%였다.

[0150] (실시예 5A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)에 3-글리시독시프로필 트리에톡시실란을 셀룰로오스 나노 섬유 고형분 중량과 동일한 중량 첨가하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수를 측정했는데, 전광선 투과율은 89%, 열선팽창 계수는 11ppm/°C, 습도 팽창 계수는 25ppm/습도%였다.

[0152] (실시예 6A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)에 티탄알록사이드를 셀룰로오스 나노 섬유 고형분 중량과 동일한 중량 첨가하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수를 측정했는데, 전광선 투과율은 88%, 열선팽창 계수는 12ppm/°C, 습도 팽창 계수는 27ppm/습도%였다.

[0154] (실시예 7A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 에폭시 수지(데나콜 EX-214L, 나가세켐텍스사제) 80중량부와 테트라메틸에틸렌디아민 5중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 80%, 열선팽창 계수는 15ppm/°C, 습도 팽창 계수는 110ppm/습도%, 팽윤율은 16배였다.

[0156] (실시예 8A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 에폭시 수지(데나콜 EX-1410L, 나가세켐텍스사제) 110중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 80%, 열선팽창 계수는 14ppm/°C, 습도 팽창 계수는 61ppm/습도%, 팽윤율은 1.8배였다.

[0158] (실시예 9A)

[0159] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 에폭시 수지(테나콜 EX-1410L, 나가세켐텍스사제) 110중량부와 테트라메틸에틸렌디아민 5중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50 μm 의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 80%, 열선팽창 계수는 12ppm/°C, 습도 팽창 계수는 90ppm/습도%, 팽윤율은 3.1배였다.

[0160] (실시예 10A)

[0161] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 에폭시 수지(테나콜 EX-1610L, 나가세켐텍스사제) 110중량부와 테트라메틸에틸렌디아민 5중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50 μm 의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 80%, 열선팽창 계수는 13ppm/°C, 습도 팽창 계수는 76ppm/습도%, 팽윤율은 2.4배였다.

[0162] (실시예 11A)

[0163] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 레졸형 폐놀수지(PR-967, 스미토모베이클라이트제) 100중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 25 μm 의 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 50%, 습도 팽창 계수는 50ppm/습도%, 팽윤율은 1.2배였다. 또한, 본 샘플은 물렸기 때문에, 열팽창 계수 측정용 샘플을 얻을 수 없었다.

[0164] (실시예 12A)

[0165] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 레졸형 폐놀수지(PR-967, 스미토모베이클라이트제) 300중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 58 μm 의 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 40%, 열선팽창 계수는 20ppm/°C, 습도 팽창 계수는 45ppm/습도%, 팽윤율은 1.2배였다.

[0166] (비)교예 1A)

[0167] 아황산 표백 침엽수 펄프를 물에 팽윤 후, 믹서로 세세하게 분산했다. 얻어진 단섬유 펄프 분산액을 감압 여과해 물을 제거하고 메탄올로 5회 치환했다. 다음에, 단섬유 펄프 메탄올 분산액을 감압 여과해 메탄올을 제거하고 열양이온 촉매(SI-100L)를 1중량부 함유하는 지환식 에폭시 모노머 90중량부로 치환하는 작업을 5회 반복했다. 그리고, 얻어진 단섬유 펄프 분산 애폭시 수지(셀룰로오스 고형분량 10중량%)를 주형에 100°C에서 2시간 가열한 후, 추가로 150°C에서 2시간 가열해 경화시켰다. 이에 의해, 두께 1mm의 복합체를 얻었다. 얻어진 복합체를 폭 10mm로 절단해 휨 강도 측정용 테스트 피스를 제작했다. 이 테스트 피스에 대해서 휨 강도를 측정하면 28N였다.

[0168] 또한, 단섬유 펄프 메탄올 분산액을 SEM으로 관찰했는데, 최대 섬유 지름이 70 μm , 수 평균 섬유 지름이 40 μm 였다.

[0169] (비)교예 2A)

[0170] 아황산 표백 침엽수 펄프를 물에 팽윤 후, 믹서로 세세하게 분산했다. 얻어진 단섬유 펄프 분산액을 감압 여과해 물을 제거하고, 추가로 동결 건조함으로써 미세 셀룰로오스 섬유를 얻었다. 다음에, 폐놀 노볼락 85중량부, 헥사메틸렌테트라민 15중량부에 미세 셀룰로오스 섬유를 15중량부 첨가해 얻어진 혼합물을 믹서로 3분간 혼합했다. 또한, 혼합물을 100°C의 2개의 가열 롤에 의해 혼련하여 열경화성 수지 성형 재료를 얻었다. 얻어진 성형 재료를 압축 성형에 의해 125°C에서 2시간 가열한 후, 추가로 150°C에서 2시간 가열해 경화시켰다. 이에 의해, 두께 1mm의 복합체를 얻었다. 얻어진 복합체를 폭 10mm로 절단해 휨 강도 측정용 테스트 피스를 제작했다. 이 테스트 피스에 대해서 휨 강도를 측정하면 40N였다.

[0171] 또한, 단섬유 펄프 메탄올 분산액을 SEM으로 관찰했는데, 최대 섬유 지름이 70 μm , 수 평균 섬유 지름이 40 μm 였다.

다.

[0172] (비)교예 3A)

[0173] 제작예 A에서 얻어진 셀룰로오스 나노 섬유 분산액(고형분량 0.15중량%)을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 125ppm/습도%, 팽윤율은 140배였다.

[0174] [미세 셀룰로오스 섬유의 제작 B]

[0175] (제작예 B)

[0176] 우선, 주로 1000nm를 넘는 섬유 지름의 셀룰로오스 섬유로 이루어지고, 건조 중량으로 2g 상당분의 미건조 필프와 0.025g의 TEMPO(2,2,6,6-테트라메틸-1-페페리딘-N-옥실)과 0.25g의 브롬화나트륨을 물 150mℓ에 분산시켜 분산액을 조제했다.

[0177] 다음에, 이 분산액에 대해서 13중량% 차아염소산 나트륨 수용액을 1g의 필프에 대해서 차아염소산 나트륨의 양이 2.5mmol가 되도록 가해 반응을 개시했다. 반응 중에는 자동 적정 장치를 이용해 0.5M의 수산화나트륨 수용액을 적하해 pH를 10.5로 유지하도록 했다. 그 후, pH에 변화가 보여지지 않게 된 시점에서 반응 종료라고 보고 0.5M의 염산 수용액으로 pH 7로 중화했다. 그리고, 반응물을 여과하고 여과물을 충분한 양의 물로 세정하는 동시에 여과를 6회 반복했다. 이에 의해, 고형분 농도 2중량%의 물을 포함하는 반응물 섬유를 얻었다.

[0178] 다음에, 얻어진 반응물 섬유에 물을 가해 0.2중량%의 반응물 섬유 분산액을 조제했다.

[0179] 이 반응물 섬유 분산액을 고압 호모지나이저(APV GAULIN LABORATORY제, 15MR-8TA형)를 이용해 압력 200bar(20MPa)로 20회 처리했다. 이에 의해, 투명한 셀룰로오스 나노 섬유 분산액을 얻었다.

[0180] 이 셀룰로오스 나노 섬유 분산액을 친수 처리를 완료한 카본막 피복 그리드 상에 캐스트 후, 2% 우라닐아세테이트로 네가티브 염색했다. 그리고, 캐스트한 셀룰로오스 나노 섬유 분산액을 TEM으로 관찰했는데, 최대 섬유 지름이 10nm, 수 평균 섬유 지름이 8nm였다.

[0181] 또, 캐스트한 셀룰로오스 나노 섬유 분산액을 건조시켰는데, 투명한 막상 셀룰로오스가 얻어졌다. 이 막상 셀룰로오스에 대해서 광각 X선 회절상을 얻었는데, 막상 셀룰로오스가 셀룰로오스 I형 결정 구조를 가지는 셀룰로오스 나노 섬유로 이루어진 것이 분명해졌다.

[0182] 또, 동일한 막상 셀룰로오스에 대해서, 전반사식 적외 분광 분석을 실시해 ATR 스펙트럼을 얻었다. ATR 스펙트럼의 패턴으로부터는 카르보닐기의 존재가 확인되어 상술한 방법에 의해 평가한 셀룰로오스 중의 알데히드기 양 및 카르복실기 양은 각각 0.31mmol/g 및 1.7mmol/g였다.

[0183] [복합체의 제작 B]

[0184] (실시예 1B)

[0185] 제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 20, 입자 지름 10~20nm, 무수 규산 함유량 20~21wt%, 낮산화학공업사제) 1중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 87%, 30°C~180°C의 범위에서의 열선팽창 계수는 9ppm/°C, 습도 팽창 계수는 70ppm/습도%, 팽윤율은 2배였다.

[0186] (실시예 2B)

[0187] 제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 N, 입자 지름 10~20nm, 무수 규산 함유량 20~21wt%, 낮산화학공업사제) 1중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오

분에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 30°C~180°C의 범위에서의 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 61ppm/습도%, 팽윤율은 1.6배였다.

[0188] (실시예 3B)

제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 0, 입자 지름 10~20nm, 무수 규산 함유량 20~21wt%, 낫산화학공업사제) 1중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 90%, 30°C~180°C의 범위에서의 열선팽창 계수는 11ppm/°C, 습도 팽창 계수는 65ppm/습도%, 팽윤율은 1.7배였다.

[0189] (실시예 4B)

제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 XS, 입자 지름 4~6nm, 무수 규산 함유량 20~21wt%, 낫산화학공업사제) 1중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 89%, 30°C~180°C의 범위에서의 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 68ppm/습도%, 팽윤율은 1.9배였다.

[0190] (실시예 5B)

제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 CM, 입자 지름 20~30nm, 무수 규산 함유량 30~31wt%, 낫산화학공업사제) 0.7중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 88%, 30°C~180°C의 범위에서의 열선팽창 계수는 11ppm/°C, 습도 팽창 계수는 70ppm/습도%, 팽윤율은 1.9배였다.

[0191] (비)교예 1B)

제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 30°C~180°C의 범위에서의 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 115ppm/습도%, 팽윤율은 100배였다.

[0192] [미세 셀룰로오스 섬유의 제작 C]

[0193] (제작예 C)

우선, 주로 1000nm를 넘는 섬유 지름의 섬유로 이루어지고, 건조 중량으로 2g 상당분의 미건조 펄프와 0.025g의 TEMPO(2,2,6,6-테트라메틸-1-페페리딘-N-옥실)과 0.25g의 브롬화나트륨을 물 150mL에 분산시켜 분산액을 조제했다.

다음에, 이 분산액에 대해서 13중량% 차아염소산 나트륨 수용액을 1g의 펄프에 대해서 차아염소산 나트륨의 양이 2.5mmol가 되도록 가해 반응을 개시했다. 반응 중에는 자동 적정 장치를 이용해 0.5M의 수산화나트륨 수용액을 적하해 pH를 10.5로 유지하도록 했다. 그 후, pH에 변화가 보여지지 않게 된 시점에서 반응 종료라고 보고 0.5M의 염산 수용액으로 pH 7로 중화했다. 그리고, 반응물을 여과하고 여과물을 충분한 양의 물에 의해 세정하는 동시에, 여과를 6회 반복했다. 이에 의해, 고형분량 2중량%의 물을 포함하는 반응물 섬유를 얻었다.

[0200] 다음에, 얻어진 반응물 섬유에 물을 가해 0.2중량%의 반응물 섬유 분산액을 조제했다.

- [0201] 이 반응물 섬유 분산액을 고압 호모지나이저(APV GAULIN LABORATORY제, 15MR-8TA형)를 이용해 압력 20MPa로 10회 처리했다. 이에 의해, 투명한 셀룰로오스 나노 섬유 분산액을 얻었다.
- [0202] 이 셀룰로오스 나노 섬유 분산액을 친수 처리를 완료한 카본막 피복 그리드 상에 캐스트 후, 2% 우라닐아세테이트로 네가티브 염색했다. 그리고, 캐스트한 셀룰로오스 나노 섬유 분산액을 TEM으로 관찰했는데, 최대 섬유 지름이 10nm, 수 평균 섬유 지름이 6nm였다.
- [0203] 또, 캐스트한 셀룰로오스 나노 섬유 분산액을 건조시켰는데, 투명한 막상 셀룰로오스가 얻어졌다. 이 막상 셀룰로오스에 대해서 광각 X선 회절상을 얻었는데, 막상 셀룰로오스가 셀룰로오스 I형 결정 구조를 가지는 셀룰로오스 나노 섬유로 이루어진 것이 분명해졌다.
- [0204] 또, 동일한 막상 셀룰로오스에 대해서, 전반사식 적외 분광 분석을 실시해 ATR 스펙트럼을 얻었다. ATR 스펙트럼의 패턴으로부터는 카르보닐기의 존재가 확인되어 상술한 방법에 의해 평가한 셀룰로오스 중의 알데히드기의 양 및 카르복실기의 양은 각각 0.31mmol/g 및 1.7mmol/g였다.
- [0205] [복합체의 제작 C]
- [0206] (실시예 1C)
- [0207] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액과 합성 스멕타이트(루센타이트 SW F)를 셀룰로오스 나노 섬유와 합성 스멕타이트의 중량비가 25 대 75가 되도록 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 50μm의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 91%이며, 30°C~180°C의 범위에서의 선팽창 계수는 4ppm/°C, 팽윤율은 15배였다.
- [0208] (실시예 2C)
- [0209] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액과 합성 스멕타이트(루센타이트 SW F)를 셀룰로오스 나노 섬유와 합성 스멕타이트의 중량비가 55 대 45가 되도록 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 20μm의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 91%이며, 30°C~180°C의 범위에서의 선팽창 계수는 5ppm/°C, 팽윤율은 48배였다.
- [0210] (실시예 3C)
- [0211] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액과 합성 사포나이트(스멕톤 SA)를 셀룰로오스 나노 섬유와 합성 사포나이트의 중량비가 25 대 75가 되도록 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 47μm의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 90%이며, 30°C~180°C의 범위에서의 선팽창 계수는 3.2ppm/°C, 팽윤율은 12배였다.
- [0212] (실시예 4C)
- [0213] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액과 합성 사포나이트(스멕톤 SA)를 셀룰로오스 나노 섬유와 합성 사포나이트의 중량비가 50 대 50이 되도록 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 41μm의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 90%이며, 30°C~180°C의 범위에서의 선팽창 계수는 5.8ppm/°C, 팽윤율은 32배였다.
- [0214] (실시예 5C)
- [0215] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 박편상 무기 재료(루센트 SWF, 코프케미컬사제) 100중량부와 에폭시 수지(테나콜 EX-214L, 나가세켐텍스사제) 600중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 24μm의 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 열선팽창 계수는 14ppm/°C, 습도 팽창 계수는 60ppm/습도%, 팽윤율은 2.1배였다.

[0216] (실시예 6C)

[0217] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 박편상 무기 재료(루센트 SWF, 코프케미컬사제) 100중량부와 에폭시 수지(테나콜 EX-214L, 나가세켐텍스사제) 200중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50 μm 의 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 92%, 열선팽창 계수는 13ppm/°C, 습도 팽창 계수는 57ppm/습도%, 팽윤율은 1.7배였다.

[0218] (실시예 7C)

[0219] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 박편상 무기 재료(스멕톤 SA, 쿠니미네공업사제) 100중량부와 에폭시 수지(테나콜 EX-214L, 나가세켐텍스사제) 600중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 열선팽창 계수는 15ppm/°C, 습도 팽창 계수는 92ppm/습도%, 팽윤율은 3.4배였다.

[0220] (실시예 8C)

[0221] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 박편상 무기 재료(스멕톤 SA, 쿠니미네공업사제) 100중량부와 에폭시 수지(테나콜 EX-214L, 나가세켐텍스사제) 200중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 58 μm 의 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 열선팽창 계수는 13ppm/°C, 습도 팽창 계수는 71ppm/습도%, 팽윤율은 2.4배였다.

[0222] (비)교예 1C)

[0223] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액을 실온에서 30분간 교반하고 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 18 μm 의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 90%이며, 30°C~180°C의 범위에서의 열선팽창 계수는 12ppm/°C, 습도 팽창 계수는 200ppm/습도%, 팽윤율은 185배였다.

[0224] [복합체의 평가]

[0225] 특성 평가 방법은 이하와 같다.

[0226] (a) 휨 강도

[0227] 휨 강도 측정용 테스트 피스의 휨 강도는 JIS K 7171에 준거해 신전간(伸展間) 거리 36mm, 크로스 헤드 속도 1 mm/분, 23°C, 상대 습도 60% 하에서 휨 강도 측정 장치((주)오리엔테크사제, UCT-30T형 텐시론)를 이용해 측정했다.

[0228] (b) 열선팽창 계수

[0229] 열응력 뒤틀림 측정 장치(세이코전자(주)제, TMA/SS120C형)를 이용하여, 질소 분위기 하, 1분간 5°C의 비율로 온도를 30°C에서 150°C까지 상승시킨 후, 일단 0°C까지 냉각하고, 다시 1분간 5°C의 비율로 온도를 상승시켜 30°C~150°C 일 때의 값을 측정해 구했다. 하중을 5g로 하고 인장 모드로 측정을 실시했다.

[0230] 또한, 실시예 1B~5B 및 비교예 1B에 대해서는 1분간 5°C의 비율로 온도를 30°C에서 200°C까지 상승시킨 후, 일단 0°C까지 냉각하고, 다시 1분간 5°C의 비율로 온도를 상승시켜 30°C~180°C 일 때의 값을 측정해 구했다.

[0231] 또한, 실시예 1C~8C 및 비교예 1C에 대해서는 1분간 5°C의 비율로 온도를 30°C에서 200°C까지 상승시킨 후, 일단 -50°C까지 냉각하고, 다시 1분간 5°C의 비율로 온도를 상승시켜 30°C~180°C 일 때의 값을 측정해 구했다.

[0232] (c) 전광선 투과율

[0233] 분광 광도계(시마즈제작소제, U3200)로 전광선 투과율을 측정했다.

- [0234] 또한, 실시예 1C~8C 및 비교예 1C에 대해서는 헤이즈미터(일본전색사제, NDH-2000)에 의해 전광선 투과율을 측정했다.
- [0235] (d) 습도 팽창 계수
- [0236] 얻어진 필름에 치수 측정의 기준이 되는 2점을 그려 실온 23°C, 습도 60%의 분위기 하에 24시간 방치하고, 그 후 100°C의 건조기에 3시간 넣어 건조했다.
- [0237] 건조 후 즉시 미리 그린 2점간의 거리를 3차원 측장기로 측정해, 이 거리를 2점간 거리의 기준으로 했다. 그 후, 건조 후의 필름을 재차 실온 23°C, 습도 60%의 분위기 하에 24시간 방치한 후, 미리 그린 2점간 거리를 3차원 측장기로 측정해 기준 거리로부터의 치수 변화율을 산출했다. 또한, 건조 후 외관의 습도를 0%로 하고, 습도 0%에서 60% 범위에서의 습도 1%당 습도 팽창 계수를 산출했다.
- [0238] (e) 팽윤율
- [0239] 얻어진 필름을 23°C의 순수에 1시간 담궈 합침 전후의 필름 두께 변화율을 측정했다. 그리고 팽윤율을 합침 후 필름 두께의 합침 전 필름 두께에 대한 배율로서 산출했다.
- [0240] 상기 측정 결과를 표 1~3에 나타낸다.

| 제조조건 및 특성 | 실시예 | | | | | | | | | | | | 비교예 단위 |
|-----------|---------------------------|-----|-----|------|------|------|------|------|------|------|------|------|-----------|
| | 1.A | 2.A | 3.A | 4.A | 5.A | 6.A | 7.A | 8.A | 9.A | 10.A | 11.A | 12.A | |
| 예주식 수식 | 지판식 예 쪽시수지 | 90 | | | | | | | | | | | 90 |
| | 대나클 EX-214L | | | | | | | 80 | | | | | |
| | 대나클 EX-1410 | | | | | | | 110 | 110 | | | | |
| | 대나클 EX-1610 | | | | | | | | | 110 | | | |
| 배수지 | 페놀노블락 | | | | | | | | | | | | 85 |
| | 리플 | | | | | | | | | | | | |
| 커플링제 | 테트라 에톡시 실란 페닐트리 에톡시 실란 | | | | | | | | | | | | |
| | 나-글리시디록시프로필 드리아에톡시 실란 | | | | | | | | | | | | |
| | 타판 알록사이드 | | | | | | | | | | | | |
| 박판상 무기재료 | 두체트 SWF | | | | | | | | | | | | |
| | 스펙톤 SA | | | | | | | | | | | | |
| 금속설파를 | 스노우택스20 | | | | | | | | | | | | |
| | 스노우택스N | | | | | | | | | | | | |
| | 스노우택스O | | | | | | | | | | | | |
| | 스노우택스XS | | | | | | | | | | | | |
| | 스노우택스CM | | | | | | | | | | | | |
| 속비 | 셀룰로오스 나노섬유 | 10 | 15 | 160 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 미세화 윌로 | | | | | | | | | | | | |
| 기교재 | SI-14QL | 1 | | | | | | | | | | | 1 |
| | 테트라메틸 에틸렌디아민 | | | | | | | | | | | | |
| | 헥사메틸렌디아민 | | | | | | | | | | | | |
| 두께 | mm | 1 | 1 | 0.63 | 0.03 | 0.03 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| | N | 48 | 60 | — | — | — | — | — | — | — | — | — | — |
| 휨강도 | % | — | — | 96 | 60 | 38 | 88 | 80 | 80 | 80 | 50 | 40 | — |
| 전력선두력을 | % | — | — | — | — | — | — | — | — | — | — | — | — |
| 열선행성계수 | ppm/ ^o C | — | — | 11 | 10 | 11 | 12 | 15 | 14 | 12 | 13 | — | — |
| 습도팽창계수 | ppm/%습도 % | — | — | 26 | 23 | 25 | 22 | 110 | 61 | 90 | 76 | 50 | 45 |
| 팽창률 | 비 | — | — | — | — | — | — | — | — | — | — | — | — |

[0241]

[0242]

표 1로부터 알 수 있는 바와 같이, 실시예 1A, 2A에서 얻어진 테스트 피스(본 발명의 복합체 조성물을 이용해 얻어진 복합체)는 모두 비교예 1A에서 얻어진 종래의 섬유상 필러를 포함하는 테스트 피스와 비교하면 기계적 강도 및 치수 안정성이 높고 각종 특성이 뛰어난 것이 확인되었다.

[0243]

또, 실시예 3A~12A에서 얻어진 필름(본 발명의 복합체 조성물을 이용해 얻어진 복합체)은 섬유상 필러와 수지 또는 커플링제(또는 커플링제의 가수분해물)를 포함하는 복합체 조성물로부터 형성된 필름이지만, 이것들은 습도 팽창 계수(흡수 치수 변화율) 및 열선행성 계수가 비교적 작고, 또한 투명성이 뛰어난 것이 확인되었다.

| 제조조건 및 특성 | | 실시예 1B | 실시예 2B | 실시예 3B | 실시예 4B | 실시예 5B | 비교예 1B |
|------------|-------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| 예폭시 수지 | 지환식 예폭시수지 | | | | | | |
| | 데나콜 EX-214L | | | | | | |
| | 데나콜 EX-1410 | | | | | | |
| | 데나콜 EX-1610 | | | | | | |
| 페놀 수지 | 페놀노블락 | | | | | | |
| | 레졸 | | | | | | |
| 커플링제 | 테트라 에톡시 실란 | | | | | | |
| | 페닐트리 에톡시 실란 | | | | | | |
| | 3-글리시도시프로필 트리에톡시 실란 | | | | | | |
| | 티탄 알콕사이드 | | | | | | |
| 박편상 무기재료 | 투센트 SWF | | | | | | |
| | 스맥톤 SA | | | | | | |
| 금속산화물 | 스노우텍스20 | 100 | | | | | |
| | 스노우텍스N | | 100 | | | | |
| | 스노우텍스O | | | 100 | | | |
| | 스노우텍스XS | | | | 100 | | |
| | 스노우텍스CM | | | | | 100 | |
| 셀룰로오스 나노섬유 | | 100 | 100 | 100 | 100 | 100 | 100 |
| 미세화 필프 | | | | | | | |
| 촉매 | SI-100L | | | | | | |
| | 테트라메틸 에틸렌디아민 | | | | | | |
| 기교재 | 헥사메틸렌테트라민 | | | | | | |
| 두께 | mm | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| 휨강도 | N | — | — | — | — | — | — |
| 전광선투과율 | % | 87 | — | 90 | 89 | 88 | 91 |
| 열선팽창계수 | ppm/ $^{\circ}\text{C}$ | 9 | 10 | 11 | 10 | 11 | 10 |
| 습도팽창계수 | ppm/습도 % | 70 | 61 | 65 | 68 | 70 | 115 |
| 팽창률 | 배 | 2 | 1.6 | 1.7 | 1.9 | 1.9 | 160 |

[0244]

[0245] 표 2로부터 알 수 있는 바와 같이, 실시예 1B~5B에서 얻어진 필름(본 발명의 복합체 조성물을 이용해 얻어진 복합체)은 모두 비교예 1B에서 얻어진 필름과 비교하면 팽윤율이 작고, 내수성이 뛰어난 것이 확인되었다.

| 제조조건 및 특성 | | 실시예 1C | 실시예 2C | 실시예 3C | 실시예 4C | 실시예 5C | 실시예 6C | 실시예 7C | 실시예 8C | 비교예 1C |
|------------|---------------------|-------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 에폭시 수지 | 지환식 에폭시수지 | | | | | | | | | |
| | 데나콜 EX-214L | | | | | 600 | 200 | 600 | 200 | |
| | 데나콜 EX-1410 | | | | | | | | | |
| | 데나콜 EX-1610 | | | | | | | | | |
| 페놀 수지 | 페놀노불락 | | | | | | | | | |
| | 레졸 | | | | | | | | | |
| 커플링제 | 테트라 에톡시 실란 | | | | | | | | | |
| | 페닐트리 에톡시 실란 | | | | | | | | | |
| | 3-글리시도시프로필 트리에톡시 실란 | | | | | | | | | |
| | 티탄 일콕사이드 | | | | | | | | | |
| 박편상 무기재료 | 루센트 SWF | 75 | 45 | | | 100 | 100 | | | |
| | 스맥론 SA | | | 75 | 50 | | | 100 | 100 | |
| 금속산화물 | 스노우텍스20 | | | | | | | | | |
| | 스노우텍스N | | | | | | | | | |
| | 스노우텍스O | | | | | | | | | |
| | 스노우텍스XS | | | | | | | | | |
| | 스노우텍스CM | | | | | | | | | |
| 셀룰로오스 나노섬유 | | 25 | 55 | 25 | 50 | 100 | 100 | 100 | 100 | 100 |
| 미세화 필름 | | | | | | | | | | |
| 촉매 | SI-100L | | | | | | | | | |
| | 테트라메틸 에틸렌디아민 | | | | | | | | | |
| 가교제 | | | | | | | | | | |
| 두께 | mm. | 0.06 | 0.02 | 0.047 | 0.041 | 0.024 | 0.05 | 0.03 | 0.058 | 0.018 |
| | N | — | — | — | — | — | — | — | — | — |
| 휨강도 | % | 91 | 91 | 90 | 90 | 91 | 92 | 91 | 91 | 90 |
| | ppm/ $^{\circ}$ C | 4 | 5 | 3.2 | 5.3 | 14 | 13 | 15 | 13 | 12 |
| 전광선투과율 | ppm/습도 % | — | — | — | — | 60 | 57 | 52 | 51 | 200 |
| | 습도팽창계수 | ppm/ $^{\circ}$ C | 15 | 48 | 12 | 32 | 2.1 | 1.7 | 3.4 | 2.4 |
| 팽창률 | | | | | | | | | | |

[0246]

[0247] 표 3으로부터 알 수 있는 바와 같이, 실시예 1C~8C에서 얻어진 필름(본 발명의 복합체 조성물을 이용해 얻어진 복합체)은 모두 비교예 1C에서 얻어진 필름과 비교하면 팽윤율이 작고, 내수성이 뛰어난 것이 확인되었다. 또, 실시예 1C~8C에서 얻어진 필름은 열선팽창 계수가 비교적 작은 것으로부터 열에 의한 치수 안정성도 뛰어나고, 또한 투명성도 높은 것이 확인되었다.

[0248] 또한, 각 실시예 및 각 비교예에서 사용된 주된 원료는 이하와 같다.

[0249] 에폭시 수지

[0250] : 세록사이드 2021 다이셀화학제

[0251] : 데나콜 EX-214L 나가세캡텍스사제

[0252] : 데나콜 EX-1410L 나가세캡텍스사제

[0253] : 데나콜 EX-1610L 나가세캡텍스사제

[0254] 페놀 수지

[0255] : 레졸형 페놀 수지 PR-967 스미토모베이클라이트제

[0256] 열양이온 촉매

[0257] : SI-100L 삼신화학제

[0258] 페놀 노불락 수지

[0259] : PR-HF-6 스미토모베이클라이트제

[0260] 커플링제

[0261] : 테트라에톡시실란 와코우순약제

[0262] : 폐널트리에톡시실란 아즈막스제

[0263] : 3-글리시도시프로필 트리에톡시실란 신에츠화학제

[0264] : 티탄알록사이드 KR-ET 아지노모토파인테크노제

[0265] 가교재(헥사메틸렌테트라민)

[0266] : 우로트로핀 스미토모정화사제

[0267] 금속 산화물

[0268] : 콜로이달 실리카 스노우텍스 20 낫산화학공업사제

[0269] : 콜로이달 실리카 스노우텍스 N 낫산화학공업사제

[0270] : 콜로이달 실리카 스노우텍스 O 낫산화학공업사제

[0271] : 콜로이달 실리카 스노우텍스 XS 낫산화학공업사제

[0272] : 콜로이달 실리카 스노우텍스 CM 낫산화학공업사제

[0273] 박편상 무기 재료

[0274] : 스멕톤 SA 쿠니미네공업제

[0275] : 루센타이트 SWF 코프케미컬

[0276] 산업상 이용 가능성

[0277] 본 발명의 복합체 조성물은 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하고, 상기 섬유상 필러의 평균 섬유 지름이 4~1000nm이다. 이 때문에, 이 복합체 조성물을 성형해서 이루어지는 복합체에는 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개가 기계적 및 화학적인 작용을 가져온다. 그 결과, 저열팽창 계수, 고강도, 고투명성, 저습도 팽창 계수(고내수성, 고치수 안정성)를 가지는 복합체가 얻어진다. 따라서, 본 발명의 복합체는 자동차 외장 및 대쉬보드 등의 자동차 부품, 철도, 항공기, 선박 등의 수송용 기기의 부품, 주택이나 오피스에서의 세시, 벽판 및 상판 등의 건재, 기둥 혹은 철근 콘크리트에서의 철근과 같은 구조 부재, 전자 회로, 표시체의 기판 등의 전자 부품, PC 및 휴대 전화 등의 가전 제품의 케이스(하우징), 문구 등의 등의 사무용 기기, 가구, 일회용 용기 등의 생활 용품, 스포츠 용품, 완구 등의 가정 내에서 사용되는 소품, 간판, 표지 등의 야외 설치물, 방탄 방패, 방탄 조끼 등의 충격 흡수 부재, 헬멧 등의 호신 용구, 인공 뼈, 의료용품, 연마제, 방음벽, 방호벽, 진동 흡수 부재, 공구, 판 스프링 등의 기계 부품, 악기, 패킹재 등에 사용할 수 있다. 따라서, 본 발명의 복합체 조성물 및 복합체는 산업상 이용 가능성을 가진다.



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DESCRIPTION KR101335758

Composite composition and composite {COMPOSITE COMPOSITIONS AND COMPOSITES}

[0001]

The present invention relates to a composite composition and composite comprising at least one of a fibrous filler and a resin, metal oxide, and flaky inorganic material.

[0002]

It is widely practiced to blend a spherical filler or a fibrous filler in order to reduce the thermal expansion coefficient of the resin or to increase the mechanical strength such as elastic modulus and flexural strength.

In recent years, studies on nanoparticles of spherical fine particles such as silica fine particles and metal fine particles, and rod-shaped whisker-type fillers as materials that replace conventional macro fillers are in full swing. However, there have been few reports of fibrous nanomaterials for these fillers.

[0003]

Recently, many plastic substitutes using cellulose have been reported. For example, a complex using microfibrils of cellulose obtained by highly miniaturizing the fibril-like material of cellulose using a device capable of applying extremely high pressure called a high pressure homogenizer, and other microfluidizer methods, A composite using microfibrils of cellulose downsized by a grinder method, freeze drying method, steel wire elastic kneading method, or ball mill grinding method as a filler. It has been reported that a molded article having a relatively high strength can be obtained by using these fillers (for example, see Patent Document 1).

[0004]

However, the conventional microfibrillation method requires a great deal of energy for the downsizing treatment, which is disadvantageous in terms of cost, and also has a relatively wide distribution in the fiber diameter of the resulting micronized fiber, resulting in incomplete degree of micronization. In some cases, coarse fibers of 1 μm or more may remain a little, so a particularly wide distribution exists in the diameter and density of the microfibril fibers, resulting in an absolute value decrease or a gap in the strength of the molded article.

[0005]

Further, as described in Patent Document 2, it is known that a fiber-reinforced composite material having a transparent and low linear expansion coefficient is obtained using bacterial cellulose from which bacteria are produced. However, as in the case of mechanically obtaining the cellulose microfibrils described above, the production speed is slow and cannot be said to be necessarily advantageous from an industrial point of view.

[0006]

Moreover, since cellulose has many hydroxyl groups on the fiber surface, hydrophilicity is high, and dimensions and physical properties are greatly changed upon absorption. For this reason, there exists a problem that the size and physical properties of the composite material are greatly changed during absorption, and the use of the composite material is limited.

Japanese Patent Application Publication No. 2003-201695 Japanese Patent Application Publication No. 2005-60680

An object of the present invention is to provide a composite composition having a low coefficient of thermal expansion, high strength, high transparency, and a low humidity expansion coefficient (high water resistance) and a composite that is a molded product thereof efficiently.

In order to achieve the above object, the present invention is a composite composition comprising at least one of a fibrous filler, a resin, a metal oxide and a flaky inorganic material, characterized in that the average fiber diameter of the fibrous filler is 4 to 1000 nm. It is a composite composition. Moreover, in the composite composition of this invention, it is preferable that the said fibrous filler is a cellulose fiber. Moreover, in the composite composition of the present invention, it is preferable that the cellulose fiber is a fiber obtained by refining a cellulose raw material by at least one of chemical treatment and mechanical treatment. Further, in the composite composition of the present invention, it is preferable that the cellulose fiber is partially oxidized to at least one of an aldehyde group and a carboxyl group in the cellulose molecule contained therein. In the composite composition of the present invention, it is preferable that the cellulose fiber is obtained by using natural cellulose as a raw material, using an N-oxyl compound as an oxidation catalyst, and oxidizing the raw material by activating a co-oxidizing agent on the raw material in water. Moreover, in the composite composition of the present invention, it is preferable that the resin is at least one of a plastic resin and a curable resin. Moreover, it is preferable that the said resin contains an epoxy resin in the composite composition of this invention. Moreover, it is preferable that the said resin contains a phenol resin in the composite composition of this invention. Further, in the composite composition of the present invention, the resin preferably contains at least one of a coupling agent and a hydrolyzate of the coupling agent. Further, in the composite composition of the present invention, it is preferable that the coupling agent is alkoxy silane or alkoxy titanium. Moreover, in the composite composition of the present invention, it is preferable that the average particle diameter of the metal oxide is 1 to 1000 nm. Further, in the composite composition of the present invention, it is preferable that the metal oxide is silicon dioxide. Further, in the composite composition of the present invention, the flaky inorganic material is mica, vermiculite, montmorillonite, iron montmorillonite, videlite, saponite, hectorite, stephensite, nontronite, margadialite, illite, kanehite. It is preferable that it is at least one selected from smectite and layered titanic acid.

Further, in the composite composition of the present invention, the content of the fibrous filler in the composite composition is preferably 0.1 to 99.9% by weight. Moreover, in the composite composition of the present invention, it is preferable that the total light transmittance at a thickness of 30 µm is 80% or more. In addition, in the composite composition of the present invention, it is preferable that the coefficient of thermal expansion at 30 °C to 180 °C is 50 ppm / °C or less. In order to achieve the above object, the present invention is made by molding the composite composition, it is a composite characterized in that the thickness is 10 ~ 2000 µm. In addition, in the composite of the present invention, it is preferable that the coefficient of thermal expansion at 30 °C to 150 °C is 0.4 to 50 ppm / °C. Moreover, in the composite of the present invention, it is preferable that the coefficient of humidity expansion is 100 ppm / % humidity or less.

[0031] Hereinafter, preferred embodiments of the composite composition and the composite of the present invention will be described in detail.

[0032] The composite composition of the present invention includes at least one of a fibrous filler and a resin, a metal oxide, and a flaky inorganic material. In addition, the composite of the present invention is produced by molding the composite composition into a predetermined shape.

[0033] <Composite composition>

[0034] (Fibrous filler)

[0035] First, the fibrous filler will be described.

[0036] The average fiber diameter of the fibrous filler used in the present invention is 4 to 1000 nm, preferably 4 to 300 nm, and more preferably 4 to 200 nm. In addition, when the average fiber diameter exceeds the upper limit, transparency is deteriorated and mechanical strength is not improved. On the other hand, although the average fiber diameter may be below the lower limit, it is difficult to obtain such a fibrous filler.

[0037] The length of the fibrous filler used in the present invention is not particularly limited, but when the average length of the fibrous filler is 100 nm or more, a reinforcing effect is easily obtained and strength is improved.

[0038] Here, the measurement of the average fiber diameter of a fibrous filler can be performed as follows.

[0039] First, a dispersion of a fibrous filler having a solid fraction of 0.05 to 0.1% by weight is prepared, and the dispersion is cast on a carbon film-coated grid to prepare a sample for TEM observation. In addition, when a fibrous filler having a large fiber diameter is included, it may be cast on glass and used as a sample for SEM observation.

[0040] Upon observation under a microscope, an electron microscope image is acquired at a magnification of any one of 5000 times, 10000 times, or 50000 times depending on the size (fiber diameter) of the fibrous filler to be constituted. When the axis of arbitrary image width is assumed in the image obtained at this time, sample conditions and observation conditions (magnification, etc.) are set so that at least 20 fibrous fillers intersect the axis.

[0041] Then, for an observed image satisfying this condition, a random axis of two vertical and horizontal axes is pulled per image, and the fiber diameter of the fibrous filler intersecting with each axis is visually read. Further, while moving the

observation positions so as not to overlap each other with respect to the sample surface, at least three observation images are acquired, and the fiber diameters are read for each image as described above. As a result, information on the fiber diameter is obtained for at least $20 \times 2 \times 3 = 120$ fibrous fillers. The average fiber diameter is calculated based on the fiber diameter data thus obtained.

[0042] The fibrous filler used in the present invention may be any fiber, but is preferably composed of cellulose fibers.

[0043] Examples of the cellulose fibers include natural cellulose fibers and regenerated cellulose fibers. On the other hand, examples of fibers other than cellulose fibers include kitchen fibers and chitosan fibers.

[0044] Of these, natural cellulose fibers include purified pulp obtained from coniferous and broad-leaved trees, cellulose fibers obtained from cotton linters and cotton lint, cellulose fibers obtained from seaweeds such as baronia and shiog, cellulose fibers obtained from Hoya, and bacteria And cellulose fibers. On the other hand, as the regenerated cellulose fiber, there is one obtained by dissolving the natural cellulose fiber once and then regenerating it into a fibrous form while maintaining the cellulose composition.

[0045] Moreover, it is preferable that the cellulose fiber used for this invention is highly crystalline. Such cellulose fibers are particularly preferably used as fibrous fillers because of their small linear expansion coefficient and high mechanical strength. Moreover, from this viewpoint, as the cellulose fiber used in the present invention, natural cellulose fiber is preferable to regenerated cellulose fiber.

[0046] Further, the cellulose fibers used in the present invention may be obtained by any known method, and the production method is not particularly limited, but as an example, a cellulose raw material (natural cellulose or regenerated cellulose) is a medium stirring mill processing apparatus and a vibration mill treatment. What is mechanically refined by various refinement apparatuses, such as an apparatus, a high pressure homogenizer processing apparatus, and an ultra high pressure homogenizer treatment apparatus, is used. As another method, the electron spinning method, steam jet method, APEX (registered trademark) technology (Polymer Group. Inc.) can also be used. However, in consideration of energy efficiency and the like, the cellulose fiber obtained by a method involving the following chemical treatment is most preferable as the cellulose raw material.

[0047] The manufacturing method of the cellulose fiber described below is a method of producing cellulose fibers (nanocellulose fibers) by dispersing them in a dispersion medium by performing a chemical treatment on the cellulose raw material and then providing it to a mechanical treatment.

[0048] Specifically, [1] an oxidation reaction process in which natural cellulose is used as a raw material, and an N-oxyl compound is used as an oxidation catalyst in water to act as a oxidizing agent to oxidize natural cellulose to obtain reactant fibers, and [2] to remove impurities It has a purification process for obtaining reactant fibers impregnated with water, and [3] a dispersion process for dispersing reactant fibers impregnated with water in a dispersion medium. Each process is explained in full detail below.

[0049] [1] Oxidation reaction process

[0050] First, in the oxidation reaction step, a dispersion liquid in which cellulose raw materials are dispersed in water is prepared. Here, the cellulose raw material to be used is preferably one that has been subjected to a treatment for increasing the surface area such as beating in advance. This is because the reaction efficiency can be increased and productivity can be increased. Moreover, it is preferable to use what was preserve | saved by Neva dry after isolation | refining and refine | purifying as a cellulose raw material. Thereby, since the convergence body of the microfibrils constituting the cellulose raw material is easily swelled, it is also possible to increase the reaction efficiency and reduce the number average fiber diameter after the refinement treatment.

[0051] In addition, when water is used as the dispersion medium for the cellulose raw material in this step, the cellulose concentration in the dispersion (reactive aqueous solution) is arbitrary as long as it is a concentration capable of sufficiently diffusing the reagent, but is usually 5% by weight or less based on the weight of the dispersion.

[0052] In addition, many N-oxyl compounds that can be used as oxidation catalysts for cellulose have been reported. For example, "Cellulose" Vol. 10, 2003TEMPO (2,2,6,) in an article titled `` Catalytic oxidation of cellulose with TEMPO derivatives: HPSEC and NMR analysis of oxidized products " by I.Shibata and A.Isogai on pages 333-341 Various N-oxyl compound catalysts of 6-tetramethyl-1-piperidine-N-oxyl), 4-acetamide-TEMPO, 4-carboxy-TEMPO and 4-phosphonooxy-TEMPO at room temperature in water It is preferably used in the reaction rate. In addition, the addition of these N-oxyl compounds is sufficient in a catalytic amount, and is preferably added to the reaction aqueous solution in the range of 0.1 to 4 mmol / l, more preferably 0.2 to 2 mmol / l.

[0053] Further, examples of the co-oxidizing agent include hypohalogenic acid or a salt thereof, halogenic acid or a salt thereof, perhalogenic acid or a salt thereof, hydrogen peroxide and perorganic acid, and the like, but in particular, alkali metal hypohalogenates, specifically Sodium hypochlorite, sodium hypobromite, and the like are preferably used. When using sodium hypochlorite, it is preferred in terms of reaction rate to proceed the reaction in the presence of an alkali metal bromide, for example sodium bromide. The amount of the alkali metal bromide added is preferably about 1 to 40 times the molar amount, more preferably about 10 to 20 times the molar amount of the N-oxyl compound.

[0054] Moreover, it is preferable to maintain the pH of the reaction aqueous solution in the range of about 8 to 11. The temperature of the aqueous solution is arbitrary in the range of about 4 to 40 ° C, but the reaction can be carried out at room temperature, and temperature control is not particularly required.

[0055] Although a carboxyl group is introduced to the cellulose molecule by the co-oxidizer to substitute a hydroxyl group, the amount of the oxidizing agent is added depending on the amount of the carboxyl group required depending on the type of the cellulose raw material in obtaining the fine cellulose fibers used in the present invention. It is sufficient to set the time for the co-oxidant to act. Specifically, the larger the amount of carboxyl groups, the smaller the maximum fiber diameter and number average fiber diameter of the finally obtained cellulose fiber, so it may be set in consideration of it.

[0056] For example, when using wood pulp and cotton pulp as the cellulose raw material, the amount of carboxyl groups required is 0.2 to 2.2 mmol / g relative to the cellulose raw material, and bacterial cellulose (BC) or cellulose extracted from Hoya is used as the cellulose raw material. In this case, the required amount of carboxyl groups is 0.1 to 0.8 mmol / g. Thus, by controlling the addition amount and reaction time of the co-oxidizing agent according to the type of the cellulose raw material, it is possible to introduce the optimum amount of carboxyl groups in each cellulose raw material.

[0057] In addition, based on the introduction amount of the carboxyl group as described above, it is possible to induce the amount of the co-oxidant added, and as an example, it is preferable to add about 0.5 to 8 mmol of the co-oxidant per 1 g of the cellulose raw material, and the reaction time is about 5 to 120 It is preferable to make it within 240 minutes even if it is minutes and long.

[0058] In addition, although the carboxyl group is introduced into the cellulose molecule through the oxidation reaction step, an aldehyde group may be introduced depending on the progress of the oxidation treatment. Therefore, after completion of the oxidation reaction process, the hydroxyl group of the cellulose molecule is replaced with at least one of an aldehyde group and a carboxyl group.

[0059] [2] Refining process

[0060] In the purification step, it is an object to remove compounds other than the reactant fibers and water contained in the reaction slurry, specifically, unreacted hypochlorous acid or various by-products. Since the reactant fibers are not normally dispersed in nanofiber units at this stage, high purity (over 99% by weight) can be achieved by repeating a conventional purification method, that is, washing and filtration.

[0061] The purification method in the present purification process may be any apparatus as long as it is a device (for example, a continuous decanter) capable of achieving the above-described object, such as a method using centrifugal dehydration. The reactant fibers thus obtained are in the range of approximately 10 to 50% by weight as the concentration of solid content (cellulose) in the squeezed state. In addition, considering dispersing in units of nanofibers in a subsequent process, it is not preferable to use a solid content concentration higher than 50% by weight because extremely high energy is required for dispersion.

[0062] [3] Dispersion process

[0063] In the above-described step, reactant fibers impregnated with water are obtained, but by dispersing them in a solvent to perform dispersion treatment, fine cellulose fibers used in the present invention are obtained in a dispersed state.

[0064] Here, the solvent as the dispersion medium is usually water, but in addition to water, alcohols (methanol, ethanol, isopropanol, isobutanol, sec-butanol, tert-butanol, methylcellosolve, ethylcello) are soluble in water depending on the purpose. Solvents, ethylene glycol, glycerin, etc.), ethers (ethylene glycol dimethyl ether, 1,4-dioxane, tetrahydrofuran, etc.), ketones (acetone, methyl ethyl ketone), N, N-dimethylformamide, N, N -Dimethylacetamide, dimethyl sulfoxide, etc. may be used. Moreover, these mixtures can also be used preferably.

[0065] In addition, when diluting and dispersing with the above-described reactant fiber solvent, a dispersion of nanofiber level fibers can be efficiently obtained by performing stepwise dispersion in which a solvent is gradually added and dispersed. Further, from the operational problem, after the dispersion step, the dispersion conditions may be selected such that the dispersion becomes a viscous state or a gel.

[0066] Here, various kinds of dispersers used in the dispersing process can be used. Although a specific example is shown, depending on the progress of the reaction in the reactant fibers (the amount of conversion to an aldehyde group or a carboxyl group), preferably under the conditions in which the reaction proceeds, such as a screw mixer, paddle mixer, disper mixer, turbine mixer, etc. A dispersion of fine cellulose fibers can be sufficiently obtained with a general-purpose disperser as an industrial production machine.

[0067] In addition, by using a device having a strong crushing ability under high-speed rotation, such as a homo mixer, a high pressure homogenizer, an ultra high pressure homogenizer, ultrasonic dispersion treatment, a beater, a disc type refiner, a conical type refiner, a double disc type refiner, and a grinder, More efficient and highly downsizing becomes possible. Furthermore, by using these devices, even if the introduction amount of the aldehyde group or the carboxyl group is relatively small (for example, 0.1 to 0.5 mmol / g as the total amount of the aldehyde group or the carboxyl group to cellulose), a dispersion of highly fine-grained fine cellulose fibers can be obtained. Can provide.

[0068] Next, a method for recovering fine cellulose fibers from a dispersion in which fine cellulose fibers are dispersed in a dispersion medium will be described.

[0069] Specifically, the fine cellulose fibers can be recovered by drying the dispersion of the fine cellulose fibers described above.

[0070] Here, for drying, for example, a freeze drying method in the case where the dispersion medium is water, or a drying by a drum dryer when the dispersion medium is a mixture of water and an organic solvent, or in some cases, spray drying by a spray dryer can be preferably used.

[0071] In addition, among the dispersions of the fine cellulose fibers described above, water-soluble polymers as binders (polyethylene oxide, polyvinyl alcohol, polyacrylamide, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, starch, natural gums, etc.) , Sugars (glucose, fructose, mannose, galactose, trehalose, etc.) may be added. Since these binder components have extremely high boiling points and have affinity for cellulose, by adding these components in a dispersion, even when they are dried by a general-purpose drying method such as a drum dryer or spray dryer, agglomeration when dispersed in a dispersion medium again This is prevented, and a dispersion of fine cellulose fibers dispersed as nanofibers can be reliably obtained. In this case, the amount of the binder added in the dispersion is preferably in the range of 10 to 80% by weight relative to the reactant fibers.

[0072] In addition, the recovered fine cellulose fibers are again mixed in a dispersion medium (water, an organic solvent, or a mixture thereof) and an appropriate dispersion force is applied (for example, dispersion is performed using various dispersers used in the dispersion process described above). It can be made into a dispersion of cellulose fibers.

[0073] In the fine cellulose fiber used in the present invention, it is preferable that a part of hydroxyl groups of cellulose is oxidized to a carboxyl group or an aldehyde group, and has a cellulose I-type crystal structure. Further, the fact that the fine cellulose fibers have an I-type crystal structure means that the fibers are finely oxidized by surface oxidation of a naturally occurring cellulose solid raw material.

[0074] In addition, the fine cellulose fibers having an I-type crystal structure have typical peaks at two positions near $2\theta = 14$ ° and $2\theta = 22$ to 23 ° in the diffraction profile obtained by measuring the wide-angle X-ray diffraction image. You can identify based on what you have. In addition, the introduction of an aldehyde group or a carboxyl group into the cellulose of the fine cellulose fiber can be confirmed by the presence of absorption (around 1608 cm⁻¹) due to the carbonyl group in the total reflection infrared spectral spectrum (ATR) of the sample completely removing moisture. In particular, when an acid-type carboxyl group (-COOH) is introduced into cellulose, absorption is present at 1730 cm⁻¹ in the above measurement.

[0075] The finer the cellulose fiber, the more the total amount of carboxyl groups and aldehyde groups present in the cellulose for the above reasons, the more stable the fiber diameter can be. For example, in the case of wood pulp or cotton pulp, the sum of the amount of carboxyl groups and aldehyde groups present in the fine cellulose fibers (hereinafter abbreviated as "total amount") is 0.2 to 2.2 mmol / g, preferably with respect to the weight of the cellulose fibers. If it is 0.5 to 2.2 mmol / g, and more preferably 0.8 to 2.2 mmol / g, cellulose fibers having excellent stability as nanofibers are obtained. Further, in the case of cellulose having a relatively large fiber diameter of microfibrils such as cellulose extracted from BC or Hoya (average fiber diameter is about 10 nm level), the total amount is 0.1 to 0.8 mmol / g, preferably 0.2 to 0.8. If it is mmol / g, cellulose fibers excellent in stability as nanofibers are obtained. In addition, when the total amount is smaller than the lower limit, the difference in physical properties (for example, dispersion stabilization effect in the dispersion) with conventionally known micronized cellulose fibers is also reduced, and at the same time, it is difficult to obtain a fiber with a small fiber diameter. Therefore, it is not preferable.

[0076] In addition, an electric repulsive force is generated by introducing a carboxyl group to the aldehyde group, which is a nonionic substituent. As a result, the tendency for microfibrils to disperse without maintaining agglutination increases, so that the stability of nanofibers as a dispersion increases. For example, in the case of wood pulp or cotton pulp, the amount of carboxyl groups present in the fine cellulose fibers is 0.2 to 2.2 mmol / g, preferably 0.4 to 2.2 mmol / g, more preferably 0.6 to relative to the weight of the cellulose fibers. If it is 2.2 mmol / g, the cellulose fiber with extremely excellent stability as nanofibers is obtained. Further, in the case of cellulose having a relatively large fiber diameter of microfibrils, such as cellulose extracted from BC or Hoya, the amount of carboxyl groups is 0.1 to 0.8 mmol / g, preferably 0.2 to 0.8 mmol / g, which provides excellent stability as nanofibers. Cellulose fibers are obtained.

[0077] Here, the amount (mmol / g) of the aldehyde group and the carboxyl group of cellulose with respect to the weight of the cellulose fiber is evaluated by the following method.

[0078] 60 ml of a slurry having a concentration of 0.5 to 1 wt% was prepared using a cellulose sample with a dry weight, the pH was adjusted to about 2.5 with an aqueous 0.1 M hydrochloric acid solution, and 0.05 M sodium hydroxide aqueous solution was added dropwise to generate the slurry. Conduct conductivity measurement. This measurement continues until the pH is about 11. The amount of functional groups is calculated from the amount of sodium hydroxide (V) consumed in the neutralization step of the weak acid with a slight change in electrical conductivity using the following equation. The functional group amount calculated here is referred to as "functional group amount 1". This functional group amount 1 represents the amount of carboxyl groups.

[0079] Functional group amount (mmol / g) = V (ml) × 0.05 / cellulose weight (g)

[0080] Next, the cellulose sample is oxidized at room temperature for an additional 48 hours in an aqueous 2% sodium chlorite solution prepared with acetic acid at a pH of 4 to 5, and the functional group amount is again calculated by the above method. The functional group amount calculated here is referred to as "functional group amount 2". Then, the functional group amount (= functional group amount 2-functional group amount 1) added by this oxidation is calculated. This functional group amount represents the amount of the aldehyde group.

[0081] (Suzy)

[0082] As the resin used in the present invention, a known one can be used, and although it is not particularly limited, those containing various curable resins, various plastic resins, and various water-soluble resins can be mentioned.

[0083] The water-soluble resin is not particularly limited as long as it is soluble in water, and examples thereof include thermoplastic resins, curable resins, and natural polymers, but are preferably polyvinyl alcohol, polyethylene oxide, polyacrylamide, and polyvinylpyrrolidone. Synthetic polymers, starches, polysaccharides such as alginic acids, natural polymers such as hemicellulose, gelatin, Nikawa, and casein, which are components of wood, and proteins.

[0084] Moreover, although it does not specifically limit as a thermoplastic resin, For example, vinyl chloride resin, vinyl acetate resin, polystyrene, ABS resin, acrylic resin, polyethylene, polyethylene terephthalate, polyethylene naphthalate, polypropylene, fluorine resin, polyamide resin , Polyesters such as thermoplastic polyimide resin, polyacetal resin, polycarbonate, polylactic acid, polyglycolic acid, poly-3-hydroxy butyrate, polyhydroxy volylate, polyethylene adipate, polycaprolactone, polypropyl lactone, And polyethers such as polyether such as polyethylene glycol, polyglutamic acid, and polylysine.

[0085] On the other hand, as the curable resin, for example, phenol resin, urea resin, melamine resin, unsaturated polyester resin, epoxy resin, acrylic resin, oxetane resin, diallyl phthalate resin, polyurethane resin, silicon resin, maleimide resin, And thermosetting polyimide resins.

[0086] Among them, as the acrylic resin, one type of acrylate or methacrylate, hydroxyethyl acrylate, etc., in addition to alkyl acrylate or alkyl methacrylate such as acrylic acid, methacrylic acid, methyl acrylate, and methyl methacrylate. The resin containing the above is mentioned.

[0087] Moreover, the phenol resin is an organic compound having one or more phenolic hydroxyl groups in the molecule. Examples include resins having novolacs or bisphenols, naphthol or naphthol in the molecule, paraxylylene-modified phenolic resins, dimethylene ether-type resols, and methylol-type resol resins. In addition, these resins are further methylolated, lignin or lignin derivatives, lignin decomposition products containing at least one phenolic hydroxyl group, lignin or lignin derivatives, modified lignin decomposition products or phenols prepared from petroleum resources. And resins including those mixed with resins.

[0088] Moreover, the epoxy resin is an organic compound having at least one epoxy group. For example, bisphenol-type epoxy resins such as bisphenol A-type epoxy resins, bisphenol F-type epoxy resins, bisphenol S-type epoxy resins, hydrates of these bisphenol-type epoxy resins, and epoxy having a dicyclopentadiene skeleton Resin, epoxy resin having triglycidyl isocyanurate skeleton, epoxy resin having kard skeleton, epoxy resin having polysiloxane structure, alicyclic polyfunctional epoxy resin, alicyclic epoxy resin having hydrogenated biphenyl skeleton, hydrogenated bisphenol And alicyclic epoxy resins having an A skeleton.

[0089] Moreover, various coupling agents may be sufficient as the resin used by this invention.

[0090] As a coupling agent, a well-known thing can be used, but a silane coupling agent, a titanium coupling agent, a zirconium coupling agent, an aluminum coupling agent, etc. are mentioned, Among these, a silane coupling agent or a titanium coupling agent is preferable. Is used. Since these are relatively easy to obtain and have high adhesion at the interface between the inorganic material and the organic material, they are very suitable as a coupling agent included in the composite composition.

[0091] Moreover, it is preferable that a silane coupling agent contains at least 1 silicon atom and 1 or more alkoxy groups as a functional group among the said coupling agents. Moreover, an epoxy group or epoxy cyclohexyl group, amino group, hydroxyl group, acrylic group, methacryl group, vinyl group, phenyl group, styryl group, isocyanate group etc. are mentioned as other functional groups. Moreover, in this invention, since the effect equivalent to a coupling agent is obtained, the tetraalkoxysilane containing four alkoxy groups is also included in a silane coupling agent.

[0092] Specific examples of the silane coupling agent include an alkyl group-containing alkoxy silane compound such as a tetraalkoxysilane compound, methyltrialkoxysilane, and dimethyldialkoxysilane, 3-glycidoxypropyl trialkoxysilane, and 3-glycidpropylmethyl dialkoxysilane , Epoxy silane compounds such as 2- (3,4-epoxycyclohexyl) ethyl trialkoxysilane, aminoalkoxysilane compounds such as 3-aminopropyl trialkoxysilane, and N-phenyl-3-aminopropyl trialkoxysilane, 3- (Meth) acrylalkoxysilane compounds such as acryloxypropyl trialkoxysilane, methacryloxypropyl trialkoxysilane, 3-methacryloxypropylmethyl dialkoxysilane, and 3-methacryloxypropyl trialkoxysilane, and vinyl trialkoxysilane Phenyl group-containing trialcohols such as vinylalkoxysilane compounds, phenyltrialkoxysilanes, diphenyldialkoxysilanes, and 4-hydroxyphenyl trialkoxysilanes. And styryl group-containing alkoxy silane compounds such as cysilane compounds and 3-isocyanatepropyl trialkoxysilane. Among these, a tetraalkoxysilane compound, an alkyl group-containing alkoxy silane compound, and a phenyl group-containing alkoxy silane compound have a high effect of increasing water resistance, and are preferable.

[0093] On the other hand, specific examples of the titanium-based coupling agent include an alkoxy titanium compound having the same substituent as the alkoxysilane compound. For example, isopropyl triisostearoyl titanate, isopropyl tridodecylbenzenesulfonyl titanate, isopropyl tri (dioctylpyrophosphate) titanate, tetraisopropyl bis (dioctylphosphite) titanate, Tetraoctyl bis (ditridecylphosphite) titanate, isopropyl trioctanoyl titanate, isopropyl dimethacryl isostearoyl titanate, isopropyl isostearoyl diacrylic titanate, isopropyl tri (di Octyl phosphate) titanate, isopropyl trixylophenyl titanate, isopropyl tri (N-aminoethylaminoethyl) titanate, dicumylphenyloxyacetate titanate, diisostearoyl ethylene titanate, bis (dioctyl Pyrophosphate) ethylene titanate, bis (dioctyl pyrophosphate) oxyacetate titanate And tetra (2,2-diallyloxymethyl-1-butyl) bis (di-tridecyl) phosphite titanate.

[0094] Moreover, you may use the hydrolyzate of a coupling agent as mentioned above instead of a coupling agent. The coupling agent or the hydrolyzate thereof may be appropriately selected in consideration of compatibility with a dispersion medium, stability of the hydrolyzate, and the like. Further, the hydrolyzate of the coupling agent can be easily prepared by stirring and mixing an acidic aqueous solution such as an acetic acid aqueous solution with the coupling agent. Moreover, as a hydrolyzate of a coupling agent, even if it is not hydrolyzed a hydrolyzable group (alkoxide group), it may be manufactured by any method as long as the molecular structure is the same as the hydrolyzate of a coupling agent.

[0095] In addition, the above-mentioned water-soluble resin, thermoplastic resin, curable resin, and coupling agent may be used individually, or two or more may be used in combination.

[0096] (Metal oxide)

[0097] The type of the metal oxide used in the present invention is not particularly limited, but includes oxides of single metals such as SiO₂ (silica), Al₂O₃ (alumina), TiO₂ (titania), ZrO₂ (zirconia), and SiO₂-Al₂O₃ (Mullite Etc.), composite oxides, such as SiO₂-TiO₂, SiO₂-ZrO₂, spinel, titania-containing silica, zirconia-containing silica, etc. are mentioned.

[0098] The metal oxide may have any shape, but is preferably in the form of particles. In this case, not only the particles of the metal oxide are composed of one kind of oxide fine particles, but also may be composed of a mixture of two or more kinds of oxide fine particles. Such oxide fine particles can be obtained by a method such as a sol-gel method, a wet method, a vapor phase method, or a dry method.

[0099] Among the metal oxides, it is preferable to use SiO₂, Al₂O₃ or a composite oxide of these. These are not only relatively inexpensive, but also can improve the mechanical strength, heat resistance and wear resistance of the composite.

[0100] In particular, it is preferable to use fine particles of Al₂O₃ as a metal oxide in order to improve the wear resistance of the composite. These fine particles are the cheapest, and they are resistant to corrosion by acids and alkalis, so that the chemical stability of the composite can be enhanced.

[0101] In addition, when the composite is used for applications such as electronic components, it is preferable to use fine particles of SiO₂ (silica fine particles) as the metal oxide. Since these fine particles have a low dielectric constant, the dielectric constant of the composite can be reduced to suppress transmission delays in electronic components.

[0102] Examples of the silica fine particles include dry powdery silica fine particles and colloidal silica (silicasol) dispersed in a solvent. From the point of dispersibility, it is preferable to use colloidal silica (silicasol) dispersed in water or an organic solvent or a mixed solvent. Examples of the solvent include alcohols such as water, methanol, ethanol, isopropyl alcohol, butyl alcohol, and n-propyl alcohol, ketones, esters, and glycol ethers, but suitable for ease of dispersion of the fibrous filler. Solvents can be selected.

[0103] The average particle diameter of such a metal oxide is preferably 1 to 1000 nm, more preferably 1 to 50 nm, more preferably 5 to 50 nm, and most preferably 5 to 40 nm in terms of balance between transparency and workability. Becomes In addition, there is a possibility that the viscosity of the produced composite composition is extremely increased below the lower limit. On the other hand, if it exceeds the above upper limit, the transparency of the composite may deteriorate significantly, which is not preferable.

[0104] When using silica fine particles as the metal oxide, it is preferable to use silica fine particles in which the proportion of silica fine particles having a primary particle size of 200 nm or more is suppressed to 5% or less in order not to lower the light transmittance at a wavelength of 400 to 500 nm. It is more preferable to set the ratio to 0%. In order to increase the filling amount of the silica fine particles, silica fine particles having different average particle sizes may be mixed and used. As the silica fine particles, a porous silica sol as shown in Japanese Patent Application Laid-Open No. 7-48117, or a composite metal oxide of silicon such as aluminum, magnesium, zinc and the like may be used.

[0105] (Plastic inorganic material)

[0106] The flaky inorganic material used in the present invention includes, for example, clay minerals made of natural or synthetic materials. Specifically, it is selected from the group consisting of mica, vermiculite, montmorillonite, iron montmorillonite, videlite, saponite, hectorite, stevensite, nontronite, margadialite, illite, carnemite, layered titanic acid, smectite, etc. At least 1 type is mentioned.

[0107] The flake-like inorganic material is a scaly flake, typically having a particle size of about 1 to 10 nm, an aspect ratio of preferably 20 to several thousand, and more preferably 20 to hundreds. When such scale-like clay particles overlap any layer in the composite, the path through which the gas passes increases, resulting in improved gas barrier properties of the composite.

[0108] Moreover, you may make it contain the cation substance which has hydrophobicity as needed between the layers of flaky inorganic materials in a composite composition. In general, clay minerals contain hydrophilic, exchangeable cations between layers. In the present invention, the hydrophilic exchangeable cation existing between the layers of the flaky inorganic material, which is a clay mineral, can be organically exchanged with a hydrophobic cation. As the hydrophobic cationic material, for example, quaternary ammonium salts such as dimethyl distearyl ammonium salt and trimethylstearyl ammonium salt, ammonium salts having a benzyl group or polyoxyethylene group are used, or phosphonium salts, pyridinium salts or imidazolium salts It is also possible to organicize using the ion-exchange property of clay.

[0109] In addition, the composite composition of the present invention may contain any of the resins, metal oxides, and flaky inorganic materials described above, or may contain two or more. For example, the composite composition of the present invention may contain a fibrous filler, a resin, a metal oxide, and a flaky inorganic material.

[0110] In the composite composition of the present invention, the content of the fibrous filler is preferably 0.1 to 99.9% by weight, and more preferably 0.1 to 75% by weight. Moreover, the content rate of a fibrous filler is not specifically limited, It is suitably adjusted according to the characteristic required when shape | molding a composite composition. In the composite composition, if the properties of the fibrous filler are to be more reflected, the content of the fibrous filler is increased, and if the properties of the resin are to be further reflected, the content of the resin may be increased.

[0111] In addition, in the case of preparing a composite used for optical use using the composite composition of the present invention, it is preferable that the average thermal expansion coefficient (average linear expansion coefficient) of 30 to 180 ° C of the composite composition is 50 ppm / ° C or less, and more preferably It is 30 ppm / ° C or less, more preferably 20 ppm / ° C or less.

[0112] Moreover, the composite composition of the present invention preferably has a total light transmittance of 80% or more at a thickness of 30 µm, more preferably 90% or more. As a result, a composite having high transparency and suitable for optical use is finally obtained.

[0113] <Composite>

[0114] The composite of the present invention is obtained by molding the composite composition of the present invention into a predetermined shape.

[0115] The composite of the present invention is used, for example, as a substrate for a solar cell, a substrate for an organic EL, a substrate for an electronic paper, or a plastic substrate for a liquid crystal display device, but in this case, the total light transmittance is preferably 70% or more, more preferably Is 80% or more, and more preferably 88% or more.

[0116] In addition, the composite of the present invention can be used, for example, in optical applications, that is, transparent plates, optical lenses, plastic substrates for liquid crystal display elements, substrates for color filters, plastic substrates for organic EL display elements, solar cell substrates, touch panels, and optical elements. , When used as an optical waveguide, LED encapsulant, etc., the average thermal expansion coefficient (average linear expansion coefficient) of 30 to 150 ° C is preferably 50 ppm / ° C or less, and more preferably 30 ppm / ° C or less. Particularly, when used for a sheet-like active matrix display element substrate, the average thermal expansion coefficient is preferably 30 ppm / ° C or less, more preferably 20 ppm / ° C or less. This is because if the above upper limit is exceeded, problems such as warping or disconnection of wiring may occur in the manufacturing process. In addition, although the lower limit is not particularly set, it is 0.4 ppm / ° C as an example.

[0117] Moreover, in the case where the composite of the present invention is used as, for example, a plastic substrate for a liquid crystal display element, a substrate for a color filter, a plastic substrate for an organic EL display element, a solar cell substrate, a touch panel, etc., the humidity expansion coefficient is preferably It is 100 ppm / humidity% or less, More preferably, it is 50 ppm / humidity% or less, More preferably, it is 30 ppm / humidity% or less. Furthermore, the swelling ratio (swelling ratio) at the time of absorption of the composite of the present invention is preferably 50 times or less, more preferably 30 times or less, still more preferably 10 times or less.

[0118] Moreover, when the composite of the present invention is molded into a plate shape, the thickness is preferably 10 to 2000 µm, more preferably 10 to 500 µm, and even more preferably 20 to 200 µm. When the thickness of the substrate is within this range, the composite of the present invention is required as a transparent substrate and also has sufficient mechanical strength and light transmittance. Moreover, by making the thickness of the substrate within the above range, the flatness is excellent, and the weight of the substrate can be reduced compared to the glass substrate.

[0119] When using the composite composition of the present invention as an optical sheet, a coating layer of resin may be provided on both surfaces for improving smoothness. It is preferable to have excellent transparency, heat resistance, and chemical resistance as the resin to be coated, and specific examples thereof include polyfunctional acrylates and epoxy resins. The average thickness of the coat layer is preferably 0.1 to 50 µm, and more preferably 0.5 to 30 µm.

[0120] Moreover, when using the optical sheet obtained from the composite composition of this invention as a plastic substrate for display elements especially, you may provide a gas barrier layer for water vapor and oxygen, or a transparent electrode layer as needed.

[0121] When the composite composition of the present invention contains a curable resin, the curing method of the curable resin is not particularly limited, but a curing accelerator such as a crosslinking agent such as an acid anhydride or an aliphatic amine, or a cationic curing catalyst or anionic curing catalyst may be used. You can.

[0122] Among them, as the cationic curing catalyst, for example, a substance that initiates cationic polymerization by heating is released (for example, an onium salt-based cationic curing catalyst or an aluminum chelate-based cationic curing catalyst) or cationic polymerization by an active energy ray. And those which release substances (for example, onium salt-based cationic curing catalysts). Specifically, examples of aromatic sulfonium salts include hexafluoroantimonate salts such as SI-60L, SI-80L, SI-100L manufactured by Samshin Chemical, and SP-66 and SP-77 manufactured by Asahi Corporation. Examples of the aluminum chelate include ethylacetate aluminum diisopropylate, aluminum tris (ethylacetate), and the like, boron trifluoride amine complex, boron trifluoride monoethylamine complex, boron trifluoride imidazole complex, And a boron trifluoride piperidine complex.

[0123] On the other hand, as an anionic curing accelerator, for example, tertiary amines such as 1,8-diaza-bicyclo (5,4,0) undecene-7 and triethylenediamine, 2-ethyl-4-methylimidazole imidazoles such as sol or 1-benzyl-2-phenylimidazole, phosphorus compounds such as triphenylphosphine, tetraphenylphosphonium tetraphenylborate, quaternary ammonium salts, organic metal salts, and derivatives thereof. , Among these, imidazoles such as phosphorus compounds and 1-benzyl-2-phenylimidazole are preferable from those excellent in transparency. These curing accelerators may be used alone or in combination of two or more.

[0124] In the composite composition of the present invention, a thermoplastic or thermosetting oligomer or polymer can be used in combination, if necessary. In addition, the composite composition of the present invention may contain a small amount of antioxidants, ultraviolet absorbers, salt pigments, fillers such as other inorganic fillers, and the like in a range that does not impair the properties as necessary.

[0125] The composite composition of the present invention is prepared by mixing each component by any method. For example, a method of mixing at least one of a fibrous filler and a resin, a metal oxide, and a flaky inorganic material as it is mentioned. Moreover, you may mix it, heating as needed.

[0126] In addition, if a method of preparing a uniform dispersion of a fibrous filler using a solvent (dispersion medium) and then performing desolvation is used, a uniform composite composition excellent in dispersibility of the fibrous filler and dispersibility of a metal oxide or flaky inorganic material Can get

[0127] As a solvent to be used, for example, a solvent capable of maintaining the dispersibility of the fibrous filler and dissolving or dispersing the resin, metal oxide, and flaky inorganic material is preferable. Examples of such a solvent include water, methyl alcohol, ethyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, diethylene glycol, dioxane, acetone, methyl ethyl ketone, methyl cellosolve, tetrahydrofuran, penta Erythritol, dimethyl sulfoxide, dimethylformamide, N-methyl-2-pyrrolidone, etc. may be mentioned, or these may be used alone or in combination of two or more. Further, it is also possible to disperse the fibrous filler in a dispersion medium of different polarity by gradually changing the polarization rate of the original dispersion medium to the polarity of the desired dispersion medium.

[0128] Furthermore, the method for obtaining a sheet having a predetermined thickness such as a substrate for a solar cell, a substrate for an organic EL, a substrate for an electronic paper, or a plastic substrate for a liquid crystal display device using the composite composition of the present invention may be a general sheet forming method, and is particularly limited. Does not work. For example, a method of directly sheeting a composite composition containing a fibrous filler and a resin, metal oxide, and flaky inorganic material, or softening a dispersion medium of the fibrous filler and removing a solvent to obtain a sheet of the fibrous filler, After that, a method of impregnating the resin or a solution containing a fibrous filler and a resin, a metal oxide, and a flaky inorganic material and a solvent is flexible, and then a solvent is removed to obtain a sheet.

[0129] One of the preferred embodiments in such a process is to prepare a dispersion by dispersing at least one of a fibrous filler, a resin, a metal oxide, and a flaky inorganic material in a solvent in advance, and then dispersing the obtained dispersion into a filter paper, membrane filter or draft net , It is a method of obtaining a sheet made of a composite composition by filtering and / or drying other components such as a solvent. In addition, in the drying process by filtration, it may be carried out under reduced pressure and under pressure in order to increase work efficiency. Moreover, when forming continuously, the method of continuously forming a thin-layer sheet using the paper machine used in the paper industry is also included.

[0130] When manufacturing a sheet by being flexible, it is preferable that the sheet formed after filtration and / or drying is produced on a substrate that can be easily peeled off. As such a base material, what is made of metal or resin is mentioned. Examples of the metal base material include a stainless steel base material, a brass base material, a zinc base material, a copper base material, and an iron base material. The resin base material includes an acrylic base material, a fluorine base material, a polyethylene terephthalate base material, and a vinyl chloride base material. , Polystyrene base materials, polyvinylidene chloride base materials, and the like.

[0131] Example

[0132] Next, specific examples of the present invention will be described.

[0133] [Production A of Micro Cellulose Fiber]

[0134] (Production Example A)

[0135] First, it is mainly composed of cellulose fibers with a fiber diameter exceeding 1000 nm, and 2 g of undried pulp and 0.025 g of TEMPO (2,2,6,6-tetramethyl-1-piperidine-N) in a dry weight. -Oxyl) and 0.25 g of sodium bromide were dispersed in 150 ml of water to prepare a dispersion.

[0136] Next, 13% by weight of sodium hypochlorite aqueous solution was added to this dispersion so that the amount of sodium hypochlorite was 2.5 mmol per 1 g of pulp, and the reaction was started. During the reaction, 0.5M sodium hydroxide aqueous solution was added dropwise to the dispersion to maintain the pH at 10.5. Thereafter, when no change in pH was observed, the reaction was deemed to be complete, and the reaction was filtered through a glass filter, and the filtrate was washed with a sufficient amount of water, and filtration was repeated 5 times. As a result, a reactant fiber containing 25% by weight of solid content was obtained.

[0137] Next, water was added to the obtained reactant fibers to prepare a 2% by weight slurry. Then, the slurry was treated with a rotary blade mixer for about 5 minutes. Since the viscosity of the slurry increased remarkably with the treatment, water was added little by little to continue dispersion treatment with a mixer until the solid content concentration was 0.2% by weight. Thereby, a cellulose nanofiber dispersion was obtained.

[0138] This cellulose nanofiber dispersion was cast on a carbon film-coated grid after hydrophilic treatment, and then negatively dyed with 2% uranyl acetate. And the cast cellulose nanofiber dispersion was observed by TEM, but the maximum fiber diameter was 10 nm and the number average fiber diameter was 6 nm.

[0139] Moreover, the cast cellulose nanofiber dispersion was dried, and transparent membrane-like cellulose was obtained. A wide-angle X-ray diffraction image was obtained for this membrane-like cellulose, and it became clear that the membrane-like cellulose was composed of cellulose nanofibers having a cellulose I-type crystal structure.

[0140] Moreover, total reflection infrared spectroscopy analysis was performed on the same membrane cellulose to obtain an ATR spectrum. In the pattern of the ATR spectrum, the presence of the carbonyl group was confirmed, and the amount of the aldehyde group and the amount of the carboxyl group in cellulose evaluated by the above-described method were 0.31 mmol / g and 0.97 mmol / g, respectively.

[0141] [Production A of Composites]

[0142] (Example 1A)

[0143] The cellulose nanofiber dispersion (solid content 10 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A was filtered under reduced pressure to remove water and replaced with methanol 5 times. Next, the cellulose nanofiber methanol dispersion was filtered under reduced pressure to remove methanol, and the operation of further replacing 90 parts by weight of an alicyclic epoxy monomer containing 1 part by weight of a thermal cationic catalyst (SI-100L) was repeated 5 times. Then, the obtained cellulose nanofiber dispersion epoxy resin (cellulose solid content 10% by weight) was molded and heated at 100 ° C for 2 hours, followed by heating at 150 ° C for 2 hours to cure. Thereby, a composite having a thickness of 1 mm was obtained. The obtained composite was cut to a width of 10 mm, and a test piece for bending strength measurement was produced. When the bending strength was measured for this test piece, it was 48N.

[0144] (Example 2A)

[0145] Cellulose nanofibers were obtained by filtering under reduced pressure the cellulose nanofiber dispersion (solids content: 15 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A and further freeze-drying. Next, the mixture obtained by adding 15 parts by weight of cellulose nanofibers to 85 parts by weight of phenol novolac resin and 15 parts by weight of hexamethylenetetramine was mixed with a mixer for 3 minutes. In addition, the mixture was kneaded by two heating rolls at 100 ° C to obtain a thermosetting resin molding material. The obtained molding material was heated at 125 ° C for 2 hours by compression molding, and then further cured by heating at 150 ° C for 2 hours. Thereby, a composite having a thickness of 1 mm was obtained. The obtained composite was cut to a width of 10 mm to produce a test piece for bending strength measurement. The bending strength of this test piece was 60N.

[0146] (Example 3A)

[0147] To the cellulose nanofiber dispersion (solid content 100 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A, tetraethoxysilane was added in the same weight as the cellulose nanofiber solid content, and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. The total light transmittance, the coefficient of thermal expansion, and the coefficient of humidity expansion were measured for this film. The total light transmittance was 90%, the coefficient of thermal expansion was 11 ppm / ° C, and the coefficient of humidity expansion was 26 ppm / humidity%.

[0148] (Example 4A)

[0149] To the cellulose nanofiber dispersion (solid content 100 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A, phenyltriethoxysilane was added in the same weight as the cellulose nanofiber solid content, and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For this film, the total light transmittance, the coefficient of thermal expansion, and the coefficient of humidity expansion were measured. The total light transmittance was 89%, the coefficient of thermal expansion was 10 ppm / ° C, and the coefficient of humidity expansion was 23 ppm / humidity%.

[0150] (Example 5A)

[0151] 3-glycidoxypropyl triethoxysilane was added to the cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight (100 parts by weight of the solid content) obtained in Production Example A and the same weight as the weight of the cellulose nanofiber solid content and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. The total light transmittance, thermal expansion coefficient, and humidity expansion coefficient were measured for this film. The total light transmittance was 88%, the thermal expansion coefficient was 11 ppm / ° C, and the humidity expansion coefficient was 25 ppm / humidity%.

[0152] (Example 6A)

[0153] Titanium alkoxide was added to the cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight (100 parts by weight of the solid content) obtained in Production Example A, and the same weight as that of the cellulose nanofiber solid content was added, followed by stirring at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For this film, total light transmittance, thermal expansion coefficient, and humidity expansion coefficient were measured. The total light transmittance was 88%, the thermal expansion coefficient was 12 ppm / ° C, and the humidity expansion coefficient was 27 ppm / humidity%.

[0154] (Example 7A)

[0155] Cellulose nanofiber dispersion (solid content of 100 parts by weight) and solid resin concentration of 0.2% by weight obtained in Production Example A were mixed with 80 parts by weight of epoxy resin (Denacol EX-214L, manufactured by Nagase Chemtex) and 5 parts by weight of tetramethylethylenediamine. The mixture was stirred for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 50 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured for this film. The total light transmittance was 80%, the thermal expansion coefficient was 15 ppm / ° C, the humidity expansion coefficient was 110 ppm / humidity%, and the swelling rate was 16 times. .

[0156] (Example 8A)

[0157] Cellulose nanofiber dispersion (solid content 100 parts by weight) and epoxy resin (Denacol EX-1410L, manufactured by Nagase Chemtex) having a solid content concentration of 0.2% by weight obtained in Production Example A were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 50 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured for this film. The total light transmittance was 80%, the thermal expansion coefficient was 14 ppm / ° C, the humidity expansion coefficient was 61 ppm / humidity%, and the swelling ratio was 1.8 times. .

[0158] (Example 9A)

[0159] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and epoxy resin (Denacol EX-1410L, manufactured by Nagase Chemtex) having a solid content concentration of 0.2% by weight obtained in Production Example A were mixed with 5 parts by weight of tetramethylethylenediamine and mixed at room temperature. The mixture was stirred for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 50 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured for this film. The total light transmittance was 80%, the thermal expansion coefficient was 12 ppm / ° C, the humidity expansion coefficient was 90 ppm / humidity%, and the swelling ratio was 3.1 times. .

[0160] (Example 10A)

[0161] Cellulose nanofiber dispersion (solid content of 100 parts by weight) and solid resin concentration of 0.2% by weight obtained in Production Example A were mixed with 110 parts by weight of epoxy resin (Denacol EX-1610L, manufactured by Nagase Chemtex) and 5 parts by weight of tetramethylethylenediamine. The mixture was stirred for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 50 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured for this film. The total light transmittance was 80%, the thermal expansion coefficient was 13 ppm / ° C, the humidity expansion coefficient was 76 ppm / humidity%, and the swelling rate was 2.4 times. .

[0162] (Example 11A)

[0163] Cellulose nanofiber dispersion (solids content of 100 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A was mixed with 100 parts by weight of resol type phenol resin (PR-967, manufactured by Sumitomo Bakelite) and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film having a thickness of 25 µm was obtained. The total light transmittance, humidity expansion coefficient, and swelling rate were measured for this film. The total light transmittance was 50%, the humidity expansion coefficient was 50 ppm /% humidity, and the swelling

rate was 1.2 times. Moreover, since this sample was bitten, a sample for measuring the thermal expansion coefficient could not be obtained.

[0164] (Example 12A)

[0165] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid resin concentration of 0.2% by weight obtained in Production Example A were mixed with 300 parts by weight of resol type phenolic resin (PR-967, manufactured by Sumitomo Bakelite) and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film with a thickness of 58 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured for this film. The total light transmittance was 40%, the thermal expansion coefficient was 20 ppm / ° C, the humidity expansion coefficient was 45 ppm / humidity%, and the swelling rate was 1.2 times. .

[0166] (Comparative Example 1A)

[0167] After the sulfurous bleached coniferous pulp was swollen in water, it was finely dispersed with a mixer. The obtained short fiber pulp dispersion was filtered under reduced pressure to remove water and replaced with methanol 5 times. Next, the operation of replacing the short-fiber pulp methanol dispersion with reduced pressure by filtration to remove methanol and replacing 90 parts by weight of an alicyclic epoxy monomer containing 1 part by weight of a cationic catalyst (SI-100L) was repeated 5 times. Then, the obtained short-fiber pulp dispersion epoxy resin (cellulose solid content 10% by weight) was molded and heated at 100 ° C for 2 hours, followed by further heating at 150 ° C for 2 hours to cure. Thereby, a composite having a thickness of 1 mm was obtained. The obtained composite was cut to a width of 10 mm to prepare a test piece for bending strength measurement. The bending strength of this test piece was 28N.

[0168] In addition, a single fiber pulp methanol dispersion was observed by SEM, and the maximum fiber diameter was 70 µm and the number average fiber diameter was 40 µm.

[0169] (Comparative Example 2A)

[0170] After the sulfurous bleached coniferous pulp was swollen in water, it was finely dispersed with a mixer. The obtained short-fiber pulp dispersion was filtered under reduced pressure to remove water, and further freeze-dried to obtain fine cellulose fibers. Next, the mixture obtained by adding 15 parts by weight of fine cellulose fibers to 85 parts by weight of phenol novolac and 15 parts by weight of hexamethylenetetramine was mixed with a mixer for 3 minutes. In addition, the mixture was kneaded by two heating rolls at 100 ° C to obtain a thermosetting resin molding material. The obtained molding material was heated at 125 ° C for 2 hours by compression molding, and then further cured by heating at 150 ° C for 2 hours. Thereby, a composite having a thickness of 1 mm was obtained. The obtained composite was cut to a width of 10 mm to produce a test piece for bending strength measurement. When the bending strength was measured for this test piece, it was 40N.

[0171] In addition, a single fiber pulp methanol dispersion was observed by SEM, and the maximum fiber diameter was 70 µm and the number average fiber diameter was 40 µm.

[0172] (Comparative Example 3A)

[0173] The cellulose nanofiber dispersion (solid content 0.15% by weight) obtained in Production Example A was evaporated with moisture in an oven at a temperature of 50 ° C according to a chalet subjected to a release treatment, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured for this film. The total light transmittance was 91%, the thermal expansion coefficient was 10 ppm / ° C, the humidity expansion coefficient was 125 ppm / humidity%, and the swelling rate was 140 times. .

[0174] [Production B of fine cellulose fibers]

[0175] (Production Example B)

[0176] First, it is mainly composed of cellulose fibers with a fiber diameter exceeding 1000 nm, and 2 g of undried pulp and 0.025 g of TEMPO (2,2,6,6-tetramethyl-1-piperidine-N) in a dry weight. -Oxyl) and 0.25 g of sodium bromide were dispersed in 150 ml of water to prepare a dispersion.

[0177] Next, 13% by weight of an aqueous sodium hypochlorite solution was added to this dispersion so that the amount of sodium hypochlorite was 2.5 mmol per 1 g of pulp, and the reaction was started. During the reaction, 0.5M sodium hydroxide aqueous solution was added dropwise using an automatic titrator to maintain the pH at 10.5. Subsequently, when no change in pH was observed, the reaction was considered to be complete, and neutralized to pH 7 with 0.5M aqueous hydrochloric acid. Then, the reaction was filtered and the filtrate was washed with a sufficient amount of water, and filtration was repeated six times. Thereby, a reactant fiber containing water having a solid content concentration of 2% by weight was obtained.

[0178] Next, 0.2% by weight of a reactant fiber dispersion was prepared by adding water to the obtained reactant fiber.

[0179] This reaction fiber dispersion was treated 20 times at a pressure of 200 bar (20 MPa) using a high pressure homogenizer (manufactured by APV GAULIN LABORATORY, type 15MR-8TA). Thereby, a transparent cellulose nanofiber dispersion was obtained.

[0180] This cellulose nanofiber dispersion was cast on a carbon film-coated grid after hydrophilic treatment, and then negatively dyed with 2% uranyl acetate. And the cast cellulose nanofiber dispersion was observed by TEM, but the largest fiber diameter was 10 nm and the number average fiber diameter was 8 nm.

[0181] Moreover, the cast cellulose nanofiber dispersion was dried, and transparent membrane-like cellulose was obtained. A wide-angle X-ray diffraction image was obtained for this membrane-like cellulose, and it became clear that the membrane-like cellulose was composed of cellulose nanofibers having a cellulose I-type crystal structure.

[0182] In addition, the same membrane-like cellulose was subjected to total reflection infrared spectroscopy to obtain an ATR spectrum. The presence of the carbonyl group was confirmed from the pattern of the ATR spectrum, and the amount of the aldehyde group and the amount of the carboxyl group in cellulose evaluated by the method described above were 0.31 mmol / g and 1.7 mmol / g, respectively.

[0183] [Production of Composite B]

[0184] (Example 1B)

[0185] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex 20, particle diameter 10-20 nm, anhydrous silicic acid content 20-21 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2 wt%) Industrial Co.) 1 part by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 87%, and the thermal expansion coefficient in the range of 30 ° C to 180 ° C was 9 ppm / ° C, and the humidity expansion coefficient was 70 ppm /% humidity, and the swelling rate was twice.

[0186] (Example 2B)

[0187] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex N, particle diameter 10-20 nm, anhydrous silicic acid content 20-21 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2% by weight) Industrial Co.) 1 part by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated to moisture in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. The thermal expansion coefficient, humidity expansion coefficient, and swelling rate of the obtained film were measured. The thermal expansion coefficient in the range of 30 ° C to 180 ° C is 10 ppm / ° C, the humidity expansion coefficient is 61 ppm /% humidity, and the swelling rate is 1.6 times.

[0188] (Example 3B)

[0189] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex O, particle diameter 10-20 nm, anhydrous silicic acid content 20-21 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2 wt%) Industrial Co.) 1 part by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated to moisture in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, the total light transmittance, the coefficient of thermal expansion, the coefficient of humidity expansion and the swelling rate were measured. Was 65 ppm /% humidity, and the swelling ratio was 1.7 times.

[0190] (Example 4B)

[0191] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex XS, particle diameter 4-6 nm, anhydrous silicic acid content 20-21 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2% by weight) Industrial Co.) 1 part by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, the total light transmittance, the coefficient of thermal expansion, the coefficient of humidity expansion and the swelling rate were measured. Was 68 ppm /% humidity, and the swelling ratio was 1.9 times.

[0192] (Example 5B)

[0193] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex CM, particle diameter 20-30 nm, anhydrous silicic acid content 30-31 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2% by weight) Industry Co., Ltd.) 0.7 parts by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 88%, and the thermal expansion coefficient in the range of 30 ° C to 180 ° C was 11 ppm / ° C, and the humidity expansion coefficient. Was 70 ppm /% humidity, and the swelling ratio was 1.9 times.

[0194] (Comparative Example 1B)

[0195] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example B was evaporated from the oven at a temperature of 50 ° C according to the chalet subjected to the release treatment, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, the total light transmittance, the coefficient of thermal expansion, the coefficient of humidity expansion and the swelling rate were measured. Was 115 ppm / % humidity, and the swelling ratio was 100 times.

[0196] [Production C of fine cellulose fibers]

[0197] (Production Example C)

[0198] First, it is mainly composed of fibers with a fiber diameter of more than 1000 nm, and by dry weight, 2 g equivalent of undried pulp and 0.025 g of TEMPO (2,2,6,6-tetramethyl-1-piperidine-N-Oxyl) and 0.25 g of sodium bromide were dispersed in 150 ml of water to prepare a dispersion.

[0199] Next, 13% by weight of an aqueous sodium hypochlorite solution was added to this dispersion so that the amount of sodium hypochlorite was 2.5 mmol per 1 g of pulp, and the reaction was started. During the reaction, 0.5M sodium hydroxide aqueous solution was added dropwise using an automatic titrator to maintain the pH at 10.5. Subsequently, when no change in pH was observed, the reaction was considered to be complete, and neutralized to pH 7 with 0.5M aqueous hydrochloric acid. Then, the reaction product was filtered and the filtrate was washed with a sufficient amount of water, and filtration was repeated 6 times. Thereby, a reactant fiber containing 2% by weight of water in a solid content was obtained.

[0200] Next, 0.2% by weight of a reactant fiber dispersion was prepared by adding water to the obtained reactant fiber.

[0201] This reactant fiber dispersion was treated 10 times at a pressure of 20 MPa using a high pressure homogenizer (manufactured by APV GAULIN LABORATORY, type 15MR-8TA). Thereby, a transparent cellulose nanofiber dispersion was obtained.

[0202] This cellulose nanofiber dispersion was cast on a carbon film-coated grid that had been subjected to hydrophilic treatment, and then negatively dyed with 2% uranyl acetate. And the cast cellulose nanofiber dispersion was observed by TEM, but the largest fiber diameter was 10 nm and the number average fiber diameter was 6 nm.

[0203] Moreover, the cast cellulose nanofiber dispersion was dried, and transparent membrane-like cellulose was obtained. A wide-angle X-ray diffraction image was obtained for this membrane-like cellulose, and it became clear that the membrane-like cellulose was composed of cellulose nanofibers having a cellulose I-type crystal structure.

[0204] In addition, the same membrane-like cellulose was subjected to total reflection infrared spectroscopy to obtain an ATR spectrum. The presence of the carbonyl group was confirmed from the pattern of the ATR spectrum, and the amount of the aldehyde group and the amount of the carboxyl group in cellulose evaluated by the method described above were 0.31 mmol / g and 1.7 mmol / g, respectively.

[0205] [Production C of Composites]

[0206] (Example 1C)

[0207] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C and synthetic smectite (lucentite SWF) were mixed so that the weight ratio of cellulose nanofiber and synthetic smectite was 25 to 75 and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated from the oven at a temperature of 50 ° C. according to a chalet subjected to a release treatment to obtain a transparent film having a thickness of 50 µm. The total light transmittance, thermal expansion coefficient, and swelling rate of the obtained film were evaluated. The total light transmittance was 91%, the coefficient of linear expansion in the range of 30 ° C to 180 ° C was 4 ppm / ° C, and the swelling rate was 15 times.

[0208] (Example 2C)

[0209] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C and synthetic smectite (lucentite SWF) were mixed so that the weight ratio of cellulose nanofiber and synthetic smectite was 55 to 45, and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated in an oven at a temperature of 50 ° C. according to a chalet subjected to a release treatment to obtain a transparent film having a thickness of 20 µm. The total light transmittance, the coefficient of thermal expansion and the swelling rate of the obtained film were evaluated. The total light transmittance was 91%, the linear expansion coefficient in the range of 30 ° C to 180 ° C was 5 ppm / ° C, and the swelling rate was 48 times.

[0210] (Example 3C)

[0211] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C and synthetic saponite (Smecton SA) were mixed so that the weight ratio of cellulose nanofiber and synthetic saponite was 25 to 75 and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated in an oven at a temperature of 50 ° C. according to a chalet subjected to a release treatment to obtain a transparent film having a thickness of 47 µm. The total light transmittance, the coefficient of thermal expansion and the swelling rate of the obtained film were evaluated. The total light transmittance was 90%, the coefficient of linear expansion in the range of 30 ° C to 180 ° C was 3.2 ppm / ° C, and the swelling rate was 12 times.

[0212] (Example 4C)

[0213] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C and synthetic saponite (Smecton SA) were mixed so that the weight ratio of cellulose nanofiber and synthetic saponite was 50 to 50 and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated in an oven at a temperature of 50 ° C. according to a chalet subjected to a release treatment to obtain a transparent film having a thickness of 41 µm. The total light transmittance, thermal expansion coefficient, and swelling rate of the obtained film were evaluated. The total light transmittance was 90%, the coefficient of linear expansion in the range of 30 ° C to 180 ° C was 5.8 ppm / ° C, and the swelling rate was 32 times.

[0214] (Example 5C)

[0215] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid flake inorganic material (from Lucent SWF, manufactured by Coff Chemical Co., Ltd.) having a solid content concentration of 0.2% by weight obtained in Production Example C and epoxy resin (Denacol EX-214L, Nagase Chemtex) Co.) 600 parts by weight were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film with a thickness of 24 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured. The total light transmittance was 91%, the thermal expansion coefficient was 14 ppm / ° C, the humidity expansion coefficient was 60 ppm / humidity%, and the swelling ratio was 2.1 times. .

[0216] (Example 6C)

[0217] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid flake inorganic material (from Lucent SWF, manufactured by Coff Chemical Co., Ltd.) having a solid content concentration of 0.2% by weight obtained in Production Example C and epoxy resin (Denacol EX-214L, Nagase Chemtex) Co.) 200 parts by weight were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a film having a thickness of 50 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 92%, the thermal expansion coefficient was 13 ppm / ° C, the humidity expansion coefficient was 57 ppm / humidity%, and the swelling rate was 1.7 times. .

[0218] (Example 7C)

[0219] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid flake inorganic material (Smecton SA, manufactured by Kunimine Industries) with a solid content concentration of 0.2% by weight obtained in Production Example C and epoxy resin (Denacol EX-214L, Nagase) Chemtex Corporation) 600 parts by weight were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film having a thickness of 30 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 91%, the thermal expansion coefficient was 15 ppm / ° C, the humidity expansion coefficient was 92 ppm / humidity%, and the swelling ratio was 3.4 times. .

[0220] (Example 8C)

[0221] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid flake inorganic material (Smecton SA, manufactured by Kunimine Industries) with a solid content concentration of 0.2% by weight obtained in Production Example C and epoxy resin (Denacol EX-214L, Nagase) Chemtex Corporation) 200 parts by weight were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film with a thickness of 58 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 91%, the thermal expansion coefficient was 13 ppm / ° C, the humidity expansion coefficient was 71 ppm / humidity%, and the swelling rate was 2.4 times. .

[0222] (Comparative Example 1C)

[0223] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C was stirred at room temperature for 30 minutes and evaporated moisture in an oven at a temperature of 50 ° C. according to the release-treated chalet to obtain a transparent film having a thickness of 18 µm. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate of the obtained film were evaluated. The total light transmittance was 90%, the coefficient of thermal expansion in the range of 30 ° C to 180 ° C was 12 ppm / ° C, the coefficient of humidity expansion was 200 ppm /% humidity, and the swelling rate was 185 times.

[0224] [Evaluation of Complexes]

[0225] The characteristic evaluation method is as follows.

[0226] (a) Flexural strength

[0227] The bending strength of the test piece for measuring the bending strength is in accordance with JIS K 7171, the extension distance 36 mm, the cross head speed 1 mm / min, 23 ° C, the bending strength measurement device under 60%

relative humidity (Note) Was measured using Orient Tech Co., Ltd., UCT-30T type tensiron).

[0228] (b) Thermal expansion coefficient

[0229] Using a thermal stress distortion measuring device (TMA / SS120C, manufactured by Seiko Electronics Co., Ltd.), the temperature was increased from 30 ° C to 150 ° C at a rate of 5 ° C for 1 minute under a nitrogen atmosphere, and then 0 After cooling to ° C, the temperature was increased at a rate of 5 ° C for 1 minute to obtain a value measured at 30 ° C to 150 ° C. The load was set to 5 g, and measurement was performed in a tensile mode.

[0230] In addition, for Examples 1B to 5B and Comparative Example 1B, after raising the temperature from 30 ° C to 200 ° C at a rate of 5 ° C for 1 minute, once cooled to 0 ° C, and again at 5 ° C for 1 minute It was obtained by measuring the value at 30 ° C ~ 180 ° C by raising the temperature at a rate.

[0231] In addition, for Examples 1C to 8C and Comparative Example 1C, the temperature was increased from 30 ° C to 200 ° C at a rate of 5 ° C for 1 minute, and then cooled to -50 ° C once again, and then 5 ° C for 1 minute. It was obtained by measuring the value at 30 ° C ~ 180 ° C by raising the temperature in the ratio of.

[0232] (c) Total light transmittance

[0233] The total light transmittance was measured with a spectrophotometer (manufactured by Shimadzu Corporation, U3200).

[0234] In addition, about Example 1C-8C and Comparative Example 1C, the total light transmittance was measured with the haze meter (made by Nippon Color Co., Ltd., NDH-2000).

[0235] (d) Humidity expansion coefficient

[0236] On the obtained film, two points, which are the basis of dimensional measurement, were drawn and left for 24 hours in an atmosphere of 23 ° C at room temperature and 60% humidity, and then dried in a dryer at 100 ° C for 3 hours.

[0237] Immediately after drying, the distance between two points drawn in advance was measured with a three-dimensional measuring instrument, and this distance was used as a reference for the distance between two points. Thereafter, the film after drying was allowed to stand for 24 hours under an atmosphere of 23 ° C and 60% humidity again, and the distance between two points drawn in advance was measured with a 3D measuring instrument to calculate the rate of dimensional change from the reference distance. In addition, the humidity of the exterior after drying was set to 0%, and the coefficient of humidity expansion per 1% of humidity in the range of 0% to 60% of humidity was calculated.

[0238] (e) swelling ratio

[0239] The obtained film was immersed in pure water at 23 ° C for 1 hour to measure the rate of change in film thickness before and after impregnation. And the swelling ratio was calculated as a magnification of the film thickness after impregnation to the film thickness before impregnation.

[0240] The measurement results are shown in Tables 1-3.

[0242] As can be seen from Table 1, the test pieces obtained in Examples 1A and 2A (composites obtained using the composite composition of the present invention) are all mechanical strength compared to the test pieces comprising the conventional fibrous filler obtained in Comparative Example 1A. And high dimensional stability and excellent various properties.

[0243] Further, the films obtained in Examples 3A to 12A (composites obtained using the composite composition of the present invention) are films formed from a composite composition comprising a fibrous filler and a resin or a coupling agent (or a hydrolyzate of the coupling agent), but these are humidity It was confirmed that the expansion coefficient (absorption dimensional change rate) and the thermal expansion coefficient were relatively small and excellent transparency.

[0245] As can be seen from Table 2, it was confirmed that the films obtained in Examples 1B to 5B (composites obtained using the composite composition of the present invention) had a small swelling ratio and excellent water resistance compared to the films obtained in Comparative Example 1B. .

[0247] As can be seen from Table 3, it was confirmed that the films obtained in Examples 1C to 8C (composites obtained using the composite composition of the present invention) had a small swelling ratio and excellent water resistance compared to the films obtained in Comparative Example 1C. . Moreover, it was confirmed that the films obtained in Examples 1C to 8C had relatively low thermal expansion coefficients, and thus excellent dimensional stability due to heat and high transparency.

[0248] In addition, the main raw materials used in each Example and each comparative example are as follows.

[0249] Epoxy resin

[0250] : Seroxide 2021 Daicel Chemical

[0251] : Denacall EX-214L manufactured by Nagase Chemtex

[0252] : Denacall EX-1410L manufactured by Nagase Chemtex

[0253] : Denacall EX-1610L manufactured by Nagase Chemtex

[0254] Phenolic resin

[0255] : Resol type phenol resin PR-967 Sumitomo Bakelite

[0256] Thermo cationic catalyst

[0257] : SI-100L Samshin Chemical

[0258] Phenol novolac resin

[0259] : PR-HF-6 Sumitomo Bakelite

[0260] Coupling agent

[0261] : Tetraethoxysilane Wako Pure Chemicals

[0262] : Phenyltriethoxysilane Azmax product

[0263] : 3-glycidoxypropyl triethoxysilane Shin-Etsu Chemical

[0264] : Titanium alkoxide KR-ET Ajinomoto Fine Technoze

[0265] Crosslinking material (hexamethylenetetramine)

[0266] : Urotropin Sumitomo Purification

[0267] Metal oxide

[0268] : Colloidal silica snowtex 20 manufactured by Nissan Chemical

[0269] : Colloidal silica snowtex N manufactured by Nissan Chemical Industries

[0270] : Colloidal silica snowtex O manufactured by Nissan Chemical

[0271] : Colloidal Silica Snowtex XS Nissan Chemical Industries Co., Ltd.

[0272] : Colloidal silica snowtex CM manufactured by Nissan Chemical Industries

[0273] Flake inorganic material

[0274] : Smecton SA Kunimine Industrial Festival

[0275] : Lucentite SWF Cope Chemical

[0276] Industrial availability

[0277] The composite composition of the present invention includes at least one of a fibrous filler and a resin, a metal oxide, and a flaky inorganic material, and the average fiber diameter of the fibrous filler is 4 to 1000 nm. For this reason, at least one of a fibrous filler, a resin, a metal oxide, and a flaky inorganic material brings mechanical and chemical action to the composite formed by molding this composite composition. As a result, a composite having a low thermal expansion coefficient, high strength, high transparency, and low humidity expansion coefficient (high water resistance, high dimensional stability) is obtained. Accordingly, the composite of the present invention is used in automobile parts such as automobile exteriors and dashboards, parts of transportation equipment such as railroads, aircraft, ships, chassis in houses or offices, building materials such as wall plates and top plates, pillars or reinforced concrete. Structural members such as reinforcing bars, electronic circuits, electronic parts such as substrates for display bodies, cases (housing) of household appliances such as PCs and mobile phones, office equipment such as stationery, household goods such as furniture, disposable containers, sports Household items such as supplies and toys, outdoor installations such as signs and signs, shock-absorbing members such as bulletproof shields, bulletproof vests, protective equipment such as helmets, artificial bones, medical supplies, abrasives, soundproof walls, protective walls, vibrations It can be used for absorbent members, tools, mechanical parts such as leaf springs, musical instruments, packing materials, and the like. Therefore, the composite composition and composite of the present invention have industrial applicability.



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CLAIMS KR101335758

1.

A composite composition comprising at least one of a cellulose fiber having an average fiber diameter of 4 to 1000 nm, and a resin, a metal oxide, and a flaky inorganic material mixed with the cellulose fiber, wherein the cellulose fiber is a co-oxidizing agent for a cellulose raw material. A composite composition characterized by being made by oxidizing and oxidizing a part of hydroxyl groups in cellulose molecules to at least one of an aldehyde group and a carboxyl group.

2.

The method according to claim 1, The total amount of the aldehyde group and the carboxyl group is 0.2 to 2.2mmol / g with respect to the weight of the cellulose fiber composite composition.

3.

The composite composition according to claim 1, wherein the cellulose fiber is further refined by mechanically treating a cellulose raw material.

4.

The method according to claim 1, The cellulose fiber is prepared by using natural cellulose as the cellulose raw material, and using an N-oxy compound as an oxidation catalyst, and oxidizing the natural cellulose by activating the co-oxidizing agent on the natural cellulose in water The composite composition obtained.

5.

The composite composition of claim 1, wherein the cellulose fiber has an I-type crystal structure.

6.

The composite composition according to claim 1, wherein the resin is at least one of a plastic resin and a curable resin.

7.

The composite composition of claim 1, wherein the resin comprises an epoxy resin.

8.

The composite composition according to claim 1, wherein the resin comprises a phenol resin.

9.

The composite composition according to claim 1, wherein the resin comprises at least one of a coupling agent and a hydrolyzate of the coupling agent.

10.

The composite composition of claim 9, wherein the coupling agent is alkoxy silane or alkoxytitanium.

11.

The composite composition according to claim 1, wherein the metal oxide has an average particle diameter of 1 to 1000 nm.

12.

The composite composition of claim 1, wherein the metal oxide is silicon dioxide.

13.

The method according to claim 1, The flaky inorganic material is mica, vermiculite, montmorillonite, iron montmorillonite, videlite, saponite, hectorite, stephensite, nontronite, margadialite, yerlite, kanehite, smectite and layered Composite composition of at least one selected from titanic acid.

14.

The composite composition according to claim 1, wherein the content of the cellulose fibers in the composite composition is 0.1 to 99.9% by weight.

15.

The composite composition according to claim 1, wherein a total light transmittance at a thickness of 30 µm is 80% or more.

16.

The composite composition according to claim 1, wherein the thermal expansion coefficient at 30 ° C to 180 ° C is 50 ppm / ° C or less.

17.

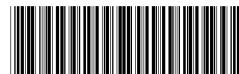
It is made by molding the composite composition according to any one of claims 1 to 16, characterized in that the thickness is 10 ~ 2000µm.

18.

The composite according to claim 17, wherein the thermal expansion coefficient at 30 ° C to 150 ° C is 0.4 to 50 ppm / ° C.

19.

The composite according to claim 17, wherein the humidity expansion coefficient is 100 ppm /% humidity or less.



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(54) 发明名称

一种纳米纤维素 / 聚乙烯醇凝胶复合材料

(57) 摘要

本发明是一种纳米纤维素 / 聚乙烯醇凝胶复合材料，其特征是包括水凝胶和气凝胶，其制备方法包括如下工艺步骤：一、化学结合机械处理法制备纳米纤维素；二、复合水凝胶的制备；三、复合气凝胶的制备。本发明的优点：复合气凝胶是由纳米级胶体粒子或高聚物分子构成的多孔性非晶固体材料，其独特的开放性纳米级多孔结构和连续的三维网状结构、使之具有极低的密度、高比表面积和高孔隙率，其中气凝胶的固体相只占总体积百分比的 0.2% ~ 20%，表现出强吸附催化能力、低热导率、低声阻抗及低折射率等特性，在航空、航天、化工、冶金、节能建筑等领域具有广泛的应用前景。

1. 一种纳米纤维素 / 聚乙烯醇凝胶复合材料, 其特征是包括水凝胶和气凝胶, 其制备方法包括如下工艺步骤 : 一、化学结合机械处理法制备纳米纤维素 ; 二、复合水凝胶的制备 ; 三、复合气凝胶的制备。

2. 根据权利要求 1 所述的一种纳米纤维素 / 聚乙烯醇凝胶复合材料, 其特征是所述的化学结合机械处理法制备纳米纤维素的工艺步骤一, 包括

(1) 化学处理法 :

1) 称取 6g 脱脂棉, 把脱脂棉尽量撕成小束状细丝放入烧杯中, 用蒸馏水浸泡 24 小时 ;

2) 向烧杯中加入 3g 亚氯酸钠, 用玻璃棒搅拌均匀后放入 75℃ 的水浴锅中加热 6 小时 ;

3) 把亚氯酸钠处理过的脱脂棉过滤至中性, 然后放入到 500ml, 5% 氢氧化钾的溶液中, 把烧杯放入调节水浴锅温度为 90℃ 的水浴锅中 6 小时, 然后取出烧杯, 将烧杯内的溶液过滤至中性 ;

4) 把过滤后的纤维颗粒加入到含有 1.5% 浓度的盐酸溶液中, 在 80℃ 的温度下处理 12 小时, 最后经盐酸处理的颗粒状纤维过滤至中性 ;

(2) 机械处理法 :

1) 把过滤至中性的颗粒状纤维利用研磨机研磨, 磨盘间隙调节至最小, 研磨 30 次至纤维悬浮液呈半蓝色, 把纤维悬浮液在室温下放置二十四小时 ;

2) 把纤维悬浮液倒入均质机中均质直至纤维悬浮液完全呈淡蓝色为止, 均质机的均质压力为 2000–2500bar, 重复均质 5 次 ;

3) 把均质好的纤维悬浮液用细胞超声波粉碎机超声, 超声时间为 10min, 超声功率为 1000W, 在超声的过程中为了防止纤维过热引发团聚, 使超声的纤维悬浮液烧杯放置在装有冰块的大烧杯中 ;

4) 最后得到的纤维悬浮液即为纳米纤维素。

3. 根据权利要求 1 所述的一种纳米纤维素 / 聚乙烯醇凝胶复合材料, 其特征是所述的复合水凝胶制备的工艺步骤二, 包括

1) 把定量的网状的纤维素纳米纤丝 (CNCs) 用蒸馏水配制成的溶液 0.10% (72ml) 、 0.16% (72ml) 、 0.28% (72ml) 、 0.45% (72ml) 、 0.61% (72ml) 和 0.98% (60ml) ; 并使其分散均匀 ;

2) 把聚乙烯醇 PVA 添加到纳米纤维素悬浮液中, 对应的 PVA:CNC 重量浓度分别为 1.2% 、 2.0% 、 3.4% 、 5.4% 、 7.3% 和 9.8% ; 在 90℃ 的温度下水域加热混合溶液 2 小时, 加热完成后通氮气脱氧 15min ;

3) 向混合溶液中分别加入引发剂过硫酸钾 (KPS) 、 亚硫酸氢钠 (SBS) 和丙烯酸 (AA) 、 交联剂 (NMBA) 各 2 ml, 在加入以上化学药品的同时持续通氮气 ;

4) 反应基本完成后用超声波处理, 超声功率为使内部的氧气完全排除 ;

5) 把原液倒入直径为 10mm 的试管中, 然后将试管置于 25℃ 冰箱中冷冻 12 小时, 取出后室温解冻 12 小时, 冻融循环六次, 即得复合水凝胶, 这样的水凝胶的机械性能达到一个稳定的值 ;

6) 制备完毕后把复合水凝胶切割成 5mm 高的统一试件, 定期更换蒸馏水保持内部纯净, 防止水凝胶被污染。

4. 根据权利要求 1 所述的一种纳米纤维素 / 聚乙烯醇凝胶复合材料, 其特征是所述的复合气凝胶的制备工艺步骤三, 包括

- 1) 切掉水凝胶表面不规则的部分, 使之放入盛有叔丁醇的培养皿中浸泡 48 小时;
- 2) 然后把浸泡好的水凝胶放入冷冻干燥箱的冷阱中冷冻 24h, 待完全冷冻后从冷阱中取出, 放入真空干燥室中真空干燥 24 小时。

一种纳米纤维素 / 聚乙烯醇凝胶复合材料

技术领域

[0001] 本发明涉及的是一种纳米纤维素 / 聚乙烯醇凝胶复合材料。

背景技术

[0002] 现有气凝胶强度较低、脆性大，限制了其作为隔热材料的推广和应用。近年来学者们致力于气凝胶与其他材料复合来制备具有一定强度又具有优良隔热性能的隔热材料，这种复合型隔热材料与气凝胶隔热材料一起都被称为纳米孔高效隔热材料。通常纳米孔高效隔热材料中添加的材料主要是纤维和遮光剂颗粒等功能添加物。植物纳米纤维因其独特的长链结构，使纤维具有很高的力学强度和弹性模量，加入纳米纤维制备的复合气凝胶材料可以大大的提高气凝胶的强度和韧性。同时植物纳米纤维素比表面积高达 $153 \sim 284\text{m}^2/\text{g}$ ，对于气凝胶吸热隔声方面具有无与伦比的作用。

发明内容

[0003] 本发明提出的是—种纳米纤维素 / 聚乙烯醇凝胶复合材料，其中纳米纤维素采用化学结合机械处理的方法，利用化学方法引发在纳米纤维表面产生自由基，然后通过交联剂作用使纳米纤维、聚乙烯醇、丙烯酸发生化学交联，形成双网结构。

[0004] 本发明的技术解决方案：—种纳米纤维素 / 聚乙烯醇凝胶复合材料，包括水凝胶和气凝胶，其制备方法包括如下工艺步骤：一、化学结合机械处理法制备纳米纤维素；二、复合水凝胶的制备；三、复合气凝胶的制备。

[0005] 本发明的优点：复合气凝胶是由纳米级胶体粒子或高聚物分子构成的多孔性非晶固体材料，其独特的开放性纳米级多孔结构和连续的三维网状结构、使之具有极低的密度、高比表面积和高孔隙率，其中气凝胶的固体相只占总体积百分比的 $0.2\% \sim 20\%$ ，表现出强吸附催化能力、低热导率、低声阻抗及低折射率等特性，在航空、航天、化工、冶金、节能建筑等领域具有广泛的应用前景。

具体实施方式

实施例

[0006] 一、用化学结合机械处理的方法制备纳米纤维素，

1、化学处理：

(1) 化学处理法：

1) 称取 6g 脱脂棉，把脱脂棉尽量撕成小束状细丝放入烧杯中，用蒸馏水水浸泡 24 小时；

2) 向烧杯中加入 3g 亚氯酸钠，用玻璃棒搅拌均匀后放入 75℃ 的水浴锅中加热 6 小时；

3) 把亚氯酸钠处理过的脱脂棉过滤至中性，然后放入到 500ml，

5% 氢氧化钾的溶液中,把烧杯放入调节水浴锅温度为 90℃的水浴锅中 6 小时,然后取出烧杯,将烧杯内的溶液过滤至中性;

4) 把过滤后的纤维颗粒加入到含有 1.5% 浓度的盐酸溶液中,在 80℃的温度下处理 12 小时,最后经盐酸处理的颗粒状纤维过滤至中性;

2、机械处理:

1) 把过滤至中性的颗粒状纤维利用研磨机研磨,磨盘间直径调节至最小,研磨 30 次至纤维悬浮液呈半蓝色,把纤维悬浮液在室温下放置二十四小时;

2) 把纤维悬浮液倒入均质机中均质直至纤维悬浮液完全呈淡蓝色为止(均质机的均质压力为 2000–2500bar,重复均质 5 次;

3) 把均质后的纤维悬浮液用细胞超声波粉碎机超声,超声时间为 10min,超声功率为 1000W,在超声的过程中为了防止纤维过热引发团聚,使超声的纤维悬浮液烧杯放置在装有冰块的大烧杯中;

4) 最后得到的纤维悬浮液即为纳米纤维素。

[0007] 二、制备复合水凝胶,包括

1) 把定量的网状的纤维素纳米纤丝(CNCs) 用蒸馏水配制成的溶液 0.10%(72ml)、0.16%(72ml)、0.28%(72ml)、0.45%(72ml)、0.61%(72ml) 和 0.98%(60ml);并使其分散均匀;

2) 把聚乙烯醇(PVA) 添加到纳米纤维素悬浮液中,对应的 PVA:CNC 重量浓度分别为 1.2%、2.0%、3.4%、5.4%、7.3% 和 9.8%;在 90℃的温度下水域加热混合溶液 2 小时,加热完成后通氮气脱氧 15min;

3) 向混合溶液中分别加入引发剂过硫酸钾(KPS)、亚硫酸氢钠(SBS) 和丙烯酸(AA)、交联剂(NMBA) 各 2 ml,在加入以上化学药品的同时持续通氮气;

4) 反应基本完成后用超声波处理,超声功率为使内部的氧气完全排除;

5) 把原液倒入直径为 10mm 的试管中,然后将试管置于 25℃冰箱中冷冻 12 小时,取出后室温解冻 12 小时,冻融循环六次,即得复合水凝胶,这样的水凝胶的机械性能达到一个稳定的值;

6) 制备完毕后把复合水凝胶切割成 5mm 高的统一试件,定期更换蒸馏水保持内部纯净,防止水凝胶被污染。

[0008] 7) 制备完毕后把凝胶切割成 5mm 高的统一试件,通过上述方法所制备的水凝胶定期更换蒸馏水保持内部纯净,防止水凝胶被污染,水凝胶制备试验选用的原料的比例见表 1。

[0009] 表 1 :本试验选用的原料的比例

| CNC 悬浮液浓度 (w/w) | PVA (g) | KBS (ml) | SBS (ml) | NBMA (ml) | AA (g) | PVA:CNC 浓度 |
|-----------------|---------|----------|----------|-----------|--------|------------|
| 0 | 6 | 0 | 0 | 0 | 0 | 0 |
| 0.10%(72ml) | 6 | 2 | 2 | 2 | 2 | 1.2% |
| 0.16%(72ml) | 6 | 2 | 2 | 2 | 2 | 2.0% |
| 0.28%(72ml) | 6 | 2 | 2 | 2 | 2 | 3.4% |
| 0.45%(72ml) | 6 | 2 | 2 | 2 | 2 | 5.4% |
| 0.61%(72ml) | 6 | 2 | 2 | 2 | 2 | 7.3% |
| 0.98%(60ml) | 6 | 2 | 2 | 2 | 2 | 9.8% |

纤维素溶液浓度对水凝胶的理化性能的影响：聚乙烯醇与纤维素七种不同配比：0, 1. 2%, 2. 0%, 3. 4%, 5. 4%, 7. 3%, 9. 8% 配制成的水凝胶，分别观察其外观的不同。

[0010] 复合水凝胶含水率和干燥速率的测定：将凝胶化完全后的复合水凝胶用蒸馏水反复清洗多次，充分洗去表面杂质，用滤纸擦干表面的溶液后，用分析天平称出凝胶的质量，记作 W_0 ，然后分别置于室温及 60℃ 烘箱干燥，并定时称重，记作 W_t ，干燥至恒重后的质量记作 W_d ，以测定含水率 (WR) 和干燥速率 (DR)：

$$WR = \frac{W_0 - W_d}{W_0} \times 100\% \quad (1)$$

$$DR = \frac{W_t - W_d}{W_0} \times 100\% \quad (2)$$

式中 W_t 为 t 时刻水凝胶的质量， W_0 为原始水凝胶的质量， W_d 为干燥至恒重后水凝胶的质量。

[0011] 不同温度值对水凝胶溶胀性能的影响：水凝胶试样在室温干燥 24h 后，放置冷冻干燥机内干燥直至凝胶达到恒重。将凝胶样品分别置于 pH 为 1.0、7.4 和 13 等三种不同缓冲溶液下，改变温度，待该温度下凝胶溶胀平衡后，滤去多余液体，用滤纸吸干凝胶表面，称重，并计算溶胀度 (SR)：

$$SR = \frac{W_0 - W_d}{W_d} \times 100\% \quad (3)$$

式中， W_d 为干凝胶在水中溶胀平衡时的质量 (g)； W_d 为干凝胶的质量 (g)。

[0012] 不同 pH 值对水凝胶溶胀性能的影响：在室温下，将水凝胶分别放置在不同 pH 值的缓冲溶液中，待凝胶溶胀平衡后，滤去多余液体，用滤纸吸干凝胶表面，称重，按式 (3) 计算其溶胀度 (SR)。

[0013] 复合水凝胶的特点：高分子水凝胶是水溶性高分子经交联或与疏水单体共聚所形成的三维网状聚合物，其在水中溶胀并在网络结构中保持大量水分而又不溶于水的高聚物。对刺激产生响应的环境敏感水凝胶称智能水凝胶，在传统凝胶材料的基础上引入纳米级纤维素晶体，首先赋予原有凝胶材料的纳米级纤维所具有的部分功能和特性：具体有

- 1) 具有纳米纤维素部分的力学性质方面的优点，如高拉伸强度、韧性以及高弹性模量；
- 2) 保持传统聚乙烯醇水凝胶的生物相容性，不刺激皮肤，对人体排斥作用小；
- 3) 是智能水凝胶的一种，在外界条件，如光、电、热、pH 值等环境下发生刺激响应；
- 4) 是一种多孔材料，并且自身孔径小，多孔性赋予了其良好的保水能力，是一种多功能性吸水材料；
- 5) 干燥成气凝胶后，其质轻、小孔隙对保温隔热、隔声具有良好的作用；
- 6) 兼有两种物质的可降解特性，对环境无污染，是一种绿色环保型材料；
- 7) 纳米纤维素、聚乙烯醇原料来源广泛，价格低廉；
- 8) 由于纳米纤维素 / 聚乙烯醇复合凝胶材料在相当广的程度上对于环境微小的物理化学刺激，如温度、电场、磁场、光、pH、离子强度、压力等，这些能够感知、处理并可响应外界环境刺激，进而凝胶随着外界的刺激而变化属于智能水凝胶材料的一种。纳米纤维素 / 聚

乙烯醇复合凝胶材料运用最广泛是在医学应用方面，其次在于组织工程，药物缓释等方面；此种水凝胶具备了高机械强度、透明性好、对磁场电场等环境具有敏感性响应等特点，因而在化学能、机械能转变方面，特别是药物释放系统、化学阀、化学机械、人工触觉系统、光阀、人工肌肉和执行元件等具有非常巨大的应用价值。

[0014] 三、制备复合气凝胶，

1) 切掉水凝胶表面不规则的部分，使之放入盛有叔丁醇的培养皿中浸泡 48 小时，2) 然后把浸泡好的水凝胶放入冷冻干燥箱的冷阱中冷冻 24h，待完全冷冻后从冷阱中取出，放入真空干燥室中真空干燥 24 小时。



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DESCRIPTION CN102786642

The invention is a nanocellulose / polyvinyl alcohol gel composite material, which is characterized by including hydrogel and aerogel, and its preparation method includes the following process steps: one, chemically combined mechanical treatment method to prepare nanocellulose; two, Preparation of composite hydrogel; 3. Preparation of composite aerogel. The advantages of the present invention: The composite aerogel is a porous amorphous solid material composed of nano-scale colloidal particles or polymer molecules. Its unique open nano-scale porous structure and continuous three-dimensional network structure make it extremely Low density, high specific surface area and high porosity, the solid phase of aerogel only accounts for 0.2% to 20% of the total volume, showing strong adsorption catalytic ability, low thermal conductivity, low acoustic impedance and low refractive index, etc. Characteristics, has broad application prospects in the fields of aviation, aerospace, chemical industry, metallurgy, energy-saving buildings and so on.

Nano cellulose / polyvinyl alcohol gel composite material

Technical field

The invention relates to a nanocellulose / polyvinyl alcohol gel composite material.

Background technique

The existing aerogel has low strength and high brittleness, which limits its promotion and application as a thermal insulation material. In recent years, scholars have devoted themselves to the composite of aerogel and other materials to prepare thermal insulation materials with certain strength and excellent thermal insulation properties. This kind of composite thermal insulation material and aerogel thermal insulation materials are called nanopores. Efficient thermal insulation material. Generally, the materials added to the nanoporous high-efficiency thermal insulation materials are mainly functional additives such as fibers and sunscreen particles. Because of its unique long-chain structure, plant nanofibers have high mechanical strength and elastic modulus. The composite aerogel material prepared by adding nanofibers can greatly improve the strength and brittleness of aerogels. At the same time, the specific surface area of plant nanocellulose is as high as 153 ~ 284m <2> / g, which has an unparalleled effect on the heat absorption and sound insulation of aerogel.

Summary of the invention

The invention proposes a nano-cellulose / polyvinyl alcohol gel composite material, in which nano-cellulose adopts chemical bonding mechanical treatment method, uses chemical method to initiate the generation of free radicals on the surface of nano-fibers, and then causes Nano-fibers, polyvinyl alcohol, and acrylic acid are chemically cross-linked to form a double-net structure.

The technical solution of the present invention: a nanocellulose / polyvinyl alcohol gel composite material, including hydrogel and aerogel, and its preparation method includes the following process steps: one, chemically combined mechanical treatment method to prepare nanocellulose; two 1. Preparation of composite hydrogel; 3. Preparation of composite aerogel.

The advantages of the present invention: the composite aerogel is a porous amorphous solid material composed of nano-scale colloidal particles or polymer molecules. Its unique open nano-scale porous structure and continuous three-dimensional network structure make it extremely polar Low density, high specific surface area and high porosity, the solid phase of aerogel only accounts for 0.2% to 20% of the total volume, showing strong adsorption catalytic ability, low thermal conductivity, low acoustic impedance and low refractive index, etc. Characteristics, has broad application prospects in the fields of aviation, aerospace, chemical industry, metallurgy, energy-saving buildings and so on.

detailed description

Examples

1. Preparation of nano-cellulose by means of chemical combined mechanical treatment,

1. Chemical treatment:

(1) Chemical treatment method:

1) Weigh 6g absorbent cotton, tear the absorbent cotton into small bundles of filament as much as possible, put it into a beaker, and soak it in distilled water for 24 hours;

2) Add 3g of sodium chlorite to the beaker, stir it evenly with a glass rod and put it in a 75 ° C water bath to heat for 6 hours;

3) Filter the absorbent cotton treated with sodium chlorite to neutral, then put it into 500ml,

5%In the solution of potassium hydroxide, put the beaker in a water bath with a temperature of 90 ° C for 6 hours, then take out the beaker and filter the solution in the beaker to neutral;

4) Add the filtered fiber particles to a hydrochloric acid solution containing 1.5% concentration, and treat at 80 ° C for 12 hours. Finally, the particulate fibers treated with hydrochloric acid are filtered to neutrality;

2. Mechanical treatment:

1) Grind the particulate fibers filtered to neutral with a grinder, adjust the diameter between the grinding discs to the minimum, grind 30 times until the fiber suspension is semi-blue, and leave the fiber suspension at room temperature for 24 hours;

2) Pour the fiber suspension into the homogenizer and homogenize until the fiber suspension is completely light blue (the homogenizer's homogenization pressure is 2000-2500 bar, repeat homogenization 5 times);

3) The homogenized fiber suspension is sonicated with a cell ultrasonic grinder with an ultrasonic time of 10 min and an ultrasonic power of 1000 W. In order to prevent the fiber from overheating and causing agglomeration during the ultrasonic process, the ultrasonic fiber suspension beaker is placed Ice cubes in a large beaker;

4) The resulting fiber suspension is nanocellulose.

2. Preparation of composite hydrogels, including

1) A solution made up of quantitative mesh cellulose nanofibrils (CNCs) with distilled water 0.10% (72ml), 0.16% (72ml), 0.28% (72ml), 0.45% (72ml), 0.61% (72ml)) And 0.98% (60ml); and make it evenly dispersed;

2) Add polyvinyl alcohol (PVA) to the nanocellulose suspension, the corresponding PVA: CNC weight concentration is 1.2%, 2.0%, 3.4%, 5.4%, 7.3% and 9.8%; at 90 ° C The mixed solution was heated in the water area for 2 hours at the temperature, and after the heating was completed, nitrogen was deoxygenated for 15min;

3) Add 2ml each of initiator potassium persulfate (KPS), sodium bisulfite (SBS) and acrylic acid (AA), cross-linking agent (NMBA) to the mixed solution, and continue to pass nitrogen while adding the above chemicals ;

4) After the reaction is basically completed, ultrasonic treatment is used, and the ultrasonic power is used to completely remove the internal oxygen;

5) Pour the original solution into a test tube with a diameter of 10mm, and then place the test tube in a 25 ° C refrigerator for 12 hours. After taking it out, thaw it at room temperature for 12 hours. Freeze and thaw cycle six times to obtain a composite hydrogel. Such water The mechanical properties of the gel reach a stable value;

6) After preparation, cut the composite hydrogel into 5mm high uniform test pieces, and regularly replace the distilled water to keep the interior pure and prevent the hydrogel from being contaminated.

7) After preparation, the gel is cut into 5 mm high uniform test pieces. The hydrogel prepared by the above method regularly replaces distilled water to keep the internal purity, to prevent the hydrogel from being contaminated. The proportion of raw materials used in the hydrogel preparation test is shown in the table 1.

Table 1: Proportion of raw materials selected for this experiment

Effect of the concentration of cellulose solution on the physical and chemical properties of hydrogel: seven different ratios of polyvinyl alcohol and cellulose: 0, 1.2%, 2.0%, 3.4%, 5.4%, 7.3%, 9.8% formulated water Observe the difference in appearance of the gel.

Determination of the water content and drying rate of the composite hydrogel: After the gelatinization is completed, the composite hydrogel is washed repeatedly with distilled water many times to fully remove the surface impurities. After drying the solution on the surface with filter paper, it is weighed out with an analytical balance The mass of the gel is recorded as Wo, then placed in an oven at room temperature and 60 ° C to dry, and weighed regularly, recorded as Wt, and the mass after drying to constant weight is recorded as Wd to determine the moisture content (WR) and drying Rate (DR):

[image] " (1)

[image] " " " (2)

Where W_t is the mass of the hydrogel at t , W_0 is the mass of the original hydrogel, and W_d is the mass of the hydrogel after drying to constant weight.

Effect of different temperature values on the swelling performance of the hydrogel. After the hydrogel sample was dried at room temperature for 24h, it was placed in a freeze dryer and dried until the gel reached a constant weight. Place the gel sample under three different buffer solutions with pH 1.0, 7.4 and 13 respectively, and change the temperature. After the gel swells and equilibrates at this temperature, the excess liquid is filtered off, the surface of the gel is blotted with filter paper and weighed. And calculate the swelling degree (SR):

[image] □ □ □ □

In the formula, W_d is the mass (g) of the xerogel when it swells in water in equilibrium; W_d is the mass (g) of the xerogel.

The effect of different pH values on the swelling performance of the hydrogel. At room temperature, place the hydrogel in a buffer solution worth of different pH. After the gel swells and balances, filter out the excess liquid and blot the surface of the gel with filter paper. Heavy, according to formula (3) to calculate the degree of swelling (SR).

The characteristics of the composite hydrogel: the polymer hydrogel is a three-dimensional network polymer formed by cross-linking or copolymerization of water-soluble polymers with hydrophobic monomers. It swells in water and maintains a large amount of water in the network structure without being soluble. High polymer for water. Environmentally sensitive hydrogels that respond to stimuli are called smart hydrogels. Nano-sized cellulose crystals are introduced on the basis of traditional gel materials. First, some functions and characteristics of nano-scale fibers of the original gel materials are given: Specific

1)

It has the advantages of the mechanical properties of the nano-cellulose part, such as high tensile strength, toughness and high elastic modulus;

2)

Maintain the biocompatibility of traditional polyvinyl alcohol hydrogel, not irritate the skin, and have little rejection effect on human body;

3)

It is a kind of smart hydrogel, which generates stimulus response under external conditions, such as light, electricity, heat, pH, etc .;

4)

It is a porous material and has a small pore size. The porosity gives it good water retention capacity and is a versatile water-absorbing material;

5)

After drying into an aerogel, its light weight and small pores have a good effect on thermal insulation and sound insulation;

6)

It has both the degradable properties of two substances, no pollution to the environment, and is a green and environmentally friendly material;

7)

Nano cellulose and polyvinyl alcohol have a wide range of raw materials and low prices;

8)

Nano-cellulose / polyvinyl alcohol composite gel materials can sense, process, and treat the physical and chemical stimuli of the environment to a considerable extent, such as temperature, electric field, magnetic field, light, pH, ionic strength, pressure, etc. It is a kind of intelligent hydrogel material that responds to external environmental stimuli and the gel changes with external stimuli.

Nanocellulose / polyvinyl alcohol composite gel materials are most widely used in medical applications, followed by tissue engineering, drug sustained release, etc .; this hydrogel has high mechanical strength, good transparency, and magnetic field electric field. The environment has the characteristics of sensitive response, etc. Therefore, in the conversion of chemical

energy and mechanical energy, especially drug release systems, chemical valves, chemical machinery, artificial tactile systems, light valves, artificial muscles and actuators have great application value.

3. Preparation of composite aerogel,

1) Cut off the irregular part on the surface of the hydrogel and place it in a petri dish containing tert-butanol for 48 hours, 2) Then put the soaked hydrogel in the cold trap of the freeze-drying box and freeze for 24h, After completely frozen, take it out of the cold trap and put it in a vacuum drying room for 24 hours under vacuum drying.



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CLAIMS CN102786642

1.

A nanocellulose / polyvinyl alcohol gel composite material, which is characterized by including hydrogel and aerogel, and its preparation method includes the following process steps: first, chemically combined mechanical treatment method to prepare nanocellulose; second, composite hydrogel Preparation of glue; 3. Preparation of composite aerogel.

2.

The nano-cellulose / polyvinyl alcohol gel composite material according to claim 1, characterized in that the first step of the process of preparing nano-cellulose by the chemical combined mechanical treatment method includes (1) chemical treatment method: 1) Weigh 6g of absorbent cotton, tear the absorbent cotton into small bundles of filament as much as possible, put it in a beaker, soak it in distilled water for 24 hours; 2) Add 3g of sodium chlorite to the beaker, stir it evenly with a glass rod and put it at 75 ° C Heat the water bath for 6 hours; 3) Filter the absorbent cotton treated with sodium chlorite to neutral, and then put it into a 500ml, 5% potassium hydroxide solution, put the beaker into the water bath to adjust the temperature to 90 ° C in the water bath for 6 hours, then take out the beaker, and filter the solution in the beaker to neutral; 4) Add the filtered fiber particles to the hydrochloric acid solution containing 1.5% concentration, and treat it at a temperature of 80 ° C 12 Hours, the granular fibers treated with hydrochloric acid are finally filtered to neutral; (2) Mechanical treatment method: 1) The granular fibers filtered to neutral are ground with a grinder, the gap between the grinding discs is adjusted to the minimum, and the fiber is suspended 30 times to the fiber suspension liquid Semi-blue, put the fiber suspension at room temperature for 24 hours; 2) Pour the fiber suspension into the homogenizer until the fiber suspension is completely light blue. The homogenization pressure of the homogenizer is 2000-2500bar, repeat homogenization 5 times; 3) The homogenized fiber suspension is sonicated with a cell ultrasonic pulverizer, the ultrasonic time is 10min, and the ultrasonic power is 1000W. During the ultrasonic process, in order to prevent the fiber from overheating and causing agglomeration, make The ultrasonic fiber suspension beaker is placed in a large beaker with ice cubes; 4) The resulting fiber suspension is nanocellulose.

3.

A nanocellulose / polyvinyl alcohol gel composite material according to claim 1, characterized in that the second step of the preparation of the composite hydrogel includes 1) the quantitative network cellulose nanofibers Silk (CNCs) solutions prepared with distilled water 0.10% (72ml), 0.16% (72ml), 0.28% (72ml), 0.45% (72ml), 0.61% (72ml), and 0.98% (60ml); and make Disperse evenly; 2) Add polyvinyl alcohol PVA to the nanocellulose suspension, the corresponding PVA: CNC weight concentration is 1.2%, 2.0%, 3.4%, 5.4%, 7.3% and 9.8%; at 90 ° C The mixed solution was heated in the water area for 2 hours at the temperature of the temperature, and deoxygenated with nitrogen for 15min after heating; 3) Add initiator potassium persulfate (KPS), sodium bisulfite (SBS) and acrylic acid (AA), cross-linking to the mixed solution respectively 2 ml each of the NMBA agent, while adding nitrogen to the above chemicals, and continue to pass nitrogen; 4) After the reaction is basically completed, use ultrasonic treatment, the ultrasonic power is to completely eliminate the internal oxygen; 5) Pour the original solution into a test tube with a diameter of 10 mm , Then place the test tube in the refrigerator at 25 ° C to freeze for 12 hours. After 12 hours of temperature thawing and six cycles of freezing and thawing, the composite hydrogel can be obtained, and the mechanical properties of such hydrogel reach a stable value; 6) After preparation, the composite hydrogel is cut into 5mm high uniform test pieces , Change the distilled water regularly to keep the interior pure and prevent the hydrogel from being contaminated.

4.

The nano-cellulose / polyvinyl alcohol gel composite material according to claim 1, wherein the composite aerogel preparation process includes step 3, including 1) cutting out irregular parts on the surface of the hydrogel , Put it in a petri dish containing tert-butanol and soak for 48 hours; 2) Then put the soaked hydrogel into the cold trap of the freeze-drying box and freeze it for 24h, and remove it from the cold trap after completely freezing, Place in a vacuum drying chamber and vacuum dry for 24 hours.



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(12) **United States Patent**
Miyawaki et al.

(10) **Patent No.:** US 8,377,563 B2
(45) **Date of Patent:** *Feb. 19, 2013

(54) **PAPERMAKING ADDITIVE AND PAPER CONTAINING THE SAME**

(75) Inventors: **Shoichi Miyawaki**, Tokyo (JP); **Shiho Katsukawa**, Tokyo (JP); **Hiroshi Abe**, Tokyo (JP); **Yuko Iijima**, Tokyo (JP); **Akira Isogai**, Tokyo (JP)

(73) Assignee: **Nippon Paper Industries Co., Ltd.**, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 239 days.

This patent is subject to a terminal disclaimer.

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§ 371 (c)(1),

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PCT Pub. Date: **Oct. 8, 2009**

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(30) **Foreign Application Priority Data**

Mar. 31, 2008 (JP) 2008-091333

(51) **Int. Cl.**

B32B 23/04 (2006.01)

(52) **U.S. Cl.** **428/532; 428/535; 428/537.5;**
427/324; 427/411

(58) **Field of Classification Search** **428/532,**
428/537.5, 535; 427/324, 411

See application file for complete search history.

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Primary Examiner — Leszek Kiliman

(74) Attorney, Agent, or Firm — Nixon & Vanderhye P.C.

(57) **ABSTRACT**

A papermaking additive comprising cellulose nanofibers whose aqueous solution at a concentration of 2% (w/v) has a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably 500 to 2000 mPa·s is used to prepare a paper having improved air resistance and smoothness. This additive is prepared by oxidizing a cellulosic material with an oxidizing agent in the presence of (1) N-oxyl compound(s) and (2) bromide, iodide or a mixture thereof to prepare oxidized cellulose, and finely grinding the oxidized cellulose in a wet condition to convert the oxidized cellulose into nanofibers.

22 Claims, 5 Drawing Sheets

Figure 1

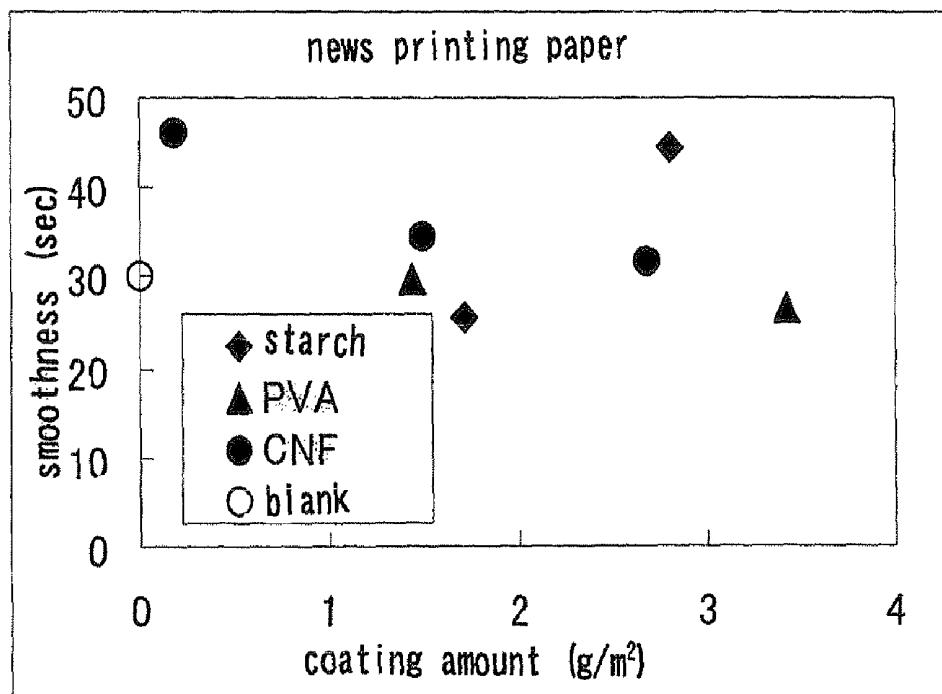


Figure 2

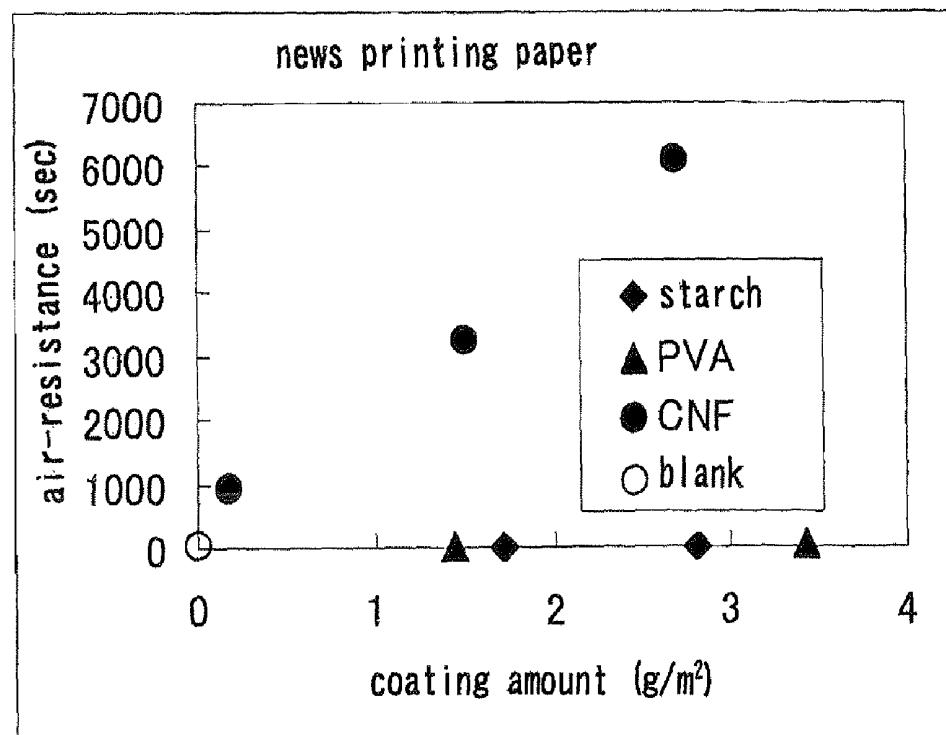


Figure 3

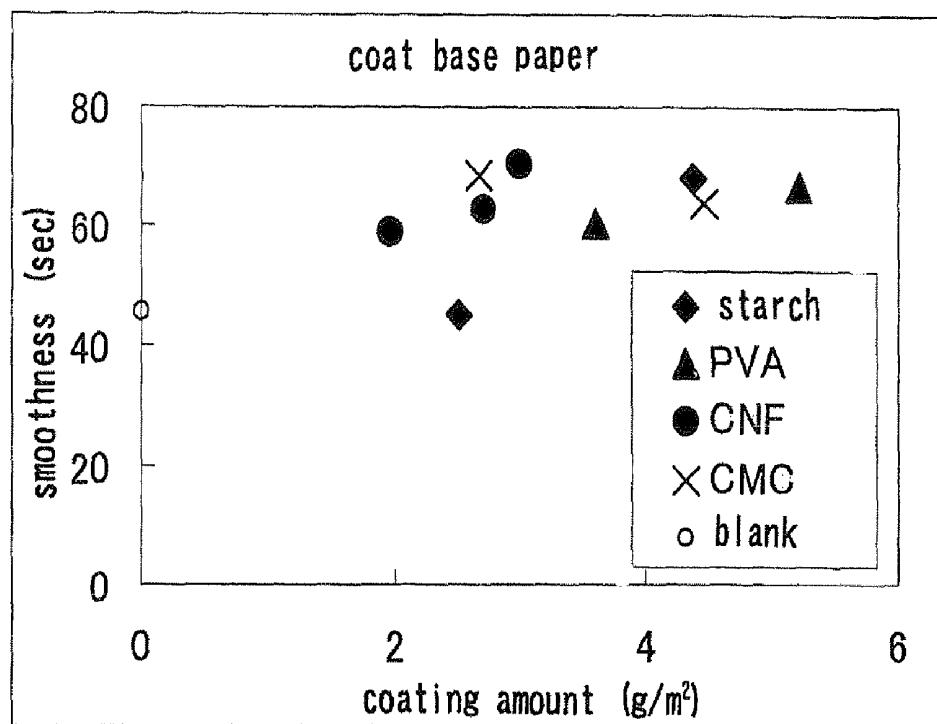


Figure 4

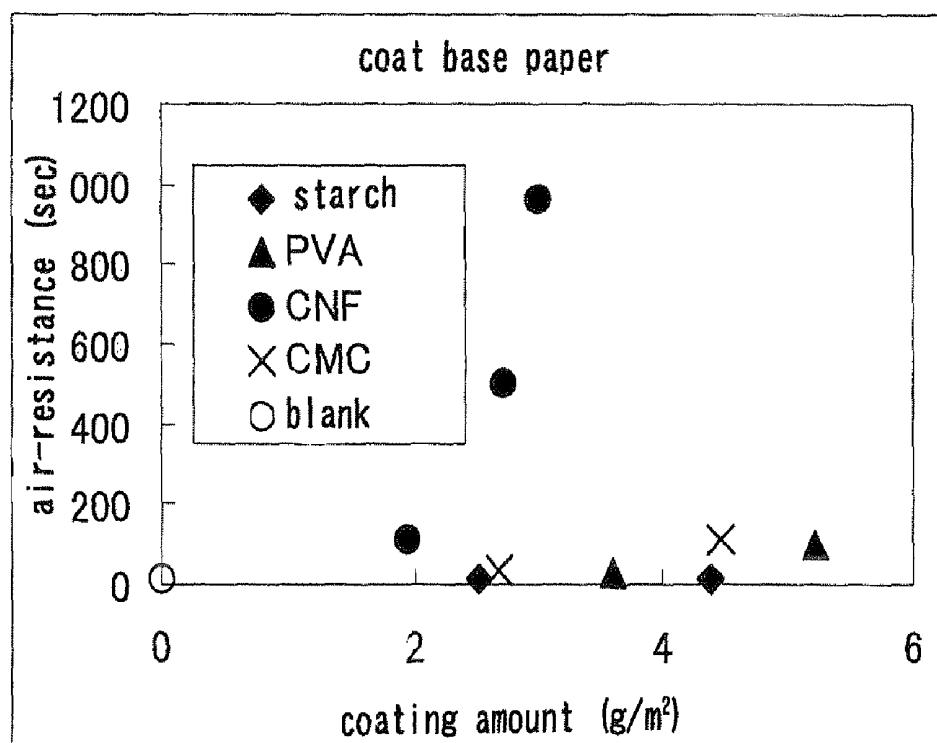


Figure 5

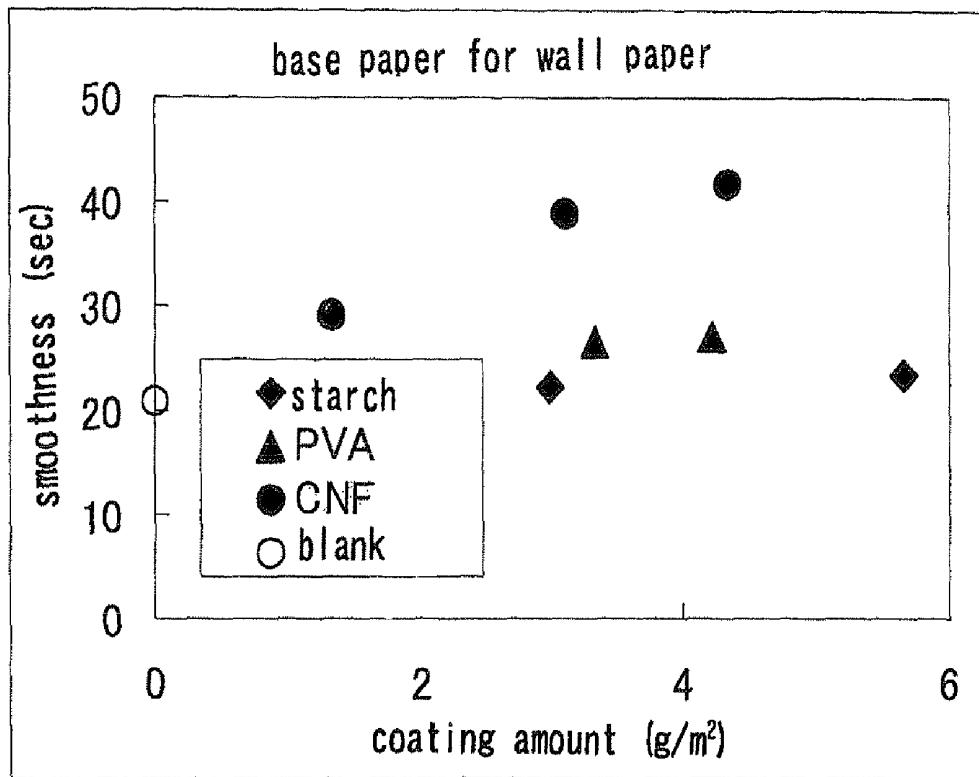


Figure 6

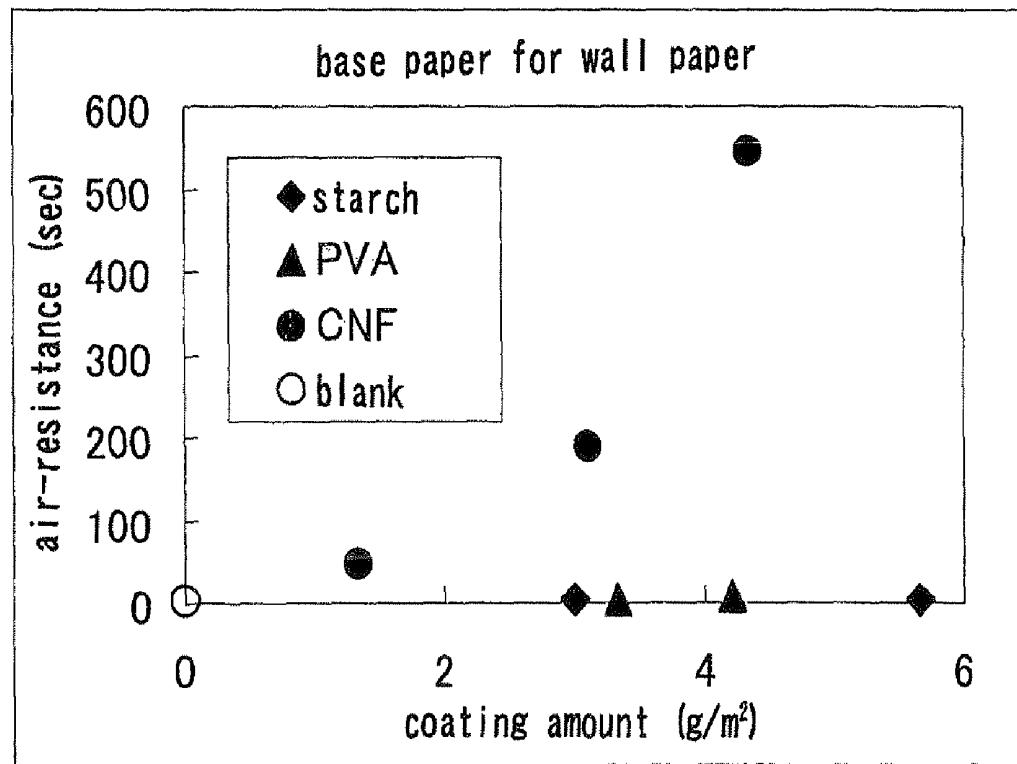


Figure 7

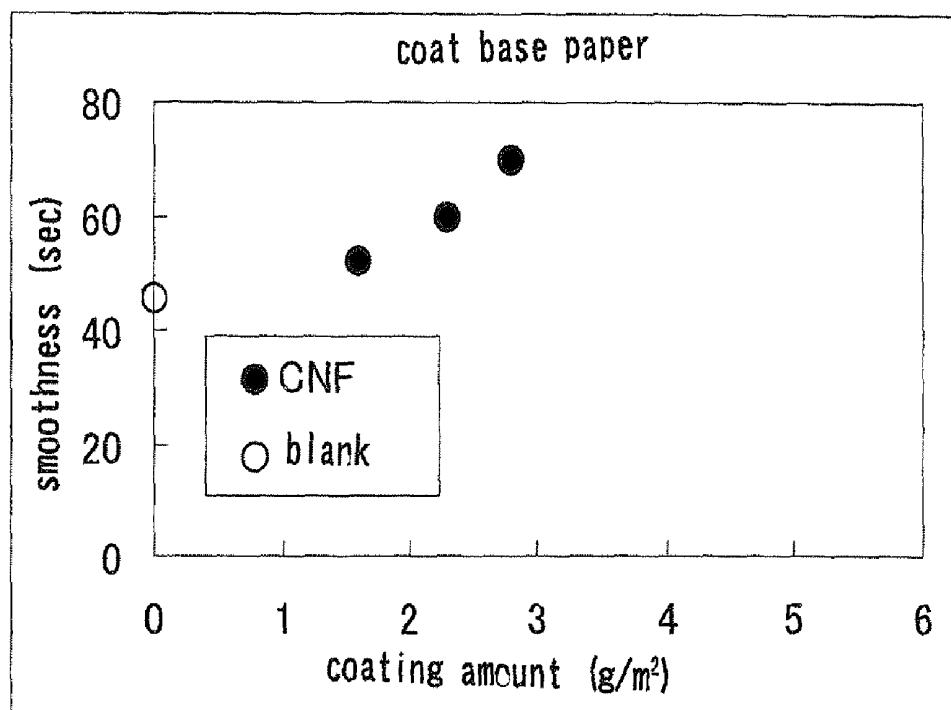


Figure 8

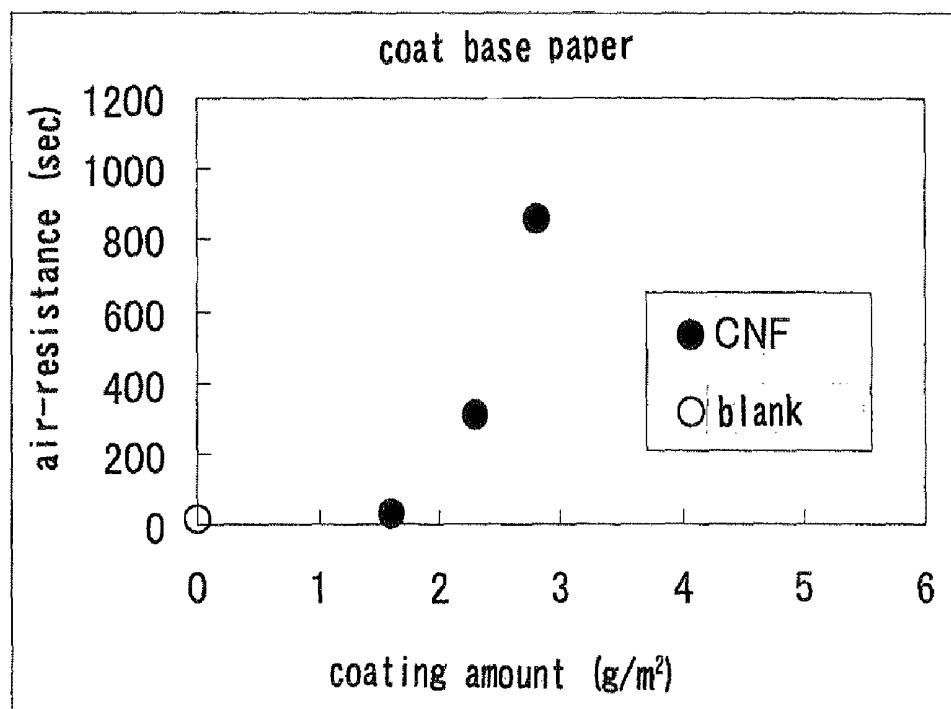


Figure 9

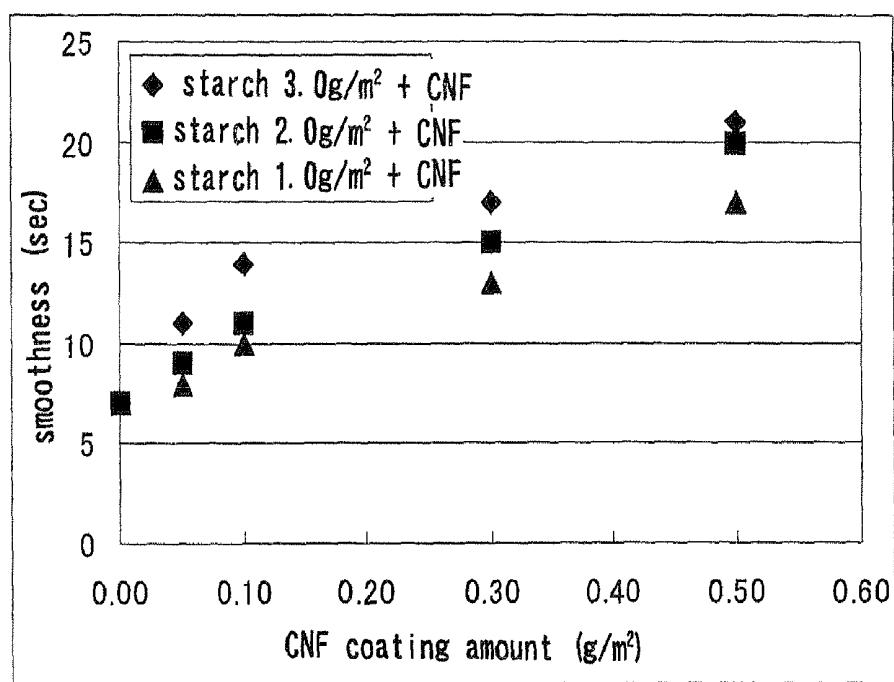
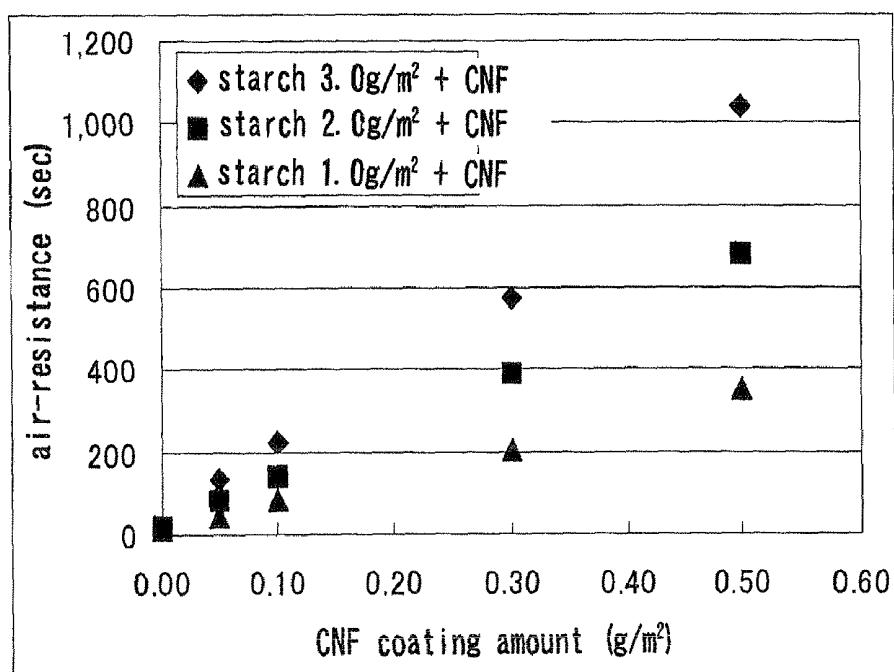


Figure 10



1

**PAPERMAKING ADDITIVE AND PAPER
CONTAINING THE SAME**

This application is the U.S. national phase of International Application No. PCT/JP2009/055967, filed 25 Mar. 2009, which designated the U.S. and claims priority to Japanese Patent Application No. 2008-091333, filed 31 Mar. 2008, the entire contents of each of which are hereby incorporated by reference.

TECHNICAL FIELD

This invention relates to a papermaking additive comprising cellulose nanofibers having a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably 500 to 2000 mPa·s at a concentration of 2%; and paper containing the papermaking additive. More specifically, the invention relates to paper containing the above papermaking additive capable of improving air resistance and smoothness, the paper which is used as printing paper, news printing paper, electrophotographic transfer paper, inkjet recording paper, thermal recording paper, pressure sensitive recording paper, converting paper, paperboard, sanitary paper, or base paper for coated paper or laminated paper.

BACKGROUND ART

Paper has voids, and the voids penetrating the paper in its thickness direction, in particular, influence barrier properties against oxygen and steam, or permeability to a coating material. Patent Literature 1 discloses use of a carboxymethylcellulose sodium salt having a degree of carboxymethyl substitution of 0.25 to 0.5 and a viscosity of 5 to 300 mPa·s as an aqueous solution at a concentration of 1%, as a permeation suppressant suppressing permeation of a paint through base paper. As a method for improving the air resistance which is an indicator of voids in paper, Patent Literature 2 discloses base paper for release paper incorporating ungelatinized granular starch. Patent Literature 3 discloses an improver for paper surface quality comprising an anionic polyacrylamide resin.

Patent Document 1: JP 2004-300624 A

Patent Document 2: JP 1992-57798 B

Patent Document 3: JP 2003-49390 A

SUMMARY OF THE INVENTION

Problems to be Solved by the Invention

However, By using the above-mentioned carboxymethylcellulose, ungelatinized granular starch, and anionic polyacrylamide resin, it is difficult to form a coating film which completely fills in the voids of paper, and a paper having sufficient air resistance has not been obtained. Other methods for improving air resistance by strengthening the beating of pulp for improving bonds between fibers, or by collapsing the voids by strong calendering, increase the density of paper, and the resulting paper is difficult to be applied other than special uses.

It is an object of the present invention to provide a papermaking additive capable of improving air resistance of paper markedly, and paper containing the additive, specifically, printing paper, news printing paper, electrophotographic transfer paper, inkjet recording paper, thermal recording paper, pressure sensitive recording paper, converting paper, paperboard, or sanitary paper; and coated paper, inkjet recording paper, thermal recording paper, pressure sensitive

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recording paper, converting paper, or laminated paper which uses the paper markedly improved in air resistance as base paper.

Means for Solving the Problems

The inventors of the present invention have found that cellulose nanofiber having a suitable B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably, 500 to 2000 mPa·s at a concentration of 2% as an aqueous dispersion, and showing moderate consistency which enables the nanofibers to be applied to a base such as paper, can be obtained by oxidizing cellulosic material with the addition of an oxidizing agent in the presence of (1) N-oxyl compound(s), and (2) compound(s) selected from bromide, iodide, or mixtures thereof, and then finely grinding the oxidized cellulosic material by a wet process to defibrate the fibers in a specific manner. The inventors also have found that incorporating a papermaking additive comprising the cellulose nanofiber into paper can improve air resistance of paper, without an increase in density of paper.

Effects of the Invention

The papermaking additive containing cellulose nanofibers according to the present invention can remarkably increase air resistance of paper, as compared to starch and polyacrylamide, and using the papermaking additive of the present invention can produce a high-quality paper having high air resistance.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a graph showing the results of measurements of the smoothnesses of news printing papers prepared in Example 2 (CNF), Comparative Example 4 (blank), Comparative Example 5 (starch), and Comparative Example 6 (PVA).

FIG. 2 is a graph showing the results of measurements of the air resistances of the news printing papers prepared in Example 2 (CNF), Comparative Example 4 (blank), Comparative Example 5 (starch), and Comparative Example 6 (PVA).

FIG. 3 is a graph showing the results of measurements of the smoothnesses of base papers for coated paper prepared in Example 3 (CNF), Comparative Example 7 (blank), Comparative Example 8 (starch), Comparative Example 9 (PVA), and Comparative Example 10 (CMC).

FIG. 4 is a graph showing the results of measurements of the air resistances of the base papers for coated paper prepared in Example 3 (CNF), Comparative Example 7 (blank), Comparative Example 8 (starch), Comparative Example 9 (PVA), and Comparative Example 10 (CMC).

FIG. 5 is a graph showing the results of measurements of the smoothnesses of base papers for wallpaper prepared in Example 4 (CNF), Comparative Example 11 (blank), Comparative Example 12 (starch), and Comparative Example 13 (PVA).

FIG. 6 is a graph showing the results of measurements of the air resistances of the base papers for wallpaper prepared in Example 4 (CNF), Comparative Example 11 (blank), Comparative Example 12 (starch), and Comparative Example 13 (PVA).

FIG. 7 is a graph showing the results of measurement of smoothness of the base papers for coated paper prepared in Example 5 and Comparative Example 7 (blank).

FIG. 8 is a graph showing the results of measurement of air resistance of the base papers for coated paper prepared in Example 5 and Comparative Example 7 (blank).

FIG. 9 is a graph showing the results of measurement of smoothness of news printing paper prepared in Examples 9 to 12 and Comparative Example 22 (fixing the coating amount of starch at 3.0 g/m², and altering the coating amount of CNF), Examples 13 to 16 and Comparative Example 23 (fixing the coating amount of starch at 2.0 g/m², and altering the coating amount of CNF), as well as Examples 17 to 20 and Comparative Example 24 (fixing the coating amount of starch at 1.0 g/m², and altering the coating amount of CNF).

FIG. 10 is a graph showing the results of measurement of air resistance of news printing paper prepared in Examples 9 to 12 and Comparative Example 22 (fixing the coating amount of starch at 3.0 g/m², and altering the coating amount of CNF), Examples 13 to 16 and Comparative Example 23 (fixing the coating amount of starch at 2.0 g/m², and altering the coating amount of CNF), as well as Examples 17 to 20 and Comparative Example 24 (fixing the coating amount of starch at 1.0 g/m², and altering the coating amount of CNF).

DESCRIPTION OF EMBODIMENTS

(Cellulose Nanofiber)

The papermaking additive of the present invention comprises cellulose nanofibers. Cellulose nanofibers are single cellulose microfibril having a width of 2 to 5 nm and a length of 1 to 5 μm, which are obtained by defibrating fibers in cellulosic material. The present invention uses, in particular, an aqueous dispersion of cellulose nanofibers having a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably 500 to 2000 mPa·s at a concentration of 2% (w/v) (that is, 2 g of cellulose nanofiber (dry weight) is contained in 100 ml of dispersion). The papermaking additive of the present invention shows moderate consistency, and can be easily prepared to a coating material by merely adjusting its concentration to a desired level. Comparatively low value of B-type viscosity of cellulose nanofibers as a 2% (w/v) aqueous dispersion is preferred since such low-viscosity nanofibers can be easily prepared to a coating material. The viscosity is preferably about 500 to 2000 MPa·s, more preferably about 500 to 1500 MPa·s, and most preferably about 500 to 1000 MPa·s.

The B-type viscosity of the cellulose nanofiber of the present invention may be measured by a known method. For example, a viscometer, VISCOMETER TV-10, available from TOKI SANGYO Corporation can be used to measure the B-type viscosity.

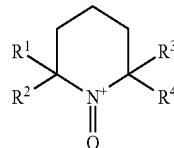
The cellulose nanofiber having a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s, preferably 500 to 2000 mPa·s as a 2% (w/v) aqueous solution, can be obtained, for example, by oxidizing a cellulosic material with the addition of an oxidizing agent in the presence of (1) N-oxyl compound(s), and (2) compound(s) selected from bromide, iodide or mixtures thereof; and then finely grinding the oxidized cellulose by a wet process to defibrate fibers in the cellulose and convert the cellulose into nanofibers.

The cellulosic material used in the present invention is not limited, and includes kraft pulp or sulfite pulp of various wood origins, powdery cellulose formed by pulverizing such pulp by a high pressure homogenizer, a mill or the like, and a microcrystalline cellulose powder formed by purifying such a material by chemical treatment such as acid hydrolysis. Among them, bleached kraft pulp, bleached sulfite pulp, powdery cellulose, and a microcrystalline cellulose powder are preferably used since comparatively low-viscosity cellulose nanofibers whose B-type viscosity is about 500 to 2000

MPa·s in an aqueous dispersion at a concentration of 2% (w/v) can be prepared effectively by using these materials. More preferably, powdery cellulose and a microcrystalline cellulose powder are used.

Powdery cellulose is a rod-like particle of microcrystalline cellulose which is obtained by removing amorphous parts from wood pulp with an acid hydrolysis treatment, and pulverizing and sieving it. In the powdery cellulose, degree of polymerization of cellulose is preferably about 100 to 500, crystallinity of powdery cellulose measured by X-ray diffraction is preferably about 70 to 90%, a mean volume diameter measured by laser diffraction is preferably not more than 100 μm, more preferably not more than 50 μm. By using powdery cellulose having a mean volume diameter of not less than 100 μm, a highly-fluid dispersion of cellulose nanofibers can be prepared. As the powdery cellulose used in the present invention, for example, a rod-like crystalline cellulose powder having a certain particle size distribution which is obtained by a method comprising subjecting a selected pulp to an acid hydrolysis treatment to obtain an undecomposed residue, and purifying, drying, pulverizing and sieving the residue, may be used, or a commercially available powdery cellulose such as KC FLOCK® available from NIPPON PAPER CHEMICALS Corporation, CEOLUS® available from ASAHI KASEI CHEMICALS Corporation, and AVICEL® available from FMC Corporation may also be used.

As the N-oxyl compound used in the present invention, any compounds which can promote desired oxidizing reaction may be used. For example, the N-oxyl compound used in the invention includes the compound represented by the following formula (1):

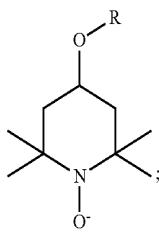


formula 1

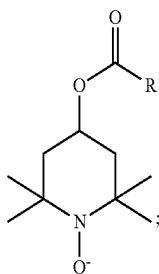
wherein R¹ to R⁴ are identical or different from each other, an alkyl group having about 1 to 4 carbon atoms.

Among the compounds represented by the formula (1), compounds which produce 2,2,6,6-tetramethyl-1-piperidin-N-oxyl radical (hereinafter referred to as TEMPO) and a 4-hydroxy-2,2,6,6-tetramethyl-1-piperidin-N-oxyl radical (hereinafter referred to as 4-hydroxy TEMPO) are preferred. In particular, derivative of 4-hydroxy TEMPO is most preferably used. As the derivatives of 4-hydroxy TEMPO, derivatives in which the hydroxyl group of 4-hydroxy TEMPO has been etherified with an alcohol containing a straight or branched carbon chain having 4 or less carbon atoms, or esterified with a carboxylic acid or a sulfonic acid, are preferably used. When etherifying 4-hydroxy TEMPO, a water-soluble derivative can be obtained by using an alcohol having 4 or less carbon atoms, regardless of the presence or absence of a saturated or unsaturated bond, and the water-soluble derivative of 4-hydroxy TEMPO can function effectively as an oxidation catalyst.

The derivatives of 4-hydroxy TEMPO include, for example, compounds represented by the following formulas 2 to 4:

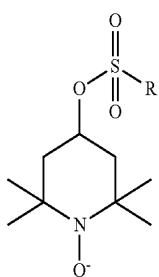


formula 2



formula 3

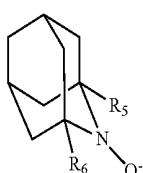
and



formula 4

wherein R is a straight or branched carbon chain having 4 or less carbon atoms.

Further, a radical of the N-oxyl compound represented by the following formula 5:



formula 5

wherein R⁵ and R⁶ are identical or different from each other, hydrogen, or a C1 to C6 straight or branched alkyl group, that is, aza-adamantane type nitroxy radical can be used preferably, since such compounds can shorten reaction time, and promote to produce a uniform cellulose nanofiber.

The amount of the N-oxyl compounds such as TEMPO and 4-hydroxy TEMPO derivatives used in the oxidation of cellulosic material is not limited, as long as it is a catalytic amount which enables the cellulosic material to be converted into nanofibers. For example, its amount is of the order of 0.01 to 10 mmols, preferably 0.01 to 1 mmol, more preferably 0.05 to 0.5 mmol, based on 1 g (absolute dry weight) of the cellulosic material.

As the bromide or iodide used in the oxidation of cellulosic material, a compound which can dissociate in water and ionize, for example, an alkali metal bromide, an alkali metal iodide or the like can be used. The amount of the bromide or iodide used can be selected within a range which can promote the oxidation reaction. For example, the amount is of the

order of 0.1 to 100 mmols, preferably 0.1 to 10 mmols, more preferably 0.5 to 5 mmols, based on 1 g (absolute dry weight) of the cellulosic material.

As the oxidizing agent used in the oxidation of cellulosic material, any oxidizing agent can be used, as long as it can proceed with the intended oxidation reaction, such as a halogen, a hypohalogenous acid, a halogenous acid, a perhalogenic acid, or a salt thereof, a halogen oxide, or a peroxide. From the viewpoint of the manufacturing cost, the preferred oxidizing agent to be used is sodium hypochlorite which is used currently most widely in industrial processes, which is inexpensive, and which imposes a minimal environmental load. The amount of the oxidizing agent used can be selected within a range which can promote the oxidation reaction. For example, the amount is of the order of 0.5 to 500 mmols, preferably 0.5 to 50 mmols, more preferably 2.5 to 25 mmols, based on 1 g (absolute dry weight) of the cellulosic material.

Oxidation of cellulosic material in the present invention is characterized that the oxidation of the cellulosic material is carried out in water with the addition of an oxidizing agent such as sodium hypochlorite in the presence of (1) N-oxyl compound(s) such as 4-hydroxy TEMPO derivative(s) and (2) compound(s) selected from the group consisting of bromide, iodide and mixtures thereof. The method has the feature that it can proceed with the oxidation reaction smoothly even under mild conditions. Thus, the reaction temperature may be room temperature of the order of 15 to 30°C. As the reaction proceeds, carboxyl groups form in the cellulose, and a decline in the pH of the reaction mixture is observed. To proceed with the oxidation reaction efficiently, it is desirable to maintain the pH of the reaction mixture at a value of 9 to 12, preferably about 10 to 11 with the addition of alkaline solution such as an aqueous solution of sodium hydroxide.

Cellulose nanofibers can be produced by finely grinding the oxidized cellulosic material which has been obtained by oxidizing cellulosic material in the presence of (1) N-oxyl compound(s) and (2) compounds selected from bromide, iodide or mixtures thereof, with the addition of an oxidizing agent, in a wet condition to defibrate it. In the wet fine grinding, mixing/stirring, emulsifying/dispersing devices, such as a high-speed shearing mixture and a high-pressure homogenizer can be used alone or in combination. In particular, an ultrahigh-pressure homogenizer which can force not less than 100 MPa, preferably not less than 120 MPa, more preferably not less than 140 MPa is preferably used in the wet fine grinding, since such a ultrahigh-pressure homogenizer can produce cellulose nanofibers having a comparatively low viscosity such as a B-type viscosity of 500 to 2000 mPa·s in an aqueous dispersion of 2% (w/v), effectively.

The cellulose nanofibers of the present invention desirably has an amount of the carboxyl groups being 0.5 mmol/g or more, preferably 0.9 mmol/g, more preferably 1.2 mmol/g, based on 1 g (absolute dry weight) of cellulose nanofibers. Such cellulose nanofibers can promote preparation of uniform dispersion. The amount of cellulose nanofibers can be measured by preparing 60 ml of slurry containing 0.5 weight % of cellulose nanofiber, adding 0.1M of hydrochloric acid to adjust the slurry's pH at 2.5, dropping 0.05N of aqueous sodium hydroxide with measuring electrical conductivity until the pH reaches 11, and determining an amount of sodium hydroxide (a) which is consumed in neutralization of weak acid when the electrical conductivity shows gentle curve, and using the following formula:

$$\text{Amount of carboxyl groups (mmol/g pulp)} = a(\text{ml}) \times 0.05 / \text{weight of oxidized pulp (g)}$$

(Paper which Contains Cellulose Nanofibers)

Incorporating the papermaking additive comprising cellulose nanofiber of the present invention into paper can improve air resistance of the paper, and can impart functions such as the suppression of permeation of a coated material, and an improvement in barrier properties. Also, when paper is coated with or impregnated with the papermaking additive of the present invention, the smoothness of the paper can be improved, thus enhancing printability. A paper prepared by coating or impregnating the papermaking additive of the cellulose nanofibers of the present invention is excellent in barrier properties and heat resistance and can be used as a packaging material.

A papermaking additive comprising the cellulose nanofibers of the present invention may be internally added or externally added to paper. However, its external addition is desirable because the external addition enables the cellulose nanofibers to be present in a larger amount in the vicinity of the paper surface and can highly improve air resistance and smoothness. In externally adding the papermaking additive, it is recommendable to coat an aqueous dispersion of the cellulose nanofibers on paper by a coating machine such as a 2-roll size press coater, a gate roll coater, a blade metering coater, or a rod metering coater, or impregnate paper with the nanofibers.

The preferred content of the papermaking additive according to the present invention is 0.1 to 10% by weight based on the dry weight of cellulose nanofibers in the dry weight of paper and, in the case of external addition, is 0.01 to 10 g/m², preferably 0.1 to 10 g/m², as the amount of coating per surface. In the case of external addition of the papermaking additive of the present invention onto a printing paper such as a news printing paper, the preferred content of the additive is 0.1 to 5 g/m² as the amount of coating per surface; in the case of external addition onto a converting paper such as base paper for wallpaper, the preferred content is 1 to 5 g/m², more preferably 2 to 5 g/m²; and in the case of external addition onto base paper for a coated paper, the preferred content is 1 to 5 g/m², more preferably 2 to 5 g/m².

Paper containing the cellulose nanofibers according to the present invention is produced by a known paper machine, and its paper making conditions are not regulated. As the paper machine, a Fourdrinier paper machine, a twin wire paper machine, or the like is used. Also, a cylinder paper machine can be used to produce multi-layer paper or a paperboard.

The paper of the present invention may be not only paper in a single layer, but also multi-layer paper in two or more layers, or a paperboard. In the multi-layer paper, the cellulose nanofibers may be contained in at least one of the layers.

The paper of the present invention uses, as a pulp component, chemical pulp (needle bleached kraft pulp (NBKP) or needle unbleached kraft pulp (NUKP), leaf bleached kraft pulp (LBKP) or leaf unbleached kraft pulp (LUKP), etc.), mechanical pulp (ground pulp (GP), thermomechanical pulp (TMP), chemithermomechanical pulp (CTMP), etc.), or recycled pulp such as deinked pulp (DIP), any of these pulps being used alone or as mixed in arbitrary proportions. During papermaking, pH may be acidic, neutral, or alkaline.

The paper of the present invention may also contain one or more filler(s). As the filler, a publicly known filler can be used, such as white carbon, talc, kaolin, clay, heavy calcium carbonate, light calcium carbonate, titanium oxide, or a synthetic resin filler. Among them, in view of protection of the environment, and improvement of preservation quality of paper, calcium carbonate is preferably used to carry out neutral papermaking, so as to make the pH of the surface of paper being 6 to 9.

Further, the paper of the present invention may, if necessary, contain aluminum sulfate, a sizing agent, a paper strength agent, a retention aid, a drainage aid, a coloring agent, a dyestuff, an anti-foaming agent, and a bulking agent.

5 (Printing Paper)

The paper of the present invention which contains cellulose nanofibers can be used as printing paper upon coating with a surface treating agent containing no pigment. Desirably, a surface treating agent consisting essentially of a water-soluble polymer, in order to improve surface strength and sizing properties. Alternatively, if a water-soluble polymer is used, the polymer may be mixed with the papermaking additive consisting of the cellulose nanofibers of the present invention, and coated therewith. When the papermaking additive is mixed with a water-soluble polymer and coated or impregnated, as compared to the case where the water-soluble polymer is used alone, a paper having high smoothness and air resistance, as well as showing high adherability of ink and low print-through in offset printing, can be obtained.

As the water-soluble polymer, a surface treating agent in common use can be used, such as starch including a starch, oxidized starch, and processed starch, carboxymethylcellulose, polyacrylamide, or polyvinyl alcohol, any of these surface treating agents being used alone or as a mixture. To the surface treating agent, in addition to the water-soluble polymer, it is possible to add a paper strength agent which can enhance water resistance and surface strength, or to externally add a sizing agent which can enhance sizing properties. If neutral papermaking is carried out, it is preferred that a cationic surface sizing agent is externally added.

The mixed ratio of the water-soluble polymer to the papermaking additive comprising cellulose nanofibers is not in particular limited, but it is preferred that the content of water-soluble polymer is 80 to 98 wt % and the content of the papermaking additive is 2 to 20 wt %, based on the solid content of the surface treating agent in the coating liquid. If the content of the papermaking additive is too high, viscosity of the coating liquid increases and the coating abilities of the coating decrease.

The surface treating agent can be coated by a coating machine, such as a 2-roll size press coater, a gate roll coater, a blade metering coater, or a rod metering coater. Of them, a film transfer type coating machine such as a gate roll coater is preferred as compared to an impregnating type coating machine such as a 2-roll size press coater, because the surface treating agent remains on the paper surface more and proves effective even in a smaller amount of coating. The preferred amount of coating with the surface treating agent is, based on 45 dry weight, 0.05 g/m² or more, but 3 g/m² or less, more preferably, 0.1 g/m² or more, but 3 g/m² or less, per surface. When the water-soluble polymer and the papermaking additive of the present invention are mixed and coated together, the preferred amount of water-soluble polymer is about 0.05 to 5 g/m² per both surfaces, and the preferred amount of cellulose nanofibers is 0.01 to 1 g/m² per both surfaces.

Further in the present invention, to improve the quality of print, it is possible to apply a coating layer containing pigments on the paper which has been internally or externally 60 provided with the papermaking additive of the present invention to make a printing paper. In addition, with the proviso that a desired effect is obtained, calendering may be performed. Calendering may be carried out with a commonly used linear pressure, but it is preferred that low linear pressure which can ensure smoothness of paper is used in order to increase a bulking property of the paper. A soft nip calendar is preferably used.

The papermaking additive comprising cellulose nanofibers of the present invention can give a printing paper high smoothness and enhance a quality of printing.

For example, a news printing paper is a kind of printing paper, and is made from 100% recycled pulp, or a mixture of recycled pulp with a mechanical pulp prepared by grinding wood and containing little amount of needle bleached pulp. Alternatively, the news printing paper is prepared by mixing the foregoing various pulps. The news printing paper is required to be hardly cut upon high-speed rotary printing, have high smoothness in both sides, high opacity, and high printing abilities. The papermaking additive of the present invention can remarkably increase the air resistance of news printing paper, and prevent the ink from excessively penetrating into the paper to prevent decrease in density of printing. In particular, if a mixture of the papermaking additive of the present invention with a water-soluble polymer is coated on the paper, cellulose nanofibers fills depressed area of the paper, the smoothness of the paper increases, and adherability of ink on the paper also increases. Also, since the cellulose nanofibers remain on the surface of the paper, the air resistance of the paper increases and, upon printing, excess penetration of ink is prevented and properties of preventing print-through is enhanced.

The papermaking additive of the present invention can also applies to a high-quality printing paper (a wood-free paper) which is made from 100% chemical pulp prepared by subjecting wood to a chemical treatment to remove lignin and consisting of cellulose and hemi-cellulose, a medium-quality printing paper (a wood containing paper) which is made from 40 to 100% of chemical pulp. Various properties of the paper may be determined depending on its use. For example, the basis weight of news printing paper is about 30 to 60 g/m². A type of printing is not limited, and any type of printing such as offset printing, gravure printing, and anastatic printing may be used. As a type of offset printing, a heat-set type of printing which includes a step of heat drying, and a cold-set type of printing which does not include heat drying, but uses an ink which is dried by penetration of the ink, may be used.

(Electrophotographic Transfer Paper, Thermal Recording Paper, Converting Paper, Paperboard, Sanitary Paper, Inkjet Recording Paper, and the Like)

The paper of the present invention can be used not only as printing paper and news printing paper, but also as electrophotographic transfer paper, inkjet recording paper, thermal recording paper, pressure sensitive recording paper, business form, converting paper, and sanitary paper. In further detail, the converting paper may be an industrial laminates base, backing paper for wall paper, or base paper for molding purposes. The sanitary paper is, in further detail, tissue paper, toilet paper, or a paper towel. The paper of the present invention can also be used as a paperboard such as a corrugating medium.

The papermaking additive of the present invention can increase smoothness and air resistance of electrophotographic transfer paper, and thereby, transferability of toner to paper is improved and quality of printing is heightened.

The papermaking additive of the present invention can increase smoothness and air resistance of inkjet recording paper, prevent an ink from excessively penetrating, avoid breeding of ink, increase fixing of ink, and heighten density of printing.

The papermaking additive of the present invention can increase smoothness and air resistance of thermal recording paper, prevent a thermal sensitive coating from excessively penetrating into the base paper, help the coating to spread on

the surface of the paper uniformly, and increase thermal insulation properties and sensitivity of the paper.

The papermaking additive of the present invention can increase smoothness and air resistance of pressure sensitive recording paper, prevent a pressure sensitive coating from excessively penetrating into the base paper, help the coating to spread on the surface of the paper uniformly, and increase sensitivity of the paper.

The papermaking additive of the present invention can increase smoothness and air resistance of backing paper for wall paper, prevent a binder such as aquatic starch paste from excessively penetrating into the base paper, avoid fuzz of the surface of the base paper, and prevent projection of resin surface.

The papermaking additive of the present invention can increase smoothness and air resistance of sanitary paper and make the surface of paper lubricant.

The papermaking additive of the present invention can increase smoothness and air resistance of paperboard such as a corrugated paperboard, and increase the printability of the paper.

(Base Paper for Coated Paper)

Further, the paper of the present invention which contains cellulose nanofibers can be used as base paper for paper having a pigment-containing coating layer such as coated paper, inkjet recording paper, thermal recording paper, pressure sensitive recording paper, or converting paper. In further detail, the coated paper may be art paper, coat paper, light-weight coated paper, cast coated paper, or a white lined board. In further detail, the converting paper may be packaging paper, moisture-proof paper, backing paper for wall paper, base paper for a paper container, or base paper for molding purposes. In particular, paper having the papermaking additive, which comprises the cellulose nanofibers according to the present invention, externally added to paper is markedly improved in air resistance and smoothness, and when this paper is used as base paper and coated with a paint, permeation of the paint is suppressed, and a smooth coating layer is obtained. Thus, coated paper with satisfactory printability can be obtained. For example, base paper for coated paper such as wood-free paper (100% chemical pulp) and wood-containing paper (mixture of chemical pulp and mechanical pulp) may be externally applied the cellulose nanofiber of the present invention, and the resulting base paper has an improved smoothness and air resistance. In such paper, a coating color consisting of pigment such as kaolin and calcium carbonate and a binder such as starch and latex is prevented from excessively penetrating into the base paper, and thus, the coated layer has a high smoothness. Such paper has a high degree of brilliance and high printability, even when the coated amount of coating color is low.

The above paper is also preferably used as base paper for inkjet recording paper, thermal recording paper, or pressure sensitive recording paper, since such papers have a smooth inkjet recording layer, a smooth thermal recording layer, or a smooth pressure sensitive recording layer. Also, the paper of the present invention which comprises cellulose nanofibers may be used as base paper for laminated paper having one or more synthetic resin layers on one surface or both surfaces thereof.

The coated paper of the present invention is paper formed by providing base paper, which contains cellulose nanofibers, with a coating layer having a pigment and a binder. The pigment used in the coating layer is an inorganic pigment such as kaolin, clay, delaminated clay, heavy calcium carbonate, light calcium carbonate, talc, titanium dioxide, barium sulfate, calcium sulfate, zinc oxide, silicic acid, silicate, col-

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loidal silica, or satin white, or an organic pigment such as plastic pigment, which has been used so far for coated paper. Any one or more of these pigments can be selected and used, as appropriate, according to needs.

The binder used in the coating layer is any of those so far used for coated paper, including synthetic adhesives such as various copolymers, for example, a styrene-butadiene copolymer, a styrene-acrylic copolymer, an ethylene-vinyl acetate copolymer, a butadiene-methyl methacrylate copolymer, and a vinyl acetate-butyl acrylate copolymer, polyvinyl alcohol, a maleic anhydride copolymer, and an acrylic acid-methyl methacrylate copolymer; proteins such as casein, soybean protein, and synthetic protein; starches such as oxidized starch, cationic starch, urea phosphoric esterified starch, etherified starch, e.g., hydroxyethyl etherified starch, and dextrin; and cellulose derivatives such as carboxymethylcellulose, hydroxyethylcellulose, and hydroxymethylcellulose. One or more of these ordinary additives for coated paper are selected as appropriate, and put to use. Any of these additives is used in an amount of the order of 5 to 50 parts by weight with respect to 100 parts by weight of the pigment. To make surface strength more satisfactory, it is preferred to contain 10 to 25 parts by weight of a copolymer latex such as styrene-butadiene. From the point of view of flexibility, the content of starch is preferably 5 parts by weight or less.

Various auxiliaries to be compounded with ordinary pigments for coated paper, such as dispersing agents, thickening agents, water retaining agents, anti-foaming agents, water resistant additives, and coloring agents, are used appropriately according to needs.

As the coating layer provided on the base paper, a single layer or two or more layers may be provided on one surface or both surfaces of the base paper. The total amount of coating with the coating layer is preferably 5 to 30 g/m², more preferably 8 to 20 g/m², per surface. The amount of coating if an undercoating layer is provided is preferably 2 to 8 g/m².

Upon application of a coating layer consisting essentially of pigment and binder(s) on a base paper, a film transfer roll coater such as a 2-roll size press coater, a gate roll coater, a blade metering size press coater, a rod metering size press coater, or Sym-Sizer; a flooded nip/blade coater, a jet fountain/blade coater, or a short dwell time applicator; a rod metering coater using a grooved rod or a plain rod instead of a blade; or a publicly known coater such as a curtain coater or a die coater. In coating an undercoating solution, the film transfer method using a gate roll coater or the like is preferred in order to impregnate the base paper with this solution moderately.

For the purpose of, for example, improving smoothness and printing quality, it is possible to carry out the surface treatment of the coated paper obtained in the above-described manner. The method of surface treatment can be to use a publicly known surface treatment apparatus such as a super-calender using a cotton roll as an elastic roll, or a soft nip calendar using a synthetic resin roll as an elastic roll.

Actions

The reason why the papermaking additive comprising cellulose nanofibers of the present invention markedly improve smoothness and air resistance of paper remains unclear. However, it is presumed that unlike a water-soluble polymer such as starch, the cellulose nanofibers are in a fibrous form, and can exist in such a crosslinked state as to fill in the voids of pulp fibers on the surface of the paper.

EXAMPLES

The present invention will be described in more detail by the following examples, which in no way limit the present invention.

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<Preparation of Cellulose Nanofiber 1>

Powdery cellulose (manufactured by NIPPON PAPER CHEMICALS CO., LTD.; particle size 24 µm) in an amount of 15 g (absolute dry weight) was added to 500 ml of an aqueous solution having 78 mg (0.5 mmol) of TEMPO (a product of Sigma Aldrich) and 755 mg (5 mmol) of sodium bromide dissolved therein, and the mixture was stirred until the powdery cellulose was uniformly dispersed. To the reaction system, 50 ml of an aqueous solution of sodium hypochlorite (available chlorine 5%) was added, and then the mixture was adjusted to pH 10.3 using a 0.5N aqueous solution of hydrochloric acid to initiate an oxidation reaction. During the reaction, the pH within the system lowers, but a 0.5N aqueous solution of sodium hydroxide was successively added to adjust the pH to 10. After the reaction was performed for 2 hours, the oxidized powdery cellulose was separated by a centrifugal operation (6000 rpm, 30 minutes, 20° C.), and thoroughly washed with water to obtain oxidized powdery cellulose. A 2% (w/v) slurry of the oxidized powdery cellulose was treated by a mixer for 15 minutes at 12,000 rpm, and the powdery cellulose slurry was further treated 5 times under a pressure of 140 MPa by an ultrahigh pressure homogenizer, whereby a transparent gel-like dispersion was obtained.

<Preparation of Cellulose Nanofiber 2>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that the powdery cellulose slurry was treated 5 times under a pressure of 120 MPa by an ultrahigh pressure homogenizer.

<Preparation of Cellulose Nanofiber 3>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that the powdery cellulose slurry was treated 5 times under a pressure of 100 MPa by an ultrahigh pressure homogenizer.

<Preparation of Cellulose Nanofiber 4>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that, in the step of the wet process finely grinding, a rotary blade mixer (rim speed: 37 m/s, NISSEI CORPORATION, processing time: 30 minutes) was used instead of the ultrahigh pressure homogenizer.

<Preparation of Cellulose Nanofiber 5>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that 4-methoxy TEMPO was used instead of TEMPO.

<Preparation of Cellulose Nanofiber 6>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 1, with the exception that a bleached, un-beaten sulfite pulp (manufactured by NIPPON PAPER CHEMICALS CO., LTD.) was used instead of the powdery cellulose, and the oxidized sulfite pulp slurry was treated 40 times under a pressure of 140 MPa by the ultrahigh pressure homogenizer.

<Preparation of Cellulose Nanofiber 7>

A cellulose nanofiber was obtained in the same manner as the preparation of cellulose nanofiber 5, with the exception that the bleached, un-beaten sulfite pulp (manufactured by NIPPON PAPER CHEMICALS CO., LTD.) was used instead of the powdery cellulose, the oxidized sulfite pulp slurry was treated by the rotary blade mixer for 5 hours.

The B-type (60 rpm, 20° C.) viscosity each of the cellulose nanofibers obtained by the foregoing preparation methods 1 to 7 was measured with the use of VISCOMETER TV-10 (TOKI SANGYO CO, LTD.), and the result is shown in Table 1.

TABLE 1

| Preparation | material | catalyst | wet process finely grinding | | cellulose nanofiber B-type viscosity (mPa · s) |
|-------------|-------------------|-----------------|---------------------------------|--------------------|--|
| | | | disperser | pressure | |
| 1 | powdery cellulose | TEMPO | ultrahigh pressure homogenizer | 140 MPa (5 times) | 890 |
| 2 | powdery cellulose | TEMPO | ultrahigh pressure homogenizer | 120 MPa (5 times) | 984 |
| 3 | powdery cellulose | TEMPO | ultrahigh pressure homogenizer | 100 MPa (5 times) | 1264 |
| 4 | powdery cellulose | TEMPO | rotary blade mixer (30 minutes) | — | 2860 |
| 5 | powdery cellulose | 4-methoxy TEMPO | ultrahigh pressure homogenizer | 140 MPa (5 times) | 850 |
| 6 | sulfite pulp | TEMPO | ultrahigh pressure homogenizer | 140 MPa (40 times) | 5568 |
| 7 | sulfite pulp | TEMPO | rotary blade mixer (5 hours) | — | 6850 |

By the preparation methods 1 to 7, cellulose nanofibers having a B-type viscosity (60 rpm, 20° C.) of 500 to 7000 mPa·s at a concentration of 2% (w/v) as an aqueous dispersion were obtained. Among them, the cellulose nanofibers obtained by the preparation methods 1 to 3, and 5 have a B-type viscosity (60 rpm, 20° C.) of 500 to 2000 mPa·s at a concentration of 2% (w/v) as an aqueous dispersion, have good flowability, and were easy to coat on a substrate such as paper. The cellulose nanofibers obtained by the preparation methods 4, 6, and 7 have a little high viscosity, and, when the nanofibers were applied on paper, penetration of the nanofibers into paper was suppressed, whereby amount of coating was decreased as compared to the case where the cellulose nanofibers obtained by the preparation methods 1 to 3, and 5, were coated on the same condition.

Next, examples of method for preparing cellulose nanofibers-containing paper by coating the cellulose nanofibers obtained by the foregoing methods on paper.

<Preparation of Wood-Free Paper Containing Cellulose Nanofibers (CNF)>

Example 1

The cellulose nanofiber dispersion obtained by the foregoing preparation method 1 was coated on wood-free paper (paper having 100% chemical pulp, manufactured by Nippon Paper Industries Co., Ltd.; basis weight 79 g/m²) by a 2-roll size press apparatus so that the amount of coating would be 1.4 g/m² on both surfaces.

Comparative Example 1

The wood-free paper used in Example 1 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 2

The wood-free paper used in Example 1 was coated with an aqueous solution of oxidized starch (commercial name:

SK200, manufactured by Nihon Cornstarch Corporation) by a 2-roll size press apparatus so that the amount of coating would be 1.4 g/m² on both surfaces.

Comparative Example 3

The wood-free paper used in Example 1 was coated with an aqueous solution of polyacrylamide (commercial name: DS4340, manufactured by SEIKO PMC CORPORATION) by a 2-roll size press apparatus so that the amount of coating would be 1.4 g/m² on both surfaces.

The thicknesses and basis weights of the papers prepared in Example 1 and Comparative Examples 1 to 3 were measured by the methods described below, and the densities were calculated based on the measured values. Further, the breaking length, Taber stiffness, whiteness, opacity, specific scattering coefficient, smoothness, and air resistance of each paper were measured by the methods described below. The results are shown in Table 2.

Thickness: Measured in accordance with JIS P8118:1998.

Basis weight: Measured in accordance with JIS P8124: 1998 (ISO 536:1995).

Density: Calculated from the measured values of the thickness and basis weight of the coated sheet.

Breaking length: Measured in accordance with JIS P8113: 1998.

Taber stiffness: Measured in accordance with JIS P8125: 1976 (ISO 2493:1992).

Whiteness: ISO whiteness was measured in accordance with JIS P8148:2001.

Opacity: Measured in accordance with JIS P8149:2000.

Specific scattering coefficient: Measured with a color-difference meter (manufactured by MURAKAMI COLOR RESEARCH LABORATORY CO., LTD.) in accordance with TAPPI T425 om-91.

Smoothness and air resistance: Measured with an Oken type smoothness/air resistance tester in accordance with Japan TAPPI Paper Pulp Testing Method No. 5-2:2000.

TABLE 2

| | density (g/cm ³) | breaking length (km) | Taber stiffness (mN) | whiteness (%) | opacity (%) | specific scattering coefficient (m ² /kg) | smooth- ness (sec.) | air resistance (sec.) |
|-----------------------|---------------------------------|----------------------------|----------------------------|------------------|----------------|---|---------------------------|-----------------------------|
| Example 1 | 0.57 | 2.97 | 0.64 | 73.5 | 95.2 | 86.1 | 43 | 49 |
| Comparative Example 1 | 0.56 | 2.55 | 0.54 | 73.2 | 95.1 | 86.2 | 27 | 6 |

TABLE 2-continued

| | density (g/cm ³) | breaking length (km) | Taber stiffness (mN) | whiteness (%) | opacity (%) | specific scattering coefficient (m ² /kg) | smooth- ness (sec.) | air resistance (sec.) |
|--------------------------|---------------------------------|----------------------------|----------------------------|------------------|----------------|---|---------------------------|-----------------------------|
| Comparative Example 2 | 0.57 | 3.01 | 0.61 | 72.9 | 95 | 83.6 | 30 | 7 |
| Comparative Example 3 | 0.57 | 3.55 | 0.67 | 72.7 | 94.9 | 82.3 | 31 | 9 |

As shown in Table 2, the paper coated with the cellulose nanofibers according to the present invention markedly improved in smoothness and air resistance as compared with the papers coated with oxidized starch or polyacrylamide.

<Preparation of News Printing Paper Containing CNF>

Example 2

News printing paper (manufactured by Nippon Paper Industries Co., Ltd.; basis weight 42 g/m², made from a little amount of mechanical pulp which contains a needle bleached pulp and a major amount of recycled pulp) was coated with the aforementioned cellulose nanofiber dispersion by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 4

The news printing paper used in Example 2 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 5

The news printing paper used in Example 2 was coated with an aqueous solution of oxidized starch (commercial name: SK200, manufactured by Nihon Cornstarch Corporation) by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 6

The news printing paper used in Example 2 was coated with an aqueous solution of polyvinyl alcohol (commercial name: PVA117, manufactured by KURARAY CO., LTD.) by a 2-roll size press apparatus, with the amount of coating being varied.

The papers prepared in Example 2 (CNF), Comparative Example 4 (blank), Comparative Example 5 (starch), and Comparative Example 6 (PVA) were measured for smoothness and air resistance. The results are shown in FIGS. 1 and 2.

<Preparation of Base Paper for Coated Paper Containing CNF>

Example 3

A coat base paper (manufactured by Nippon Paper Industries Co., Ltd.; basis weight 70 g/m², wood-containing paper made from chemical and mechanical pulps) was coated with the aforementioned cellulose nanofiber dispersion by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 7

The coat base paper used in Example 3 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 8

15 The coat base paper used in Example 3 was coated with an aqueous solution of oxidized starch (commercial name: SK200, manufactured by Nihon Cornstarch Corporation) by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 9

20 The coat base paper used in Example 3 was coated with an aqueous solution of polyvinyl alcohol (commercial name: PVA117, manufactured by KURARAY CO., LTD.) by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 10

25 The coat base paper used in Example 3 was coated with an aqueous solution of carboxymethylcellulose (commercial name: F01MC, manufactured by NIPPON PAPER CHEMICALS CO., LTD.) by a 2-roll size press apparatus, with the amount of coating being varied.

30 The papers prepared in Example 3 (CNF), Comparative Example 7 (blank), Comparative Example 8 (starch), Comparative Example 9 (PVA), and Comparative Example 10 (CMC) were measured for smoothness and air resistance. The results are shown in FIGS. 3 and 4.

<Preparation of Backing Paper for Wall Paper Containing CNF>

Example 4

45 Base paper for wall paper (manufactured by Nippon Paper Industries Co., Ltd.; basis weight 64 g/m²) was coated with the aforementioned cellulose nanofiber dispersion by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 11

50 The base paper for wall paper used in Example 4 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 12

55 The base paper for wallpaper used in Example 4 was coated with an aqueous solution of oxidized starch (commercial name: SK200, manufactured by Nihon Cornstarch Corporation) by a 2-roll size press apparatus, with the amount of coating being varied.

Comparative Example 13

60 The base paper for wall paper used in Example 4 was coated with an aqueous solution of polyvinyl alcohol (com-

mercial name: PVA117, manufactured by KURARAY CO., LTD.) by a 2-roll size press apparatus, with the amount of coating being varied.

The papers prepared in Example 4 (CNF), Comparative Example 11 (blank), Comparative Example 12 (starch), and Comparative Example 13 (PVA) were measured for smoothness and air resistance. The results are shown in FIGS. 5 and 6.

As shown in FIGS. 2, 4 and 6, the coating with the cellulose nanofibers of the present invention markedly improved air resistance, compared with the coating with oxidized starch, polyvinyl alcohol, or carboxymethylcellulose, regardless of the type of paper coated (news printing paper, coat base paper, base paper for wall paper). Thereby, in the case of the news printing paper, decrease in density of printing was prevented and quality of printing was improved; in the case of base paper for a coated paper, excessive penetration of a coated material was prevented and the printability was improved; and in the case of base paper for wall paper, excessive penetration of binders was prevented and workability of the wall paper was improved. Further, as shown in FIG. 5, the base paper for wall paper coated with the cellulose nanofibers of the present invention has a high smoothness, as compared with the base paper for wall paper coated with the other compounds. Thereby, fuzz of the base paper for wall paper was suppressed, and a wall paper having a smooth surface was obtained.

<Preparation of Base Paper for Coated Paper Containing CNF>

Example 5

The coat base paper used in Example 3 was with the cellulose nanofiber dispersion obtained by the foregoing preparation method 3 by a 2-roll size press apparatus, with the amount of coating being varied. The smoothness and air resistance of the resulting paper were measured, and the results are shown in FIGS. 7 and 8.

<Preparation of Thermal Recording Paper of which Base Paper Contains CNF>

Example 6

A thermal sensitive coating color having the following composition was coated on the paper obtained by Example 1 which has been coated with the cellulose nanofibers, by a Meyer bar so that the amount of coating would be 6 g/m², and then the resulting paper was dried and calendered so that the Oken type smoothness would be 500 seconds, to obtain a thermal recording paper having a thermal sensitive layer.

| Composition of the thermal sensitive layer: | |
|---|------------|
| Dispersion of color developer (dispersion A) | 36.0 parts |
| Dispersion of leuco dye (dispersion B) | 13.8 parts |
| Dispersion of sensitizer (dispersion C) | 36.0 parts |
| 10% of aqueous solution of absolutely saponified polyvinyl alcohol (commercial name: PVA117, manufactured by KURARAY CO., LTD.) | 25.0 parts |

Compositions of each of the dispersions of color developer (dispersion A), leuco dye (dispersion B), and sensitizer (dispersion C) are as follows, and the dispersions were prepared separately by wet-grinding with a sand grinder so that their average particle size would be 0.5 micron.

| Dispersion A (dispersion of color developer) | |
|--|------------|
| 4-hydroxy-4'-isopropoxy-diphenylsulfone | 6.0 parts |
| 10% of aqueous solution of polyvinyl alcohol | 18.8 parts |
| water | 11.2 parts |
| Dispersion B (dispersion of basic and colorless dye) | |
| 3-dibutylamino-6-methyl-7-anilinofluorane (ODB-2) | 3.0 parts |
| 10% of aqueous solution of polyvinyl alcohol | 6.9 parts |
| water | 3.9 parts |
| Dispersion C (dispersion of sensitizer) | |
| dibenzyl oxalate | 6.0 parts |
| 10% of aqueous solution of polyvinyl alcohol | 18.8 parts |
| water | 11.2 parts |

Comparative Example 14

A thermal recording paper was prepared in the same manner as Example 6, with the exception that the thermal sensitive coating color was coated on the paper obtained by Example 3 which has been coated with water alone.

The sensitivity of the papers prepared in Example 6 and Comparative Example 14 were measured in the manner described below. The results are shown in Table 3.

Sensitivity: Printing was performed with a TH-PMD (manufactured by OHKURA DENKI CORPORATION, a tester for thermal recording paper equipped with a thermal head manufactured by KYOCERA CORPORATION) under the applied energy of 0.41 mJ/dot. Density of printing was measured with a Macbeth densitometer (RD-914, equipped with an amber filter).

TABLE 3

| sensitivity | |
|------------------------|------|
| Example 6 | 1.39 |
| Comparative Example 14 | 1.21 |

As shown in Table 3, the thermal recording paper using base paper coated with the cellulose nanofiber of the present invention (Example 6) has an markedly improved sensitivity, as compared with the thermal recording paper using base paper coated with water. The reason for this is considered that smoothness and air resistance of the base paper coated with the cellulose nanofiber (Example 1) is much higher than the base paper coated with water (Comparative Example 1), and therefore, in the case of thermal recording paper (Example 6) which uses the base paper coated with the cellulose nanofiber, excessive penetration of the thermal sensitive coating color into the base paper is suppressed, and the thermal sensitive coating color is coated uniformly on the base paper to provide thermal insulation effect with the paper and the sensitivity is improved.

<Preparation of a Wood-Free, Off-Set Printing Paper Containing CNF>

Example 7

100 parts of leaf bleached kraft pulp (LBKP, freeness: 400 ml) was defiberized to prepare a pulp slurry. To the pulp slurry, calcium carbonate was added in an amount of 5.0% based on the absolutely dried pulp. Neutral papermaking was carried out with a twin-wire paper machine so that the basis weight would be 62 g/m² to obtain a wood free base paper. The ash content of the resulting base paper was 9.5%.

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To the base paper, a coating material containing hydroxyethylated starch and the cellulose nanofiber prepared in the preparation method 1 in an amount (solid content) shown in Table 4 was coated by a 2-roll size press apparatus so that the coating amount (solid content) of starch and the cellulose nanofiber would be 2.0 g/m² and 0.1 g/m², respectively (both surfaces), to obtain a wood-free offset printing paper.

Comparative Example 15

The base paper used in Example 7 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 16

The base paper used in Example 7 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 2.0 g/m² on both surfaces.

Comparative Example 17

The base paper used in Example 7 was coated with an aqueous solution of polyacrylamide (commercial name:

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Adherability of ink (unevenness in printing) was evaluated by visual observation in accordance with the following basis:

◎: Highly even printing is obtained.

○: Even printing is obtained.

Δ: Printing is uneven.

X: Printing is markedly uneven.

<Test for RI Printing—Print Through>

Printing was carried out with an offset eco-ink, high viscosity AF ink manufactured by TOYO INK MFG. CO., LTD, by an RI printer (4-color printer) manufactured by ISHIKAWAJIMA INDUSTRIAL MACHINERY CO., LTD. The level of print through was evaluated by visual observation in accordance with the following basis:

◎: Penetration of ink to the back side of the printing is not observed.

○: Penetration of ink to the back side of the printing is almost not observed.

Δ: Penetration of ink to the back side of the printing is a little observed.

X: Penetration of ink to the back side of the printing is observed.

TABLE 4

| | composition of | | | | coating amount | | | | | RI printing test | |
|------------------------|------------------|-------------------|-------|-----------------|----------------------------------|----------------------|---------------------------|----------------|--------------------|--|----------------------------------|
| | coating material | | | (both surfaces) | polyacryl-amide g/m ² | CNF g/m ² | density g/cm ³ | smoothness sec | air resistance sec | adherability of ink visual observation | print through visual observation |
| | starch % | polyacryl-amide % | CNF % | | | | | | | | |
| Example 7 | 9.5 | 0 | 0.5 | 10.0 | 2.0 | 0 | 0.10 | 0.604 | 22 | 92 | ◎ |
| Comparative Example 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0.594 | 11 | 8 | X | X |
| Comparative Example 15 | 10.0 | 0 | 0 | 10.0 | 2.0 | 0 | 0 | 0.600 | 13 | 12 | Δ |
| Comparative Example 16 | 10.0 | 0 | 0 | 10.0 | 2.0 | 0 | 0 | 0.601 | 15 | 14 | Δ |
| Comparative Example 17 | 0 | 10.0 | 0 | 10.0 | 0 | 2.0 | 0 | 0.601 | 14 | 14 | Δ |

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DS4340, manufactured by SEIKO PMC CORPORATION) by a 2-roll size press apparatus so that the coating amount of the polyacrylamide would be 2.0 g/m² on both surfaces.

Test

The thickness and basis weights of the papers prepared in Example 7 and Comparative Examples 15 to 17 were measured by the methods described below, and the densities were calculated based on the measured values. Further, the smoothness, air resistance, adherability of ink, and print through were measured by the methods described below. The results are shown in Table 4.

<Measurement of Basis Weight, Thickness and Density>

Basis weight: Measured in accordance with JIS P8124:1998 (ISO 536:1995).

Thickness: Measured in accordance with JIS P 8118:1998.

Density: Calculated from the measured values of the thickness and basis weight of the coated sheet.

<Measurement of Smoothness and Air Resistance>

The smoothness and air resistance were measured with an Oken type smoothness/air resistance tester in accordance with Japan TAPPI Paper Pulp Testing Method No. 5-2:2000.

<Test for RI Printing—Adherability of Ink>

Printing was carried out with an offset eco-ink, high viscosity AF ink manufactured by TOYO INK MFG. CO., LTD, by an RI printer (4-color printer) manufactured by ISHIKAWAJIMA INDUSTRIAL MACHINERY CO., LTD.

45

As shown in Table 4, the paper coated with a mixture of the cellulose nanofiber of the present invention and the starch has a higher smoothness and air resistance than those of the papers coated with starch alone or polyacrylamide, and has a good adherability of ink and prevention of print through, while the density is not increased.

<Preparation of a Wood-Containing, Offset Printing Paper Containing CNF>

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Example 8

95 parts of thermomechanical pulp (TMP, freeness: 100 ml) and 5 parts of needle bleached kraft pulp (nBKP, freeness: 600 ml) were mixed and defiberized to prepare a pulp slurry.

To the pulp slurry, calcium carbonate was added in an amount of 5.0% based on the absolutely dried pulp. Neutral paper-making was carried out with a twin-wire paper machine so that the basis weight would be 53 g/m² to obtain a wood-containing base paper. The ash content of the resulting base paper was 4.4%.

To the base paper, a coating material containing hydroxyethylated starch and the cellulose nanofiber prepared in the preparation method 1 in an amount (solid content) shown in Table 5 was coated by a 2-roll size press apparatus so that the coating amount (solid content) of starch and the cellulose nanofiber would be 2.0 g/m² and 0.1 g/m², respectively (both surfaces), to obtain a wood-containing offset printing paper.

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Comparative Example 18

The base paper used in Example 8 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 19

The base paper used in Example 8 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 2.0 g/m² on both surfaces.

Comparative Example 20

The base paper used in Example 8 was coated with an aqueous solution of polyacrylamide (commercial name: DS4340, manufactured by SEIKO PMC CORPORATION) by a 2-roll size press apparatus so that the coating amount of the polyacrylamide would be 2.0 g/m² on both surfaces.

Test

The thickness and basis weights of the papers prepared in Example 8 and Comparative Examples 18 to 20 were measured by the methods described below, and the densities were calculated based on the measured values. Further, the smoothness, air resistance, adherability of ink, and print through were measured by the methods described above. The results are shown in Table 5.

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coating amount (solid content) of starch and the cellulose nanofiber would be 3.0 g/m² and 0.5 g/m², respectively (both surfaces), to obtain an off-set news printing paper.

Example 10

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 3.0 g/m² and 0.3 g/m², respectively.

Example 11

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 3.0 g/m² and 0.1 g/m², respectively.

Example 12

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 3.0 g/m² and 0.05 g/m², respectively.

Example 13

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating

TABLE 5

| | composition of | | | | coating amount | | | | RI printing test | | |
|------------------------|------------------|--------------------------|----------|-----------------------|----------------------------|---|-------------------------|------------------------|--------------------------|---------------------------------|---|
| | coating material | | | (both surfaces) | | | | smooth- ness sec | air resistance sec | of ink visual observation | print through visual observation |
| | starch % | polyacryl- amide % | CNF % | solid content % | starch g/m ² | polyacryl- amide g/m ² | CNF g/m ² | | | | |
| Example 8 | 9.5 | 0 | 0.5 | 10.0 | 2.0 | 0 | 0.10 | 0.372 | 15 | 86 | ◎ |
| Comparative Example 18 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.366 | 7 | 5 | X |
| Comparative Example 19 | 10.0 | 0 | 0 | 10.0 | 2.0 | 0 | 0 | 0.373 | 9 | 7 | Δ |
| Comparative Example 20 | 10.0 | 10.0 | 0 | 10.0 | 2.0 | 2.0 | 0 | 0.369 | 9 | 7 | Δ |

As shown in Table 5, the paper coated with a mixture of the cellulose nanofiber of the present invention and the starch has a higher smoothness and air resistance than those of the papers coated with starch alone or polyacrylamide, and has a good adherability of ink and prevention of print through, while the density is not increased.

<Preparation of a News Printing Paper>

Example 9

80 parts of deinked pulp (DIP, freeness: 180 ml) and 15 parts of TMP (freeness: 100 ml) and 5 parts of needle bleached kraft pulp (NBKP, freeness: 600 ml) were mixed and defibrated to prepare a pulp slurry. To the pulp slurry, calcium carbonate was added in an amount of 7.5% based on the absolutely dried pulp. Neutral papermaking was carried out with a twin-wire paper machine so that the basis weight would be 42 g/m² to obtain a news printing base paper. The ash content of the resulting base paper was 12.5%.

To the base paper, a coating material containing hydroxyethylated starch and the cellulose nanofiber prepared in the preparation method 1 in an amount (solid content) shown in Table 6 was coated by a 2-roll size press apparatus so that the

amount of starch and the cellulose nanofiber was changed to 2.0 g/m² and 0.5 g/m², respectively.

Example 14

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 2.0 g/m² and 0.3 g/m², respectively.

Example 15

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 2.0 g/m² and 0.1 g/m², respectively.

Example 16

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 2.0 g/m² and 0.05 g/m², respectively.

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Example 17

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 1.0 g/m² and 0.5 g/m², respectively.

Example 18

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 1.0 g/m² and 0.3 g/m², respectively.

Example 19

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating amount of starch and the cellulose nanofiber was changed to 1.0 g/m² and 0.1 g/m², respectively.

Example 20

An off-set news printing paper was prepared in the same manner as in Example 9, with the exception that the coating

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Comparative Example 23

The base paper used in Example 9 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 2.0 g/m² on both surfaces.

Comparative Example 24

The base paper used in Example 9 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 1.0 g/m² on both surfaces.

Test

The thickness and basis weights of the papers prepared in Examples 9 to 20 and Comparative Examples 21 to 24 were measured by the methods described below, and the densities were calculated based on the measured values. Further, the smoothness, air resistance, adherability of ink, and print through were measured by the methods described above. The results are shown in Table 6, and FIGS. 9 and 10.

TABLE 6

| | composition of | | | | | | | | RI printing test | | |
|------------------------|------------------|-------|-----------------|-------------------------|----------------------|---------------------------|----------|----------------|--------------------|--------------|---------------|
| | coating material | | | coating amount | | | | smooth- | air | adherability | print |
| | solid | | (both surfaces) | | starch | CNF | density | | | | |
| | starch % | CNF % | content % | starch g/m ² | CNF g/m ² | density g/cm ³ | ness sec | resistance sec | visual observation | of ink | print through |
| Example 9 | 10.8 | 1.2 | 12.0 | 3.0 | 0.50 | 0.576 | 21 | 1038 | ◎ | ◎ | |
| Example 10 | 11.1 | 0.9 | 12.0 | 3.0 | 0.30 | 0.579 | 17 | 573 | ◎ | ◎ | |
| Example 11 | 11.5 | 0.5 | 12.0 | 3.0 | 0.10 | 0.571 | 14 | 227 | ◎ | ◎ | |
| Example 12 | 11.7 | 0.3 | 12.0 | 3.0 | 0.05 | 0.578 | 11 | 132 | ○ | ○ | |
| Example 13 | 8.8 | 1.2 | 10.0 | 2.0 | 0.50 | 0.574 | 20 | 684 | ◎ | ◎ | |
| Example 14 | 9.1 | 0.9 | 10.0 | 2.0 | 0.30 | 0.569 | 15 | 392 | ◎ | ◎ | |
| Example 15 | 9.5 | 0.5 | 10.0 | 2.0 | 0.10 | 0.575 | 11 | 141 | ◎ | ◎ | |
| Example 16 | 9.7 | 0.3 | 10.0 | 2.0 | 0.05 | 0.580 | 9 | 84 | ○ | ○ | |
| Example 17 | 5.8 | 1.2 | 7.0 | 1.0 | 0.50 | 0.577 | 17 | 348 | ◎ | ◎ | |
| Example 18 | 6.1 | 0.9 | 7.0 | 1.0 | 0.30 | 0.576 | 13 | 207 | ◎ | ◎ | |
| Example 19 | 6.5 | 0.5 | 7.0 | 1.0 | 0.10 | 0.571 | 10 | 81 | ○ | ○ | |
| Example 20 | 6.7 | 0.3 | 7.0 | 1.0 | 0.05 | 0.581 | 8 | 42 | ○ | ○ | |
| Comparative Example 21 | 0 | 0 | 0 | 0 | 0 | 0.576 | 6 | 10 | X | | X |
| Comparative Example 22 | 12.0 | 0 | 12.0 | 3.0 | 0 | 0.581 | 7 | 19 | Δ | Δ | |
| Comparative Example 23 | 10.0 | 0 | 10.0 | 2.0 | 0 | 0.577 | 7 | 17 | Δ | Δ | |
| Comparative Example 24 | 7.0 | 0 | 7.0 | 1.0 | 0 | 0.574 | 7 | 13 | Δ | X | |

amount of starch and the cellulose nanofiber was changed to 1.0 g/m² and 0.05 g/m², respectively.

Comparative Example 21

The base paper used in Example 9 was coated with water alone by a 2-roll size press apparatus.

Comparative Example 22

The base paper used in Example 9 was coated with an aqueous solution of hydroxyethylated starch by a 2-roll size press apparatus so that the coating amount of the starch would be 3.0 g/m² on both surfaces.

As shown in Table 6, the paper coated with a mixture of the cellulose nanofiber of the present invention and the starch has a higher smoothness and air resistance than those of the papers coated with starch alone or polyacrylamide, and has a good adherability of ink and prevention of print through, while the density is not increased.

The invention claimed is:

1. A cellulose nanofiber obtained by a method comprising the steps of:
oxidizing a cellulosic material with an oxidizing agent in the presence of:

25

- (1) N-oxy compound(s), and
 (2) compound(s) selected from the group consisting of bromide, iodide and mixtures thereof to prepare an oxidized cellulose; and
 finely grinding the oxidized cellulose in a wet condition to convert the oxidized cellulose into nanofibers having an amount of carboxyl groups of 1.2 mmol or more, based on 1 g absolute dry weight of the cellulose nanofibers, and whose B-type viscosity (60 rpm, 20° C.) as an aqueous solution at a concentration of 2% (w/v) is from 500 to 10 7000 mPa·s.
2. The cellulose nanofiber according to claim 1 whose B-type viscosity (60 rpm, 20° C.) as an aqueous solution at a concentration of 2% (w/v) is from 500 to 2000 mPa·s.
3. The cellulose nanofiber according to claim 1 wherein the step of finely grinding comprises defibrating the oxidized cellulose with an ultrahigh pressure homogenizer under a pressure of not less than 100 MPa.
4. A papermaking additive comprising the cellulose nanofiber according to claim 1.
5. Paper containing the cellulose nanofiber according to claim 1.
6. Paper according to claim 5 which is used as a printing paper.
7. A thermal recording paper using the paper according to claim 5 as a base paper.
8. A coated paper using the paper according to claim 5 as a base paper.
9. The paper according to claim 5 which is used as a news printing paper.
10. The paper according to claim 5 which is used as a converting paper.
11. The paper according to claim 5 which is used as an electrophotographic transfer paper.
12. The paper according to claim 5 which is used as a paper board.
13. The paper according to claim 5 which is used as a sanitary paper.

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14. The paper according to claim 5 which is used as an inkjet recording paper.
15. The paper according to claim 5 which is used as a thermal recording paper.
16. The paper according to claim 5 which is used as a pressure sensitive recording paper.
17. An inkjet recording paper using the paper according to claim 5 as a base paper.
18. A pressure sensitive recording paper using the paper according to claim 5 as a base paper.
19. A laminated paper having one or more layers of synthetic resin on a surface or both surfaces of the paper according to claim 5 as a base paper.
20. A method for preparing cellulose nanofiber having an amount of carboxyl groups of 1.2 mmol or more, based on 1 g absolute dry weight of the cellulose nanofibers and whose B-type viscosity (60 rpm, 20° C.) as an aqueous solution at a concentration of 2% (w/v) is from 500 to 7000 mPa·s, comprising the steps of:
 oxidizing a cellulosic material with an oxidizing agent in the presence of:
 (1) N-oxy compound(s), and
 (2) compound(s) selected from the group consisting of bromide, iodide and mixtures thereof to prepare an oxidized cellulose; and
 finely grinding the oxidized cellulose in a wet condition to convert the oxidized cellulose into nanofibers.
21. The process according to claim 20 wherein the B-type viscosity (60 rpm, 20° C.) of the cellulose nanofiber as an aqueous solution at a concentration of 2% (w/v) is from 500 to 20 mPa·s.
22. The process according to claim 20 wherein the step of finely grinding comprises defibrating the oxidized cellulose with an ultrahigh pressure homogenizer under a pressure of not less than 100 MPa.

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(54) METHOD FOR PRODUCING FURNISH, FURNISH AND PAPER

VERFAHREN ZUR HERSTELLUNG EINES PAPIERSTOFFS, PAPIERSTOFF UND PAPIER

PROCÉDÉ DE PRODUCTION DE COMPOSITION DE FABRICATION, COMPOSITION DE
FABRICATION ET PAPIER

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DescriptionField of the Invention

5 [0001] The present invention relates to a method for preparing aqueous furnish to be used in paper or paper board manufacturing. The invention also relates to furnish prepared by the method according to the invention, and to paper or paper board manufactured from the furnish.

Background of the Invention

10 [0002] For economical reasons, the trend in paper industry is to increase the proportion of filler in paper products and thereby to reduce the use of fibres. In addition to low price and good availability, fillers also increase the printability and optical properties of paper. However, a problem related to the increasing of the filler proportion is that the filler addition leads to a deterioration in the mechanical properties of the paper product. These mechanical properties of paper depend 15 on inter-fibre bonding, and fillers inhibit partly this inter-fibre bonds formation due to their rigidity and poor capability of hydrogen bond formation. Increasing the binding between fibres and fillers is thus essential to improve the strength of filled paper. Furthermore, better affinity between the fibres and the fillers will also lead to a better retention of fillers.

20 [0003] The interactions between fibres and fillers have been widely studied, and many different solutions for improving the inter-fibre bonding have been presented. The loss of the paper strength has been reduced, among other things, by using thinner filler particles. Another solution to this problem is to add starch into the fibre suspension, because the adsorption of starch on fibres increases paper strength by increasing the strength of inter-fibre bonds. Although starch is very cost-effective, it cannot be used in high concentrations because of the problems of significant sticky behaviour of starch on forming wire. Furthermore, the addition of fines in paper is another effective way to compensate for the strength loss which is caused by the presence of the fillers. However, added fines may induce dewatering problems.

25 [0004] A publication EP 1936 032 A1 discloses a method of producing a laminate paper comprising at least two layers, said method comprising (i) providing an aqueous suspension comprising cellulosic fibers (ii) adding to the suspension microfibrillar polysaccharide in an amount to yield from about 0.05 to about 50 wt percent based on the weight of the cellulosic fibers (iii) dewatering the obtained suspension and forming a first layer having a density from about 150 to about 500 kg/m³ of said laminate paper product

30 [0005] A publication WO 00/47628 A2 discloses a method for producing derivatized microfibrillar polysaccharide, where the electrostatic forces are provided by anionic charge or by a combination of both anionic and cationic charge, by stabilizing and/or microfibrillating a polysaccharide starting material.

35 [0006] As described above, many different solutions have been presented to improve interactions between fibres and fillers in order to enhance the strength of the filled paper. However, there is still a need for a method that makes it possible to use a high content of the filler so that the strength of the final paper product will not decrease and so that the method will not cause any other unwanted effects on the manufacturing process.

Summary of the Invention

40 [0007] It is an aim of the present invention to provide a novel method for preparing aqueous furnish to be used in paper and paper board manufacturing in such a way that the paper product manufactured from the furnish has a high loading of filler, with good mechanical strength. The aim of the invention is also to provide a novel method for preparing a furnish in order to improve the interactions between fibres and fillers.

45 [0008] To achieve these aims, the method according to the invention for preparing aqueous furnish is characterized in what will be presented in the characterizing portion of claim 1.

[0009] The invention also relates to furnish prepared by the method according to the invention, and to paper or paper board manufactured from the furnish prepared by the method according to the invention.

50 [0010] The invention is based on the modification of the fibre and/or filler surfaces in such a way that the fibre-filler bonding will be enhanced, because the poor capability of fillers to form bonds with fibres is greatly responsible for the low retention of fillers and for the loss of mechanical properties of filled paper. In the method according to the invention, at least the filler surface is modified by adsorption of cationic polyelectrolyte and nanofibrillated cellulose (NFC) during the furnish preparation. This modification creates a bilayer of cationic polyelectrolyte and NFC around the fillers, which improves the affinity between fillers and fibres. Also, the fibre surfaces can be treated equally by forming the bilayer of cationic polyelectrolyte and NFC around the fibres.

55 [0011] Filler and/or fibres are treated with cationic polyelectrolyte and nanofibrillated cellulose during the furnish preparation. The modification can be carried out in different ways. The treatment of the filler with cationic polyelectrolyte and NFC can be carried out by mixing the filler with the cationic polyelectrolyte and NFC before adding them to the fibre suspension. Alternatively, the modification of the fibre and filler surfaces can be carried out at the same time in the fibre

suspension without separate mixing steps, or the fibre surfaces can be treated with cationic polyelectrolyte and NFC before the addition of the filler to the fibre suspension. It is also possible to treat filler and fibres separately one with cationic polyelectrolyte and other with nanofibrillated cellulose. The way of the modification can be chosen according to the convenience, for example based on the existing paper mill layout.

5 [0012] One alternative way is to modify the filler surfaces by forming cationic polyelectrolyte and NFC bilayer as described above and in parallel, to modify the fibre surfaces by adsorption of cationic polyelectrolyte, because the adsorption of cationic polyelectrolyte on fibres increases the strength of inter-fibre bonds and increases the affinity of the modified filler to the cellulose fibres. Therefore, the modification of filler surface by cationic polyelectrolyte and NFC combined with the modification of fibres by cationic polyelectrolyte enhances significantly the filler-fibre bonding and thus the filler retention and the mechanical properties of the final paper product, particularly in Z-direction.

10 [0013] Any of the conventional cationic polyelectrolytes used in paper manufacturing are suitable for the method according to the invention. Preferably, cationic polyelectrolyte is cationic starch.

15 [0014] In the furnish preparation, at least a part of the filler conventionally used is replaced with the filler containing cationic starch and nanofibrillated cellulose absorbed to the surface of the filler. In addition to the modified filler, the furnish can also contain other fillers, sizing materials and additives as known by a skilled person in the art.

20 [0015] The modification of filler and/or fibre surfaces with cationic polyelectrolyte and nanofibrillated cellulose leads to increased fibre-filler bonding. This increase enhances significantly the retention of fillers and the strengthening effect of the cationic polyelectrolyte. Furthermore, when the strength of paper is increased, the nanofibrillated cellulose is beneficial in maintaining the bulk of the paper. Finally, it can also be mentioned that the strength and retention values of the paper that are achieved with the combination of cationic starch and NFC are similar to those obtained with a quantity of cationic starch not conceivable, because of stickiness problems induced by an addition of such a high amount of starch.

Description of the Drawings

25 [0016] The present invention will now be described in more detail with reference to the appended drawings, in which:

- | | |
|-------------------|--|
| Fig. 1 | shows a strategy of mixing different components which are used in the Example 1, |
| Fig. 2 | shows the amount of PCC retained in handsheets as a function of the added amount of PCC (Example 1), |
| 30 Fig. 3 | shows the tensile strength and Scott bond of handsheets as a function of filler content (Example 1), |
| Fig. 4 | shows the tensile strength of handsheets as a function of the density of handsheets (Example 1), |
| Fig. 5 | shows the tensile strength of handsheets as a function of filler content (Example 1), |
| Fig. 6 | shows the tensile strength of handsheets as a function of filler content (Example 1), |
| 35 Figs. 7a to 7g | show strategies of mixing different components which are used in Example 2, |
| Figs. 8a and 8b | show the tensile strength of the handsheets as a function of filler content (example 2), and |
| Fig. 9 | shows the tensile strength and Scott bond of the handsheets as a function of filler content (Example 2). |

Detailed Description of the Invention

40 [0017] In the method according to the invention, the filler and/or fibre surfaces are modified by adsorption of cationic polyelectrolyte and nanofibrillated cellulose (NFC) during the furnish preparation in order to improve the interaction between fibres and fillers. It has been observed that cationic polyelectrolyte and nanofibrillated cellulose can be absorbed on the surface of fillers and fibres used for paper and paper board manufacture during simple processing suitable for a paper mill process.

45 [0018] The modification of filler and/or fibre surfaces can be carried out by mixing them with cationic polyelectrolyte and nanofibrillated cellulose. Preferably, the filler and fibres are treated first with cationic polyelectrolyte and secondly with nanofibrillated cellulose by adding them to the fibre-filler suspension. Alternatively, the filler is treated with cationic polyelectrolyte and nanofibrillated cellulose before adding it to fibre suspension. Also in this case, the filler is preferably treated first with cationic polyelectrolyte and secondly with nanofibrillated cellulose by adding them to the filler suspension. The fibres can be treated with cationic polyelectrolyte before adding the modified fillers to the fibre suspension in order to increase the strength of inter-fibre bonds.

50 [0019] The term nanofibrillated cellulose refers to a collection of isolated cellulose microfibrils or microfibril bundles derived from cellulose raw material. Nanofibrillated cellulose have typically high aspect ratio: the length might exceed one micrometer while the number-average diameter is typically below 200 nm. The diameter of nanofibril bundles can also be larger but generally less than 5 µm. The smallest nanofibrils are similar to so called elementary fibrils, which are typically 2-12 nm in diameter. The dimensions of the fibrils or fibril bundles are dependent on raw material and disintegration method. The nanofibrillated cellulose may also contain some hemicelluloses; the amount is dependent

on the plant source. Mechanical disintegration of nanofibrillated cellulose from cellulose raw material, cellulose pulp, or refined pulp is carried out with suitable equipment such as a refiner, grinder, homogenizer, colloider, friction grinder, ultrasound sonicator, fluidizer such as microfluidizer, macrofluidizer, or fluidizer type homogenizer. Nanofibrillated cellulose can also be directly isolated from certain fermentation processes. The cellulose-producing micro-organism of the present invention may be of the genus *Acetobacter*, *Agrobacterium*, *Rhizobium*, *Pseudomonas* or *Alcaligenes*, preferably of the genus *Acetobacter* and more preferably of the species *Acetobacter xylinum* or *Acetobacter pasteurianus*. Nanofibrillated cellulose can also be any chemically, enzymatically or physically modified derivate of cellulose microfibrils or microfibril bundles. The chemical modification could be based for example on carboxymethylation, oxidation, esterification, or etherification reaction of cellulose molecules. Modification could also be realized by physical adsorption of anionic, cationic, or non-ionic substances or any combination of these on cellulose surface. The described modification can be carried out before, after, or during the production of microfibrillar cellulose.

[0020] Nanofibrillated cellulose can also be called nanocellulose, nanofibrillar cellulose, cellulose nanofiber, nano-scale fibrillated cellulose, microfibrillar cellulose, cellulose nanofibrils (CNF) or microfibrillated cellulose (MFC). In addition, nanofibrillated cellulose produced by certain microbes has also various synonyms, for example, bacterial cellulose, microbial cellulose (MC), biocellulose, nata de coco (NDC), or coco de nata. Nanofibrillated cellulose described in this invention is not the same material as so called cellulose whiskers, which are also known as: cellulose nanowhiskers, cellulose nanocrystals, cellulose nanorods, rod-like cellulose microcrystals or cellulose nanowires. In some cases, similar terminology is used for both materials, for example by Kuthcarlapati et al. (*Metals Materials and Processes* 20(3):307-314, 2008) where the studied material was called "cellulose nanofiber" although they clearly referred to cellulose nanowhiskers.

Typically these materials do not have amorphous segments along the fibrillar structure as nanofibrillated cellulose, which leads to more rigid structure.

[0021] The filler can be any filler used in paper manufacturing, e.g. precipitated calcium carbonate (PCC), ground calcium carbonate (GCC), kaolin, talcum or gypsum. Preferably, the filler is precipitated calcium carbonate (PCC).

[0022] In the method according to the invention, the filler is added to the furnish in an amount of 1 to 60% by the dry weight of the fibres in the furnish, preferably 20 to 40% by the dry weight of the fibres. The nanofibrillated cellulose is added in an amount of 0.01 to 20% by the dry weight of the fibres in the furnish, preferably 1 to 10%, and most preferably 1 to 3%.

[0023] Cationic polyelectrolyte can be any retention or strength polymer used in paper manufacturing, e.g. cationic starch, cationic polyacrylamide (CPAM) or polydimethylallyl ammonium chloride (PDADMAC). Also, the combinations of the different polyelectrolytes can be used. Preferably, the cationic polyelectrolyte is cationic starch (CS).

[0024] The cationic polyelectrolyte is added in an amount of 0.01 to 5% of dry weight of fibres in the furnish, preferably approximately 2 to 4%.

[0025] The furnish prepared by the method according to the invention can be used as such in paper or paper board making. However, the furnish can also contain non-treated fillers and other components, including e.g. conventional auxiliary agents and retention agents. The filler modified with cationic polyelectrolyte and nanofibrillated cellulose can be used in combination with conventional untreated fillers in filled paper grades.

[0026] The furnish prepared by the method according to the invention is used for manufacturing of a paper or paper board product. In the paper or paper board machine, the furnish is fed into a forming section and water is removed from the furnish by allowing the furnish to drain through a water permeable forming wire, and after that, the paper web thus produced is dried and finished to produce a final paper or paper board product with good mechanical strength properties and a high filler content.

[0027] The following examples were carried out to illustrate the present invention. The examples are not intended to limit the scope of the invention.

45 Example 1

[0028] This example was carried out to demonstrate that the method according to the invention clearly increases the filler retention and strength of paper sheets with a high filler content.

[0029] The materials used in this experiment were the following:

50 **Fibres**

[0030] Dried hardwood (birch) bleached chemical pulp was used in the experiments. About 360 g (o.d.) of pulp was soaked overnight in 5 l of water and beaten for 50 minutes at a consistency of 1.6% in a Valley beater (ISO 5264-1) to the Shopper-Riegler (SR) number (ISO 5267-1) of about 42. Afterwards 2 l of water was used to remove the last fibres remaining in the beater and added to the fibre suspension. This suspension was fractionated in a Bauer McNett classifier (SCAN-CM 6:05) using a 200 mesh wire to remove the fines fraction. At this point the SR number was about 18. Finally, the pulp was washed, first by acidic treatment (0.01 M hydrochloric acid) to remove metal ions and afterwards the fibres

were converted to sodium form with 1 mM of sodium bicarbonate. After these two treatments, the pulp was washed thoroughly with deionised water.

[0031] The fractioning and washing were done in order to prevent possible interference of varying fines content, pH or salts that would hamper interpretation of the results.

5

Fillers

[0032] The filler was commercial scalenohedral precipitated calcium carbonate (PCC). According to the manufacturer, the average particle size of this PCC was 2.3 µm, the brightness 95% and the dry matter content was 19.9%.

10

Nanofibrillated cellulose (NFC)

[0033] Nanofibrillated cellulose was obtained by high pressure homogenisation of fully bleached softwood including an enzymatic pre-treatment step. The principles of this approach have been published in Pääkkö, et al., Enzymatic hydrolysis combined with mechanical shearing and high pressure homogenization for nanoscale cellulose fibrils and strong gels, Biomacromolecules (8), pp. 1934-1941, 2007. Just before use, NFC-gel (about 1-2 % solid content) was diluted with deionised water and disintegrated with Branson Digital Sonifier (Branson Ultrasonics Corporation, Danbury, USA) with an amplitude setting of 25 % for 2 minutes.

20

Cationic starch

[0034] Cationic starch (CS) with a degree of substitution of 0.035 was supplied by Ciba Specialty Chemical, Raisio, Finland. Before use, 2 g (o.d.)/l starch solution was cooked in an autoclave at 120 °C for 20 minutes.

25

Water

[0035] The water used in all the experiments was deionised water.

[0036] During the preparation of pulp slurry, 1.63 g (o.d.)/l of fibres were mixed together with starch in a vessel for 15 minutes. In parallel, nanofibrillated cellulose (NFC) was mixed together with PCC for 15 minutes. Afterwards, both contents were poured into the same vessel and mixed for 15 minutes. This mixing strategy is illustrated in Figure 1.

[0037] To the preparation of the different test points (presented in Table 1), four different compositions of pulp slurry were used:

- one reference with fibre dispersion only (reference sample),
- one with fibres and cationic starch (samples CS2.5, CS5 and CS10),
- one with fibres and NFC (samples NFC25 and NFC 50), and
- one with fibres, cationic starch and NFC (samples CS2.5+NFC25 and CS2.5+NFC50).

[0038] According to the test points, three different amounts of cationic starch: 25, 50 and 100 mg/g (o.d.) of fibres and two different amounts of NFC: 25 and 50 mg/l (o.d.) were added to the suspensions. In Table 1, sample compositions CS2.5, CS5, CS10 with fibres and cationic starch comprise different amounts of cationic starch as mentioned above. Also, sample compositions NFC25 and NFC 50 with fibres and NFC comprise above mentioned amounts of NFC. Sample CS2.5+NFC25 comprises fibres, 25 mg/g CS and 25 mg/l NFC, and sample CS2.5+NFC50 comprises fibres, 25 mg/g CS and 50 mg/l NFC.

45

[0039] To these four different mixtures various amount of PCC were also added. The amount of the fibres added was 1.63 g in each case.

Table 1. Summary of the experiments carried out.

50

| sample | PCC added (g/g of paper) | NFC added (mg/sheet or mg/l) | NFC (mg/g paper) | CS added (% dry fibres) | CS (mg/g paper) | Ash content(% sheet) |
|-----------|-----------------------------|------------------------------------|---------------------|----------------------------|--------------------|-------------------------|
| reference | 0 | 0 | 0 | 0 | 0 | 0 |
| | 2.00 | 0 | 0 | 0 | 0 | 25.9 |
| | 3.49 | 0 | 0 | 0 | 0 | 31.7 |
| | 5.97 | 0 | 0 | 0 | 0 | 35.9 |
| CS2.5 | 0 | 0 | 0 | 2.5 | 24 | 0 |

(continued)

| | sample | PCC added (g/g of paper) | NFC added (mg/sheet or mg/l) | NFC (mg/g paper) | CS added (% dry fibres) | CS (mg/g paper) | Ash content(% sheet) |
|----|-----------------|-----------------------------|------------------------------------|---------------------|----------------------------|--------------------|-------------------------|
| 5 | | 0.70 | 0 | 0 | 2.5 | 19 | 23.2 |
| | | 1.71 | 0 | 0 | 2.5 | 15 | 39.2 |
| | | 3.68 | 0 | 0 | 2.5 | 12 | 50.5 |
| 10 | CS5 | 0,00 | 0 | 0 | 5 | 48 | 0 |
| | | 0.58 | 0 | 0 | 5 | 32 | 32.0 |
| | | 1.39 | 0 | 0 | 5 | 23 | 52.7 |
| 15 | CS10 | 0,00 | 0 | 0 | 10 | 91 | 0 |
| | | 0.49 | 0 | 0 | 10 | 55 | 39.5 |
| | | 1.25 | 0 | 0 | 10 | 40 | 55.7 |
| 20 | NFC25 | 0 | 25 | 15 | 0 | 0 | 0 |
| | | 0.89 | 25 | 11 | 0 | 0 | 27.1 |
| | | 1.62 | 25 | 1 | 0 | 0 | 33.6 |
| | | 2.67 | 25 | 9 | 0 | 0 | 38.5 |
| 25 | NFC50 | 0 | 50 | 30 | 0 | 0 | 0 |
| | | 0.68 | 50 | 22 | 0 | 0 | 25.6 |
| | | 1.48 | 50 | 17 | 0 | 0 | 41.7 |
| | | 4.27 | 50 | 17 | 0 | 0 | 42.3 |
| 30 | CS2.5+ NFC25 | 0 | 25 | 15 | 2.5 | 24 | 0 |
| | | 0.28 | 25 | 12 | 2.5 | 20 | 17.4 |
| | | 0.87 | 25 | 8 | 2.5 | 13 | 45.5 |
| | | 1.78 | 25 | 7 | 2.5 | 11 | 53.4 |
| 35 | CS2.5+ NFC50 | 0 | 50 | 29 | 2.5 | 24 | 0 |
| | | 0.26 | 50 | 23 | 2.5 | 19 | 20.5 |
| | | 0.64 | 50 | 16 | 2.5 | 13 | 44.2 |
| | | 1.00 | 50 | 14 | 2.5 | 11 | 51.7 |

[0040] After furnish preparation, handsheets were formed. Sheets were formed in a laboratory sheet former, Lorentzen & Wettre AB, Sweden (ISO 5269-1) with a 100 mesh wire. The grammage of sheets was adjusted to about 60 g/m² by dilution of the suspension when necessary. The sheets were wet pressed under 4.2 bar for 4 minutes and dried in a frame to avoid shrinkage during drying (105 °C for 3 minutes). The samples were conditioned according to the standard SCAN_P 2:75.

[0041] All the sheet properties were measured according to SCAN or ISO standards. The grammage (ISO 536:1995 (E)), the thickness and the bulk were determined with Lorentzen & Wettre micrometer (ISO 534:2005(E)). The tensile strength, the stretch and the stiffness were determined with Alwetron TH1 (ISO 1924-2:1994(E)). The tear index was measured with Lorentzen & Wettre tearing tester (SE009 Elmendorf)(SCAN-P 11:73), and optical properties were determined by Lorentzen & WettreElrepopho. The ash content was measured according to the standard ISO 1762:2001 (E) to determine the amount of retained fillers in paper sheets.

[0042] The main objective of the above described experiments was to evaluate the effect of the modification of filler surface by NFC and CS on the fibre-filler bonding. Several strength properties as well as filler retention were measured for handsheets obtained after various treatments.

[0043] Figure 2 shows the PCC retained in handsheets as a function of the added amount of PCC. The curves illustrate results obtained from a sheet containing no additives (reference: +) and from sheets prepared either with cationic starch alone (CS2.5: Δ) or with a mixture of cationic starch and NFC (CS2.5+NFC25: ●). The PCC retained is obtained from the value of ash content at 525 °C. As shown in Figure 2, the combination of cationic starch and NFC (sample CS2.5+NFC25) allows a very great improvement of PCC retention. If we look at 0.36 g/g of paper of PCC retained (equivalent to 35% of filler content), the amount of PCC added is about 10 times less than with combination of cationic starch and NFC than with reference. The retention is also significantly higher (more than twice) than that obtained by addition of starch alone.

[0044] Figure 3 shows the tensile strength and Scott bond of handsheets as a function of filler content. The curves illustrate results obtained from sheet containing no additives (reference: +) and from sheets prepared either with cationic starch alone (CS2.5: Δ) or with a mixture of cationic starch and NFC (CS2.5+NFC25: ●). The combination of cationic starch and NFC (sample CS2.5+NFC25) leads to an increase in strength properties, particularly in Z-direction, as shown by Scott bond results.

[0045] The strength of paper is usually proportional to the sheet density. The enhancement of the strength properties also increases the density of the sheet. It would be optimal if stronger paper could be obtained without a significant increase in density. Figure 4 shows the tensile strength of handsheets as a function the density. In Figure 4, the curves also illustrate results obtained from sheet containing no additives (reference: +) and from sheets prepared either with cationic starch alone (CS2.5: Δ) or with a mixture of cationic starch and NFC (CS2.5 + NFC25: ●). From Figure 4, it can be observed that the combination of cationic starch and NFC (sample CS2.5 + NFC25) has the steepest slope. NFC is thus beneficial in maintaining the bulk.

[0046] In order to determine the influence of the NFC amount on the strength properties, the added amount of NFC was varied (see Figure 5). NFC was either mixed in the pulp together with cationic starch or added alone as such. In Figure 5, the curves illustrate results obtained from sheet containing no additives (reference: +) and from sheets prepared either with two different amounts of NFC (NFC25: Δ and dotted line, NFC50: A) or with a mixture of cationic starch and different amounts of NFC (CS2.5 +NFC25: o and dotted line, CS2.5 +NFC50: ●). When NFC is used alone, a slight improvement of tensile strength can be seen. However, the value is much lower than that obtained with the combination of cationic starch and NFC.

[0047] On the other hand, in order to compare the effect of cationic starch either alone or combined with NFC, on paper strength, three different amounts of starch were used. These results are illustrated in Figure 6. In Figure 6, the curves illustrate results obtained from sheet containing no additives (reference: +) and from sheets prepared either with three different amounts of cationic starch (CS2.5: Δ and dotted line, CS5: □ and dashed line, and CS10:○) or with a mixture of cationic starch and NFC (CS2.5 +NFC25: ●). Very high amounts of cationic starch are needed in order to obtain a similar sheet strength to using the combination of cationic starch and NFC proposed here. Thus, the combination of the cationic starch and nanofibrillated cellulose is a preferable combination for improving the tensile strength and Z-directional strength of the paper product.

Example 2

[0048] The aim of this example was to test different strategies of mixing filler and fibres with cationic starch and nanofibrillated cellulose in order to determine their influence on paper strength. Another aim was to illustrate the effect of combining NFC and cationic starch for improving the strength of filled paper in situations where fines are present.

[0049] The materials used in the experiments are the following:

Fibres

[0050] Dried hardwood (birch) bleached chemical pulp was also used in this example. About 360 g pulp was soaked overnight in 5 l of water and beaten for 50 minutes at a consistency of 1.6% in a Valley beater (ISO 5264-1) to the Shopper-Riegler (SR) number (ISO 5267-1) of about 42. Afterwards, 2 l of water was used to rinse the beater and added to the fibre suspension. Finally, the pulp was washed, first by acidic treatment (0.01 M hydrochloric acid) to remove metal ions, and afterwards, the fibres were converted to sodium form with 1 mM of sodium bicarbonate. After these two treatments, the pulp was thoroughly washed with deionized water.

[0051] The difference to the fibres used in Example 1 is that fines were not removed in this Example.

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Nanofibrillated cellulose (NFC)

[0052] Never dried hard wood was disintegrated using a Masuko supermass colloid with 200 µm gap between the stones at 3% consistency. The NFC used for paper sheets was obtained after five passes through the colloid.

[0053] The nanofibril gel was delivered at a dry content of 2%. Just before use, NFC was diluted with deionized water and dispersed with Branson Digital Sonifier (Branson Ultrasonics Corporation, Danbury, USA) with an amplitude setting of 25% for 2 minutes.

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Cationic starch

[0054] Cationic starch (CS) with a degree of substitution of 0.035 (Raisamyl 50021) was supplied by Ciba Specialty Chemical, Raisio, Finland. Before use, 2 g (o.d.)/l starch solution was cooked in an autoclave at 120°C for 20 minutes.

Fillers

[0055] Commercial scalenothedral precipitated calcium carbonate (PCC). According to the manufacturer, the average particle size of this PCC was 2.3 µm, the brightness 95% and the dry matter content 19.9%.

[0056] In this example, seven different mixing strategies were chosen in order to prepare the pulp slurry (Figs. 7a to 7g):

- Strategy 1 (Fig. 7a): Fibres were put in suspension in a vessel with deionized water. In parallel, cationic starch was diluted with deionized water in a vessel and mixed together with PCC for 15 minutes. Afterwards, these premixed suspensions were poured into a vessel and mixed for 15 minutes.
- Strategy 2 (Fig. 7b): Fibres were put in suspension in a vessel with deionized water. In parallel, cationic starch was diluted with deionized water in a vessel and mixed together with PCC for 15 minutes. Afterwards, NFC was added to this suspension and all was mixed again for 15 minutes. Finally, both contents were poured into a vessel and mixed for 15 minutes.
- Strategy 3 (Fig. 7c): Fibres were put in suspension in a vessel with deionized water. In parallel, cationic starch (CS) was diluted with deionized water in a vessel and mixed together with NFC and PCC for 15 minutes (added simultaneously into the vessel). Afterwards, both contents were poured into a vessel and mixed for 15 minutes.
- Strategy 4 (Fig. 7d): Fibres were put in suspension in a vessel with deionized water. Afterwards, PCC, cationic starch and NFC were added successively to the fibre suspension and mixed for 15 minutes.
- Strategy 5 (Fig. 7e): this strategy is similar to strategy 3, but this time the total amount of starch is divided equally between the fibre suspension vessel and the NFC and PCC one.
- Strategy 6 (Fig. 7f): Fibres were put in suspension with deionized water in a vessel and mixed together with starch for 15 minutes. In parallel, NFC was put in suspension with deionized water in a vessel and mixed together with PCC for 15 minutes. Afterwards, both contents were poured into a vessel and mixed for 15 minutes.
- Strategy 7 (Fig. 7g): Fibres were put in suspension with deionized water in a vessel and mixed together with PCC for 15 minutes. This is used as Reference sample.

[0057] To perform furnish of these seven strategies, 1.63 g/l of fibres were used. 20 or 40 mg of cationic starch per g of fibres and two different amounts of NFC: 15 and 30 mg/g of fibres were used. In all steps, the pH of the slurry was adjusted to about 9 with a sodium bicarbonate buffer solution, and the ionic strength was measured. To be able to compare results from paper testing, the furnish was further diluted with water to obtain a paper sheet grammage between 55 and 65 g/m².

[0058] After the furnish preparation, handsheets were formed from different furnishes as in the Example 1. The sheet properties were measured using the same methods as presented in Example 1.

[0059] The purpose of the two first strategies, was to determine the optimal amounts of cationic starch and NFC. Figures 8a and 8b show tensile strength of the handsheets as a function of filler content. The curves of Figure 8a illustrate results obtained from sheets prepared with two different content of cationic starch: 2% (dashed line) and 4% (continuous line). The curves of Figure 8b illustrate results obtained from sheets prepared with two different contents of cationic starch and NFC: 2% CS and 15% NFC (◊ and dotted line), 4% CS and 15% NFC (◊ and continuous line), 2% CS and 30% NFC (□ and dashed line), 4% CS and 30% NFC (□ and continuous line). The lines in these figures are only drawn to guide the eye and do not illustrate the actual trend. The increase of cationic starch content does not give significant improvement of the tensile strength. Furthermore, too high starch content may cause problems in the papermaking process, such as stickiness, the lower starch content is thus chosen for the other experiments. The same conclusion can be made for the NFC content, indeed, a higher amount of NFC does not further increase the tensile strength and the content chosen for further experiments was hence the lowest one.

[0060] The tensile strength and Scott bond obtained with the different mixing strategies are summarized in Figure 9. Figure 9 shows tensile strength and Scott bond of the handsheets as function of filler content. The curves illustrate results obtained from sheets prepared with starch alone i.e. strategy 1 (▲ and continuous line), the strategy 2 (□ and dashed line), the strategy 3 (△ and dotted line), the strategy 4 (■ and continuous line), the strategy 5 (+ and dotted line), the strategy 6 (○ and dashed line) and the reference i.e. strategy 7 (● and continuous line). The changes in tensile strength between the two filler contents are obviously not following a straight line but these lines have been drawn in order to see the trend of change more easily.

[0061] The strength properties obtained with the strategy 4 presented in Fig. 7d (mixing fibres and fillers and then adding first CS and then NFC) stands out from the other strategies by its improvement, indeed, if we compare with cationic starch alone for 30% filler content, the tensile strength is increased by 17% and the Scott bond by 26%.

[0062] Another efficient way is to treat the fillers with first CS and then NFC (forming a bilayer on the filler surface) and then to add these modified filler particles to the fibre suspension (strategy 2 presented in Fig. 7b). In this case the fibres may be unmodified or modified with CS.

[0063] Also other strategies increase the strength of the paper sheets but the most efficient way is to form a bilayer

of CS and NFC on at least the filler surface but preferably also the fibre surface.

Claims

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1. A method for preparing aqueous furnish to be used in paper or paper board manufacturing, in which method the furnish is prepared by adding at least filler to a fibre suspension, wherein the filler and/or the fibres are treated with cationic polyelectrolyte and nanofibrillated cellulose, **characterized in that** the filler and the fibres are treated first with cationic polyelectrolyte and secondly with nanofibrillated cellulose by adding them to the fibre-filler suspension.

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2. The method according to claim 1, **characterized in that** the filler content is 1 to 60% of the dry weight of the fibres in the furnish, preferably 20 to 40%.
3. The method according to any of the preceding claims, **characterized in that** the filler is precipitated calcium carbonate (PCC).
4. The method according to any of the preceding claims, **characterised in that** the nanofibrillated cellulose is added in an amount of 0.01 to 20% of the dry weight of the fibres in the furnish, preferably 1 to 10% and most preferably 1 to 3%.

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5. The method according to any of the preceding claims, **characterized in that** the cationic polyelectrolyte is added in an amount of 0.01 to 5% of the dry weight of fibres in the furnish, preferably approximately 2 to 4%.
6. The method according to any of the preceding claims, **characterized in that** the cationic polyelectrolyte is cationic starch.
7. Furnish, which is prepared by the method according to any of the preceding claims.
8. Paper or paper board manufactured from the furnish prepared by the method according to any of claims 1 to 6.

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Patentansprüche

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1. Verfahren zur Herstellung eines bei der Papier- oder Pappeherstellung zu verwendenden wässrigen Stoffeintrags, in welchem Verfahren der Stoffeintrag durch Zusetzen zumindest eines Füllstoffs zu einer Fasersuspension hergestellt wird, wobei der Füllstoff und/oder die Fasern mit kationischem Polyelektrolyt und nanofibrillierter Cellulose behandelt werden, **dadurch gekennzeichnet, dass** der Füllstoff und die Fasern zuerst mit kationischem Polyelektrolyt und zweitens mit nanofibrillierter Cellulose durch deren Zusetzen zu der Faser-Füllstoff-Suspension behandelt werden.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** der Füllstoffgehalt 1 bis 60 % des Trockengewichts der Fasern in dem Stoffeintrag, vorzugsweise 20 bis 40 %, beträgt.
3. Verfahren nach irgendeinem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** der Füllstoff ausgefällt Calciumcarbonat (PCC, precipitated calcium carbonate) ist.
4. Verfahren nach irgendeinem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** die nanofibrillierte Cellulose in einer Menge von 0,01 bis 20 % des Trockengewichts der Fasern in dem Stoffeintrag, vorzugsweise 1 bis 10 % und am meisten bevorzugt 1 bis 3 %, zugesetzt wird.
5. Verfahren nach irgendeinem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** der kationische Polyelektrolyt in einer Menge von 0,01 bis 5 % des Trockengewichts der Fasern in dem Stoffeintrag, vorzugsweise ungefähr 2 bis 4 %, zugesetzt wird.
6. Verfahren nach irgendeinem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** der kationische Polyelektrolyt kationische Stärke ist.
7. Stoffeintrag, welcher durch das Verfahren nach irgendeinem der vorangehenden Ansprüche hergestellt ist.

8. Papier oder Pappe, hergestellt aus dem durch das Verfahren nach irgendeinem der Ansprüche 1 bis 6 hergestellten Stoffeintrag.

5 **Revendications**

1. Procédé pour préparer une composition de fabrication aqueuse à utiliser dans la fabrication du papier ou du carton, procédé dans lequel on prépare la composition de fabrication en ajoutant au moins une matière de charge à une suspension fibreuse, la matière de charge et/ou les fibres étant traitée(s) avec un polyélectrolyte cationique et de la cellulose nanofibrillaire, **caractérisé en ce que** la matière de charge et les fibres sont traitées en premier lieu avec un polyélectrolyte cationique et en deuxième lieu avec de la cellulose nanofibrillaire en les ajoutant à la suspension de fibre-matière de charge.
2. Procédé selon la revendication 1, **caractérisé en ce que** la teneur en matière de charge représente de 1 à 60 % du poids à sec des fibres dans la composition de fabrication, de préférence de 20 à 40 %.
3. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la matière de charge représente du carbonate de calcium précipité (PCC, precipitated calcium carbonate).
4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la cellulose nanofibrillaire est ajoutée en une quantité de 0,01 à 20 % du poids à sec des fibres dans la composition de fabrication, de préférence de 1 à 10 % et de manière de loin préférée de 1 à 3 %.
5. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le polyélectrolyte cationique est ajouté en une quantité de 0,01 à 5 % du poids à sec des fibres dans la composition de fabrication, de préférence d'approximativement 2 à 4 %.
6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le polyélectrolyte cationique est de l'amidon cationique.
7. Composition de fabrication que l'on prépare via le procédé selon l'une quelconque des revendications précédentes.
8. Papier ou carton fabriqué à partir de la composition de fabrication préparée via le procédé selon l'une quelconque des revendications 1 à 6.

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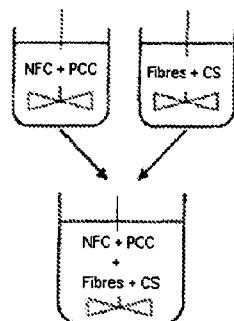


Fig. 1

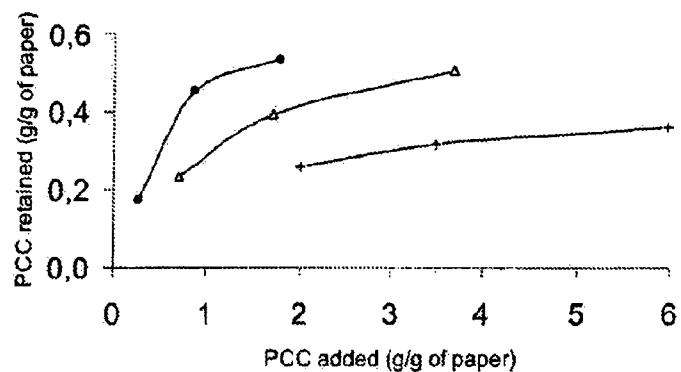


Fig. 2

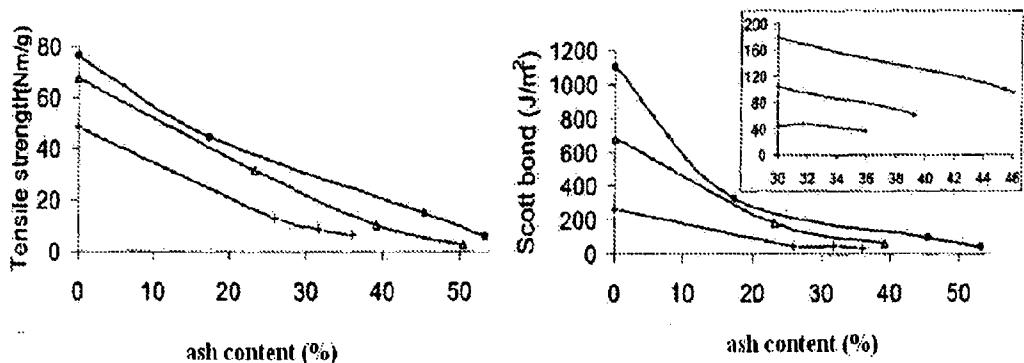


Fig. 3

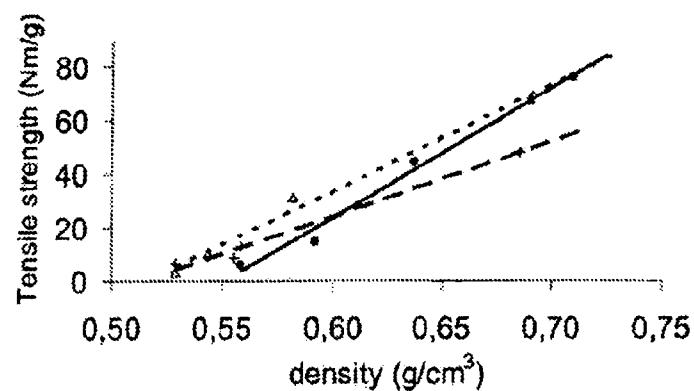


Fig. 4

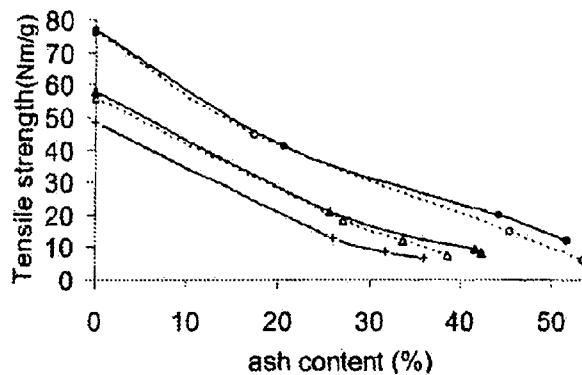


Fig. 5

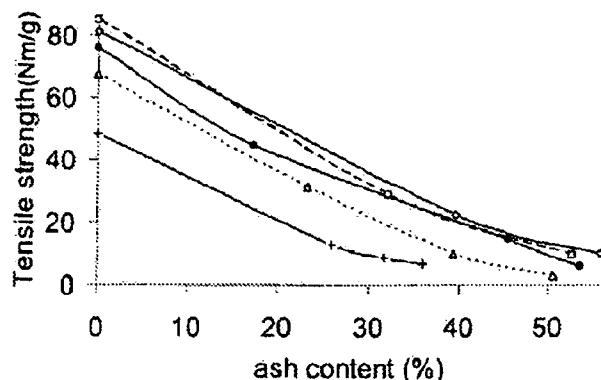
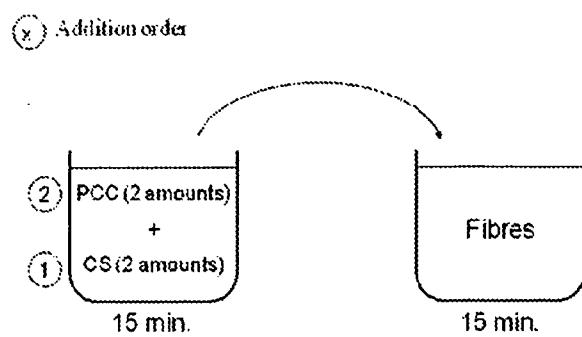
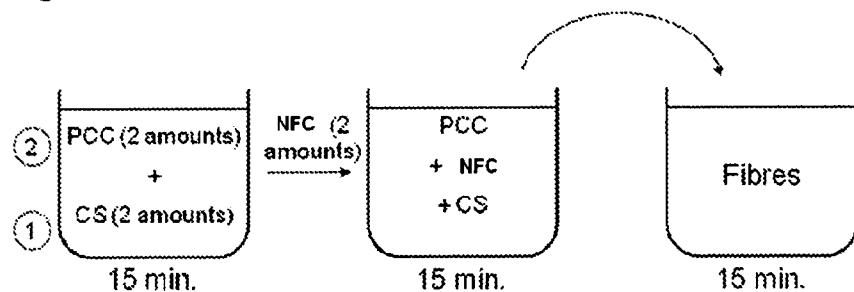
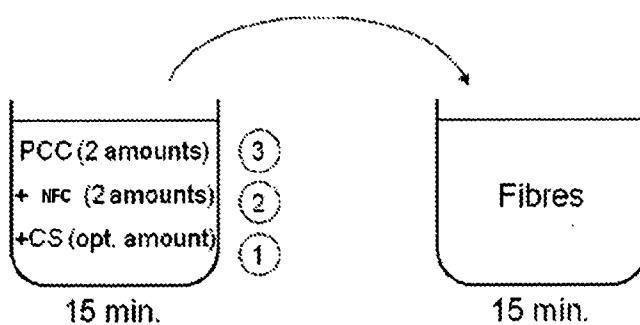
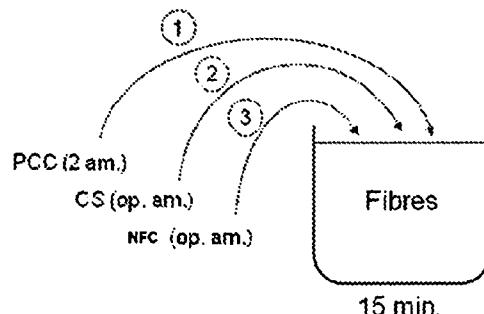


Fig. 6

**Fig. 7a****Fig. 7b****Fig. 7c****Fig. 7d**

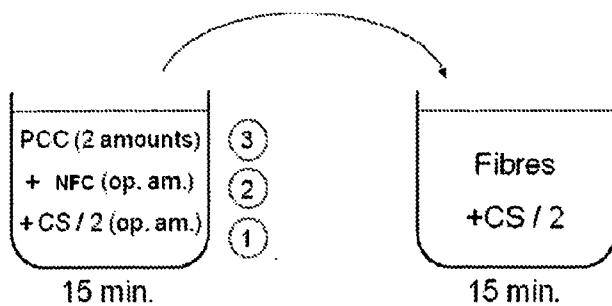


Fig. 7e

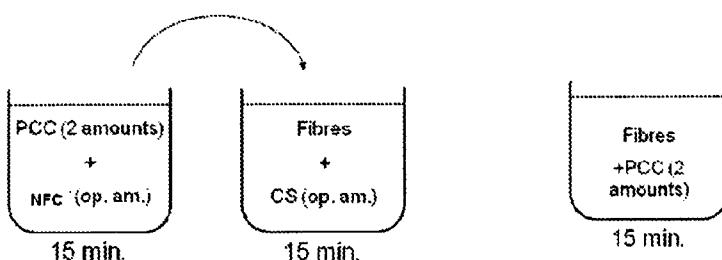


Fig. 7f

Fig. 7g

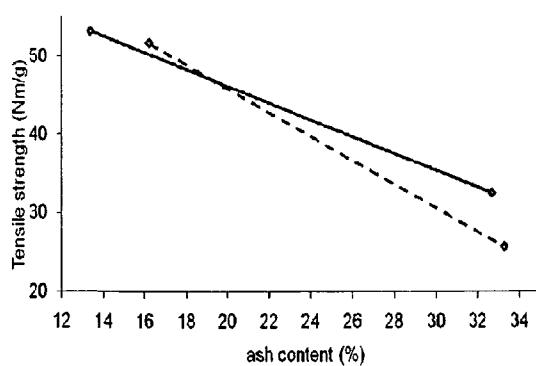


Fig. 8a

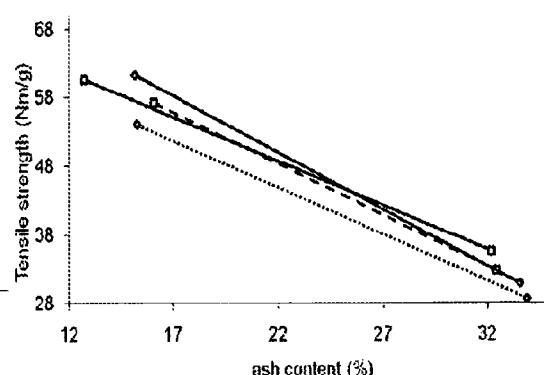


Fig. 8b

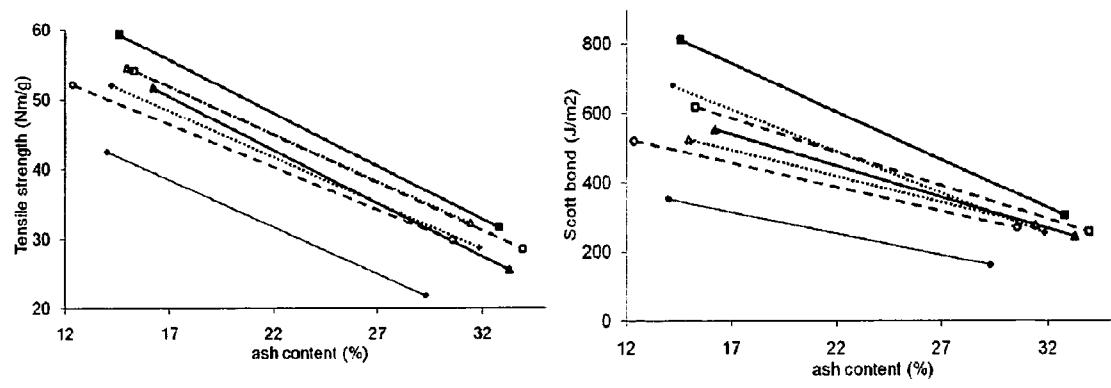


Fig. 9

REFERENCES CITED IN THE DESCRIPTION

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(54) Titre : MATIERE CELLULOSIQUE RESISTANTE AU FEU

(54) Title: FIRE-RESISTANT CELLULOSE MATERIAL

(57) Abrégé/Abstract:

A new approach for improving fire resistance of cellulosic materials is provided, especially when the cellulosic material is to be used in polymer composites. Cellulosic material is treated with an aqueous mixture of alkali metal or ammonium hydroxide and alkaline earth or aluminum metal salt simultaneously with or within a short period of time of preparing the mixture. The treated cellulosic material becomes self-extinguishing and may also have improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents and/or improved resistance to damage by ultra-violet light. The fire-resistant cellulosic material may also be treated with a layered nanoparticulate material either simultaneously with, subsequent to or prior to treatment with the aqueous mixture of alkali metal or ammonium hydroxide and alkaline earth or aluminum metal salt to impart further fire resistance to the cellulosic material. Polymer composites produced from cellulosic material treated according to the present invention have significantly improved fire resistance with small negative impact on the mechanical performance of the composite, and may have the added benefit of improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents and/or improved resistance to damage by ultra-violet light.

ABSTRACT

- A new approach for improving fire resistance of cellulosic materials is provided, especially when the cellulosic material is to be used in polymer composites. Cellulosic material is treated with an aqueous mixture of alkali metal or ammonium hydroxide and 5 alkaline earth or aluminum metal salt simultaneously with or within a short period of time of preparing the mixture. The treated cellulosic material becomes self-extinguishing and may also have improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents and/or improved resistance to damage by ultra-violet light.
- 10 The fire-resistant cellulosic material may also be treated with a layered nanoparticulate material either simultaneously with, subsequent to or prior to treatment with the aqueous mixture of alkali metal or ammonium hydroxide and alkaline earth or aluminum metal salt to impart further fire resistance to the cellulosic material. Polymer composites produced from cellulosic material treated according to the present invention have significantly 15 improved fire resistance with small negative impact on the mechanical performance of the composite, and may have the added benefit of improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents and/or improved resistance to damage by ultra-violet light.

FIRE-RESISTANT CELLULOSIC MATERIAL

Cross-reference to Related Applications

This application claims the benefit of United States Provisional patent application serial number 61/504,779 filed July 6, 2011, the entire contents of which is herein
5 incorporated by reference.

Field of the Invention

The present invention relates to a process for producing a fire-resistant cellulosic material, the fire-resistant cellulosic material produced by the process and the use of the fire-resistant cellulosic material in fire-resistant polymer composites.

10 Background of the Invention

Cellulosic materials (natural and synthetic) in different forms (fiber, film, powder, particle, pellet, chip, etc) at different sizes (nano, micro or macro) are often flammable and have low thermal resistance. They can be burned and also can spread the fire in the presence of oxygen. Thus, their use either in direct or non-direct form is limited in
15 applications requiring fire resistance. Due to their flammability, the use of cellulosic materials in polymer composites is also limited in certain applications.

Cellulosic materials are treated with different flame retardants depending on the application, for example in furniture, textiles or composites. The most commonly used flame retardants are based on halogen (e.g. WO 2004/1097088), phosphorous (e.g. US
20 3,899,483; US 6,524,653; US 4,228,202; US 5,238,464; US 2005/0215152; US 2004/0094279; WO 2002/1044470; US 6,352,786), boron (e.g. WO 2005/1042840; US 4,228,202; US 2009/0156073), ammonium (e.g. US 4,228,202; US 6,524,653; WO 2002/1044470), graphite (e.g. JP 09-031887; EP 0735187), alkaline-earth metallic compounds (e.g. US 5,434,200) or mixtures thereof. To improve fire resistance of
25 organic polymer composites, the incorporation of flame retardants based on halogen, phosphorous, metallic hydroxide (magnesium hydroxide, aluminum hydroxide, calcium hydroxide, layer double hydroxide), metallic oxide (antimony oxide, boron oxide), silicate (clay, talc), etc, in the polymer matrix has been widely used.

Among the compounds listed above, halogen based flame retardants are well
30 known to be the most efficient as they can be used at a low concentration in the final composition thus limiting their impact on other properties of the product. However, halogen compounds are considered to be harmful to the environment. Boron compounds

are supposed to be efficient, however they tend to be washed off due to their good solubility in water. Less harmful flame retardants based on phosphorous, graphite or alkaline-earth metallic compounds are much less efficient, thus a large amount of those additives must be used in the formulation. The use of flame retardant incorporated in a 5 polymer matrix alone does not satisfactorily resolve the flammability problem in cellulose-polymer composites, especially when the concentration of cellulose is quite significant in the formulation of the composite.

It is generally known that metal hydroxides, including barium hydroxide, can be used as a flame retardant for cellulosic materials (e.g. US 2009-298370; US 671,548; 10 Chen 1991; Mostashari 2008) and for polymer materials (e.g. US 7,354,958). Further, CA 2,079,302 discloses a flame retardant composition for cellulosic material comprising sodium hydroxide and a metal salt of boron among other ingredients. The metal salt of boron is defined as borax which is a sodium tetraborate. US 3,973,074 discloses a flame-proofing composition comprising potassium hydroxide and/or potassium carbonate and 15 possibly a small amount of sodium hydroxide and/or sodium carbonate and may include another potassium salt. US 5,480,587 discloses inorganic additives to impart flame resistance to polymers. The additives include hydroxides and metal salts that evolve gas. One such metal salt is barium chloride dihydrate. US 4,567,242 discloses the use of a mixture of a polycondensate of a halogenated phenol and an alkaline earth metal halide 20 in a flame retarding composition.

US 2003-0220515 discloses flame retardant compositions in which ancillary flame retardant additives may be used alone or in combination, such as metal hydroxides and metal salts, including alkaline earth metal salts. There is no disclosure of the use of an aqueous mixture of alkali metal hydroxides with alkaline earth metal salts.

25 US 4,064,317 discloses the use of "alkali compounds" for use in flame resistant plaster board. The "alkali compounds" are defined as at least one of an alkali metal hydroxide, alkali metal salt, alkaline earth metal hydroxide or alkaline earth metal salt. It is preferred to use a mixture of alkali metal salts and alkaline earth metal salts, for example a mixture of sodium and calcium formate. The combination of alkali metal 30 hydroxide and alkaline earth metal salt, especially barium salts, is not specifically disclosed.

The abstract of CN 1869154 discloses a flame retardant composition which initially involves the step of making magnesium hydroxide from the reaction of magnesium sulfate and sodium hydroxide. However, this document does not disclose

treating a cellulosic material with an aqueous reaction mixture of an alkali metal hydroxide and alkaline earth metal salt simultaneously with or shortly after mixing the alkali metal hydroxide with alkaline earth metal salt.

It is known that treatment of cellulosic materials with alkaline earth metal carbonates (e.g. barium carbonate) imparts fire resistance to the cellulosic material (e.g. Mostashari 2004-2005). Here, the alkaline earth metal carbonate is applied to the cellulosic material by first coating the cellulosic material with an alkaline earth metal chloride and then treating the so-coated material with sodium carbonate. It is also known to use both a clay and a metal hydroxide in a fire retarding composition comprising a polymer material (e.g. GB 2367064; JP 2002-180374).

There remains a need for an environmentally friendlier, effective approach to producing fire-resistant cellulosic materials.

Summary of the Invention

The present invention provides a new approach for improving fire resistance of cellulosic materials, especially when the cellulosic material is to be used in polymer composites. Cellulosic material is treated with an aqueous mixture of alkali metal or ammonium hydroxide and alkaline-earth or aluminum metal salt simultaneously with or within a short period of time of preparing the mixture. The treated cellulosic material becomes self-extinguishing and may also have improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to damage by ultra-violet light and/or reduced negative impact on fiber strength and/or modulus. The fire-resistant cellulosic material may also be treated with a layered nanoparticulate material either simultaneously with, subsequent to or prior to treatment with the aqueous mixture of alkali metal or ammonium hydroxide and alkaline-earth or aluminum metal salt to impart further fire resistance to the cellulosic material. Polymer composites produced from cellulosic material treated according to the present invention have significantly improved fire resistance with small negative impact on the mechanical performance of the composite, and may have the added benefit of one or more of improved thermal stability, improved interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents and improved resistance to damage by ultra-violet light.

Thus, in one aspect of the present invention there is provided a process of producing a fire-resistant cellulosic material comprising: treating a cellulosic material with

an aqueous reaction mixture of an alkali metal or ammonium hydroxide and an alkaline earth or aluminum metal salt, wherein the treating is done simultaneously with or within a short period of time of mixing the alkali metal or ammonium hydroxide and alkaline earth metal or aluminum salt; and, drying the treated cellulosic material.

- 5 In another aspect of the present invention there is provided a fire-resistant cellulosic material produced by the process of the present invention.

In yet another aspect of the present invention there is provided a polymer composite comprising a polymer matrix and the fire-resistant cellulosic material of the present invention dispersed in the polymer matrix.

- 10 Alkali metal hydroxides are the hydroxides of Group IA metallic elements and include, for example, lithium hydroxide, sodium hydroxide, potassium hydroxide and cesium hydroxide. Sodium hydroxide and potassium hydroxide are particularly preferred, especially sodium hydroxide. Ammonium hydroxide is NH₄OH. The alkali metal or ammonium hydroxide will be referred to herein as the hydroxide. The hydroxide is
15 preferably present in the aqueous reaction mixture in an amount of about 20 wt% or less, based on weight of the reaction mixture. More preferably, the amount is in a range of from about 0.1 wt% to about 10 wt%. Even more preferably, the amount is in a range of from about 0.5 wt% to about 4 wt%.

- 20 Alkaline earth metal salts or aluminum metal salts, or mixtures thereof are used in conjunction with the alkali metal salts to produce the fire-resistant cellulosic material. Alkaline earth metal salts and aluminum metal salts are ionic compounds that dissociate in an aqueous environment and comprise one or more cations and one or more counter anions. Alkaline earth metal salts are preferred. Alkaline earth metals include, for example, beryllium, magnesium, calcium, strontium and barium. Magnesium, calcium and
25 barium are particularly preferred, especially magnesium and calcium. Counter anions may be any suitable negatively charged elements or radicals or combinations thereof. Counter anions include, for example, halides (e.g. fluoride, chloride, bromide, iodide), nitrate and sulfate. Chloride and nitrate are particularly preferred. Chloride is most preferred. The alkaline earth metal or aluminum salt is preferably present in the aqueous
30 reaction mixture in an amount of about 20 wt% or less, based on weight of the reaction mixture. More preferably, the amount is in a range of from about 0.1 wt% to about 15 wt%. Even more preferably, the amount is in a range of from about 0.5 wt% to about 10 wt%.

In addition the ratio between the hydroxide and alkaline earth or aluminum metal salt can play an important role. The molar ratio between the hydroxide and the alkaline earth or aluminum metal salts is preferably in a range of from about 0.2 to about 4. More preferably, the molar ratio is in a range of from about 0.5 to about 2. The ratio between
5 the hydroxide and alkaline earth or aluminum metal salt can also be expressed on a weight basis, and is preferably in a range of from about 0.9 wt% to about 1.1 wt%.

In addition, the concentration of the product of the aqueous reaction mixture of the hydroxide and the alkaline earth or aluminum metal salt is preferably about 0.5 wt% or more, more preferably about 1.5 wt% or more, even more preferably in a range of from
10 about 1.5 wt% to about 20 wt%, yet more preferably about 1.5 wt% to about 15 wt%, based on weight of the reaction mixture.

Treating the cellulosic material with the aqueous reaction mixture is preferably done simultaneously with mixing the hydroxide and alkaline earth or aluminum metal salt. However, the reaction mixture remains effective within a short period of time of mixing.
15 The maximum desirable length of time after mixing and before treating is 1 day, preferably 5 hours or less, more preferably 5 seconds to 5 hours. More preferably, the time is in a range of from about 5 seconds to about 30 minutes, or about 5 seconds to about 10 minutes, or about 30 seconds to about 24 hours, or about 1 minute to about 5 hours.

20 The cellulosic material may be obtained from any suitable source. Cellulosic materials may be natural or synthetic, may have different forms (e.g. fiber, shives, film, powder, particle, pellet, chip, etc.) and may have different size distributions (e.g. nano, micro or macro). Some suitable sources of cellulosic include, for example, wood sources (e.g. pulp, wood flour such as sawdust, wood shavings, etc. from softwood and/or
25 hardwood, etc), agricultural sources (e.g. fruits, grain crops (e.g. triticale and flax), vegetables, cotton, hemp, grass, rice straw, etc.), synthetic sources (e.g. nanocrystalline cellulose, cellulose triacetate, cellulose propionate, cellulose acetate propionate, cellulose acetate butyrate, nitrocellulose, cellulose sulfate, methylcellulose, ethylcellulose, ethyl methyl cellulose, hydroxypropyl cellulose, hydroxyethyl methyl cellulose, hydroxypropyl
30 methyl cellulose, carboxymethyl cellulose, etc.), recycled paper and cardboard. The cellulosic material may be used alone or mixed with cellulosic materials from different sources. It is apparent to one skilled in the art that cellulosic materials from natural sources, for example wood and vegetable fibers, contain significant amount of lignin (in some case more than 30 wt%) and that such "lignocellulose materials" are encompassed
35 by the present invention. A particularly preferred form are cellulosic material is fibers. For

use in polymer composites, non-fibrous cellulosic material having an average particle size of from about 0.001-20 mm, more particularly from about 0.01-5 mm are generally suitable. Non-fibrous cellulosic material may be in the form of cellulosic nanocrystals. When the cellulosic material is fibrous, the average diameter of the fiber is preferably in a 5 range of from about 0.001 micron to 400 micron, more preferably from about 0.001 to 100 micron. Fibrous cellulosic material may be in the form of cellulosic nanofibers or nanowhiskers.

After treating with the aqueous reaction mixture, treated cellulosic material is dried to produce fire-resistant cellulosic material of the present invention. Prior to drying, the 10 treated cellulosic material may be cleaned, for example with water, if desired or required. Drying may be done by any suitable method, for example, air drying at ambient temperature and pressure, drying at elevated temperature, drying under a pressurized stream of air or other gas or a combination thereof. Specialized equipment such as fluid bed, rotary, spray and vacuum dryers may be used.

15 To further improve fire resistance of the cellulosic material, the cellulosic material may be further treated with a layered nanoparticulate material. Treating the cellulosic material with the layered nanoparticulate material may be done before, at the same time as or after treating the cellulosic material with the aqueous reaction mixture. Preferably, the cellulosic material is treated with layered nanoparticulate material after treatment with 20 the aqueous reaction mixture as this leads to a more durable fire-resistant coating. This further treatment with layered nanoparticulate material is particularly useful when the fire-resistant cellulosic material is to be used in a polymer composite as it significantly improves the fire-resistance of the composite in comparison to using fire-resistant cellulosic material that has only undergone treatment with the aqueous reaction mixture.

25 Any suitable layered nanoparticulate material may be used. Layered clays are particularly preferred. Layered clays are hydrated aluminum or aluminum-magnesium silicates comprised of multiple platelets. Layered clays may be natural, semi-synthetic or synthetic layered silicates. Suitable layered clays include, for example, bentonite, kaolinite, dickite, nacrite, staspulite, illite, halloysite, montmorillonite, sepiolite, 30 palygorskite, hectorite, fluorohectorite, nontronite, beidellite, saponite, volkonskoite, magadiite, medmontite, kenyaite, saucomite, muscovite, vermiculite, mica, fluoromica, hydromica, phegite, bramalite, celadonite, layered double hydroxides, etc., or a mixture thereof. Particularly preferred are layered double hydroxides, montmorillonite, sepiolite, palygorskite, bentonite, fluoromica or a mixture thereof. Layered double hydroxides, 35 montmorillonite or mixtures thereof are even more particularly preferred. The layered

nanoparticulate material is used in a sufficient amount to provide an improvement to the fire-resistance of the cellulosic material or composite in which the cellulosic material is used. The layered nanoparticulate material is preferably present in the aqueous mixture in an amount of about 15 wt% or less, based on weight of the mixture. More preferably, 5 the amount is in a range of from about 0.1 wt% to about 10 wt%. Even more preferably, the amount is in a range of from about 0.5 wt% to about 5 wt%.

The cellulosic material may be mixed with the aqueous mixture, and layered nanoparticulate material if desired, in any suitable way known in the art. Various systems are known in the art and include, for example, high shear mixers, in-line mixers, batch 10 mixers, colloid mills, stirrers, agitators and blending systems.

A polymer composite of the present invention comprises the fire-resistant cellulosic material dispersed in a polymer matrix. The polymer matrix may comprise one or more suitable organic or inorganic polymers, preferably one or more organic polymers. Organic polymers may be natural or synthetic and may be obtained from non-renewable 15 or renewable sources. Natural polymers include cellulose, lignin, starch, protein, etc. Polymer matrices may be classified in a number of other different ways. A suitable polymer matrix may comprise a homopolymer, a copolymer, a terpolymer, or a mixture thereof. The polymer matrix may comprise amorphous or crystalline polymers. The polymer matrix may comprise hydrophobic or hydrophilic polymers. The polymer matrix 20 may comprise linear, branched, star, cross-linked or dendritic polymers or mixtures thereof. Polymer matrices may also be conveniently classified as thermoplastic, thermoset and/or elastomeric polymers. It is clear to one skilled in the art that a given polymer matrix may be classifiable into more than one of the foregoing categories.

Thermoplastic polymers generally possess significant elasticity at room 25 temperature and become viscous liquid-like materials at a higher temperature, this change being reversible. Some thermoplastic polymers have molecular structures that make it impossible for the polymer to crystallize while other thermoplastic polymers are capable of becoming crystalline or, rather, semi-crystalline. The former are amorphous thermoplastics while the latter are crystalline thermoplastics. Some suitable 30 thermoplastic polymers include, for example, olefins (i.e., polyolefins), vinyls, styrenics, acrylonitrilics, acrylics, cellulosics, polyamides, thermoplastic polyesters, thermoplastic polycarbonates, polysulfones, polyimides, polyether/oxides, polyketones, fluoropolymers, copolymers thereof, or mixtures thereof.

Some suitable olefins (i.e., polyolefins) include, for example, polyethylenes (e.g., LDPE, HDPE, LLDPE, UHMWPE, XLPE, copolymers of ethylene with another monomer (e.g., ethylene-propylene copolymer)), polypropylene, polybutylene, polymethylpentene, or mixtures thereof. Some suitable vinylics include, for example, polyvinylchloride, 5 chlorinated polyvinylchloride, vinyl chloride-based copolymers, polyvinylidenechloride, polyvinylacetate, polyvinylalcohol, polyvinyl aldehydics (e.g., polyvinylacetal), polyvinylalkylethers, polyvinylpyrrolidone, polyvinylcarbazole, polyvinylpyridine, or mixtures thereof. Some suitable styrenics include, for example, polystyrene, polyparamethylstyrene, polyalphamethylstyrene, high impact polystyrene, styrene-based 10 copolymers, or mixtures thereof. Some suitable acrylonitrilics include, for example, polyacrylonitrile, polymethylacrylonitrile, acrylonitrile-based copolymers, or mixtures thereof. Some suitable acrylics include, for example, polyacrylicacid, polymethacrylicacid, polymethacrylate, polyethylacrylate, polybutylacrylate, polymethylmethacrylate, polyethylmethacrylate, cyanoacrylate resins, 15 hydroxymethylmethacrylate, polacrylamide, or mixtures thereof. Some suitable cellulosics include, for example, cellulose, cellulose esters, cellulose acetates, mixed cellulosic organic esters, cellulose ethers, methylcellulose, ethylcellulose, carboxymethylcellulose, hydroxyethylcellulose, or mixtures thereof. Some suitable polyamides include, for example, aliphatic polyamides (i.e., nylons), aromatic polyamides, 20 transparent polyamides, or mixtures thereof. Some suitable thermoplastic polyesters/polycarbonates are, for example, polyalkylene terephthalates (e.g., polyethylene terephthalate, polybutylene terephthalate), polycyclohexanedimethanol terephthalates, polyarylesters (e.g., polyarylates), polycaprolactones, polyactides, polyhydroxyalkanoates (e.g. polyhydroxybutanoate), polycarbonate, or mixtures thereof. 25 Some suitable polysulfones include, for example, diphenylsulfone, polybisphenolsulfone, polyethersulfone, polyphenylethersulfones, or mixtures thereof. Some suitable polyimides include, for example, polyamideimide, polyetherimide, or mixtures thereof. Some suitable polyether/oxides include, for example, polymethyleneoxides, polyethyleneoxide, polypropyleneoxide, polyphenyleneoxides, or mixtures thereof. Some 30 suitable polyketones include, for example, polyetheretherketone-1. Some suitable fluoropolymers include, for example, polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylfluoride, polyvinylidenefluoride, polyperfluoroalkoxy, polyhexafluoropropylene, polyhexafluoroisobutylene, fluoroplastic copolymers, or mixtures thereof.

Thermoset polymers (thermoset resins) generally arise from a complex 35 combination of polymerization and cross-linking reactions, which convert low- or relatively low-molecular weight molecules into three-dimensional networks. The reaction is

irreversible and the resulting polymeric species is generally hard. The polymerization and cross-linking reactions may be temperature-activated, catalyst-activated or mixing-activated. Some suitable thermosets include, for example, phenolic systems, formaldehyde systems, furan systems, allyl systems, alkyd systems, unsaturated polyester systems, vinylester systems, epoxy systems, urethane/urea systems, isocyanurate systems or mixtures thereof.

Some suitable phenolic systems include, for example, phenol-formaldehyde resins, phenol acetaldehyde resins, alkylphenol-formaldehyde resins, lignin formaldehyde resins or mixtures thereof. Some suitable formaldehyde systems include, for example, 10 urea-formaldehyde resins, melamine-formaldehyde resins, phenol-formaldehyde resins, or mixtures thereof. Some suitable furan systems include, for example, furan resins, furfural resins, furfuryl alcohol resins, or mixtures thereof. Some suitable allyl systems include, for example, diallyl phthalate, diallyl isophthalate, diethyleneglycol bis(allyl carbonate), or mixtures thereof. Some suitable alkyd systems include, for example, the 15 reaction product of ethylene glycol, glycerol and phthalic acid with fatty acids. Some suitable unsaturated polyester systems include, for example, one component which is a polyester product of a reaction between a difunctional acid or anhydride (e.g., maleic acid, maleic anhydride, phthalic anhydride, terephthalic acid) with a difunctional alcohol (e.g., ethylene glycol, propylene glycol, glycerol), and, a second component which is a 20 monomer capable of polymerizing and reacting with unsaturations in the polyester component (e.g., styrene, alphamethylstyrene, methylmethacrylate, diallylphthalate). Some suitable vinylester systems include, for example, the reaction of diglycidyl ether of bisphenol A with methacrylic acid. Some suitable epoxy systems include, for example, the reaction between epichlorohydrin and a multifunctional acid, amine or alcohol. Some 25 suitable urethane/urea systems include, for example, the reaction product of a liquid or solid isocyanate (e.g., 2,4-toluenediisocyanate, 2,6-toluenediisocyanate, methylene diisocyanate monomer or oligmer of different molecular weight) with a polyol (e.g., polyethylene ether glycol, polypropylene ether glycol).

Elastomeric polymers (elastomers) can generally be defined as materials capable 30 of large elastic deformations and are often referred to as rubbers. Elastomers may be classified as vulcanizable elastomers, reactive system elastomers and thermoplastic elastomers. Some suitable elastomers include, for example, polyisoprene, polybutadiene, polychloroprene, polyisobutylene, styrene-butadiene rubber, acrylonitrile-butadiene rubber, ethylene-propylene rubber, ethylene-propylene-diene rubber, 35 chlorinated polyethylene, chlorosulfonated polyethylene, ethylene-vinylacetate copolymer,

ethylene-acrylate copolymer, fluoroelastomers (e.g., polyvinylidene fluoride, polychlorotrifluoroethylene), silicone polymers (e.g., polydimethylsiloxane), acrylic rubber, epichlorohydrin rubber, polysulfide rubbers, propyleneoxide rubbers, polynorbornene, polyorganophosphazenes, olefinic thermoplastic rubbers, styrenic thermoplastic rubbers, 5 urethane thermoplastic rubbers, etherester thermoplastic rubbers, etheramide thermoplastic rubbers, copolymers of an elastomer, or mixtures thereof.

Particularly preferred polymer matrices include, for example, homopolymers and copolymers of PP, PE, PET, PBT, PHA, PHB, PLA, PA, PS, PVC, PVF, PVA, PVAc, polybutadiene, polychloroprene, polyisobutylene, styrene-butadiene rubber, acrylonitrile-10 butadiene rubber, ethylene-propylene rubber, ethylene-propylene-diene rubber, chlorinated polyethylene, chlorosulfonated polyethylene, ethylene-vinylacetate copolymer, ethylene-acrylate copolymer, phenolformaldehyde, ligninformaldehyde, ureformaldehyde, melamine formaldehyde, epoxide, unsaturated polyester, vinylester, PU, polyisocyanurate, lignin, starch or mixtures thereof.

15 For thermoplastics, the number average molecular weight (M_n) of the polymer matrix may vary considerably depending on the specific type of polymer and the use to which the polymer composite is to be put. Preferably, the number average molecular weight is greater than about 500. Polymer matrices having a number average molecular weight of from about 1,300 to about 15,000,000 are suitable for a number of applications. 20 In one embodiment, the number average molecular weight may be from about 1,500 to about 2,000,000. In another embodiment, the number average molecular weight may be from about 1,500 to about 500,000.

25 Compatibility of the fire-resistant cellulosic material with the polymer matrix in a composite may be improved by treating the fire-resistant cellulosic material with a surfactant. The surfactant may improve compatibility through primary or secondary interactions between the fire-resistant cellulosic material and the polymer matrix. Where a layered nanoparticulate material is also employed, the fire-resistant cellulosic material may be treated with the surfactant before or after, preferably after, treatment with the layered nanoparticulate material. Suitable surfactants for a given case will depend on the 30 nature of the polymer matrix and the nature of the layered nanoparticulate material, if any, and are within the abilities of one skilled in the art to determine for any particular combination.

Surfactants generally comprise a functional group and a hydrocarbon chain. The functional group may be provided in the form of a positively charged ion (e.g. ammonium

or phosphonium ions) or a negatively charged ion (e.g. carboxylate, sulfonate or phenolate) depending on the charge availability on the surface. The hydrocarbon chain preferably comprises 1 or more carbon atoms, more preferably from 6 to 20,000 carbon atoms, even more preferably from 10 to 40 carbon atoms. Hydrocarbon chains may be
5 linear, branched or cyclic and may be substituted or unsubstituted. The surfactant may comprise one or more functional groups. The one or more functional groups interact with the clay surface and the polymer matrix and/or compatibilizer.

Some suitable surfactants include, for example, amines (e.g. dimethyldioctadecyl ammonium (DMDODA) salts, octadecyl amine (ODA) or its salts, trimethyloctadecyl ammonium salts, trimethylhexadecyl ammonium salts, dimethylhexadecyl amine or its salts, hexadecyl amine or its salts, dimethylbenzyloctadecyl ammonium salts, methyloctadecyldihydroxyethyl ammonium salts, methylamine or its salts, dimethylbenzyl amine or its salts, tribenzyl amine or its salts, glycine or its salts), di- and poly-functional amines (e.g. diethylenetriamine or its salts, ethylenediamine or its salts, Jeffamine™ T-
10 403 or its salts, Jeffamine™ D-2000 or its salts), alkanolamines (e.g. ethanolamine or its salts, triethanolamine or its salts), acids or carboxylates (e.g. lauric acid, palmitic acid, stearic acid, stearate, oleic acid, oleate, linoleic acid, linoleate, ricinoleic acid) or mixtures thereof.
15

Polymer composites may also include other suitable additives normally used in polymers. Such additives may be employed in conventional amounts and may be added directly to the process during formation of the polymer composite. Illustrative of such additives known in the art are processing aid agents, colorants, pigments, carbon black, fibers (glass fibers, carbon fibers, aramid fibers), fillers, impact modifiers, antioxidants, stabilizers, flame retardants, reheat aids, crystallization aids, acetaldehyde reducing
20 compounds, recycling release aids, oxygen scavengers, anti-UV agents, plasticizers, flexibilizers, nucleating agents, foaming agents, mold release agents, and the like, or their combinations.
25

The amounts of polymer matrix, fire-resistant cellulosic material and additives present in the polymer composite will depend on the particular use to which the polymer composite is put and the particular polymer matrix. The polymer matrix may be present in an amount from about 0.1 to about 99.9 weight percent based on the total weight of the polymer composite, or from about 20 to about 99 weight percent, or from about 40 to about 98 weight percent. The fire-resistant cellulosic material may be present in an amount from about 0.1 to about 99.9 weight percent based on the total weight of the
30

polymer composite, or from about 1 to about 80 weight percent, or from about 10 to about 60 weight percent.

Standard polymer processing techniques may be used to prepare the polymer composites of the present invention. Such techniques are generally known in the art
5 (Charrier 1991; Manas-Zloczower 1994; Rauwendaal 1998). Standard composite forming techniques may be used to fabricate products from the polymer composites of the present invention. For example, melt spinning, casting, vacuum molding, sheet molding, injection molding and extruding, melt blowing, spun bonding, blow molding, overmolding, compression molding, resin transfer molding (RTM), L-DFT, spraying, gel spinning,
10 thermo-forming, roll-forming and co- or multilayer extrusion may all be used.

Advantageously, the process of the present invention is less harmful to the environment due to the absence of halogen compounds, organic solvents and toxic chemicals while the cellulosic materials treated according to the present invention pose less health risk to animals and human than boron and phosphorous compounds. Self-
15 extinguishing cellulosic materials can be produced in accordance with the present invention using less harmful chemicals at significantly reduced concentrations. In addition, while the process involves the use of an aqueous mixture comprising a hydroxide and an alkaline earth or aluminum metal salt, and optionally a layered nanoparticulate material, fire resistance of the treated cellulosic material is not unduly
20 compromised even after washing the fire-resistant cellulosic material several times with water, which is a significant advantage compared to other traditional water soluble flame retardants based on boron or phosphorous compounds. In addition, fire-resistant cellulosic material according to the present invention and their polymer composites may also have improved mechanical properties, improved thermal stability, improved
25 interfacial thermal resistance, improved resistance to damage by oxidants and other chemical agents, improved resistance to biological agents (e.g. bacteria, mold, fungi, termites and other insects) and/or improved resistance to damage by ultra-violet light. Overall, the present invention provides several improvements to fire-resistant cellulosic materials and their polymer composites, which have not been realized before.

30 Commercial applications for the present invention are extensive, including applications in the textile (e.g. cloth, tapis, matte), transportation, aerospace, marine, construction, household and agriculture industries. Fire-resistant cellulosic materials of the present invention may be used with commercially available polymer materials and existing conventional equipment, thereby reducing capital investment and investment risk

involved with the production of polymer composites. This opens new opportunities for cellulose composites in more demanding fields such as the aerospace industry.

Further features of the invention will be described or will become apparent in the course of the following detailed description.

5 Brief Description of the Drawings

In order that the invention may be more clearly understood, embodiments thereof will now be described in detail by way of example, with reference to the accompanying drawings, in which:

Fig. 1A depicts a graph comparing flexural modulus (GPa) of laminates prepared
10 by compression of various polypropylene (PP)-flax fiber composites; and,

Fig. 1B depicts a graph comparing flexural strength (MPa) of laminates prepared by compression of various polypropylene (PP)-flax fiber composites.

Description of Preferred Embodiments

Without being held to any particular mode of action, there may be one or more possible explanations for the efficacy of the present invention. It is currently believed that alkalinity of the aqueous reaction mixture causes the surface of the cellulosic material to swell and possibly generate anionic groups in the cellulosic material, possibly due to the reaction of the hydroxide with -CH₂OH groups of glucose and fructose units in the cellulose polymer. Alkaline earth metal or aluminum cations can then more easily penetrate the surface as the surface is swollen by alkalinity and the cations possibly form ionic bonds or otherwise interact with anions created by the hydroxide or with hydroxyl groups available on the fiber surface. Subsequent drying or heating then shrinks the surface of the cellulosic material further immobilizing the alkaline earth or aluminum metal on the cellulosic material. In this manner, a durable coating of alkaline earth or aluminum metal is formed on the cellulosic material giving rise to a self-extinguishing cellulosic material in which the coating is not easily washed off. In contrast, simply treating the cellulosic material with an alkaline earth metal salt or even an alkaline earth metal hydroxide that was pre-prepared does not lead to satisfactory self-extinguishing properties and the coating of alkaline earth metal is easily washed off eliminating what little effect the coating did have. Where a layered nanoparticulate material is employed, the layered nanoparticulate material may be attached chemically to the cellulosic material by ionic bonds (for example when montmorillonite (MMT) is used) or by strong van der

Waals interactions including hydrogen bonds (for example when a layered double hydroxide (LDH) is used). Layered double hydroxides are particularly preferred since they provide greater surface coverage. When a surfactant is used to improve compatibility of the fire-resistant cellulosic material with a polymer matrix, the surfactant can bind to the 5 surface of the layered nanoparticulate material.

Example 1: Materials

Table 1 provides a description of chemicals and Table 2 provides a description of the fibers used in the following examples.

10

Table 1 – Description of Chemicals

| Chemicals | Company | Purification |
|--|-----------------------------|--|
| CaCl ₂ .2H ₂ O | Fisher | - |
| Ca(NO ₃) ₂ .4H ₂ O | Aldrich | ≥ 99% |
| Ca(OH) ₂ | Aldrich | ≥ 96% |
| MgCl ₂ | Sigma Life Science | - |
| MgSO ₄ | Sigma-Aldrich | ≥ 99.5% |
| Mg(NO ₃) ₂ .6H ₂ O | Fluka | ≥ 99% |
| Mg(OH) ₂ | Alfa Aesar | 95-100.5% |
| NaOH | Aldrich | ≥ 98% |
| KOH | Sigma-Aldrich | ≥ 90% |
| Al(OH) ₃ | Aldrich | Reagent grade, Al ₂ O ₃ : 50-57% |
| AlCl ₃ | Sigma-Aldrich | 98% |
| NH ₄ OH | Sigma-Aldrich | ACS reagent, NH ₃ : 28-30% |
| BaCl ₂ | Fisher | Lab grade |
| BaCl ₂ .2H ₂ O | JTBaker Chemical | 100.5% |
| Ba(OH) ₂ | Aldrich | ~95% |
| Clay MMT | Southern Clay Products, Inc | Montmorillonite Cloisite Na™ clay (CEC: 92 meq/100 g) |
| Clay LDH | AkzoNobel | Layered Double Hydroxides (LDH)-anionic clay |

Table 2 – Description of Cellulosic Fibers

| Sample | Fiber | Weight (g/m ²) |
|--------|---|-------------------------------|
| C1 | Belgium flax fabric C 20M-2/2 twill from Moss Composites received in 2008. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 149 |
| C2 | Belgium flax fabric C 20M-2/2 twill from Moss Composites received in 2010. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 149 |
| C3 | Belgium flax fabric C10M-8H satin from Moss Composites received in 2010. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 258 |
| C4 | France unidirectional flax fiber Mutistrat MRCL1-180/17 UD 45° from Conseil Recherche Supstrats Textiles (CRST) received in 2010. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 180 |
| C5 | France bi-directional flax fiber Mutistrat MRL2-250/12 bi biais 2x45° from Conseil Recherche Supstrats Textiles (CRST) received in 2009. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 250 |
| C6 | Canada woven flax fabric from JBMatin received in 2010. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 240 |
| C7 | Hemp mat 1 supplied by CIC. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 350 |
| C8 | Hemp mat 2 supplied by CIC. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 500 |
| C9 | Paper 1CHR from Whatman received in 2008. | 85 |
| C10 | Cotton pad from Govmark for UL94 test received in 2009. | 210 |
| C11 | Belgium flax fabric C 007M twill from Moss Composites received in 2012. It was cleaned with the cleaning product at 80°C for 2 hours then rinsed three times with demineralized water. | 180 |

Example 2: General Procedure for Treatment of Fibers

Solution preparation:

In a single component solution, only one chemical is dissolved in demineralized water. For example, A2% means 2wt% of this chemical A in demineralized water.

5 In a single component suspension, only one mineral (e.g. clay) is dispersed in demineralized water. For example, X2% means 2wt% of mineral X in demineralized water.

In a bi-component solution or a bi-component suspension, separate solutions or suspensions of each of the two chemicals were prepared in an equal amount of
10 demineralized water and then they were mixed together. If both of the solutions could produce hydroxide product, the ratio of the amount of the chemicals in the first and the second solutions was calculated based on the assumption that the reaction between the chemicals in the first and the second solutions was quantitative to form the hydroxide without excess amount of any chemical left over. For example, (A+B)2% means 2wt% of
15 the hydroxide product produced by the reaction between A and B assuming that the reaction was quantitative without having any excess amount of A or B in the product. If the two systems could not produce hydroxide product the concentrations of the chemical in the first and the second solutions or suspensions were equal.

Treatment processes:

20 In one-step treatment processes (P1), about 10 g of cellulosic fiber was soaked in about 60 ml of a single component solution or a single component suspension or a bi-component solution for a period of time. The fibers were then dried in air for 6 hours and then in an oven at 120°C for 2 hours prior to testing.

25 Two types of two-step treatment processes (P2-1 and P2-2) were used. In P2-1, 10 g of cellulosic fiber was soaked in about 60 ml of a single component solution or a single component suspension or a bi-component solution or a bi-component suspension for 5 to 300 seconds. The fibers were then removed from the treating medium and allowed to dry in air for 6 hours, and then dried in an oven at 120°C for 2 hours. The dried fibers were then soaked in about 60 ml of another single component solution or a single
30 component suspension or a bi-component solution or a bi-component suspension for 5 to 300 seconds. Finally the fibers were dried in air for 6 hours and then in an oven at 120°C

for 2 hours prior to testing. The concentrations of the first and the second solutions or suspensions were equal.

In P2-2, 10 g of cellulosic fiber was soaked in about 30 ml of a single component solution or a single component suspension or a bi-component solution or a bi-component suspension for 5 to 300 seconds. Then, about 30 ml of another single component solution or a single component suspension or a bi-component solution or a bi-component suspension was added into the system and mixed. The fibers were soaked for 5 to 300 seconds then removed them from the treating medium. Finally the fibers were dried in air for 6 hours, and then in an oven at 120°C for 2 hours prior to testing.

10 *Example 3: General Procedure for Preparation of Fiber/Polymer Composite Plaques*

For fiber/phenolic resin composites, fibers were dried in an oven at 120°C for about 2 hours to remove humidity before use. Phenolic resin was then wetted on the fibers and dried in an oven to remove solvent from the resin and to let the resin transfer to stage B before compression. Wabash PC 100-2418-2TM compression was used to fabricate the composites under 100 psi pressure at 150°C. The amounts of polymer and fiber in the final product were about 60 wt% and 40 wt%, respectively. The thickness of the composite plaque was about 3 mm.

For fiber/polypropylene composites, fibers were dried in an oven at 120°C for about 2 hours to remove humidity before use. Laminate composites were prepared with Basell Profax 1274 PCD by compression molding with Wabash PC 100-2418-2TM under 100 psi pressure at 190°C. The amounts of polymer and fiber used were about 60 wt% and 40 wt%, respectively. The thickness of the composite plaque was about 3 mm.

For fiber/epoxy composites, fibers were dried in an oven at 120°C for about 2 hours to remove humidity before use. Laminate composites were prepared with Shell Epon 828 by compression molding with Wabash PC 100-2418-2TM under 100 psi pressure at 80°C. The amounts of polymer and fiber used were about 60 wt% and 40 wt%, respectively. The thickness of the composite plaque was about 3 mm.

For fiber/unsaturated polyester (UPE) composites, fibers were dried in an oven at 120°C for about 2 hours to remove humidity before use. Laminate composites with Progress RL 2710 resin were prepared by compression molding with Wabash PC 100-2418-2TM under 100 psi pressure at 50°C. The amounts of polymer and fiber used were about 70 wt% and 30 wt%, respectively. The thickness of the composite plaque was about 3 mm. The UPE resin contains 20 wt% alumina trihydrate Hubert SB332.

Example 4: General Procedure for Burning Tests

A Govmark UL94 and vertical chamber were used to conduct burning tests. For each example, results are provided using numbers and the terms "NB" and "G". The term "NB" means "no burning" and is an indication that there was no flame and no glow after removing the flame. "NB" represents excellent fire resistance as the sample did not continue to burn appreciably after the external flame source was removed, thus the sample was self-extinguishing. The term "NB/B" means that some fiber did not burn and that some fiber did burn. The term "G" means "glow" and is an indication that the sample continued to glow after removal of the flame. The numbers are the time in seconds that the sample continued to glow after removal of the flame.

UL94 Horizontal Burning Test (HB):

For fiber samples, five specimens having width x length (WxL) of 0.5x6.0 inch (12.7x152.4 mm) were cut from bulk fiber. Specimens were held at one end in a horizontal position and tilted at 45° with marks at 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 inch from the free end. A flame was applied to the free end of the specimen for 30 seconds or until the flame front reached the 1 inch mark. If combustion continued, the duration was timed between each 0.5 inch mark. A thin metallic wire was inserted to support the specimen.

For polypropylene, epoxy and unsaturated polyester (UPE) composite samples, five specimens having width x length (WxL) of 0.5x6.0 inch (12.7x152.4 mm) were cut from the 3 mm thick composite plaque prepared as described in Example 3. Specimens were held at one end in a horizontal position and tilted at 45° with marks at 1, 2.0, 3.0, 4.0, 5.0 inch from the free end. A flame was applied to the free end of the specimen for 30 seconds or until the flame front reached the 1 inch mark. If combustion continued, the duration was timed between each 1.0 inch mark.

UL94 Vertical Burning Test (VB):

For phenol formaldehyde composite samples, five specimens having width x length (WxL) of 0.5x6.0 inch (12.7x152.4 mm) were cut from the 3 mm thick composite plaque prepared as described in Example 3. Specimens were held at one end in the vertical position. The flame was applied for ten seconds and then removed until flaming stopped, at which time the flame was reapplied for another ten seconds and then removed. The combustion time and burning length were recorded.

Vertical Burning Test (VC-2):

For phenol formaldehyde composite samples, three specimens having width x length (WxL) of 3x12 inch (76.2x304.8 mm) were cut from the 3 mm thick composite plaque prepared as described in Example 3. Specimens were held at one end in the vertical position. The flame was applied for sixty seconds and then removed until flaming stopped. The combustion time and burning length was recorded. If the specimen has burning length and burning time less than 8 inch and 15 seconds, respectively, it is considered to be passed the standard (self-extinguished).

Example 5: General Procedure for Mechanical Tests**10 Fibers:**

Tensile tests on fibers were conducted on a tow (strand) disassembled from the fabric. The tows in the longitudinal direction in the fabric were separated from the ones in the orthogonal direction. Tests were carried out for both series separately. The tensile properties of the fiber tow were determined at room temperature and 50% relative humidity on an Instron 5548 micro-tester machine, with crosshead distance of 50 mm and speeds of 120 mm/min. The maximum load at break was recorded for each specimen. A minimum 10 specimens were tested for each type of sample.

Composites:

The tensile properties of the composites were determined at room temperature and 50% relative humidity on an Instron 5500R machine, with crosshead speeds of 5 mm/min according to ASTM 3039-00. A minimum 5 specimens were tested for each type of sample.

Example 6: Fibers Treated with Single Component Solutions - Comparative

Belgium flax fiber samples C1 as described in Table 2 were treated with different single component solutions as indicated in Table 3 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 3. It is evident from Table 3 that all of the C1 fibers treated with various single component systems are not self-extinguishing, although these treatments slowed down flame propagation.

30 Belgium flax fiber samples C2 as described in Table 2 were treated with different single component systems as indicated in Table 4 for 120 s using the process P1.

Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 4. It is evident from Table 4 that all of the fibers treated with a single component system, including a barium hydroxide system (C1-6/P1), are not self-extinguishing. Fibers treated with NaOH or KOH did not continue to burn but did continue to glow. Fibers treated with NaOH and then washed with water did continue to burn, demonstrating that any fire resistant effect afforded by an alkali metal hydroxide alone is easily removed if the fibers get wet.

Collectively, Tables 3 and 4 demonstrate that single component systems of metal hydroxides, metal salts or clays do not impart self-extinguishing properties on fibers treated with the systems.

Table 3 - C1 Fibers Treated with Single Component Solutions

| Sample | Description | Burning Length (inches) | | | | | | |
|---------|--|-------------------------|-----|-----|-----|-----|-----|-----|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 |
| | | Burning Time (seconds) | | | | | | |
| C1 | Untreated C1 | 3 | 7 | 10 | 14 | 17 | 21 | 25 |
| C1-1/P1 | C1+clay MMT2%/P1 | 5 | 9 | 14 | 18 | 22 | 26 | 31 |
| C1-2/P1 | C1+clay MMT4%/P1 | 5 | 9 | 14 | 18 | 22 | 27 | 31 |
| C1-3/P1 | C1+clay LDH2%/P1 | 5 | 9 | 14 | 20 | 25 | 30 | 34 |
| C1-4/P1 | C1+clay LDH4%/P1 | 6 | 13 | 19 | 25 | 30 | 38 | 44 |
| C1-5/P1 | C1+(BaCl ₂)2%/P1 | 4 | 7 | 11 | 15 | 18 | 22 | 26 |
| C1-6/P1 | C1+(Ba(OH) ₂)2% | 5 | 8 | 14 | 18 | 23 | 27 | 32 |
| C1-7/P1 | C1+(BaCl ₂)2% then washed with water | 4 | 7 | 10 | 14 | 17 | 21 | 25 |
| C1-8/P1 | C1+(Ba(OH) ₂)2% then washed with water | 5 | 8 | 14 | 18 | 22 | 26 | 31 |

Table 4 - C2 Fibers Treated with Single Component Solutions

| Sample | Description | Burning Length (inches) | | | | | | | | |
|--------------------------------|------------------------------------|-------------------------|-----|-----|------|------|------|------|------|-------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| Average Burning Time (seconds) | | | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-1/P1 | C2+(Ba(OH) ₂)2% | 3.2 | 6.1 | 8.9 | 11.9 | 15 | 17.6 | 20.4 | 23.3 | 26.5 |
| C2-2/P1 | C2+(BaCl ₂)2% | 2.3 | 5.0 | 7.1 | 9.1 | 11.0 | 13.3 | 15.3 | 17.5 | 19.8 |
| C2-3/P1 | C2+(BaCl ₂)2% twice | 4.0 | 7.3 | 9.8 | 12.6 | 14.7 | 17.8 | 20.1 | 22.4 | 25.2 |
| C2-4/P1 | C2+(MgNO ₃)2% | 2.3 | 4.8 | 7.1 | 9.4 | 11.4 | 14.0 | 16.0 | 18.1 | 20.3 |
| C2-5/P1 | C2+(MgCl ₂)2% | 3.7 | 6.1 | 8.8 | 11.7 | 15.3 | 18.2 | 21.7 | 24.6 | 27 |
| C2-6/P1 | C2+(MgSO ₄)2% | 2.6 | 5.2 | 7.3 | 9.5 | 11.5 | 14.0 | 16.2 | 18.1 | 19.5 |
| C2-7/P1 | C2+(Mg(OH) ₂)2% | 3.0 | 6.2 | 8.2 | 10.1 | 12.1 | 14.6 | 16.4 | 18.8 | 20.6 |
| C2-8/P1 | C2+(Ca(NO ₃)2% | 2.6 | 4.8 | 7.0 | 8.7 | 10.9 | 12.6 | 14.6 | 16.3 | 18.1 |
| C2-9/P1 | C2+(CaCl ₂)2% | 2.8 | 5.1 | 7.5 | 9.5 | 11.6 | 14.3 | 16.6 | 19.0 | 21.0 |
| C2-10/P1 | C2+(KOH)2% | G | G | G | G | G | G | G | G | G-250 |
| C2-11/P1 | C2+(NaOH)2% | G | G | G | G | G | G | G | G | G-250 |
| C2-12/P1 | C2+(NaOH)2% twice | G | G | G | G | G | G | G | G | G-280 |
| C2-13/P1 | C2+(NaOH)2% then washed with water | 2.8 | 5.5 | 7.7 | 10.0 | 12.5 | 14.5 | 17.0 | 19.7 | 22.0 |
| C2-14/P1 | C2+(AlCl ₃)2% | 3.6 | 6.5 | 9.2 | 12.3 | 15.4 | 18.4 | 21.3 | 24.8 | 27.8 |
| C2-15/P1 | C2+(Al(OH) ₃)2% | 2.8 | 5.3 | 7.8 | 10.2 | 11.8 | 14.7 | 16.6 | 18.6 | 20.9 |

*Example 7: Fibers Treated with Bi-component Solutions**C1 Fibers Treated with Barium-containing Bi-component Systems:*

5 Belgium flax fiber samples C1 as described in Table 2 were treated with different barium-containing bi-component systems as indicated in Table 5 for 120 s using the processes P1 and P2-1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 5. It is evident from Table 5 that all of the C1 fibers treated with bi-component systems involving the mixture of barium chloride and sodium hydroxide are self-extinguishing. Fibers treated with barium chloride alone then with clay or barium hydroxide alone then with clay are not self-extinguishing. Thus, single component systems are not self-extinguishing, even with the subsequent addition of clay. A mixture of both the alkaline metal salt and the alkali metal hydroxide is needed to make the fibers self-extinguishing. It is further clear that washing the fibers after treatment with a bi-component system does not remove the self-extinguishing properties imparted by the

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treatment. Further, the order in which clay is introduced into the bi-component does not affect the self-extinguishing properties of the fibers after treatment.

Table 5 - C1 Fibers Treated with Barium-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | |
|------------|---|-------------------------|-----|-----|-----|-----|-----|-----|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 |
| | | Burning Time (seconds) | | | | | | |
| C1 | Untreated C1 | 3 | 7 | 10 | 14 | 17 | 21 | 25 |
| C1-9/P2-1 | C1+(BaCl ₂)2% then +clay MMT2% | 4 | 8 | 13 | 17 | 21 | 26 | 31 |
| C1-10/P2-1 | C1+(Ba(OH) ₂)2% then +clay LDH2% | 5 | 11 | 15 | 20 | 25 | 30 | 35 |
| C1-11/P1 | C1+(BaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB |
| C1-12/P1 | C1+(BaCl ₂ +NaOH)2% then washed with water | NB | NB | NB | NB | NB | NB | NB |
| C1-13/P2-1 | C1+(BaCl ₂ +NaOH)2% then +clay MMT2% | NB | NB | NB | NB | NB | NB | NB |
| C1-14/P2-1 | C1+(BaCl ₂ +NaOH)2% then +clay LDH2% | NB | NB | NB | NB | NB | NB | NB |
| C1-15/P2-1 | C1+clay MMT2% then +(BaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB |
| C1-16/P2-1 | C1+clay LDH2% then +(BaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB |

5 C2 Fibers Treated with a Barium-containing Bi-component System:

Nine different specimens of Belgium flax fiber samples C2 as described in Table 2 were treated with one barium-containing bi-component systems as indicated in Table 6 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 6. It is evident from Table 6 that fiber quality is not always consistent even in the same batch, and that fire resistance behavior of fibers treated with a bi-component system (BaCl₂+NaOH)2% can vary from specimen to specimen. Some specimens are self-extinguishing while others are not, although they were all treated at the same time.

Table 6 - C2 Fibers Treated with a Barium-containing Bi-component System

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|---|-------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-16/P1 | C2+(BaCl ₂ +NaOH)2% specimen 1 | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| | C2+(BaCl ₂ +NaOH)2% specimen 2 | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| | C2+(BaCl ₂ +NaOH)2% specimen 3 | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| | C2+(BaCl ₂ +NaOH)2% specimen 4 | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| | C2+(BaCl ₂ +NaOH)2% specimen 5 | 5.0 | 8.5 | 11.0 | 13.5 | 16.5 | 19.5 | 22.0 | 26.0 | 31.0 |
| | C2+(BaCl ₂ +NaOH)2% specimen 6 | 4.5 | 10.5 | 14.5 | 18.5 | 21.5 | 27.5 | 31.5 | 35.5 | 39.5 |
| | C2+(BaCl ₂ +NaOH)2% specimen 7 | 4.0 | 8.5 | 11.5 | 14.5 | 18.5 | 22.5 | 26.5 | 30.0 | 34.0 |
| | C2+(BaCl ₂ +NaOH)2% specimen 8 | 4.5 | 8.5 | 11.0 | 14.0 | 17.5 | 21.0 | 24.5 | 27.0 | 31.5 |
| | C2+(BaCl ₂ +NaOH)2% specimen 9 | 5.0 | 8.5 | 11.5 | 14.5 | 18.5 | 21.0 | 24.5 | 28.5 | 32 |

C2 Fibers Treated with a Calcium-containing Bi-component System at Different Treatment Periods:

- 5 Belgium flax fiber samples C2 as described in Table 2 were treated with calcium-containing bi-component systems as indicated in Table 7 for different treatment periods from 5-300 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 7. It is evident from Table 7 that fibers treated with bi-component system
 10 (CaCl₂+NaOH)2% at different treatment periods (5-300 s) are all self-extinguishing. Further, the (CaCl₂+NaOH)2% system appears to have greater tolerance to cellulosic fiber quality than the (BaCl₂+NaOH)2% system (compare Table 6 to Table 7).

Table 7 - C2 Fibers Treated with a Calcium-containing Bi-component System at Different Treatment Periods

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|---|-------------------------|-----|-----|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-17/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 5s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-18/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 10s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-19/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 30s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-20/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 60s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-21/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 120s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-22/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 180s | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-23/P1 | C2+(CaCl ₂ +NaOH)2% impregnated 300s | NB | NB | NB | NB | NB | NB | NB | NB | NB |

C2 Fibers Treated with a Calcium-containing Bi-component System at Different

5 *Concentrations:*

Belgium flax fiber samples C2 as described in Table 2 were treated with one calcium-containing bi-component systems at different concentrations from 1 wt% to 3 wt% of the hydroxide product of the alkaline metal salt and alkali metal hydroxide as indicated in Table 8 for 120 s using the process P1. Burning tests were conducted in 10 accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 8. It is evident from Table 8 that to obtain self-extinguishing fibers treated with the bi-component system (CaCl₂+NaOH) for 120s using the process P1, the minimum concentration must be 1.5%.

Table 8 - C2 Fibers Treated with a Calcium-containing Bi-component System at Different Concentrations

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|----------------------------------|-------------------------|-----|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-24/P1 | C2+(CaCl ₂ +NaOH)1% | 4.0 | 7.6 | 11.5 | 13.9 | 17.0 | 20.0 | 23.2 | 25.7 | 28.4 |
| C2-25/P1 | C2+(CaCl ₂ +NaOH)1.5% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-21/P1 | C2+(CaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-26/P1 | C2+(CaCl ₂ +NaOH)3% | NB | NB | NB | NB | NB | NB | NB | NB | NB |

C2 Fibers Treated with Magnesium-containing Bi-component Systems at Different

5 *Concentrations:*

Belgium flax fiber samples C2 as described in Table 2 were treated with magnesium sulfate-containing bi-component systems at 1 wt% and 2 wt% of the hydroxide product of the alkaline metal salt and alkali metal hydroxide as indicated in Table 9 for 120 s using the process P1. Burning tests were conducted in accordance with 10 the general procedure described in Example 4 and the results from the burning tests are also shown in Table 9.

Table 9 - Fibers Treated with a Magnesium Sulfate-containing Bi-component System at Different Concentrations

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|------------------------------------|-------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-27/P1 | C2+ (MgSO ₄ +NaOH)1% | 4.4 | 8.3 | 11.6 | 14.6 | 18.3 | 21.8 | 25.6 | 28.7 | 32.3 |
| C2-28/P1 | C2+ (MgSO ₄ +NaOH)2% | 5.1 | 10.6 | 14.6 | 19.5 | 24.7 | 29.5 | 33.7 | 38.7 | 43.4 |

15 Belgium flax fiber samples C2 as described in Table 2 were treated with magnesium chloride-containing bi-component systems at 1 wt% and 2 wt% of the hydroxide product of the alkaline metal salt and alkali metal hydroxide as indicated in Table 10 for 120 s using the process P1. Burning tests were conducted in accordance

with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 10.

Table 10 - Fibers Treated with a Magnesium Chloride-containing Bi-component System at Different Concentrations

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|------------------------------------|-------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-29/P1 | C2+ (MgCl ₂ +NaOH)1% | 5.1 | 11.0 | 15.2 | 19.3 | 24.0 | 30.4 | 34.7 | 39.9 | 47.0 |
| C2-30/P1 | C2+ (MgCl ₂ +NaOH)2% | 7.0 | 14.0 | NB |

5

It is evident from Table 9 that all fibers treated with the (MgSO₄+NaOH) system burned at a slower rate than the untreated one but they are not self-extinguishing. From Table 10, it is evident that fibers are self-extinguishing after treatment with the bi-component system (MgCl₂+NaOH) for 120s using the process P1 at 2.0% solution, but 10 not for the 1.0% solution. Thus, (MgCl₂+NaOH) is more effective than the (MgSO₄+NaOH). Therefore, sulfate is not as good a counter anion in the alkaline metal salt as chloride.

C2 Fibers Treated with NaOH and CaCl₂ or NaOH and Clay

Belgium flax fiber samples C2 as described in Table 2 were treated sequentially 15 with calcium chloride and sodium hydroxide in different orders as indicated in Table 11 for 120 s using the process P2-2. Likewise, C2 fibers were treated with sodium hydroxide and then clay as indicated in Table 11 for 120 s using the process P2-2. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 11. It is evident from Table 11 20 that fibers treated first with NaOH and then with CaCl₂ are self-extinguishing, but this is not the case for the reverse order although the burning time is slower when compared to untreated fiber. Further, fibers treated with a 2.0% solution of NaOH and then a 2.0% suspension of MMT clay are not self-extinguishing but the burning time is slower when compared to untreated fiber.

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Table 11 - Fibers Treated with NaOH and CaCl₂ or NaOH and Clay

| Sample | Description | Burning Length (inches) | | | | | | | | |
|------------|--|-------------------------|-----|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-31/P2-2 | (C2+NaOH) then add CaCl ₂ | G 125 | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-32/P2-2 | (C2+CaCl ₂) then add NaOH | 4.4 | 8.4 | 12.6 | 15.2 | 17.8 | 20.6 | 22.6 | 25.0 | 28.0 |
| C2-33/P2-2 | C2+(NaOH)2% then add clay MMT2% | 4.1 | 7.6 | 10.6 | 13.5 | 16.6 | 19.9 | 22.9 | 25.7 | 29.0 |

C2 Fibers Treated with Different Aluminum-containing Bi-component Systems

Belgium flax fiber samples C2 as described in Table 2 were treated with aluminum chloride-containing bi-component systems at different concentrations (0.75-2 wt%) of the hydroxide product of the aluminum salt and hydroxide as indicated in Table 12 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 12. It is evident from Table 12 that aluminum chloride together with ammonium hydroxide at a concentration of 0.75% or more resulted in fibers that were self-extinguishing, but this is not the case with aluminum chloride with sodium hydroxide, although the rate of burning was slowed relative to untreated fibers.

Table 12 - Fibers Treated with Aluminum-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|---|-------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-34/P1 | C2+ (AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-35/P1 | C2+ (AlCl ₃ +NH ₄ OH)1.5% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-36/P1 | C2+ (AlCl ₃ +NH ₄ OH)1.0% | G | NB |
| C2-37/P1 | C2+ (AlCl ₃ +NH ₄ OH)0.75% | G 7.9 | NB |
| C2-38/P1 | C2+ (AlCl ₃ +NaOH)0.5% | 3.2 | 6.7 | 11.1 | NB/B | NB/B | NB/B | NB/B | NB/B | NB/B |
| C2-39/P1 | C2+ (AlCl ₃ +NaOH)2% | 6.7 | 12.9 | 16.9 | 20.4 | 24.6 | 28.7 | 32.7 | 36.4 | 40.0 |

C2 Fibers Treated with Bi-component Systems Containing Different Magnesium and Calcium Salts

Belgium flax fiber samples C2 as described in Table 2 were treated with bi-component systems containing different magnesium and calcium salts at 2 wt% of the hydroxide product of the alkaline earth metal salt and hydroxide as indicated in Table 13 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 13. It is evident from Table 13 that fibers treated with $(\text{MgCl}_2+\text{NaOH})2\%$ and with $(\text{CaCl}_2+\text{NaOH})2\%$ are self-extinguishing. Fibers treated with $(\text{Mg}(\text{NO}_3)_2+\text{NaOH})2\%$ and with $(\text{Ca}(\text{NO}_3)_2+\text{NaOH})2\%$ did not burn but continued to glow. Fibers treated with $(\text{MgSO}_4+\text{NaOH})2\%$ continued to burn, but at a slower rate than untreated fibers. The efficiency of the $(\text{MgCl}_2+\text{NaOH})2\%$ system is greater than the $(\text{Mg}(\text{NO}_3)_2+\text{NaOH})2\%$ system, which is greater than the $(\text{MgSO}_4+\text{NaOH})2\%$ system. This is also similar for the calcium-containing systems where the efficiency of the $(\text{CaCl}_2+\text{NaOH})2\%$ system is greater than the $(\text{Ca}(\text{NO}_3)_2+\text{NaOH})2\%$ system. Thus, chloride is the most preferred counter anion for the alkaline earth metal cation.

Table 13 - Fibers Treated with Mg- and Ca-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|--|-------------------------|------|------|------|------|------|------|------|------------------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-30/P1 | C2+ $(\text{MgCl}_2+\text{NaOH})2\%$ | 7.0 | 14.0 | NB |
| C2-40/P1 | C2+ $(\text{Mg}(\text{NO}_3)_2+\text{NaOH})2\%$ | G | G | G | G | G | G | G | G | G 180- 260 |
| C2-28/P1 | C2+ $(\text{MgSO}_4+\text{NaOH})2\%$ | 5.1 | 10.6 | 14.6 | 19.5 | 24.7 | 29.5 | 33.7 | 38.7 | 43.4 |
| C2-21/P1 | C2+ $(\text{CaCl}_2+\text{NaOH})2\%$ | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C2-41/P1 | C2+ $(\text{Ca}(\text{NO}_3)_2+\text{NaOH})2\%$ | G | G | G | G | G | G | G | G | G 50- 300 |

Different Fibers Treated with a Calcium-containing Bi-component Systems

Various fiber samples C2, C3, C4 and C7 as described in Table 2 were treated with a calcium-containing bi-component systems as indicated in Table 14 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure 5 described in Example 4 and the results from the burning tests are also shown in Table 14. It is evident from Table 14 that all of the fibers were self-extinguishing after treatment with the (CaCl₂+NaOH)2% system.

Table 14 - Different Fibers Treated with a Calcium-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|--------------------------------|--|------------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-21/P1 | C2+(CaCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C3 | Untreated C3 | 4.6 | 8.5 | 12.0 | 15.5 | 19.0 | 22.9 | 26.6 | 30.2 | 34.1 |
| C3-1/P1 | C3+(CaCl ₂ +NaOH)2% | G 20-85 | G 20-85 | NB |
| C4 | Untreated C4 | Burned fast and whole sample was fired | | | | | | | | 12 |
| C4-1/P1 | C4+(CaCl ₂ +NaOH)2% | NB-G 10-15 | NB | NB | NB | NB | NB | NB | NB | NB |
| C7 | Untreated C7 | 2.9 | 5.7 | 8.0 | 10.0 | 12.4 | 14.8 | 17.2 | 19.6 | 22.6 |
| C7-1/P1 | C7+(CaCl ₂ +NaOH)2% | G 25-80 | NB | NB | NB | NB | NB | NB | NB | NB |

10 *Different Fibers Treated with a Magnesium-containing Bi-component Systems*

Various fiber samples C2, C3, C4, C6 and C7 as described in Table 2 were treated with a magnesium-containing bi-component systems as indicated in Table 15 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown 15 in Table 15. It is evident from Table 15 that all of the fibers were self-extinguishing after treatment with the (MgCl₂+NaOH)2% system. Taken together, Tables 14 and 15 show that the treatments are useful across a range of cellulosic materials.

Table 15 - Different Fibers Treated with a Magnesium-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|------------------------------------|--------------------------------------|------|------|------|------|------|------|------|------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-30/P1 | C2+ (MgCl ₂ +NaOH)2% | 7.0 | 14.0 | NB |
| C3 | Untreated C3 | 4.6 | 8.5 | 12.0 | 15.5 | 19.0 | 22.9 | 26.6 | 30.2 | 34.1 |
| C3-2/P1 | C3+ (MgCl ₂ +NaOH)2% | G 80-110 | NB |
| C4 | Untreated C4 | Burn fast and whole sample was fired | | | | | | | | 12 |
| C4-2/P1 | C4+ (MgCl ₂ +NaOH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C6 | Untreated C6 | 2.6 | 4.8 | 6.7 | 8.4 | 10.3 | 12.0 | 13.9 | 15.6 | 18.0 |
| C6-2/P1 | C6+ (MgCl ₂ +NaOH)2% | G 35-215 | NB |
| C7 | Untreated C7 | 2.9 | 5.7 | 8.0 | 10.0 | 12.4 | 14.8 | 17.2 | 19.6 | 22.6 |
| C7-2/P1 | C7+ (MgCl ₂ +NaOH)2% | G 20-70 | NB |

Different Fibers Treated with an Aluminum-containing Bi-component Systems

Various fiber samples C2-C11 as described in Table 2 were treated with an aluminum-containing bi-component systems as indicated in Table 16 for 120 s using the process P1. Burning tests were conducted in accordance with the general procedure described in Example 4 and the results from the burning tests are also shown in Table 16. It is evident from Table 16 that all of the fibers were self-extinguishing after treatment with the (AlCl₃+NH₄OH)2% system. Taken together, Tables 14, 15 and 16 show that the treatments are useful across a range of cellulose materials.

Table 16 - Different Fibers Treated with an Aluminum-containing Bi-component Systems

| Sample | Description | Burning Length (inches) | | | | | | | | |
|----------|---|--------------------------------------|-----|------|------|------|------|------|------|-------|
| | | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 |
| | | Burning Time (seconds) | | | | | | | | |
| C2 | Untreated C2 | 2.8 | 5.4 | 7.6 | 10.1 | 12.6 | 15.2 | 17.6 | 20.1 | 22.5 |
| C2-34/P1 | C2+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C3 | Untreated C3 | 4.6 | 8.5 | 12.0 | 15.5 | 19.0 | 22.9 | 26.6 | 30.2 | 34.1 |
| C3-3/P1 | C3+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C4 | Untreated C4 | Burn fast and whole sample was fired | | | | | | | | 12 |
| C4-3/P1 | C4+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C5 | Untreated C5 | Whole sample was fired | | | | | | | | 40 |
| C5-3/P1 | C5+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C6 | Untreated C6 | 2.6 | 4.8 | 6.7 | 8.4 | 10.3 | 12.0 | 13.9 | 15.6 | 18.0 |
| C6-3/P1 | C6+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C7 | Untreated C7 | 2.9 | 5.7 | 8.0 | 10.0 | 12.4 | 14.8 | 17.2 | 19.6 | 22.6 |
| C7-3/P1 | C7+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C8 | Untreated C8 | Burn fast and whole sample was fired | | | | | | | | 10-15 |
| C8-3/P1 | C8+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C9 | Untreated C9 | 1.9 | 3.7 | 5.4 | 6.8 | 8.5 | 10.2 | 11.8 | 13.0 | 14.2 |
| C9-3/P1 | C9+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C10 | Untreated C10 | Burn fast and whole sample was fired | | | | | | | | 7.6 |
| C10-3/P1 | C10+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |
| C11 | Untreated C11 | 4.5 | 9.7 | 15.3 | 20.7 | 26.3 | 31.8 | 38.2 | 43.3 | 48.7 |
| C11-3/P1 | C11+(AlCl ₃ +NH ₄ OH)2% | NB | NB | NB | NB | NB | NB | NB | NB | NB |

Example 8: Tensile Properties of Fiber Tows

Tensile properties of untreated Belgium flax fiber samples C2 as described in
5 Table 2 and of various treated C2 fiber samples were measured in accordance with the procedure described in Example 5. Table 16 lists the fiber tows that were tested as well

as their tensile properties. The tows in the longitudinal direction in the fabric are denoted as parallel, whereas the ones in the orthogonal direction are denoted as perpendicular.

It is evident from Table 17 that the tensile properties did not change much for most of the systems indicating that treatment did not generally have a detrimental effect 5 on tensile properties. However, for fibers treated with alkali metal hydroxide alone (e.g. (KOH)2% and (NaOH)2%) or treated with aluminum-containing salt (e.g. (AlCl₃+NH₄OH)2%), there is a significant loss in tensile properties. It is clear, therefore, that cellulosic materials treated with both alkaline earth metal salt and alkali metal hydroxide are advantageously very fire retardant, often self-extinguishing, while retaining 10 good tensile properties, in contrast to fibers treated only with alkali metal hydroxide or treated with another metal salt. Drying at lower temperature of 100°C could help to maintain the tensile properties of the fiber treated with (AlCl₃+NH₄OH)2%).

Table 17 – Tensile Strength of Tows of Treated C2 Fibers

| Fiber | Description | Tensile Properties | |
|--------------------------|---|--------------------|---------------|
| | | Parallel | Perpendicular |
| C2 | Untreated C2 | 20.4 ± 3.3 | 23.8 ± 4.1 |
| C2-1/P1 | C2+(Ba(OH) ₂)2% | 21.7 ± 3.2 | 24.1 ± 4.4 |
| C2-2/P1 | C2+(BaCl ₂)2% | 21.1 ± 3.1 | 25.1 ± 2.9 |
| C2-7/P1 | C2+Mg((OH) ₂)2% | 19.2 ± 3.4 | 23.6 ± 2.7 |
| C2-10/P1 | C2+(KOH)2% | 15.8 ± 2.1 | 20.2 ± 2.9 |
| C2-11/P1 | C2+(NaOH)2% | 15.8 ± 1.4 | 19.0 ± 2.6 |
| C2-13/P1 | C2+(NaOH)2% then washed with water | 13.2 ± 1.9 | 18.4 ± 4.8 |
| C2-15/P1 | C2+(Al(OH) ₃)2% | 22.8 ± 1.8 | 23.6 ± 2.7 |
| C2-21/P1 | C2+(CaCl ₂ +NaOH)2% | 19.5 ± 3.4 | 24.9 ± 3.1 |
| C2-28/P1 | C2+(MgSO ₄ +NaOH)2% | 23.0 ± 3.6 | 25.8 ± 3.3 |
| C2-30/P1 | C2+(MgCl ₂ +NaOH)2% | 21.3 ± 3.2 | 23.7 ± 3.2 |
| C2-31/P2-2 | (C2+NaOH) then add CaCl ₂ | 23.0 ± 2.6 | 27.4 ± 3.9 |
| C2-32/P2-2 | (C2+CaCl ₂) then add NaOH | 22.4 ± 3.2 | 24.2 ± 3.4 |
| C2-34/P1 | C2+(AlCl ₃ +NH ₄ OH)2% | 16.9 ± 1.6 | 16.0 ± 1.5 |
| C2-34/P1 dry at 100°C | C2+(AlCl ₃ +NH ₄ OH)2% dried at 100°C | 24.1 ± 0.6 | 24.1 ± 5.9 |
| C2-40/P1 | C2+(Mg(NO ₃) ₂ +NaOH)2% | 23.8 ± 3.5 | 25.5 ± 4.7 |
| C2-41/P1 | C2+(Ca(NO ₃) ₂ +NaOH)2% | 24.4 ± 3.8 | 24.8 ± 3.9 |

*Example 9: Properties of Fire-resistant Flax Fiber/Polymer Composites**Phenol formaldehyde (PF)/flax fiber composites*

Phenol formaldehyde/flax fiber composites were prepared as indicated in Table 18 in accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 60% and 40% by weight, respectively. UL94 vertical burning tests were conducted in accordance with the procedure described in Example 4, and the results are shown in Table 18. Sample PF-C1 is a comparative example of a PF composite containing untreated flax fiber. PF-C1-1/P1 and PF-C1-3/P1 are comparative examples of PF composites containing flax fibers treated two different clays. PF-C1-11/P1 is an example of a PF composite of the present invention containing flax fibers treated with a bi-component barium-containing system. PF-C1-13/P2-1 is an example of a PF composite of the present invention containing flax fibers treated with a bi-component barium-containing system and then clay.

In this example, burning time is the time it takes for the sample to self-extinguish after the external flame is removed. Thus, a shorter burning time is indicative of a more fire resistant sample. Phenol formaldehyde is a phenolic thermoset resin which itself has considerable resistance to fire. Because of the fire resistance of phenol formaldehyde, it is the flax fiber that primarily burns during the burning test. As is evident from Table 18, fire-resistant flax fibers of the present invention provide a tremendously significant greater resistance to burning in the phenol formaldehyde matrix than untreated flax fibers or flax fibers treated just with clays. The fire-resistance effect is particularly pronounced when the flax fibers are treated with both an aqueous mixture of BaCl₂ and NaOH and an aqueous suspension of clay (PF-C1-13/P2-1).

Table 18 - Phenol Formaldehyde/Flax Fiber Composites

| Sample | Composition | Burn Time (s) 5 inch length |
|---------------|--|--------------------------------|
| PF-C1 | Phenol formaldehyde matrix Flax fabric C1 (untreated) | 118 |
| PF-C1-1/P1 | Phenol formaldehyde matrix Flax fabric C1-1/P1 (C1+clay MMT2%) | 119 |
| PF-C1-3/P1 | Phenol formaldehyde matrix Flax fabric C1-3/P1 (C1+clay LDH2%) | 101 |
| PF-C1-11/P1 | Phenol formaldehyde matrix Flax fabric C1-11/P1 (C1+(BaCl ₂ +NaOH)2%) | 74 |
| PF-C1-13/P2-1 | Phenol formaldehyde matrix Flax fabric C1-13/P2-1 (C1+(BaCl ₂ +NaOH)2%+clay MMT2%) | 10 |

Mechanical properties of the phenol formaldehyde/flax fiber composite samples are shown in Table 19. It is evident from Table 19 that PF composites containing fibers treated in accordance with the present invention have good mechanical properties. However, due to impregnation difficulties during the preparation of the composites, it is 5 difficult to draw completely accurate conclusions about the mechanical properties of the samples listed in Table 19. Once the impregnation difficulties are resolved, the mechanical properties of composites containing fire-resistant fibers of the present invention are expected to improve.

Table 19 –Mechanical Properties of Phenol Formaldehyde/Flax Fiber Composites

| Sample | Young Modulus (GPa) | Tensile Strength (MPa) | Strain at max load (%) | Energy to break point (J) | Density (g/cm ³) |
|---------------|---------------------|------------------------|------------------------|---------------------------|------------------------------|
| PF-C1 | 9.20 (0.38) | 95.66 (10.59) | 2.90 (0.70) | 6.63 (2.17) | 1.563 (0.022) |
| PF-C1-1/P1 | 7.89 (0.27) | 70.81 (1.57) | 4.03 (0.23) | 8.45 (0.69) | 1.494 (0.005) |
| PF-C1-3/P1 | 10.46 (0.28) | 87.71 (4.64) | 1.88 (0.35) | 4.15 (1.08) | 1.442 (0.002) |
| PF-C1-11/P1 | 9.20 (1.98) | 77.36 (5.09) | 2.15 (0.52) | 4.33 (1.05) | 1.387 (0.001) |
| PF-C1-13/P2-1 | 6.25 (0.66) | 66.67 (1.42) | 3.22 (0.29) | 5.67 (0.64) | 1.473 (0.010) |

10

Phenol formaldehyde/flax fiber composites were prepared another time as indicated in Table 20 in accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 60% and 40% by weight, respectively. Vertical VC-2 burning tests were conducted in accordance with the procedure described in 15 Example 4, and the results are shown in Table 20. Sample PF-C2 is a comparative example of a PF composite containing untreated flax fiber. PF-C2-34/P2-2% and PF-C2-34/P2-23% are examples of PF composites of the present invention containing flax fibers treated with a bi-component aluminum-containing system at 2 and 3%.

In this example, burning time is the time it takes for the sample to self-extinguish 20 after the external flame is removed. Thus, a shorter burning time is indicative of a more fire resistant sample. Phenol formaldehyde is a phenolic thermoset resin which itself has considerable resistance to fire. Because of the fire resistance of phenol formaldehyde, it is the flax fiber that primarily burns during the burning test. As is evident from Table 20, fire-resistant flax fibers of the present invention provide a tremendously significant greater 25 resistance to burning in the phenol formaldehyde matrix than untreated flax fibers that allows the obtained composites with the treated flax fibers to be classified as self-extinguished.

Table 20 - Phenol Formaldehyde/Flax Fiber Composites

| Sample | Composition | Max flame time (s) | Max burn length (inches) | Glow | Pass VC-2 test |
|-----------------|---|--------------------|--------------------------|------|----------------|
| PF-C2 | Phenol formaldehyde matrix Flax fabric C2 (untreated) | 35.8 ± 8.2 | 1.3 ± 0.1 | No | No |
| PF- C2-34/P1-2% | Phenol formaldehyde matrix Flax fabric C2-34/P1-2% (C2+(AlCl ₃ +NH ₄ OH)2%) | 7. 5± 5.6 | 0.5 ± 0.1 | No | Yes |
| PF- C2-34/P1-3% | Phenol formaldehyde matrix Flax fabric C2-34/P1-3% (C2+(AlCl ₃ +NH ₄ OH)3%) | 2.1 ± 2.4 | 0.2 ± 0.1 | No | Yes |

Mechanical properties of the phenol formaldehyde/flax fiber composite samples are shown in Table 21. It is evident from Table 21 that PF composites containing fibers
5 treated with a bi-component aluminum-containing system at 2% in accordance with the present invention have comparable flexural properties with the reference. However, due to impregnation difficulties during the preparation of the composite containing fibers treated with a bi-component aluminum-containing system at 3%, the flexural strength of this sample reduced.

10 Table 21 -Mechanical Properties of Phenol Formaldehyde/Flax Fiber Composites

| Sample | Composition | Flexural strength (MPa) | Flexural modulus (GPa) |
|-----------------|---|-------------------------|------------------------|
| PF-C2 | Phenol formaldehyde matrix Flax fabric C2 (untreated) | 129.8 ± 8.2 | 10.2 ± 0.3 |
| PF- C2-34/P1-2% | Phenol formaldehyde matrix Flax fabric C2-34/P1-2% (C2+(AlCl ₃ +NH ₄ OH)2%) | 118.1± 4.2 | 10.1 ± 0.8 |
| PF- C2-34/P1-3% | Phenol formaldehyde matrix Flax fabric C2-34/P1-3% (C2+(AlCl ₃ +NH ₄ OH)3%) | 65.9 ± 2.6 | 9.5 ± 0.3 |

Polypropylene (PP)/flax fiber composites

Polypropylene/flax fiber composites were prepared as indicated in Table 22 in
15 accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 60% and 40% by weight, respectively. Sample PP-C1 is a comparative example of a PP composite containing untreated flax fiber. PP-C1-3/P1 is a comparative example of PP composite containing flax fibers treated only with LDH clay. PP-C1-6/P1 is a comparative example of a PP composite containing flax fibers treated only with Ba(OH)₂. PP-C1-10/P2-1 is a comparative example of a PP composite containing flax fibers treated with Ba(OH)₂ and then LDH clay. PP-C1-11/P1 is an example of a PP composite of the present invention containing flax fibers treated with a bi-component barium-containing system. PP-C1-13/P2-1 is an example of a PP

composite of the present invention containing flax fibers treated with a bi-component barium-containing system and then MMT clay. PP-C1-14/P2-1 is an example of a PP composite of the present invention containing flax fibers treated with a bi-component barium-containing system and then LDH clay. Horizontal burning tests were conducted in 5 accordance with the procedure described in Example 4, and the results are shown in Table 23. Burning time represents the amount of time it took for the sample to burn the stated length. Thus, a longer time to burn a given length is an indication of better fire resistance. It is evident from Table 23 that the fire-resistant flax fibers of the present invention have less effect on the fire resistance of a polypropylene composite as 10 compared to a phenol formaldehyde composite (see Table 18). This is likely due to the fact that polypropylene itself is highly flammable, thus the matrix burns in any event. However, the inclusion of clay in the polypropylene/flax fiber composite of the present invention does offer a marked improvement over composites having fire-resistant flax fibers of the present invention but not including clay, and over composites having clay 15 and regular flax fibers.

Table 22 - Composition of Polypropylene/Flax Fiber Composites

| Sample | Composition |
|---------------|--|
| PP-C1 | Polypropylene matrix Flax fabric C1 (untreated) |
| PP-C1-3/P1 | Polypropylene matrix Flax fabric C1-3/P1 (C1+clay LDH2%) |
| PP-C1-6/P1 | Polypropylene matrix Flax fabric C1-6/P1 (C1+Ba(OH) ₂ 2%) |
| PP-C1-10/P2-1 | Polypropylene matrix Flax fabric C1-10/P2-1 (C1+Ba(OH) ₂ 2%+clayLDH2%) |
| PP-C1-11/P1 | Polypropylene matrix Flax fabric C1-11/P1 (C1+(BaCl ₂ +NaOH)2%) |
| PP-C1-13/P2-1 | Polypropylene matrix Flax fabric C1-13/P2-1 (C1+(BaCl ₂ +NaOH)2%+clay MMT2%) |
| PP-C1-14/P2-1 | Polypropylene matrix Flax fabric C1-13/P2-1 (C1+(BaCl ₂ +NaOH)2%+clay LDH2%) |

Table 23 - Burning Tests on Polypropylene/Flax Fiber Composites

| Sample | Burning length (inches) | | | | | |
|---------------|-------------------------|-----|-----|-----|-----|-----|
| | 0.0 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| | Burning Time (seconds) | | | | | |
| PP-C1 | 0 | 103 | 186 | 263 | 344 | 382 |
| PP-C1-3/P1 | 0 | 112 | 190 | 270 | 351 | 399 |
| PP-C1-6/P1 | 0 | 117 | 186 | 255 | 332 | 370 |
| PP-C1-10/P2-1 | 0 | 108 | 174 | 246 | 322 | 365 |
| PP-C1-11/P1 | 0 | 103 | 182 | 268 | 351 | 369 |
| PP-C1-13/P2-1 | 0 | 125 | 201 | 276 | 352 | 386 |
| PP-C1-14/P2-1 | 0 | 147 | 230 | 313 | 409 | 446 |

Mechanical properties of the polypropylene/flax fiber composite samples are shown in Fig. 1A (flexural modulus) and Fig. 1B (flexural strength). It is evident from Fig.

5 1A and Fig. 1B that polypropylene composites containing flax fibers treated in accordance with the present invention have significantly better flexural modulus than the comparative samples, while maintaining a flexural strength that is at least as good as the comparative samples.

Epoxy/flax fiber composites

10 Epoxy/flax fiber composites were prepared as indicated in Table 24 in accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 60% and 40% by weight, respectively. Sample Epo-C2 is a comparative example of an epoxy composite containing untreated flax fiber. Epo-C2-34/P1 is a comparative example of epoxy composite containing flax fibers treated only with a bi-component aluminum-containing system at 2%. Epo-C2-34-Clay/P2 is a comparative example of epoxy composite containing flax fibers treated only with a bi-component aluminum-containing system at 2% and then MMT clay. Horizontal burning tests were conducted in accordance with the procedure described in Example 4, and the results are shown in Table 25. Burning time represents the amount of time it took for the sample to burn the stated length. Thus, a longer time to burn a given length is an indication of better fire resistance. It is evident from Table 25 that the fire-resistant flax fibers of the present invention have stopped the composites from burning. Mechanical properties of the epoxy/flax fiber composite samples are shown in Table 26. It is evident from Table 26 that epoxy composites containing flax fibers treated in accordance with the present invention have very slightly reduction in tensile strength and modulus than the

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comparative samples, while improving the energy to break which represents the composite toughness.

Table 24 - Composition of Epoxy/Flax Fiber Composites

| Sample | Composition |
|-------------------|--|
| Epo-C2 | Epoxy matrix Flax fabric C2 (untreated) |
| Epo-C2-34/P1 | Epoxy matrix Flax fabric C2-34/P1 (C2+(AlCl ₃ +NH ₄ OH)2%) |
| Epo-C2-34-Clay/P2 | Epoxy matrix Flax fabric C2-34/P1 (C2+(AlCl ₃ +NH ₄ OH)2%+clay MMT2%) |

5

Table 25 - Burning Tests on Epoxy/Flax Fiber Composites

| Sample | Burning length (inches) | | | | | |
|-------------------|-------------------------|-----|-----|-----|-----|-----|
| | 0.0 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| | Burning Time (seconds) | | | | | |
| Epo-C2 | 0 | 111 | - | - | 425 | 542 |
| Epo-C2-34/P1 | 0 | NB | NB | NB | NB | NB |
| Epo-C2-34-Clay/P2 | 0 | NB | NB | NB | NB | NB |

Table 26 - Mechanical Properties of Epoxy/Flax Fiber Composites

| Sample | Tensile stress (MPa) | Tensile modulus (GPa) | Energy to break (J) |
|-------------------|----------------------|-----------------------|---------------------|
| EPO-C2 | 117.7 ± 4.0 | 9.8±0.6 | 33.7±2.0 |
| Epo-C2-34/P1 | 106.4 ± 1.0 | 7.2±0.3 | 36.7±2.6 |
| Epo-C2-34-Clay/P2 | 103.7 ± 4.2 | 8.4±0.2 | 36.7±2.6 |

Unsaturated polyester/flax fiber composites

10 UPE/flax fiber composites were prepared as indicated in Table 27 in accordance with the procedure described in Example 3. The resin (matrix) and fiber in composites are about 70% and 30% by weight, respectively. Sample UPE-C2 is a comparative example of an epoxy composite containing untreated flax fiber. UPE-C2-34/P1 is a comparative example of epoxy composite containing flax fibers treated only with a bi-component aluminum-containing system at 2%. Horizontal burning tests were conducted in accordance with the procedure described in Example 4, and the results are shown in Table 28. Burning time represents the amount of time it took for the sample to burn the

15

stated length. Thus, a longer time to burn a given length is an indication of better fire resistance. It is evident from Table 28 that the fire-resistant flax fibers of the present invention have stopped the composites from burning.

Table 27 - Composition of UPE/Flax Fiber Composites

| Sample | Composition |
|--------------|---|
| UPE-C2 | UPE matrix Flax fabric C2 (untreated) |
| UPE-C2-34/P1 | UPE matrix Flax fabric C2-34/P1 (C2+(AlCl ₃ +NH ₄ OH)2%) |

5

Table 28 - Burning Tests on UPE/Flax Fiber Composites

| Sample | Burning length (inches) | | | | | |
|--------------|-------------------------|-----|-----|-----|-----|-----|
| | 0.0 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| | Burning Time (seconds) | | | | | |
| UPE-C2 | 0 | 114 | - | - | 421 | 522 |
| UPE-C2-34/P1 | 0 | NB | NB | NB | NB | NB |

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20 Other advantages that are inherent to the structure are obvious to one skilled in the art. The embodiments are described herein illustratively and are not meant to limit the scope of the invention as claimed. Variations of the foregoing embodiments will be evident to a person of ordinary skill and are intended by the inventor to be encompassed by the following claims.

Claims:

1. A process of producing a fire-resistant cellulosic material comprising: treating a cellulosic material with an aqueous reaction mixture of an alkali metal or ammonium hydroxide and an alkaline earth or aluminum metal salt, wherein the treating is done

5 simultaneously with or within a short period of time of mixing the alkali metal or ammonium hydroxide and alkaline earth or aluminum metal salt; and, drying the treated cellulosic material.

2. The process according to claim 1, wherein the alkaline earth or aluminum metal salt comprises alkaline earth metal salt.

10 3. The process according to claim 2, wherein the alkaline earth metal salt comprises magnesium or calcium.

4. The process according to any one of claims 2 to 3, wherein the alkaline earth metal salt is a chloride, a fluoride, a bromide, an iodide or a nitrate.

15 5. The process according to claim 2, wherein the alkaline earth metal salt is calcium or magnesium chloride.

6. The process according to claim 1, wherein the alkaline earth or aluminum metal salt comprises aluminum chloride.

7. The process according to any one of claims 1 to 6, wherein the hydroxide is an alkali metal hydroxide.

20 8. The process according to any one of claims 1 to 6, wherein the hydroxide is NaOH.

9. The process according to any one of claims 1 to 6, wherein the hydroxide is NH₄OH.

25 10. The process according to claim 1, wherein the hydroxide is NH₄OH and the metal salt is AlCl₃.

11. The process according to any one of claims 1 to 10, wherein the aqueous reaction mixture utilizes 0.5-10 wt% of the alkaline earth or aluminum metal salt and 0.5-4 wt% of the alkali metal or ammonium hydroxide, and wherein a product of the reaction of the alkaline earth or aluminum metal salt and the alkali metal or ammonium hydroxide is present in an amount of 0.5 wt% or more.

12. The process according to any one of claims 1 to 11, wherein the short period of time is 1 day or less.

13. The process according to any one of claims 1 to 11, wherein the short period of time is 5 seconds to 5 hours.

5 14. The process according to any one of claims 1 to 11, wherein the short period of time is 5 seconds to 30 minutes.

15. The process according to any one of claims 1 to 11, wherein the short period of time is 5 seconds to 10 minutes.

10 16. The process according to any one of claims 1 to 11, wherein the short period of time is from 1 minute to 5 hours.

17. The process according to any one of claims 1 to 16, wherein the cellulosic material is fibrous.

15 18. The process according to any one of claims 1 to 17, wherein the cellulosic material comprises material from wood sources, agricultural sources, synthetic sources, recycled paper or recycled cardboard.

19. The process according to any one of claims 1 to 18, wherein the cellulosic material is further treated with a layered nanoparticulate material before, at the same time or after treating with the aqueous reaction mixture.

20. The process according to claim 19, wherein treating with the layered nanoparticulate material is done after treating with the aqueous reaction mixture.

21. The process according to any one of claims 19 to 20, wherein the layered nanoparticulate material comprises a layered clay.

25 22. The process according to any one of claims 19 to 20, wherein the layered nanoparticulate material comprises a layered double hydroxide, montmorillonite, sepiolite, palygorskite, bentonite, fluoromica or a mixture thereof.

23. The process according to any one of claims 19 to 20, wherein the layered nanoparticulate material comprises a layered double hydroxide, montmorillonite or a mixture thereof.

24. A fire-resistant cellulosic material produced by the process as defined in any one of claims 1 to 23.

25. The fire-resistant cellulosic material according to claim 24 which is self-extinguishing.

5 26. A polymer composite comprising a polymer matrix and the fire-resistant cellulosic material as defined in claim 24 or 25 dispersed in the polymer matrix.

27. The polymer composite according to claim 26, wherein the polymer matrix comprises an organic polymer.

10 28. The polymer composite according to claim 26, wherein the polymer matrix comprises a thermoset resin.

29. The polymer composite according to claim 26, wherein the polymer matrix comprises a polyolefin or a phenolic resin.

30. The polymer composite according to claim 26, wherein the polymer matrix comprises a polypropylene or a phenol formaldehyde.

15 31. The polymer composite according to claim 26, wherein the polymer matrix comprises an unsaturated polyester or an epoxy polymer.

32. The polymer composite according to any one of claims 26 to 31 further comprising a surfactant for improving compatibility of the fire-resistant cellulosic material with the polymer matrix.

20 33. The polymer composite according to claim 32, wherein the surfactant comprises an amine, a di-functional amine, a poly-functional amine, an alkanolamine, an acid, a carboxylate or any mixture thereof.

34. The polymer composite according to any one of claims 26 to 32, wherein the polymer matrix is present in an amount from about 0.1 to about 99.9 weight percent
25 based on total weight of the polymer composite.

35. The polymer composite according to any one of claims 26 to 32, wherein the polymer matrix is present in an amount from about 40 to about 98 weight percent based on total weight of the polymer composite.

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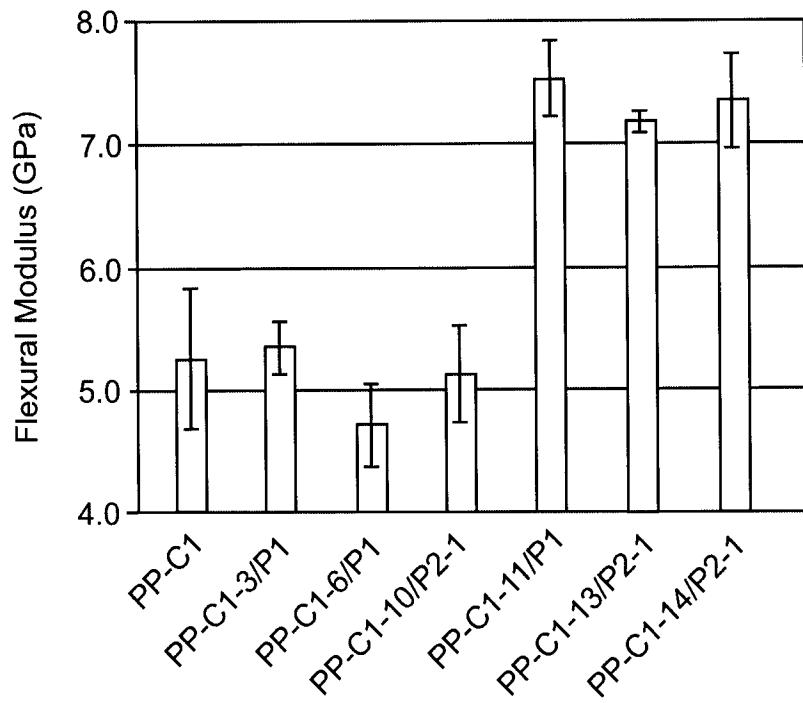


Fig. 1A

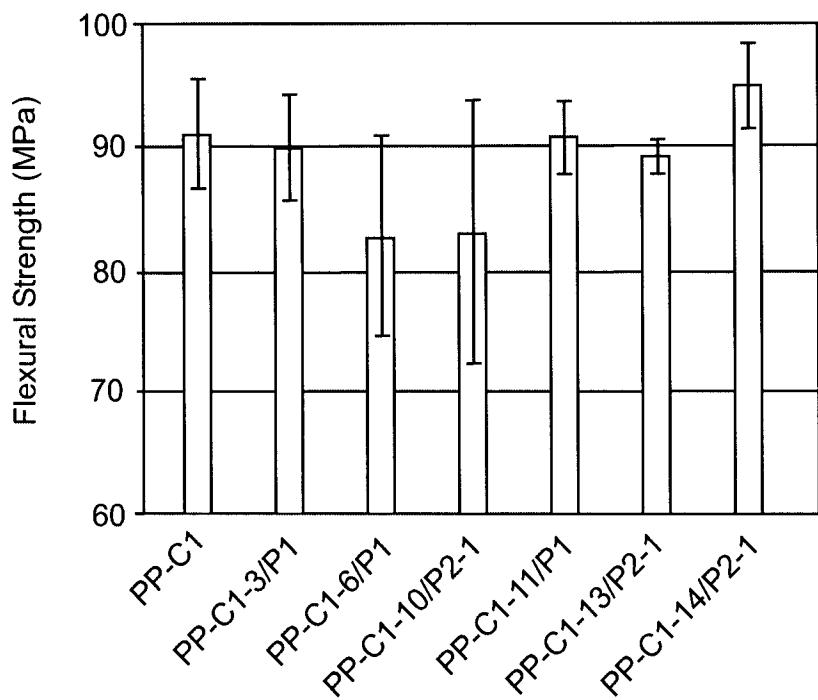


Fig. 1B



US 20130130049A1

(19) United States

(12) Patent Application Publication

Moilanen et al.

(10) Pub. No.: US 2013/0130049 A1

(43) Pub. Date: May 23, 2013

(54) FABRICATION AND APPLICATION OF POLYMER-GRAFHTIC MATERIAL NANOCOMPOSITES AND HYBRIDE MATERIALS

(76) Inventors: Pasi Moilanen, Jyvaskyla (FI); Jorma A. Virtanen, Las Vegas, NV (US)

(21) Appl. No.: 13/518,781

(22) PCT Filed: Dec. 22, 2010

(86) PCT No.: PCT/FI10/00077

§ 371 (c)(1),
(2), (4) Date: Jun. 22, 2012

(30) Foreign Application Priority Data

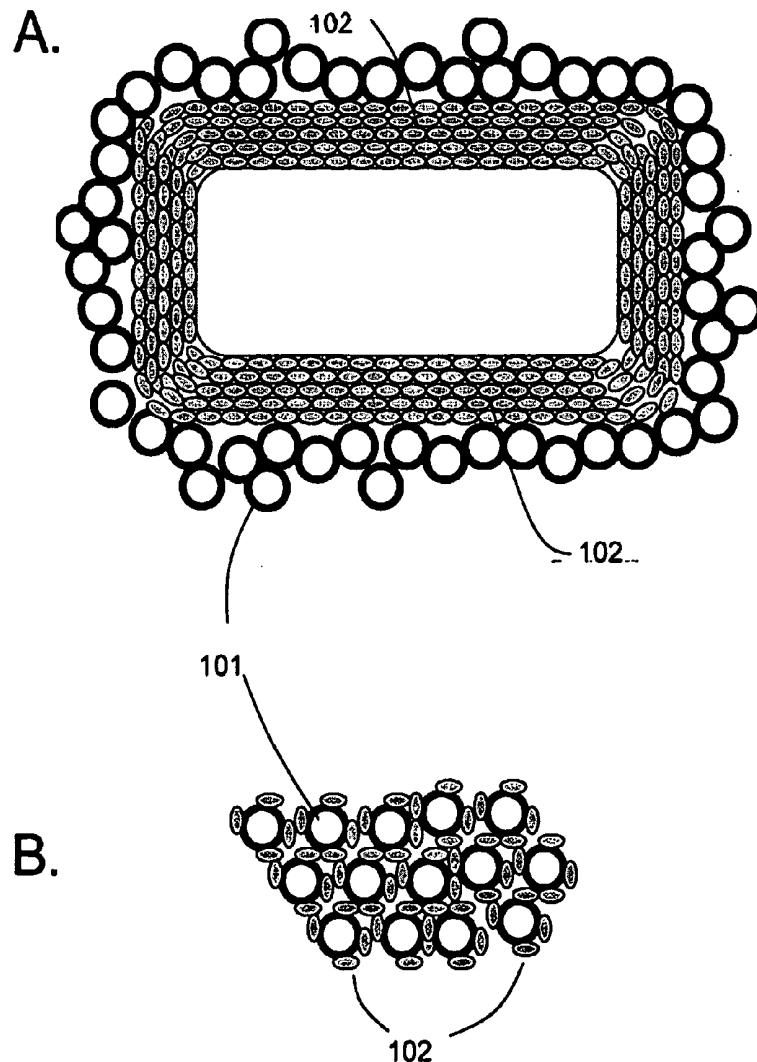
Dec. 22, 2009 (FI) 20090495
Apr. 9, 2010 (FI) 20100143
Oct. 18, 2010 (FI) 20106077

Publication Classification

(51) Int. Cl.
H01G 9/042 (2006.01)
H01G 9/00 (2006.01)
(52) U.S. Cl.
CPC *H01G 9/042* (2013.01); *H01G 9/155* (2013.01)
USPC 428/532; 252/509; 252/62.51R; 361/502

(57) ABSTRACT

The present invention describes a nanocomposite and hybride material of functionalized carbon nanotubes and cellulose and associated methods for the fabrication of that nanocomposite or hybride material containing electromagnetically active nanoparticles. The fabrication is fast, environmentally friendly, and economical. These nanocomposites are strong and electrically conducting, and have many materials and electronic applications.



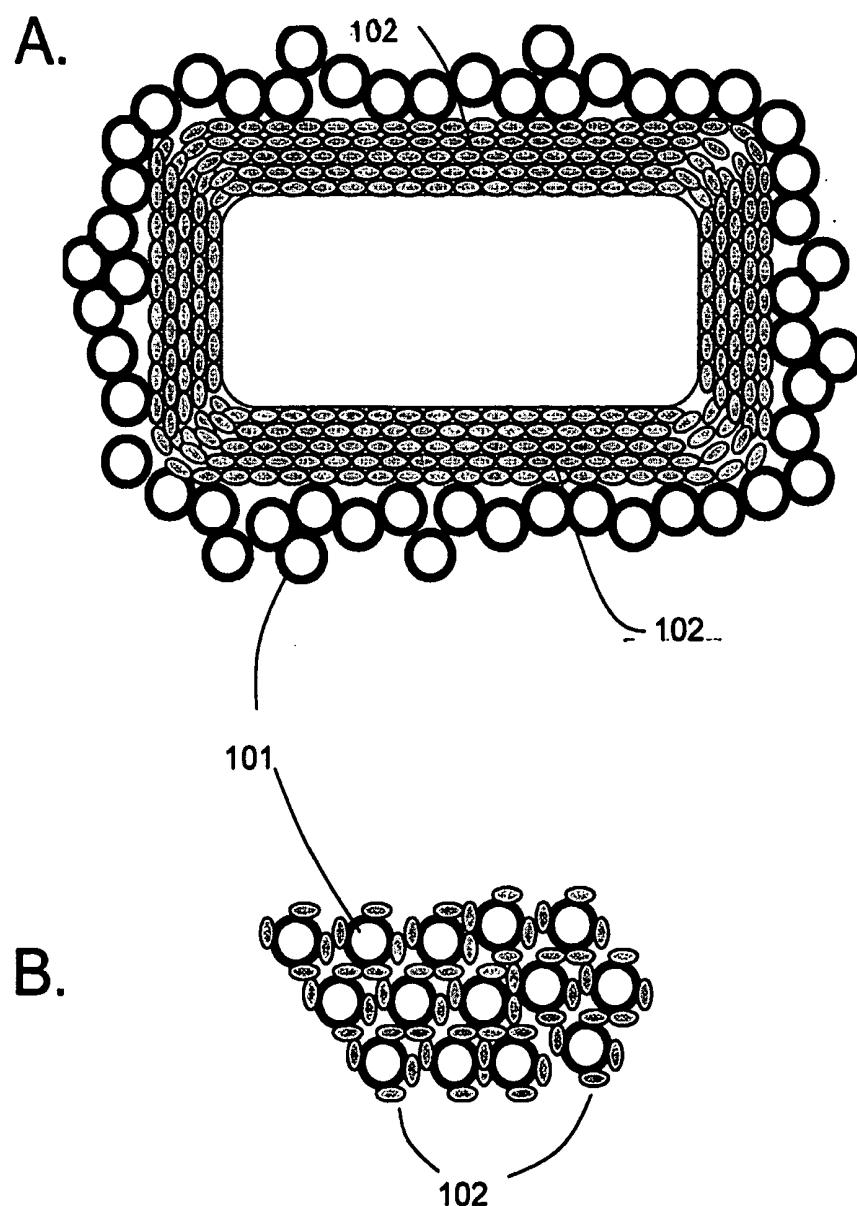


Fig.1

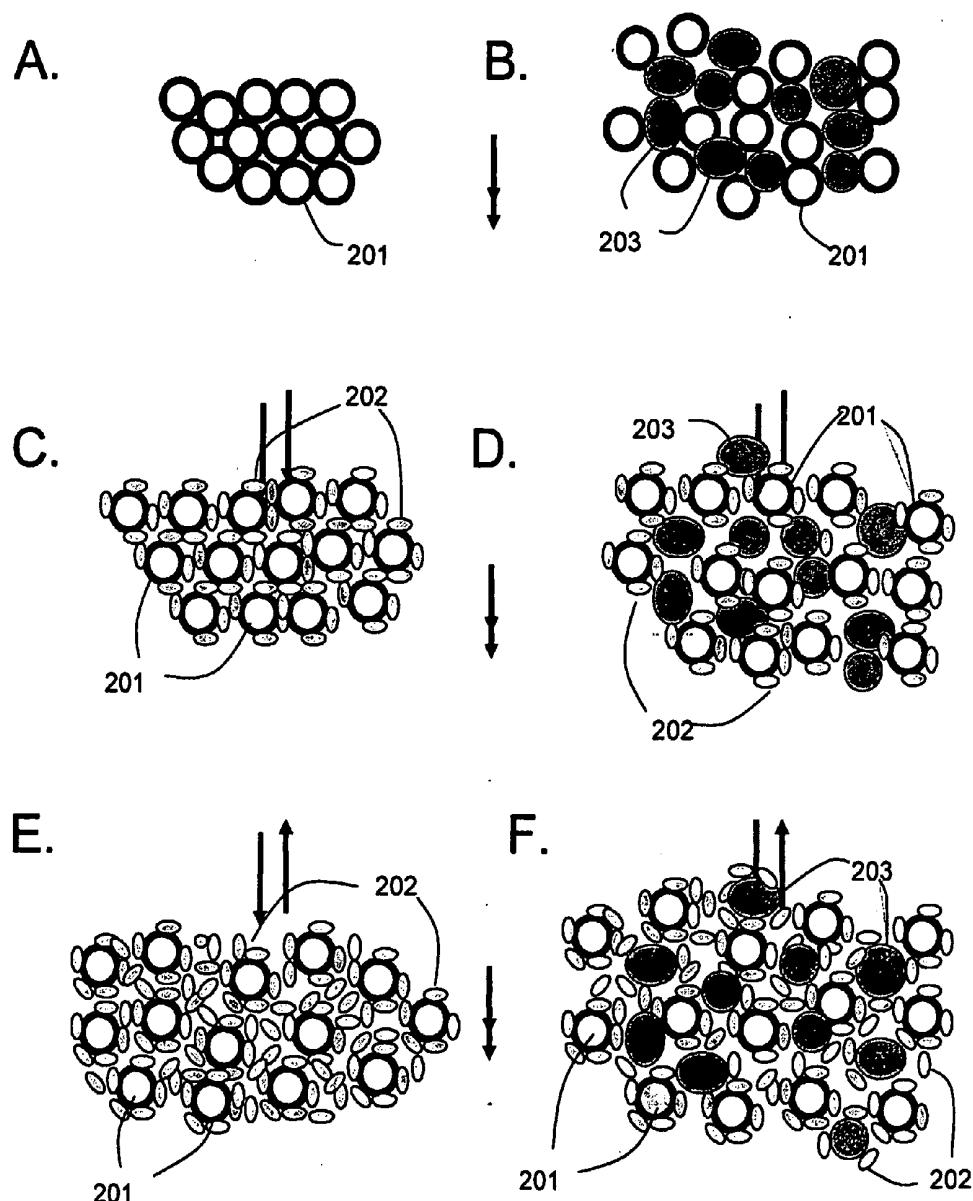


Fig.2

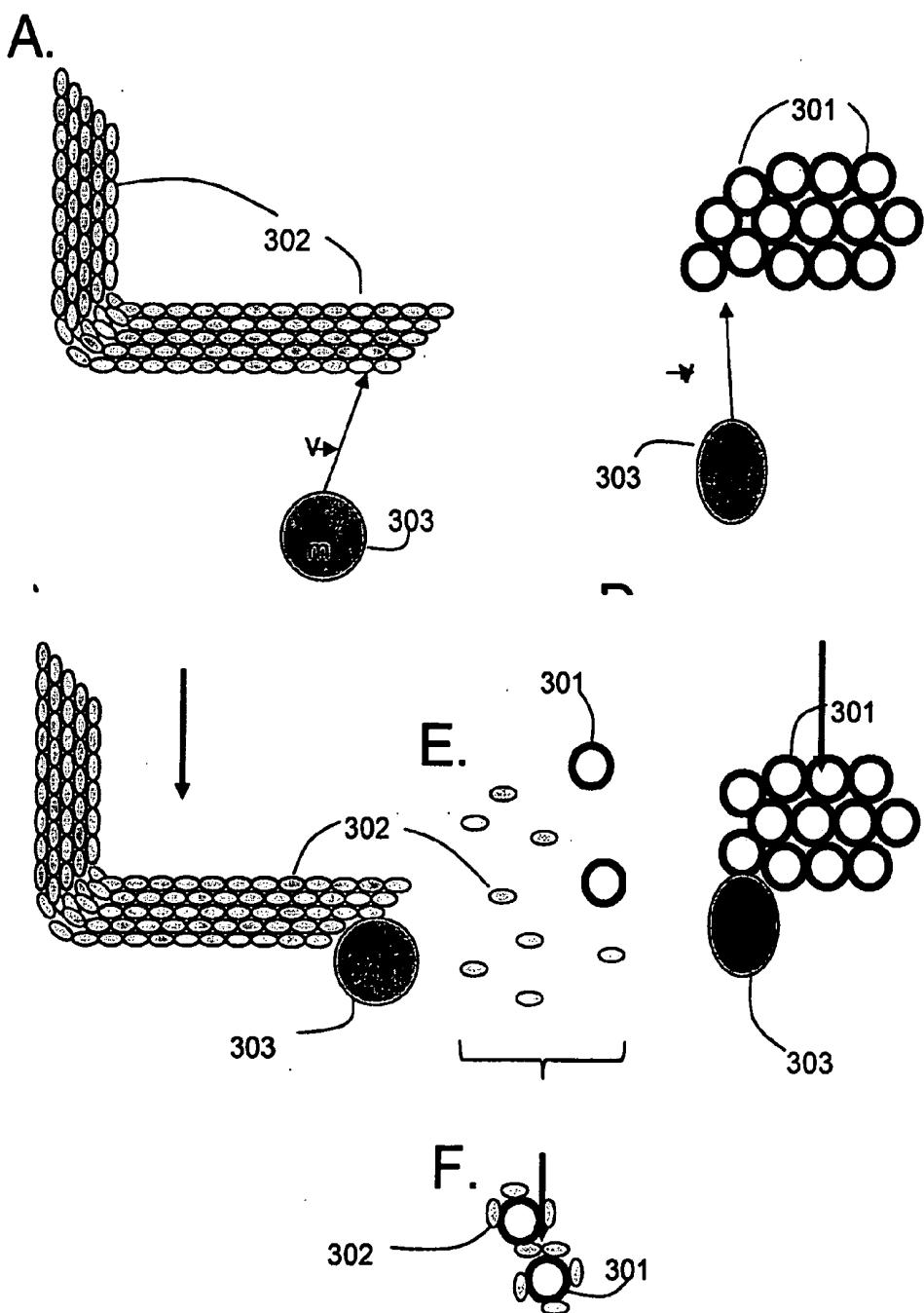


Fig.3

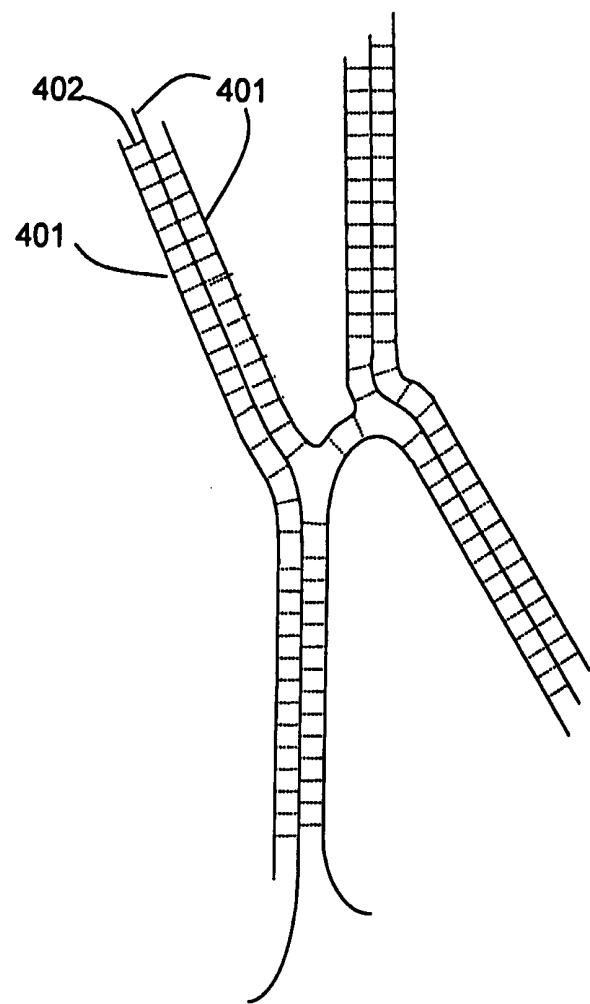


Fig.4

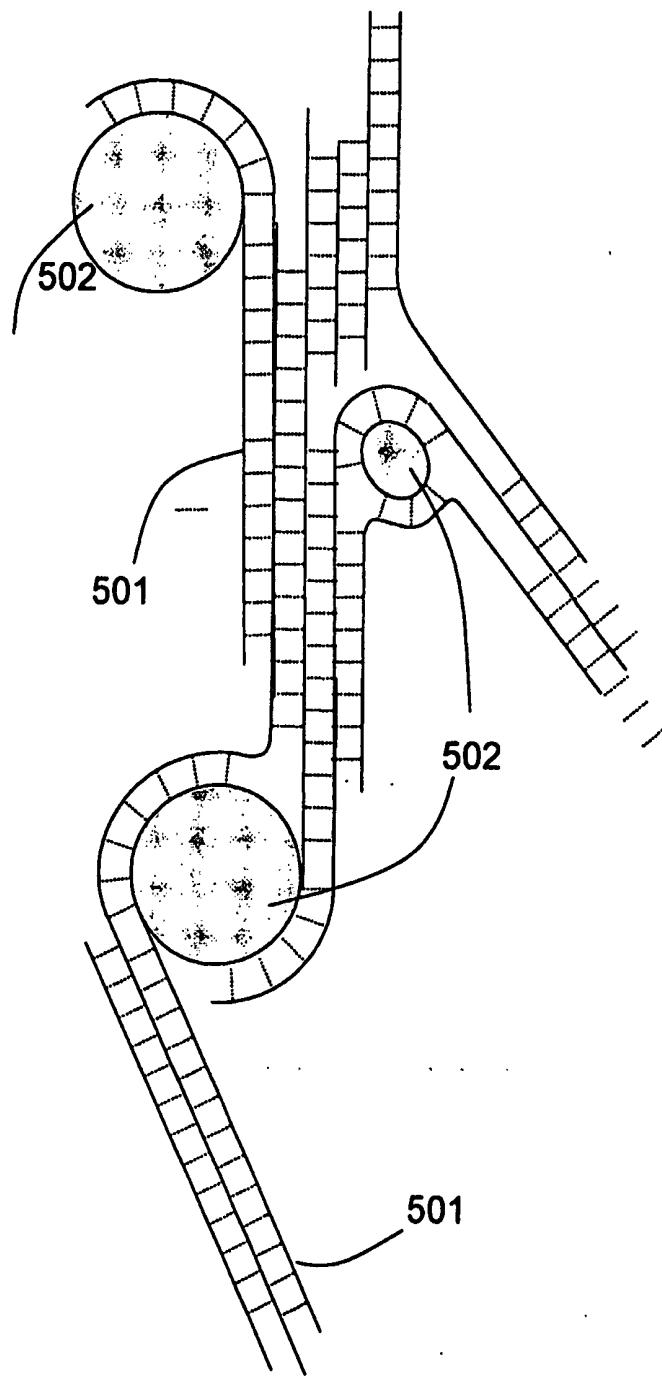


Fig.5

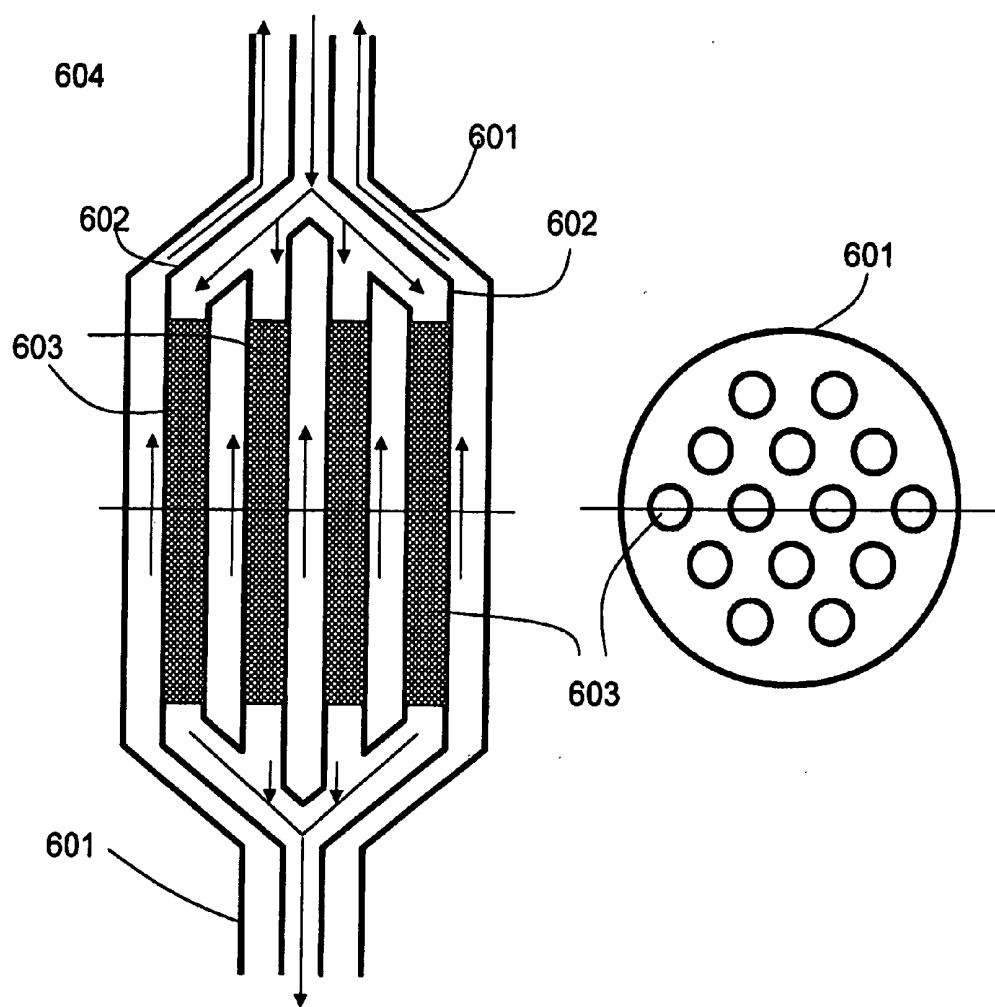


Fig.6

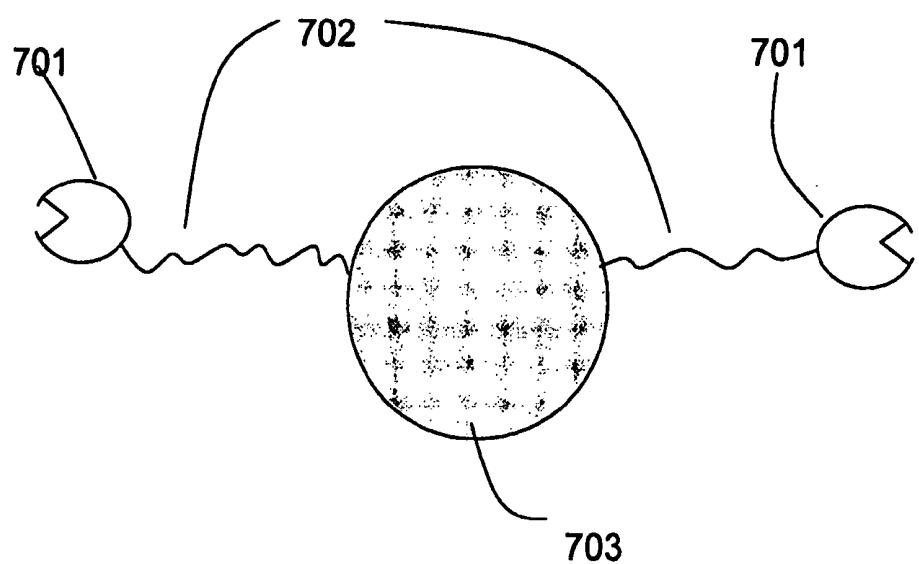


Fig.7

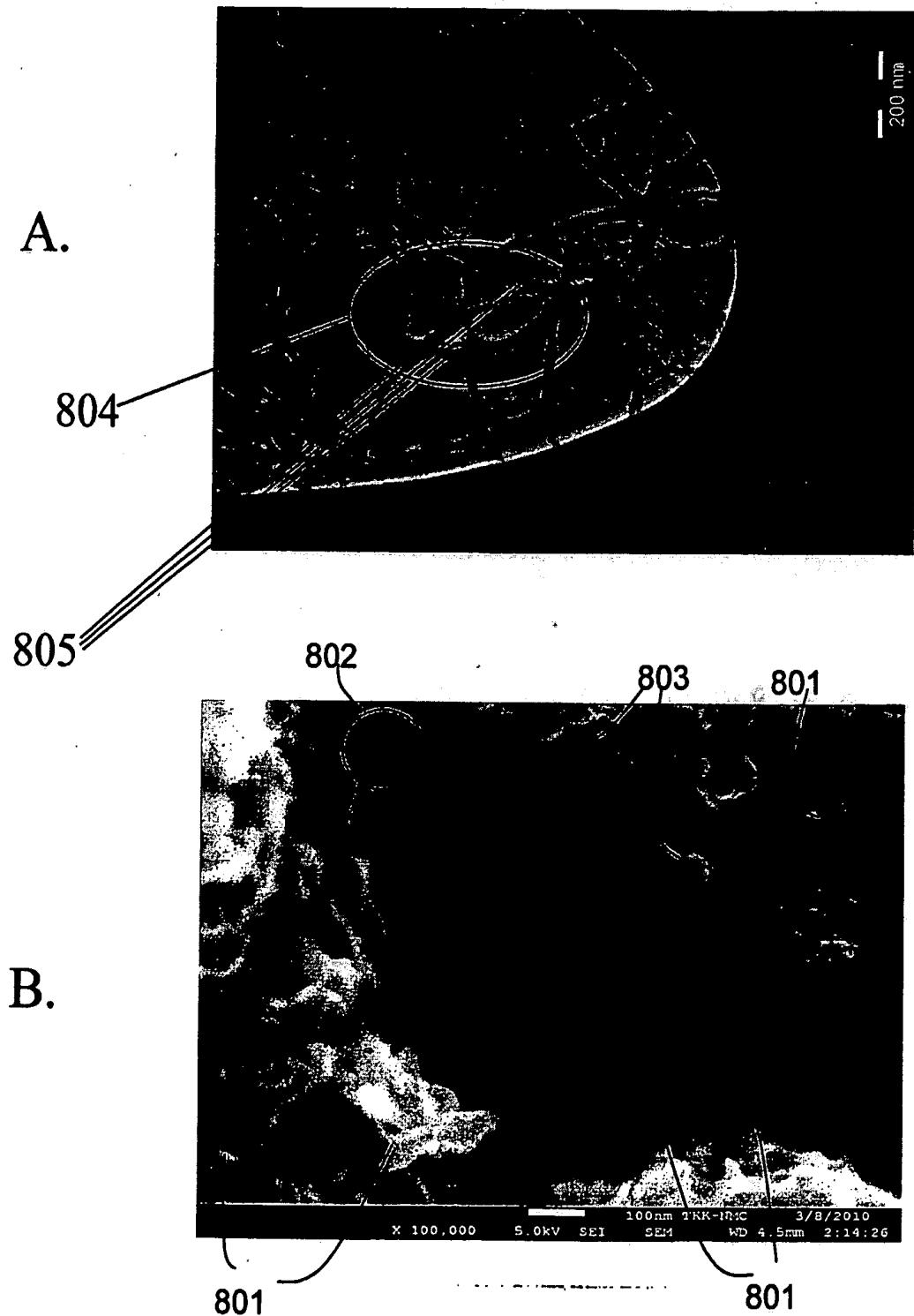


Fig.8

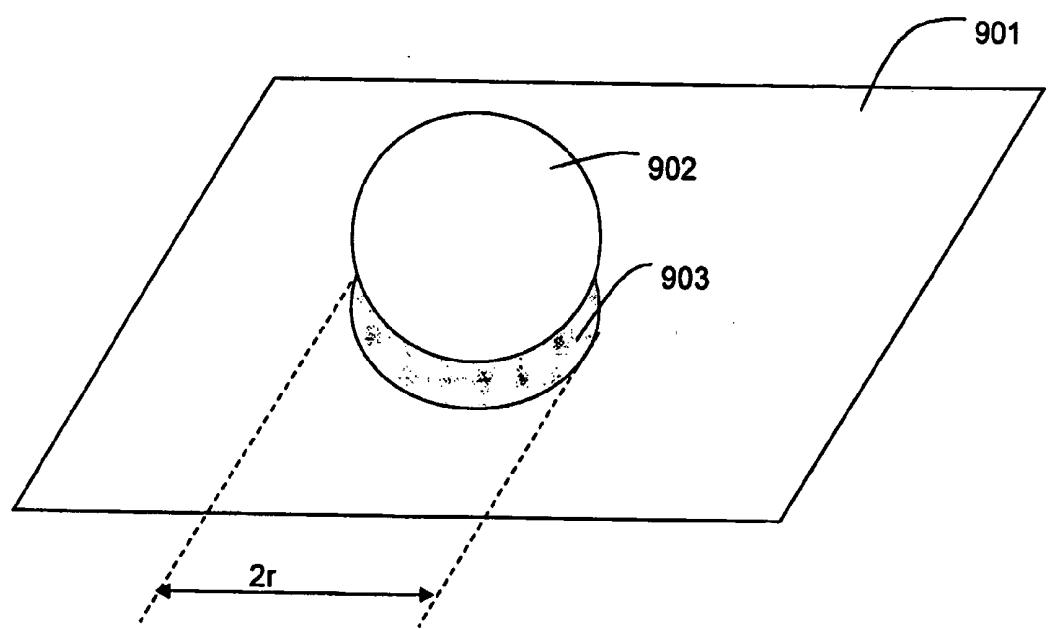


Fig.9

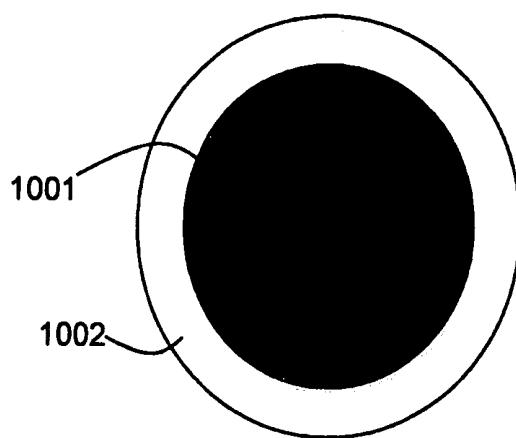


Fig.10

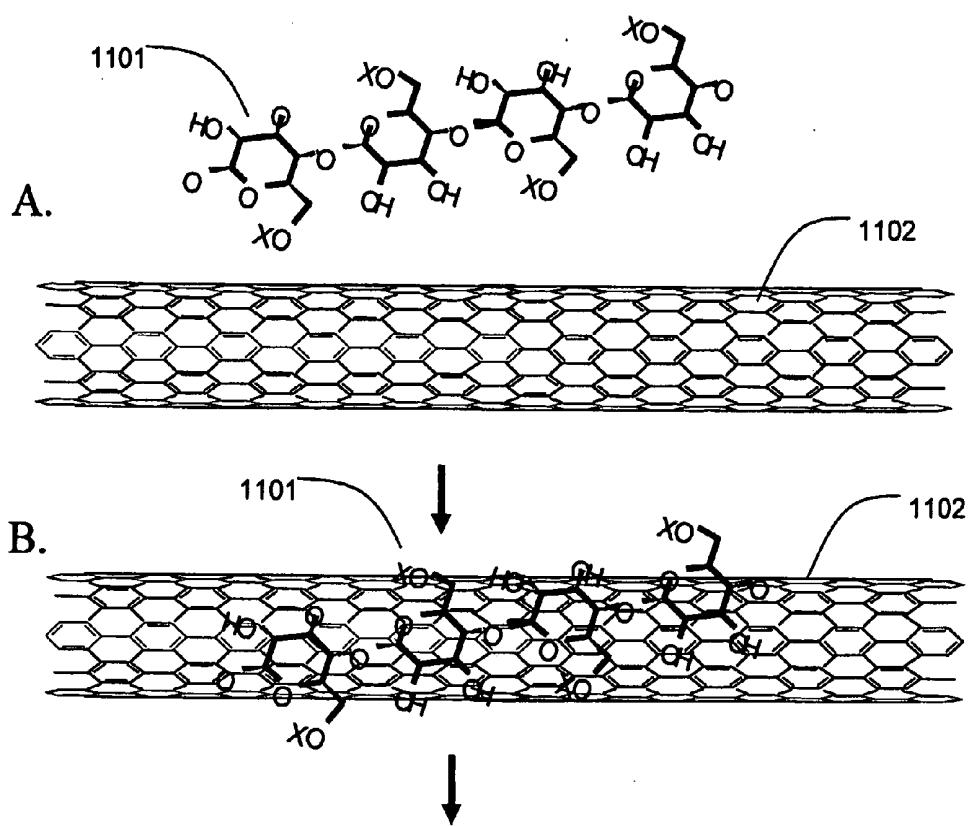


Fig.11

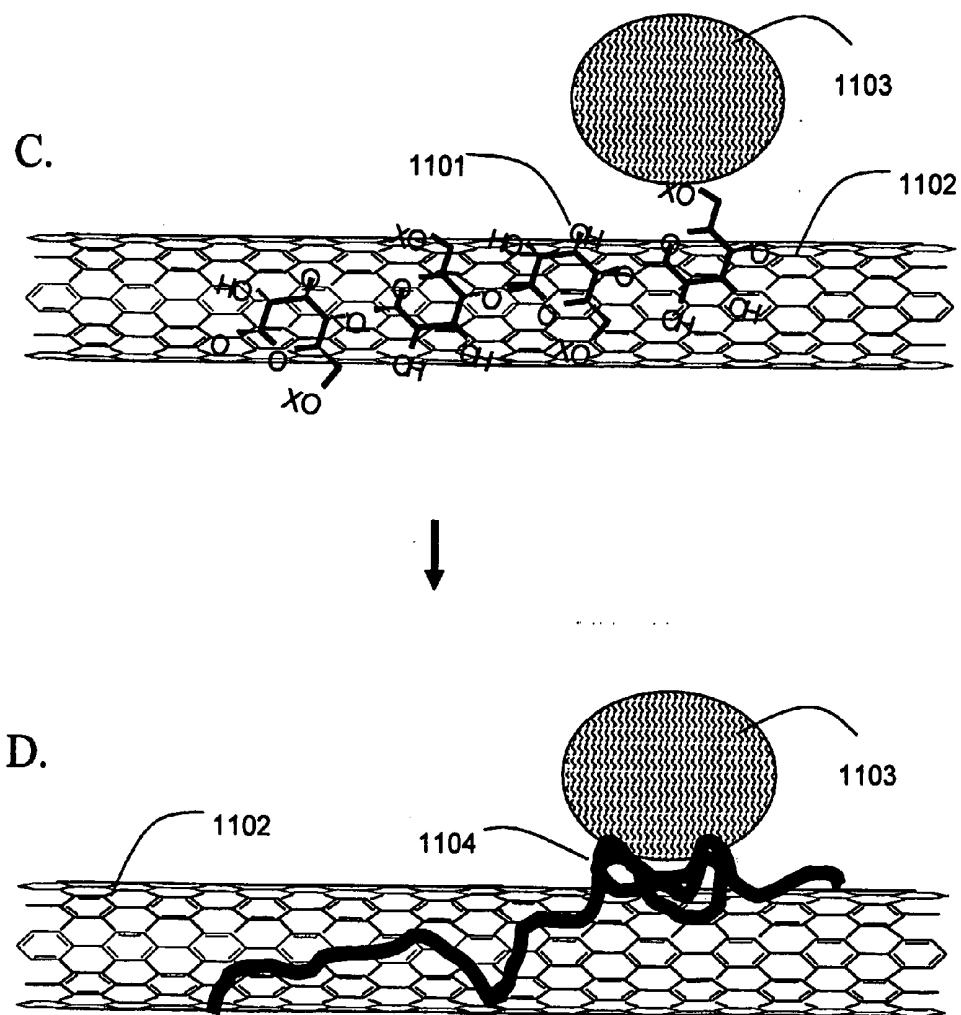


Fig.11

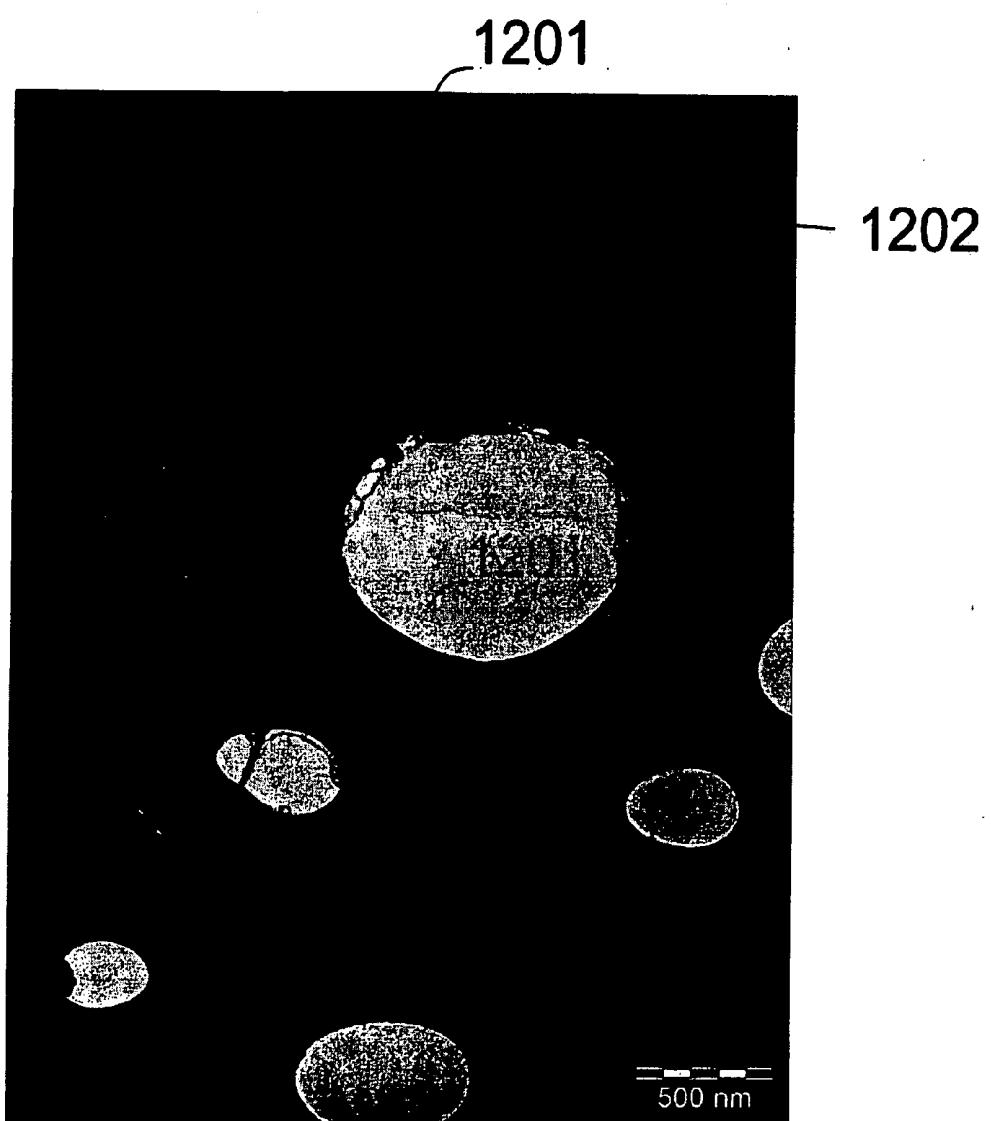


Fig.12

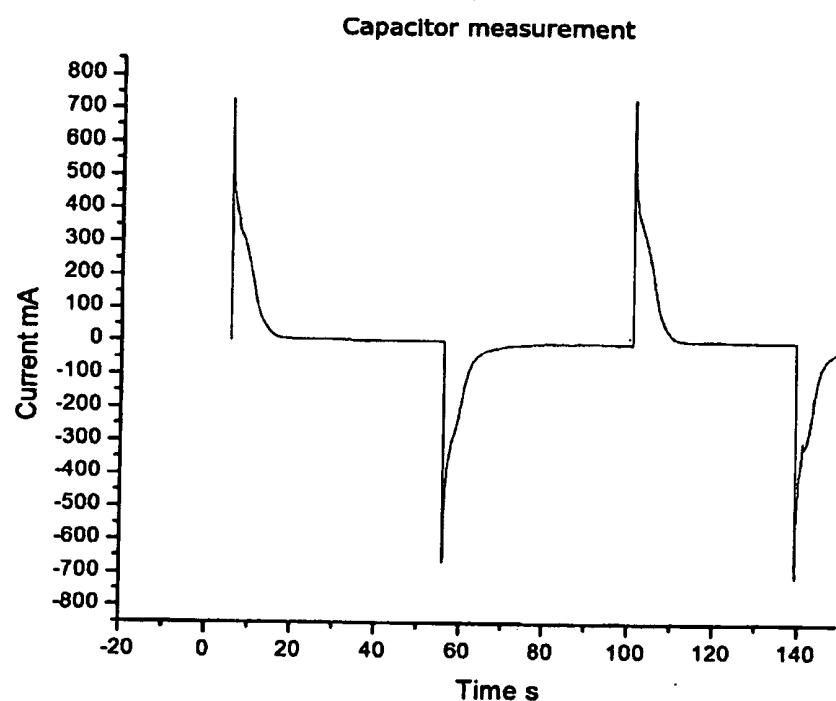


Fig.13

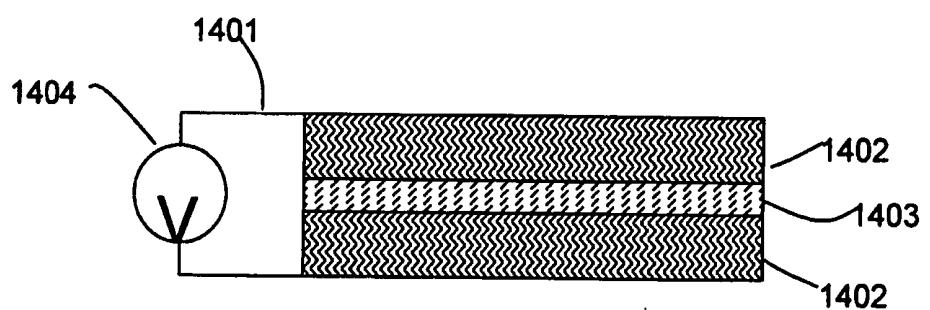


Fig.14

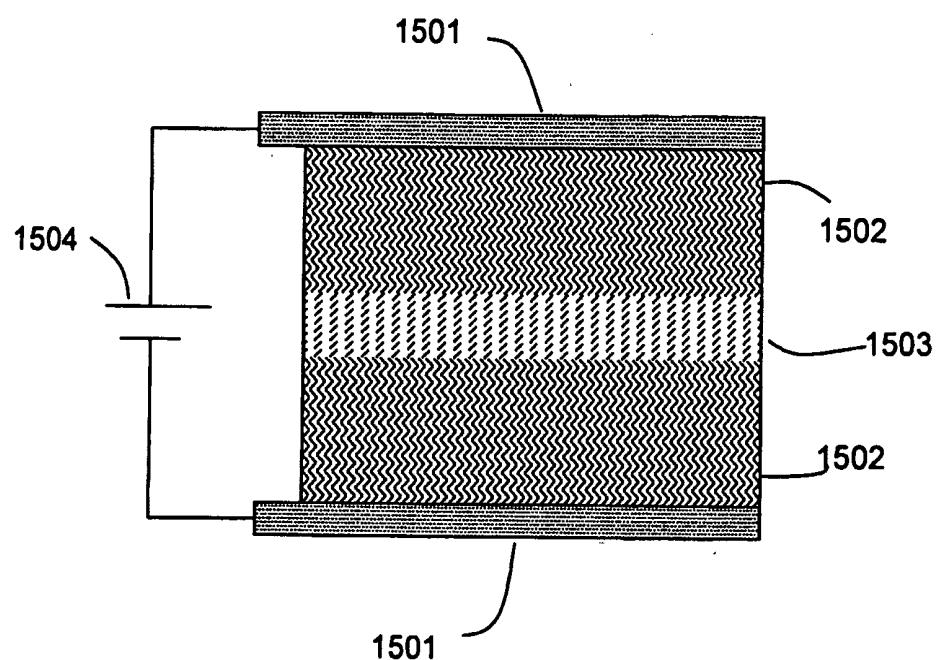


Fig.15

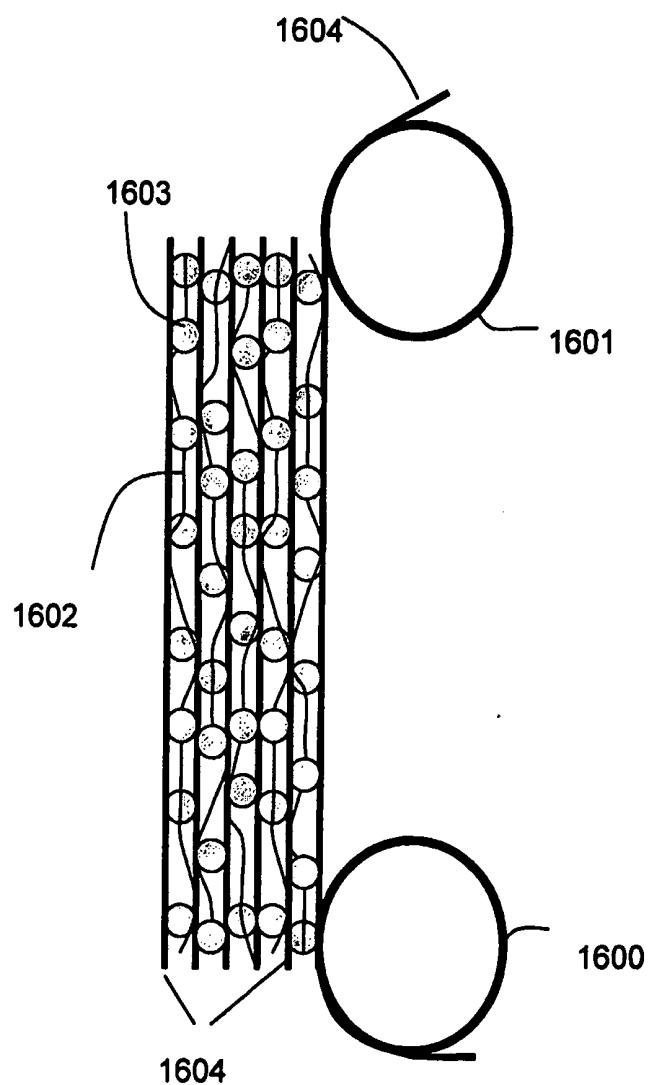


Fig. 16

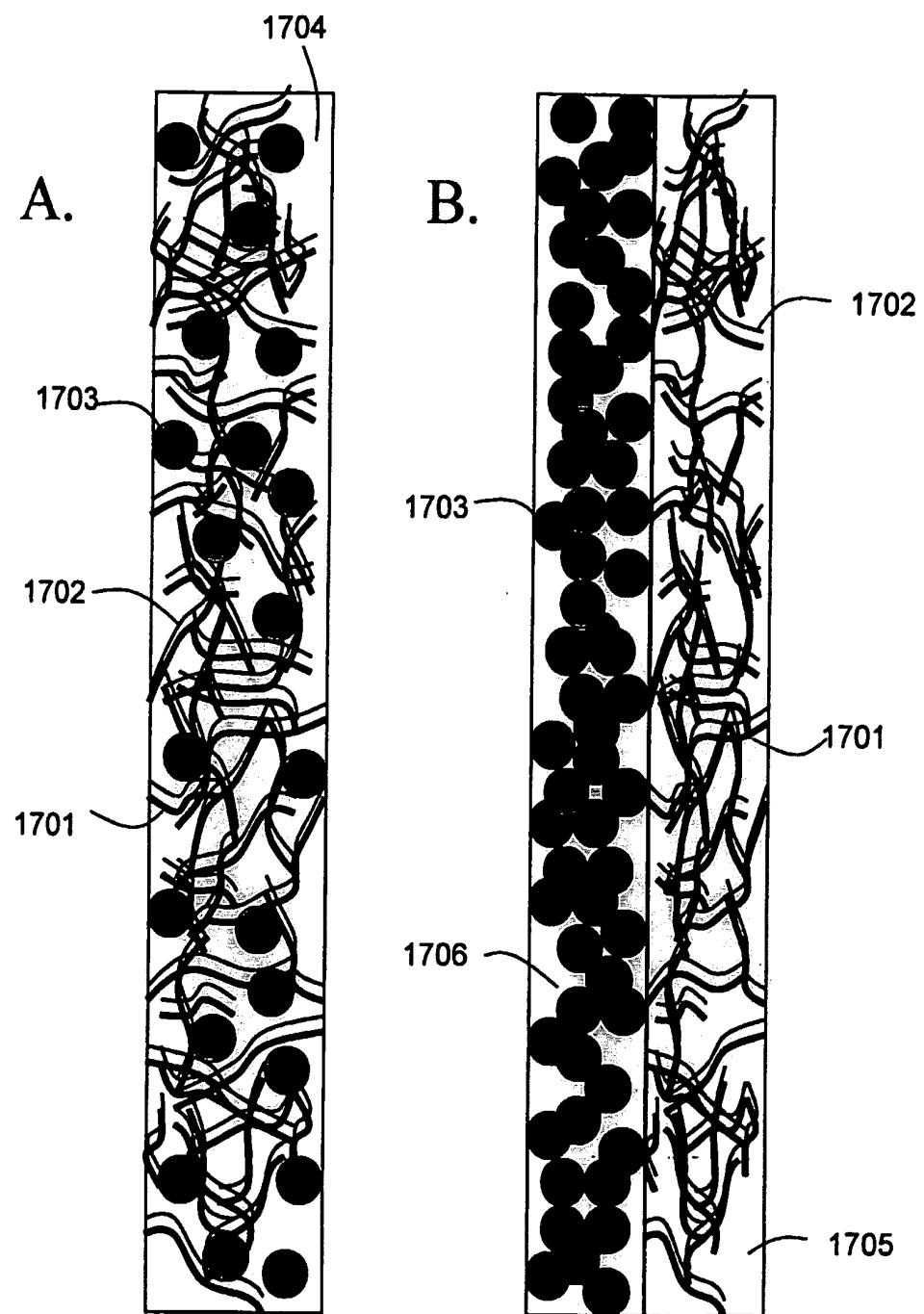


Fig.17

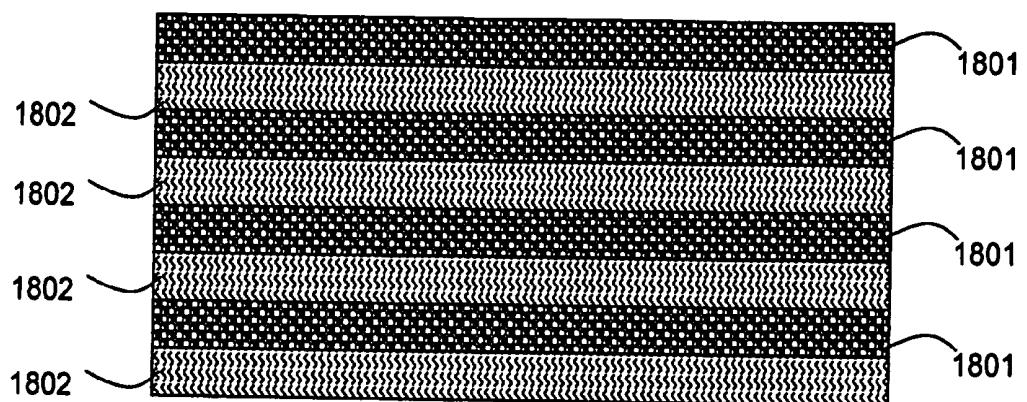


Fig.18

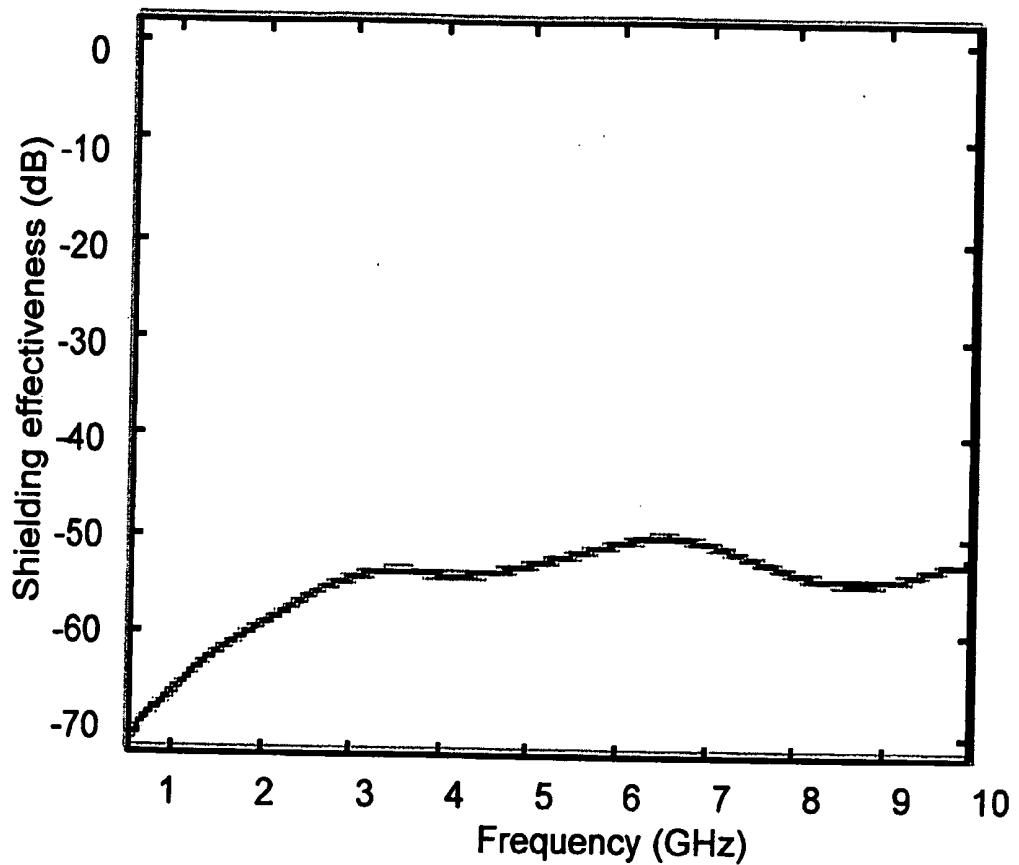
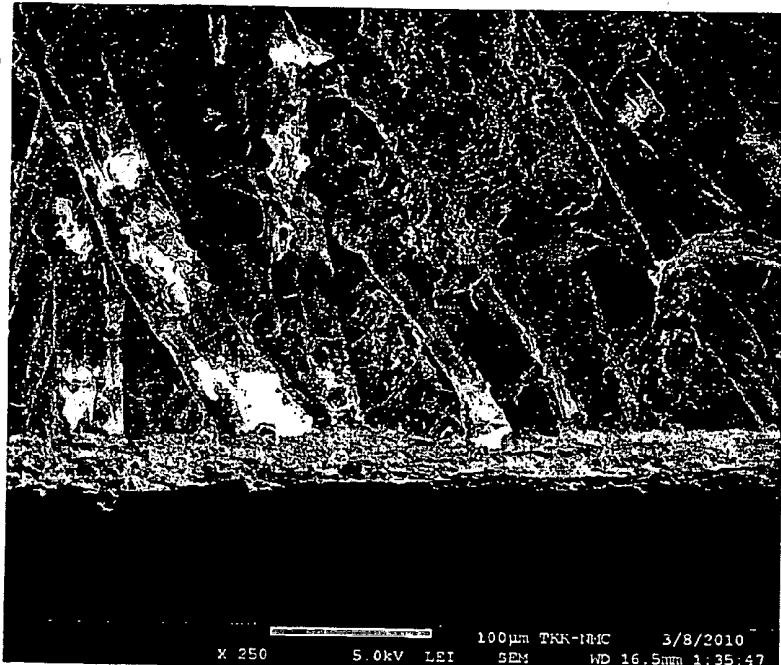


Fig.19

A.



B.

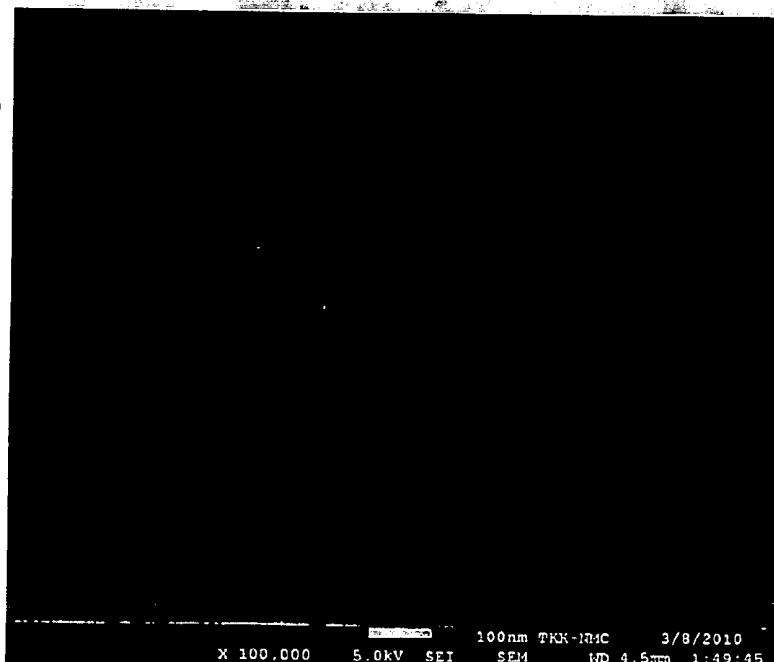


Fig.20

FABRICATION AND APPLICATION OF POLYMER-GRAFHTIC MATERIAL NANOCOMPOSITES AND HYBRIDE MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from Finnish Application Serial No. 20090495, filed Dec. 22, 2009, and Finnish Application Serial No. 20100143, filed Apr. 9, 2010, and
Finnish Application Serial No. 20106077, filed Oct. 18, 2010, and
U.S. Provisional application Ser. No. _____, filed January 2010, titled Fabrication and Application of Functionalized cellulose-carbon nanotube nanocomposite and Hybride Materials

BACKGROUND

[0002] 1. Field of Invention

[0003] This invention relates to the fabrication of nanocomposites from two or more materials that have low solubility in a liquid milieu and large scale structures of these materials. More specifically fabrication of nano-composites or hybride materials of polymer and graphitic material using nanoparticles as dispersion facilitators is described. In addition, the present invention involves the electromagnetic utilization graphitic material-polymer nanocomposites for supercapacitors and electromagnetic shielding.

[0004] 2. Prior Art and Overall Description

[0005] Fabrication of nanocomposites of two or more materials is not straightforward. Often these materials do not have a common solvent. Even, when both or all materials have a common solvent, their deposition will most probably result into a random structure, in which both components can be clustered as well as mixed in a nanoscale. The present invention solves this problem using carbon nanotubes and cellulose as examples. Efficient dispersion of graphitic materials, such as carbon nanotubes (CNTs) and graphite into polymers continues to be problematic. Graphitic materials tend to aggregate, especially, if their concentration exceeds 10% in the medium. Aggregation prevents the full utilization of the graphitic material. For example, a capacitance of supercapacitor depends on the available surface area of the graphitic material. Aggregate has much less available surface area than individually separated graphitic particles have combined surface area. Electromagnetic interference (EMI) protection efficiency is hampered by clustering. Material strength is much better served by individually dispersed graphitic particles than by clusters.

[0006] This invention provides very efficient dispersion methods and materials that are often accompanied by functionalization of graphitic particles. Currently preferred embodiments are almost exclusively related to the fabrication of CNT-cellulose nanocomposite, i.e., graphitic material consists of CNTs, and polymer is cellulose or modified cellulose. Although scanning electron microscope (SEM), and transmission electron microscope (TEM) images prove good dispersion, more importantly, capacitances of supercapacitors, EMI shielding efficacy, and material strength are practically important implications of the efficacy of the dispersion method. Carbon nanotubes (CNTs) can be single walled (SWNT), double walled (DWNT) or multiwalled (MWNT).

They can have diameters that range from subnanometer to over 100 nm. Also CNTs have a multitude of chiralities. Thus, there are hundreds of different kind of CNTs. Some CNTs are metallic conductors and some are semiconducting. Many CNTs are better electrical conductors than silver at room temperature. All CNTs are very strong, and the tensile strength of the CNTs is tens of times better than that of steel.

[0007] CNTs can be functionalized by several methods. One commonly used method is oxidation with the mixture of sulfuric and nitric acids to form carboxylic groups (R. E. Smalley, et al., Method for forming an array of single-wall carbon nanotubes and compositions thereof, US2002/0159943 A1). Many moieties can be attached with carboxylic groups. In another method radicals are generated from diazonium salts, and these radicals react with the CNTs (J. M. Tour, et al., Process for functionalizing carbon nanotubes under solvent-free conditions, Int. Appl. WO 2004/007364). In a co-owned method (J. Virtanen et al. PCT/FI2005/000437) CNTs are cut, and the nascent dangling bonds react with a reagent that is present. These are just some examples that are well known in-the-art. Functionalized CNTs are not really CNTs anymore. They will also be called hybride nanotubes (HNTs) in this context. The term HNT-cellulose material will be used all hybride materials of the present invention.

[0008] CNTs and cellulose are sparingly soluble into all solvents. Due to large particle size they form suspensions rather than solutions, although terms solubility, solution and solubilization will be used here frequently as well as more accurate term dispersion.

[0009] CNTs can be solubilized into water using detergents, and into organic solvents as such or using compounds, such as pyrene, that increase the solubility of the CNTs. Detergents may hamper the good properties of CNT-cellulose materials.

[0010] Cellulose and its derivatives can be used to disperse CNTs, and cellulose-CNT composites have been used as supercapacitors, and EMI protection cellulose is renewable material, and its annual production in the nature might be more than the production of any other natural or man-made polymer. In wood cellulose is intertwined with lignin that is an aromatic polyether. Pure cellulose fibers are few micrometers long, and they have a rectangular cross-section. The cellulose fibers are hollow. Cellulose fibers bind with each other by hydrogen bonds. Because of the large number of hydrogen bonds the interaction is strong. However, water is able to break at least partially the hydrogen bonding network between fibers, and wet paper is very weak.

[0011] When nanoparticles or fibers are mixed, composite is formed. If the mixing is efficient, so that the components are mixed also in nanoscale, a nanocomposite will be formed. Fabrication of nanocomposites is not trivial, because often each component tends to separate into clusters that do not contain or contain very little of the other component(s). When the nanocomponents are chemically bound, the material is classified as a hybride material. The main focus of this invention is the fabrication and applications of HNT-cellulose nanocomposites and hybride materials.

[0012] It is possible to fabricate cellulose nanofibers that have diameters between 5-100 nm. They are still several micrometers long, and are called microfibrillated cellulose (M. Ankerfors, et al., A manufacturing method for microfibrillated cellulose, 6th International Paper and Coating Chemistry Symposium, 2006).

[0013] It is possible to fabricate even smaller bundles of cellulose. Cellulose fragment gel is made of cellulose by cutting the long cellulose molecules shorter and disintegrating the original cellulose fibers into amorphous structures.

[0014] One currently preferred method is acid hydrolysis of δ -cellulose in order to produce microcrystalline cellulose that has polymerization degree between 200 and 1000 α -glucose units, preferably between 300 and 500.

[0015] Another currently preferred cutting method is enzymatic. Cellulose fragment gel forms very strong nanocomposite with CNTs and HNTs. We have found that in the presence of CNTs and nanoparticles, individual molecular fragments of chemically, enzymatically, or biologically fragmented cellulose will be separated and reassembled around CNTs and nanoparticles. This form of fragmented cellulose is currently favored for the dispersion of CNTs. This kind of product is different from other known forms of cellulose composites, and is cellulose-nanoparticle gel, and is called Celose. Cellulose fragments form an amorphous continuum, and the material is mechanically very strong cellulose fragment-nanoparticle gel is essential for the present invention, and separates it from the prior art that utilizes various forms of cellulose. Carboxymethyl cellulose alone or mixed with cellulose gives good results, but we found that cellulose fragment gel is clearly better. In cellulose fiber hundreds of cellulose molecules are bound together. If cellulose fibers are used as carrier material for CNTs, only the surface of the fibers will be utilized, and the CNT/cellulose mass ratio is small. Despite of small CNT/cellulose ratio the CNTs are not well separated in two directions, although they are excessively separated in third direction (FIG. 1). The situation will be improved, if microfibrillated or nanocellulose will be used. Even nanocellulose has tens of (cut) cellulose molecules in one nanofiber. In cellulose fragment gel molecules are equally separated in all directions, and separation can adjusted at molecular accuracy by choosing the desired CNT/cellulose ratio. Cellulose fragments interact individually with CNTs by wrapping around the CNTs. Thus, the CNT/cellulose ratio will be maximized. Although nano-, and microparticles are useful for the dispersion they are not mandatory, especially for the short chained cellulose fragments, such as some forms of microcrystalline cellulose. Organic ionic solvents are good solvents for both cellulose and CNTs. Their high price is a serious drawback for several practical applications. Also during various deposition processes some CNTs and cellulose molecules form homoaggregates. The same problem is encountered with many other methods, in which cellulose is solubilized. When molecular components are well solvated, their mutual interaction in solution is suppressed. While solubilized cellulose is not properly wrapping CNTs, and deposition results at least into partial phase separation. When the deposition is induced by an outside effect, the product tends to be under kinetic control. In the method of present invention two water insoluble solids, fragmented cellulose and CNTs, are mixed in water using uneven distribution of kinetic energy that is able to separate cellulose fragments as well as CNTs from their own fibers and clusters. Cellulose molecular fragments will wrap around individual CNTs under thermodynamic control. Advantageously, nano- or microparticles will be used to enhance the effect of the kinetic energy. The resulting CNT-cellulose nanocomposite is stable enough so that the components do not separate under the conditions that are used in this invention.

[0016] The situation with various forms of cellulose is somewhat analogous to various forms of iron, such as chemically pure iron, cast iron, steel, stainless steel, and acid resistant steel. There are several subspecies of each of these. They have different mechanical properties, malleability, molding properties, chemical resistance, electrical conductivity, and magnetic properties. In some applications it might be possible to choose between two or more kinds of iron. However, in many applications only one kind of iron may be used. Similarly, we have found that out of several kinds of cellulose and its derivatives, cellulose nanoparticle gel (Celose) is best for the electrical applications of this invention, although some other forms of cellulose can be used with partial success.

[0017] In a co-owned patent application is described the fabrication of CNT-cellulose nanocomposite that contains also electrically conducting nanoparticles (J. A. Virtanen and P. Moilanen, WO/2008/034939). Combination of CNTs and electrically conducting nanoparticles is not enough. For several applications, including supercapacitors and EMI protection, there must be a good electrical contact between CNTs and nanoparticles. Mixing of the components even at nanoscale does not guarantee always the good electrical contact.

[0018] The composites of the present invention are also based on CNT-cellulose nanocomposite that contains electrically conducting nanoparticles. In the present invention the methods and compositions will be provided that ensure good electrical contact between CNTs and electrically conducting nanoparticles. Thus, the full utility of electrically conducting nanoparticles is obtained.

[0019] This nanocomposite may contain also paramagnetic particles, such as magnetite particles, or these particles may be advantageously in an adjacent layer. Thus, the macrostructure will contain both electrically and magnetically active particles providing superior protection against electromagnetic interference (EMI protection).

[0020] Magnetic particles can be made from iron, nickel, or cobalt, for example. Paramagnetic particles are typically ferrites. Magnetite is one specific example.

[0021] One major class of supercapacitors utilizes carbon nanoparticles (CNPs). Because CNPs have poor electrical conductance, only thin layers can be used. Similarly one class of EMI protecting materials is based on CNPs. CNPs give a random structure that can not be the best possible structure. More control of the structure is obtained, if CNTs or graphene will be used. However, so far the results have been disappointing mainly because CNTs and graphene tend to aggregate.

[0022] Prior art, all of which are given here as reference in their entirety:

[0023] M. Ankerfors, et al., US Patent Application 20090221812

[0024] Method for the Manufacture of Microfibrillated cellulose

cellulose was enzymatically (endoglucanase) cut, refined, and homogenized with high pressure fluidizer/homogenizer. The resulting product is micro- (or nano) fibrous cellulose that is different from the product of the present invention. Although the methods resemble each other, the different product can be explained by the presence of CNTs and/or nanoparticles in the methods of the present invention. CNTs and nanoparticles bind individual cellulose molecules and prevent their recombination into fibers after they have been separated even temporarily.

[0025] J. Engelhardt, et. al., WO 2009/021687 A1

Nanoparticles of amorphous cellulose

[0026] Fabrication of amorphous cellulose nanoparticles is described by a method that resembles that of Ankerfors et al. except that chemical cleaving of cellulose is used instead of enzymatic cleaving. However, the method of Engelhardt et al. provides amorphous nanoparticles instead of nano- or microfibers. One reason is shearing and ultrasonic vibration of fragmented cellulose. In the present invention the formation of cellulose particles, even nanoparticles, is undesirable. The formation of cellulose particles is avoided, because cellulose molecules wrap around of CNTs and nanoparticles.

[0027] H. Tennent, et al., US Application 856657

[0028] Graphitic nanofibers in electrochemical capacitors.

[0029] The capacitor in which nanofibers are coated with a thin coating layer of carbonaceous polymer. Polymer can be cellulosic polymer. However, no example is given.

[0030] C. Niu, et al., Appl. Phys. Lett. 70 (1997) 1480

[0031] CNT electrodes for high power electrochemical capacitors

[0032] P. Glatkowski, et al., U.S. Pat. No. 6,265,466

[0033] EMI shielding composite containing CNTs and polymer is described. Disclosure and examples limit the concentration of CNTs to 15%. Higher concentration require new methods, such as described in the present invention that allows any concentration between 0 and 100%. Glatkowski et al. require also orientation of CNTs by a shearing force. The present invention provides so good dispersion that enough CNTs will be oriented into every direction for EMI protection.

[0034] W. Li, H. Pröbstle, and J. Fricke, J. Non-Crystalline Solids 325 (2003) 1.

carbon aerogel supercapacitor is described.

[0035] C. H. Cooper et al., US Patent Application 20050272856 Jul. 7, 2004

[0036] CNT containing materials and articles containing such materials for altering electromagnetic radiation,

[0037] Claims are limited for the case, in which the length of CNTs is more than half the wavelength. In the present invention this requirement is not necessary. As a matter of fact the CNTs that are one hundredth of this limit work well, when the present method is used. This will make the materials of the present invention much more economical.

[0038] P. J. Glatkowski, et al., U.S. Pat. No. 7,118,693 Oct. 10, 2006

[0039] Conformal coatings comprising CNTs.

[0040] CNT diameter is claimed to be smaller than 3.5 nm that essentially requires that the CNTs are SWNTs. Very low loadings were used that are far lower than optimal concentration. One reason that can be the inefficient dispersion of CNTs over 1% and difficult dispersion over 10%. cellulose is mentioned as a possible polymer, but is not described in Experimental section. Sonication of CNTs into toluene solution, and mixing this solution with epoxy, polyurethane, acrylic, or silicone coatings was described by Glatkowski et al. cellulose was not an example. Repeating the method of Glatkowski et al. for cellulose was performed by the inventors of this invention. CNTs were dispersed either into water or 2-propanol in the absence or presence of cellulose. One typical example is in FIG. 20. The results were very different from those of the present invention. In FIG. 20 cellulose fibers are virtually intact (FIG. 20 A), and CNTs are lying on the surface of

cellulose fibers (FIG. 20 B, schematics in FIG. 1A). Thus, the EMI shielding efficacy obtained by Glatkowski et al. is limited by dispersion method.

[0041] P. J. Glatkowski, et al., U.S. Pat. No. 7,118,693

[0042] Conformal EMI shielding coating is described. CNTs have outer diameter 3.5 nm or less, while in the present invention the diameter is 3.5 nm or more. Glatkowski et al. require also insulating layer. While one embodiment of the present invention also contains CNT-polymer layer and an insulating layer that layer contains magnetically active particles. A three layer structure of the present invention has an insulating layer sandwiched between two CNT-polymer layers, and destructive interference of electromagnetic radiation is created between two CNT-polymer layers. This is totally new effect that is not described by Glatkowski et al.

[0043] C. Du and N. Pan, nanotechnology 17 (2006)5314

[0044] Electrophoretic deposition of carbon nanotubes on electrodes is described.

[0045] C.-C. Hu, et al., J. Phys. Chem. Solids 68 (2007) 2353.

[0046] Modification of MWNTs for electric double-layer capacitors.

[0047] S. Yoshimitsu, U.S. Pat. No. 7,382,601 Jun. 3, 2008

[0048] Electric double layer capacitor and method of manufacturing same.

[0049] Incorporating fullerene into CNT electrodes by microwave radiation is described.

[0050] J. S. Douglas, US Patent Application 20080044651

[0051] A coating or ink comprising CNTs is described. Dispersion may also contain nanoparticles and polymers including cellulose. cellulose is only mentioned by name without further definition or enabling embodiments. Also surface roughness is required to be about 100 nm or less. This is almost impossible to achieve with a mixture CNTs and cellulose, because both are fibrous solids.

[0052] W. Lu and H. Kent Douglas, US Patent Application 20080192407

[0053] Ultracapacitors with carbon nanomaterials and ionic liquids.

[0054] Ionic liquids are used as electrolytes. Polymers are carrier materials so that the supercapacitor is largely solid. Inorganic material is used to prevent crystallization of polymeric material.

[0055] P. M. Ajayan, et al., US Patent Application 20080212261

[0056] Energy storage devices and composite articles associated with the same.

[0057] Method claims of Ajayan et al. require polymer is dissolved into a liquid. That is in sharp contrast of the present invention, in which the polymer is advantageously poorly soluble into the liquid. Importantly, no kinetic energy input is mentioned in disclosure or in any embodiments.

[0058] US Patent Application 20080254362

[0059] Nano-Composite structures, methods of making, and use thereof.

[0060] Nanocomposite containing CNTs and semiconducting or metallic nanoparticles is described. Also polymeric binder may be included. Apparently no polymers are defined in the disclosure, and no examples of their use is given. However, several specific polymers are claimed, but cellulose is not included.

[0061] U.S. Pat. No. 7,553,341 Jun. 30, 2009
 [0062] High power density supercapacitors with carbon nanotube electrodes.
 [0063] Electrophoretic deposition of CNTs.
 [0064] J. S. Glatkowski, et al., US Patent Application 20090131554
 [0065] EMI shielding CNT-polymer composite is provided. In strong contrast with present invention the composite has low or essentially no bulk conductivity. Glatkowski et al. realized that entanglement of CNTs is essential for good EMI protection. Entanglement is difficult to obtain with high loadings. This problem has been solved in the present invention, and high concentrations of CNTs can be used, and CNT-polymer nanocomposite has also good bulk conductivity.
 [0066] K.-L. Jiang and S.-S. Fan, US Patent Application 20090168302
 [0067] Electrochemical capacitor with CNTs.
 [0068] Use of cellulose in porous middle membrane is mentioned. However, Membrane is not integrated with CNT layers.
 [0069] J.-H. Kwon, et al, U.S. Pat. No. 7,588,700
 [0070] Specific EMI shielding material comprising epoxy or polyimide resin and CNTs that contain both C=O and N—H functionalities. Composition may further comprise metal particles.
 [0071] A. G. Rinzler, et al., U.S. Pat. No. 7,704,479
 [0072] Highly accessible, nanotube electrodes for large surface area contact applications. Fabrication of porous CNT-membrane is described. Sacrificial nano- or microparticles are used. These particles will be removed after the fabrication of a film. Dispersion method is not specified, but the requirement is that CNTs and particles do not flocculate from suspension. This is in sharp contrast to the present invention, in which the CNT-polymer-nanoparticle nanocomposite flocculates advantageously from suspension. Also in the present invention nano- or microparticles will be used to focus kinetic energy, and they must have density that is advantageously twice that of the solvent. Rinzler et al. use nano-, and microparticles only as spacers, and the density is not important, unlike in the present invention.

FIGURE CAPTIONS

[0073] FIG. 1. Schematic cross-section of A. CNT-cellulose composite, in which CNTs have been deposited onto a cellulose fiber surface, B. CNT-cellulose nanocomposite, in which components are mixed at molecular scale.
 [0074] FIG. 2. Schematic depiction of fabrication (F to A) of nanocomposite of this invention, and final control of the composition (reverse direction, i.e., A to F, but not necessarily in alphabetical order).
 [0075] FIG. 3. Schematic depiction of kinetic energy focusing at molecular level by using nanoparticles.
 [0076] FIG. 4. Schematics of binding of cellulose fragments via hydrogen bonded segments. Each fragment can change direction suddenly, and bind with several different other cellulose fragments.
 [0077] FIG. 5. Schematics of a structure of cellulose fragment-nanoparticle nanocomposite or gel.
 [0078] FIG. 6. Schematics of one embodiment of a countercurrent flow reactor that can be used to fabricate CNT-cellulose fragment gel of this invention.
 [0079] FIG. 7. Schematics of a micro- or nanoparticle that is at least partially coated with enzymes.

[0080] FIG. 8. TEM image (A), scale bar is 200 nm and SEM (B) image of amorphous CNT-cellulose-nanoparticle nanocomposite of this invention, 100 000 fold magnification.
 [0081] FIG. 9. Schematic demonstration of the increase of the area achieved by coating a flat surface by spherical particles.
 [0082] FIG. 10. Schematic depiction of a particle 1001 that is coated with a layer 1002.
 [0083] FIG. 11. Schematic depiction of one embodiment of the nanocomposite fabrication method. A. Functionalized cellulose 1101 and carbon nanotube 1102, B. Combination of CNT and functionalized cellulose. C. Precursor nanoparticle 1103 is attached with functionalized cellulose. D. Amorphous carbon 1104 is formed from functionalized cellulose 1101 after pyrolysis, and precursor nanoparticle is enlarged and attached with CNT 1102.
 [0084] FIG. 12. TEM micrograph of MWNT-cellulose-CMC-Prussian Blue nanocomposite. Prussian blue nanoparticle 1201, carbon nanotube 1202
 [0085] FIG. 13. Graph of charging cycles of a supercapacitor that was made of MWNT-cellulose-CMC-Prussian Blue gel.
 [0086] FIG. 14. Schematics of one embodiment of the present invention. Two layers of CNT-molecular cellulose-nanoparticle nanocomposite 1402 of the invention are separated by an ion permeable membrane 1403. The electric wires 1401 are connected directly with nanocomposite layers 1402, and no separate electrodes will be needed.
 [0087] FIG. 15. Schematics of another embodiment of the present invention, in which CNT-molecular cellulose-nanoparticle layers 1502 have been integrated into one continuous layer via a center layer that consists of molecular cellulose that may contain nanoparticles, but no CNTs.
 [0088] FIG. 16. Schematics of a cross-section of two CNTs 1600 and 1601 that are connected electronically by a graphite sheet 1604, that is stacked by several graphite sheets 1604. Intercalated between graphite sheets are nanoparticles 1603 and molecular cellulose fragment 1602.
 [0089] FIG. 17. Schematic structure of A., Single layer composite containing both electric 1701 and magnetic particles 1703 in the same layer, B., Double layer structure, in which the electric 1701 and magnetic particles 1703 are in different layers.
 [0090] FIG. 18. Schematic depiction of multilayer alternating structure.
 [0091] FIG. 19. Graph of EMI shielding efficiency of DWNT-fragmented cellulose paper vs. frequency.
 [0092] FIG. 20. SEM images of CNT-cellulose fiber composite A. 250x magnification, and B. 100 000 magnification of the area, in which CNTs are visible. Schematic FIG. 1 A is drawn on the basis of this SEM image. This figure is provided as a reference, and does not represent the present invention.

DEFINITIONS

[0093] Cellulose fiber is a hollow fiber consisting thousands of cellulose molecules.
 [0094] Nanocellulose is a nanofiber consisting of tens of cellulose molecules, diameter is about 5 nm.
 [0095] Cellulose molecule is less than 1 nm thick, and several micrometers long.
 [0096] In common language cellulose refers often to a pulp consisting of cellulose fibers. In this disclosure cellulose means individual cellulose molecules.

[0097] Cellulose fragment has between 200 and 4000 glucose units.

[0098] Amorphous cellulose does not have crystalline or even fibrous structure, and no long range order. Few molecules can run parallel a short distance (FIG. 4).

[0099] Cellulose gel is amorphous cellulose that contains solvent.

[0100] Cellulosic material is any polymer or oligomer fabricated from cellulose.

[0101] Nanoparticle has a diameter between 10 and 100 nm.

[0102] Graphitic material consists almost entirely of sp^2 hybridized carbon atoms arranged into hexagonal network. Some heteroatoms may be especially at the edges. Examples are graphite, graphene, carbon nanotubes, and nanohorns.

[0103] Material is slightly soluble, if the solubility is less than 0.5% (w/w) as molecules.

[0104] Material is sparingly soluble, if the solubility is less than 0.05% (w/w) as molecules.

Acronyms:

[0105] CAP is cellulose acetate propionate

CMC is carboxymethyl cellulose

CNP is carbon nanoparticle

CNT is carbon nanotube

EMI is electromagnetic interference

ESD is electrostatic dissipation

HNT is Hybride nanotube, HNT will include CNTs unless otherwise specified.

SUMMARY OF THE PRESENT INVENTION

[0106] The present invention provides methods for the fabrication of nanocomposites and hybride materials from two materials in a liquid into which both materials are slightly or sparingly soluble.

[0107] The present invention provides methods and compositions for the efficient, fast, and economical fabrication of polymer-graphitic material nanocomposites using nanoparticles for the facilitation of dispersion especially, if both materials are sparingly soluble.

[0108] In the currently preferred method polymer is cellulose or modified cellulose, and graphitic material consists of CNTs or functionalized CNTs, and CNT/cellulose ratio is more than 1:10.

[0109] In another currently preferred embodiment CNTs, chemically or enzymatically cut cellulose, and nanoparticles, such as calcium carbonate nanoparticles, will be first mechanically mixed, and then hydrodynamically mixed so that the amount of CNTs and cellulose is about equal, and the amount of nanoparticles is more than the combined amount of CNTs and cellulose. Depending on actual components and applications the relative amounts can be varied considerably.

[0110] Still another embodiment allows to increase the concentration of CNTs by the partial or total removal of some nanoparticles, such as calcium carbonate nanoparticles, by acid treatment, and partial or total removal of cellulose by pyrolysis that generates only volatile components. CNT concentration can be increased up to 100%, but in order to avoid reaggregation CNT concentration will be preferably under 75%.

[0111] In one aspect of the present invention the materials of the present invention can be advantageously used in supercapacitors, for EMI protection, and dispersion of graphitic materials into other polymers.

[0112] In one embodiment that is especially useful for EMI protection the material may contain magnetic or paramagnetic nanoparticles.

[0113] In another embodiment of the present invention the material that is useful for supercapacitors, contains electrically active nanoparticles, such as magnetite, Prussian blue, cobalt oxide, lead(II,II,IV)oxide, carbon nanoparticles, ruthenium oxide, titanium oxide, tin oxide, or manganum oxide.

[0114] In one advantageous embodiment of the present invention cellulose derivatives, such as cellulose fragment gel, cellulose acetate, nitrate, methyl cellulose, carboxymethyl cellulose, or ethyleneoxide cellulose are mixed or reacted with HNTs. In one currently preferred embodiment the cellulose derivative is cellulose acetate propionate that can be melted without decomposition, and the HNTs can be mixed with the melted cellulose derivative without using any solvents. Magnetic or paramagnetic nanoparticles can be deposited or mixed with these composites.

[0115] It is a further aspect of the present invention to improve the mechanical properties by chemical cross-linking cellulose or functionalized cellulose with HNTs and/or HNTs with each other, and magnetic nanoparticles. Cross-linked material is hybride material.

[0116] In one embodiment the HNT-cellulose fragment gel that is used in supercapacitors is also mechanically strong so that is also a structural component in various devices and vehicles, while the main purpose is storing electricity. Mechanical strength can be further increased by carbon fibers that will also have dual function, because they are able to distribute electric current evenly into a supercapacitor.

[0117] In another aspect of the present invention, a supercapacitor is electrically connected with two or three electrical potential sources. The first potential source is used to charge the supercapacitor. The second potential source forms a closed circuit with the first electrode of the supercapacitor. Optionally, the third potential source forms a closed circuit with the second electrode of the supercapacitor. This kind of supercapacitor may be flat, cylindrical, or some other form, and can be used to conduct electricity longitudinally.

[0118] In still another aspect of the present invention a layered structure is formed from HNT-cellulose nanocomposite and a dielectric material. If dielectric material contains paramagnetic material, a dual layer structure is useful. If no paramagnetic particles are included, a triple layer structure, in which dielectric layer is sandwiched between two HNT-cellulose nanocomposite layers is useful. This kind of layered structure can be used advantageously for the protection against electromagnetic interference (EMI).

[0119] In one advantageous embodiment HNT-cellulose nanocomposite is embedded inside a thermoplastic or thermoset resin, combining good material properties and EMI protection, and possibly also electrical storage.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0120] Fabrication of Graphitic Material-Polymer Nanocomposite The present invention provides graphitic material-polymer nanocomposites, in which individual molecules of graphitic material will not be clustered. Thus, a full utility of

graphitic material for many applications will be obtained. In most currently preferred embodiments graphitic material consists of CNTs, and polymer is cellulose or modified cellulose.

[0121] The essence of one embodiment of the present invention is a material, in which graphitic material **101** (CNTs in FIG. 1) is wrapped in molecular polymer **102** so that the surface of the graphitic material is maximally exposed at molecular level, i.e., it is not covered by another graphitic molecule, except at small areas that provide bulk conductivity. In these examples polymer is cellulose or fragmented cellulose. Cellulose provides a porous and hydrophilic structure, in which several types nanoparticles can be incorporated. Also ions can move easily in a porous and hydrophilic milieu. The distance of graphitic material particles can be adjusted very accurately by the mass ratio of graphitic material and fragmented cellulose provided that fragmented cellulose is not clustered (FIG. 1 B.). This is achieved by cutting cellulose fibers chemically, biochemically, biologically, and/or physically. Advantageously, dispersion is done in the presence of nano- or microparticles, such as alumina, silica, calcium carbonate, calcium sulfate, calcium phosphate, iron phosphate, iron oxide (ferrite), tin oxide, titanium oxide, or zinc oxide. These particles amplify the dispersion of graphitic material and cellulose, and act as spacers that prevent their recombination into homoclusters. Some of these nanoparticles are electromagnetically useful in applications. Fabrication is depicted in FIG. 2, in which cross-sections of the components are shown for simplicity. CNTs are examples of graphitic material, and the cross-section of a CNT is a circle **201**. FIG. 2 A depicts a bundle of CNTs. Nanoparticles **203** are added from left to right (FIG. 2 A to B, C to D, and E to F). Molecular cellulose is added downward (FIG. 2 A to C, B to D, C to E, and D to F). In the fabrication methods of this invention all these components are present at the same time, because positive cooperative effect. nanoparticles **203** would not mix very well with CNTs **201**. However, their high relative density promotes detachment of molecular cellulose **202** from cellulose fibers, and cellulose encapsulates both CNTs and nanoparticles.

[0122] Dispersion and the resulting interaction of two insoluble solids, graphitic material and cellulose, is achieved in this invention by using unevenly distributed kinetic energy. Many forms of mechanical or hydrodynamic mixing can be used, including blade mills, ball mills, millstones, blasting with ceramic or polymeric particles, powerful liquid jets, and ultrasonic vibration. In one currently favored method the cellulosic material is mixed with graphitic material, alumina nanoparticles, and enzyme, such as endocellulobiose, or chemicals, such as sodium hypochlorite, in water and milled with very fast blades. The mixture is further subjected into ultrasonic vibration. Nano- and microparticles have much higher density than the solvent, cellulose, or CNTs. They will greatly amplify the mixing effect, and will make the large scale fabrication of CNT-cellulose nanocomposite economical and practical. nano- and microparticles can be considered as kinetic energy concentrators that can focus the kinetic energy to individual molecules, CNTs (FIG. 3 B), and cellulose fragments (FIG. 3 A, cellulose fiber has already been cut mechanically). Kinetic energy is required for the separation of individual cellulose molecular fragments and CNTs (FIG. 3 E) or other graphitic particles. Because they are sparsely soluble into water, or other solvents that can be used in this context, they will recombine very fast, and under these con-

ditions they combine often to form CNT-cellulose nanocomposite (FIG. 3 F), in which cellulose fragment molecules are helically wrapped around CNTs. Cellulose is not only amorphous, but is molecular form, i.e., divided into smallest possible units that are molecules. Cellulose fragment molecules are not easily detached any more from the CNTs. This method works really well, when cellulose is partially cut. Intact cellulose is very difficult to separate as individual molecules. Although detergents will be avoided, but not totally forbidden in conjunction of the present invention, some other soluble agents that will help partial dissolution of the starting materials may be used. Examples are polyvinyl alcohol, polyallyl amine, CMC, scarbonch, and hemicellulose. SEM image (FIG. 8 B) proves that cellulose does not form fibers or crystallites in this material. Most of material surface is structureless and resembles the circled area **802**. This image is taken from a hole, in which several features can be seen. CNTs are in this image similar to sparsely deposited CNTs (not shown), expect that they are coated by a thin layer of molecular cellulose. Thicker layer will appear white. Some nanoparticles (calcium carbonate) **803** are also visible. The material is amorphous, and is very different from microfibrillated cellulose or nanocellulose. TEM image (FIG. 8 A) is taken from same sample. The coating layer of cellulose is very readily visible in circled area **804**. Cellulose can be seen as uneven shape around very well visible edges of MWCNT's **805**. Microcrystalline cellulose can also be advantageously used as a starting material. Microcrystalline cellulose is obtained from β -cellulose by acid hydrolysis. Kinetic energy is directly proportional to the mass m and second power of the velocity of the particle **303** (FIG. 3 A). Nanoparticles follow the liquid flow very closely. If the kinetic energy of a nanoparticle is compared with a equal volume element of a liquid, that nanoparticle can have several times bigger kinetic energy, if the density of the nanoparticle is much higher than that of liquid. Nanoparticle **303** will hit only one or few molecules, and the kinetic energy of the nanoparticles is transferred to few molecules (FIG. 3 E), while surrounding molecules experience much smaller impact from liquid. This mechanism works really well only, if the density of nano- or microparticles is considerably higher than that of the solvent. Advantageously the density of particles is at least twice the density of the solvent. This will lead to an efficient separation of molecules from a cluster or bulk material. Nanoparticles **303** will also be incorporated into the nanocomposite.

[0123] Some nanoparticles that are used during the fabrication of CNT-cellulose nanocomposite can be easily removed. For example, calcium carbonate can be removed by acid. Calcium chloride is soluble in water and is largely or totally removed during filtration, and washing. Alumina and silica can be removed with sodium hydroxide. Because cellulose can be partially or totally removed by pyrolysis, the CNT content of the final product can be deliberately adjusted anywhere between 0-100%. This is one further aspect of the present invention. Using excess of inert solid material for the dispersion of the CNTs or other graphitic materials, gives a better dispersion (FIG. 2 F). When the excess of intervening solid is removed, CNTs will still stay separated, provided that too much of cellulose **202** and/or solid nano- or microparticles **203** will not be removed (FIG. 2 B or C). Instead of totally removing nanoparticles **203** their size can be reduced. Because nanoparticles will be incorporated into the nanocomposite, and they will be consumed, their amount is advantageously quite large, typically over 50% of the total mass.

This is not mandatory, and the amount can be much smaller. Large amount of nanoparticles, such as calcium carbonate, is not problematic, because many of them are inexpensive, and can easily be removed by acid or base. Acid is consumed in the process of removing calcium carbonate, and the end product will be neutral. Soluble products can be filtered away. Moreover, dielectric nanoparticles act as spacers between CNTs like cellulose does.

[0124] When powerful solvents, such as ionic liquids, are used to solubilize CNTs and cellulose, they do not really separate CNTs completely, or CNTs will cluster with each other, when the ionic liquid is removed. Although cellulose will often be amorphous, when deposited from solution, it is still strongly clustered. Solubilized cellulose will wrap around CNTs only partially. This kind of method is under kinetic control, unlike the method of the present invention that is thermodynamically controlled. In kinetic control large molecules, CNTs and cellulose molecules, cluster with the molecules that happen to be closest, when deposited by lower temperature of addition of poor solvent. Partial reassociation of CNTs can not be prevented under kinetic control. Thermodynamic control gives good quality CNT-polymer nanocomposite as is evidenced by the present invention. If cellulose wrapped CNTs are thermodynamically stable, as experimental results of this invention demonstrate, virtually all CNTs will be wrapped inside cellulose. They can still have contact points that provide bulk electrical conductance.

[0125] One currently favored embodiment of the present invention provides electrically well conducting CNT or HNT network that is coated with electrically conducting nanoparticles so that there is a good electrical contact between HNTs and nanoparticles. Currently most advantageous particles are CNPs. Some other possibilities, cuprous iodide, cobalt oxide and Prussian blue. Graphite is one special type of CNP. Graphite is exfoliated graphite that has very good electrical conductivity, and surface area per gram is 2600 m²/g, if both sides of the sheet are included. CNPs can be made in several methods. One currently preferred method is to cutting HNTs very short, and then oxidizing them in nitric acid-sulfuric acid mixture even shorter. Some of them will exfoliate so that they are intermediates of HNTs and graphene.

[0126] In supercapacitors the role of nanoparticles is straightforward. The purpose is to increase the surface area that can be charged electrically. If the particle is spherical, it has the surface area that is four times larger than it covers on the HNT (FIG. 5). In addition many nanoparticles are porous, and the effective area is many times larger. Graphene is flat and can connect two or more HNTs. Contact area between graphene and CNTs is relatively large, while contact between two cylindrical CNTs is point-like and very small.

[0127] For EMI protection the role of the electromagnetically active nanoparticles is less obvious. The EMI protection can be obtained by two different mechanisms, reflection or absorption. Metals reflect electromagnetic fields. HNTs behave somewhat similarly. However, absorption is preferred. HNTs will be excited to higher energy levels by electromagnetic waves transiently, but they will relax by emitting electromagnetic waves. Part of the electromagnetic energy will be reflected back. When HNTs are coated with nanoparticles that are able to absorb the excitation energy from the HNTs, there will be minimal reflection. Nanoparticles act as sinks for the electromagnetic energy. This is the ideal situation, because it is desirable to minimize electromagnetic background from all electrical devices. Reflectors, such as

metals and pure CNTs do not achieve this goal, they only redirect the electromagnetic energy.

[0128] In order to obtain the full merit of these nanoparticles, a good electrical contact between HNTs and nanoparticles is necessary. This can be obtained by various means. When CNPs are used, they are well dispersed with CNTs using a dispersing agent. Cellulose fragment gel and carboxymethyl cellulose (CMC, X=CH₂COOH in FIG. 11) are currently preferred. Also cellulose succinate, maleate, and other dicarboxylic acid esters are applicable. One glucose unit may contain 1-3 acidic or other substituents. One currently preferred method for the creating a good electrical contact is pyrolysis of CMC or another cellulose derivative (FIG. 11). Cellulose and its derivatives 1101 start to decompose at temperatures above about 260° C. Cellulose will decompose mainly into volatile small molecules. Although the chemical structure of the decomposition products of cellulose derivatives are not currently known, the electrical contact between HNTs 1102 and precursor nanoparticles 1103 will be improved. Precursor nanoparticle can be nanoparticle, such as carbon including graphite, titanium dioxide, lead dioxide, lead(II,II,IV)oxide, iron phosphate, tin dioxide, magnesium dioxide, cadmium sulfide. It can be a single ion, for example, copper(II), iron(II), iron(III), or lanthanum that serves as a nucleus for the growing nanoparticle. These are nonlimiting examples. The term precursor nanoparticle is used, because the particle can be so small that it is not a nanoparticle in the strict sense of definition. During pyrolysis the precursor nanoparticle will be partially or totally coated with amorphous carbon. The chemical composition and structure of the pyrolysis product may depend strongly on the temperature of pyrolysis. We suppose that at higher temperatures, about 800° C., the product will resemble amorphous carbon 1104, and call the pyrolysis product amorphous carbon even, if the pyrolysis temperature is lower than 800° C. (FIG. 11). The result will also depend on heating method to some extent. Joule heating is fairly even. IR- or microwave heating may heat some components, CNTs and CNPs, very strongly, while having virtually no direct effect on cellulose or modified cellulose itself. However, the junction of CNT and CNP will be strongly heated, and vicinal cellulose will be pyrolyzed to provide a seal for the junction. We consider this process to be analogous to soldering. Instead of tin the soldering is performed by a decomposition product of CMC or some other functionalized cellulose. Before the pyrolysis, the CMC molecules can be connected with metal ions, such as copper, zinc, aluminum, or alike. Presence of metal ions will create cavities during pyrolysis. Acid treatment will form hydrogen bonds between CMC molecules. Additional advantage of the pyrolysis is that most of the cellulose backbone will decompose into small molecules that evaporate. Still the porosity is largely retained. Thus, the final weight of the product is reduced considerably, while quality is improved.

[0129] Another method for the connecting HNTs and electrically conducting nanoparticles, is to deposit nanoparticles directly on the surface of the HNTs. Especially, if the HNTs are dispersed using CMC, many metal ions bind with CMC that is tightly bound with HNT, and the nanoparticles can be fabricated directly onto the surface of HNTs. Currently cuprous iodide, magnetite, Prussian blue, tin oxide, and cobalt oxide nanoparticles are favored. For EMI protection also magnetite nanoparticles are advantageous. In these cases the precursor nanoparticle can be a single metal ion that is

attached with functionalized cellulose or HNT. The nanoparticle will grow around this ion, when more reagents will be added.

[0130] Currently cellulose and its derivatives are used advantageously to disperse HNTs and in some cases also electromagnetically active nanoparticles. cellulose provides also porosity that is useful especially for supercapacitors.

[0131] Still another mixing method is provided by shear force that can be especially strong in a high pressure dispersion apparatus, which is commercially available, for example DeBEE 2000 Pilot Homogenizer. The pressure gradients in these devices can be hundreds of bars.

[0132] Mechanical mixing is ineffective at very short distances because the molecules move together about the same speed, although counterstroke mixer alleviates partly this problem. The ultrasonic vibration agitates molecules and particles by accelerating them back and forth in a rapid succession. Thus, the diffusion gradients of the reagents are diminished. This greatly increases the rate of the diffusion dependent collision and binding of particles.

[0133] The power of one sonotrode can be between 0.1 and 50 kW, most advantageously between 1 and 20 kW. When multiple sonotrodes are used, the power may vary with time so that interference pattern will change all the time. Thus, the whole reaction mixture can be more evenly agitated. Ultrasonic processes can be easily scaled up and optimized (Hielscher T., Ultrasonic production of nano-size dispersions and emulsions, ENS'05, Paris, France, 14-16 Dec. 2005).

[0134] Cellulose xanthate is used industrially for the fabrication of cellulose fibers. Cellulose acetate, pthalate, acrylate, and nitrate are also much better soluble into organic solvents than cellulose. Sulfonation, carboxylation, amination, and many other functionalizations increase the solubility of the CNTs into water several orders of magnitude. All these and other functionalized cellulose derivatives and CNTs can be used as additives in the context of the present invention. Often the primary hydroxyl group is easiest to functionalize (X in FIG. 11), although other hydroxyl groups can also be functionalized.

Currently Preferred Embodiment for the Fabrication of Modified Cellulose Fragment-Nanoparticle Gel

[0135] The starting material for the method of this invention can be cellulose that is made from wood, grass, or any other plant material. Also bacterial cellulose, such as produced by *Acetobacter xylinum*, can be used. Because of low cost, one preferred starting material is the finely divided suspension that is not retained in paper during the fabrication of paper that also contains nanoparticles. Microcrystalline cellulose is another preferred starting material, because of consistent good quality.

[0136] Cellulose molecules consists of about 5 000 β -glucose moieties. Vicinal cellulose molecules are strongly hydrogen bonded, and separation of individual cellulose molecules is nearly impossible. Hydrolysis of β -glucoside bonds produces fragments that are easier to separate. Fragments should be long enough so that they are still interesting for the materials applications, i.e., they should form strong hydrogen bonded network and be slightly or sparingly soluble into water. Hydrolysis can be performed by chemical means, for example, catalyzed by acids, such as sulfuric or hydrochloric acids, or enzymatically. Also certain molecules or ions, including boric acid, aluminum, iron, zinc, magnesium, and calcium ions, will catalyze the hydrolysis. Cellulose is also

thermally unstable above 260° C. Superheated steam above 260° C. will be able to cut cellulose molecules.

[0137] Separation of the cellulose fibers and cellulose fragments (fragmented cellulose) is essential for the fast reaction. Otherwise the product will inhibit the further reaction. Boric acid under basic conditions will assist the transfer of cellulose fragment. Chaotropic agents will also break hydrogen bonds that keep cellulose molecules and fibers together. One of the most powerful chaotropic agent is guanidinium isothiocyanate. Ultrasonic vibration is one currently preferred method for the detachment of fragments from cellulose fibers. Temperature has also a significant effect on the breaking of hydrogen bonds.

[0138] Reactions rely on diffusion on a molecular scale. Mechanical mixing is ineffective at very short distances because the molecules move together about the same speed. The ultrasonic vibration agitates molecules and particles by accelerating them back and forth in a rapid succession. Thus, the diffusion gradients of the reagents are diminished. This greatly increases the rate of the diffusion dependent reactions. The separation of large molecules and nanoparticles benefits even more from the ultrasonic agitation. For example, diffusion of an enzyme is relatively slow, but ultrasonic vibration promotes the movement of an enzyme to and from the surface of a cellulose fiber. The cellulose fragment that is partly or totally detached from the cellulose fiber will have different acceleration in the same oscillating medium than the remaining aggregate. Thus, they are pulled apart. If the process relies on the diffusion alone, it would take much longer time. One aspect of the present invention is to use enzymes 701 that are conjugated with spacers, such as PEG, with nanoparticles 703 (FIG. 7). Conjugation of enzymes with nanoparticles is well known in the art. These kind of particles act simultaneously mechanically and biochemically.

[0139] Also purely chemical reaction, such as acid hydrolysis, can be accelerated by nanoparticles that loosen the structure of a cellulose fiber. This will further promote the chemical reaction and separation of components. Nanoparticles must be tolerant against the chemical milieu of the process. For example, hydroxyapatite nanoparticles tolerate basic conditions, and silica particles are resistant to acidic conditions. Earth alkali sulfates are suitable in the presence of sulfuric acid, because the excess of the sulfate ions prevents the dissolution of these particles. Some carbonates, such as calcium or barium carbonates, may be used especially, if the solution contains soluble carbonate, such as sodium carbonate.

[0140] Removal of the reaction product is not enough, if the product can diffuse back onto the cellulose fibers. Nanoparticles can assist the removal by bonding the cellulose fragments. Also CNTs will be coated by cellulose fragments. Binding of cellulose fragments by particles is advantageous for the hydrolysis of cellulose, but also fragments can be further hydrolyzed. In order to prevent further fragmentation of primary cellulose fragments flow through reactor is currently preferred (FIG. 6).

[0141] In the simplest form the flow reactor has outer and inner tube. A part of the inner tube is tubular grid that has mesh size between 200 and 2000. A thick slurry of cellulose starting material that contains catalytic agent, such as acid, enzyme, or microbe, and nanoparticles flows downward. Water that might contain nanoparticles or CNTs flows upward in the outer tube. The content is agitated, preferably by ultrasonic vibration. Cellulose fragments will be trans-

ferred from inner tube into the outer tube. Catalytic agent may be bound onto a solid substrate so that it is retained inside the inner tube. For example, an enzyme may be bound by a spacer onto a relatively large particle, or ion exchange resin may be used to carry protons or catalytic metal ions. In order to facilitate the transfer the product through the grid, the pressure between the two tubes may oscillate so that there is back and forth flow between the inner and outer tube. Oscillation can be accomplished by coordination of pumps or valves that are part of the system. In an alternative embodiment cellulose and CNTs are mixed mechanically, and the mixture is suspended into water, and flows in the inner tubular grid. It is obvious that the role of inner and outer tube may be reversed, and also any combination of flow directions will be applicable.

[0142] Flow reactor that has more throughput is depicted in FIG. 6. It has 14 tubular grids. The starting material is pumped into one tube that is divided into 14 tubes, and after passing the grids inside the reaction chamber these tubes are connected into one tube again.

[0143] Although the continuous reactor (FIG. 6) is currently preferred, it is obvious that the ultrasonic method of this invention is applicable also in bath type reactors. The ultrasonic vibration is more efficient at higher pressures. The pressure can be increased in continuous reactors by hydrostatic pressure. About 10 m high column of water based liquid in a tube or pipe corresponds to one bar (megapascal) of pressure. The pressure can be between 1 and 50 bar and most advantageously between 2 and 5 bars. Excessively long tubular reactor can be avoided, if the reactor is closed and pumps are used.

[0144] The ultrasonic vibrator generates heat, and the temperature can actually increase slightly in the reactor. External or internal heating is also possible in the reactor. The heating can be accomplished by the methods that are well known in the art. Also electromagnetic radiation can be used, especially IR-, or microwave radiation. The wavelength is preferably chosen so that cellulose, nanoparticles, or CNTs absorb it effectively. This radiation may be advantageously directed into the reaction chamber.

[0145] The reactor may contain a mechanical mixer. The mixer may have blades, propellor, or screw. The motor is advantageously outside the reactor and on the top, and the shaft comes into the reactor. Mechanical mixing can be used with or without ultrasonic vibration.

[0146] While cellulose molecules are strongly hydrogen bonded within one cellulose fiber, the interaction of molecules between two fibers is much weaker, i.e., the structure is granular. On the contrary, when solid material is reconstructed from individual cellulose fragment molecules, they can form continuous 3D network, in which vicinal molecules will be strongly hydrogen bonded, and essentially a continuous, isotropic material will be formed. Although some molecules bind parallel with each other, no significant fibrous structure is formed. The material is amorphous gel-like. This is clear distinction with nano-, and microfibrillated cellulose, and, of course, with cellulose itself. Very strong paper, boards, and other pieces that have more complicated shapes can be produced from cellulose fragment gel. Nanoclay, and other micro- or nanoparticles, including but not limited to silica, alumina, magnetite, titanium dioxide or silicate, cadmium sulfide, Prussian blue, CNTs, carbon, and graphite, can be mixed with fragmented cellulose mass advantageously during fragmentation. Mixing of particles and cellulose frag-

ments can also be done before the fabrication solid objects. These particles can give desired additional properties, such as increased modulus, color, magnetic or electric properties. The product is Celose™ in all cases. If it contains CNTs, for example, it can be specified as CNT-Celose™.

[0147] If only ESD is required, mixing of 0.1-2% of CNTs will be sufficient. Good EMI protection is obtained if the material contains about 10-40% of CNTs. Because CNTs reflect microwave radiation, addition of carbon nanoparticles is advantageous so that the microwave radiation is mostly absorbed. Magnetic protection will require 1-20% of ferrite particles. Ferrite particle can be quite large, up to 50 µm, and they may be coated with silica or alumina layer. Material that is used for heating elements should have specific resistance around 1 Ωcm, which is obtained, when the CNT content is 10-30%. Supercapacitors are advantageously made of CNT-cellulose nanocomposite that contains 20-70% of CNTs. Conducting ink for printable electronics should contain 20-70% of CNTs. Product that contains 70% of CNTs and 30% cellulose (molecular fragments) is still paper-like and can be easily handled and formatted into various shapes. However, the good properties of CNT-cellulose nanocomposite do not increase linearly with CNT content. Instead it seems that capacitance and EMI protection reach optimum around 50% of CNTs.

[0148] While fragmented cellulose is advantageous for the dispersion of nanoparticles and CNTs, part of it or all of it can be removed after dispersion process. For example, the weight of supercapacitors should be minimized, and cellulose or cellulose fragments do not have active role in the electric storage function. The excess cellulose can be removed by further fragmentation so that the fragments become soluble, and can be washed away, or are transformed into carbon that is actually active in the supercapacitor (FIG. 2 F to D, or E to C). In the extreme case the thermal fragmentation can go so far that fragments will evaporate. Enzymatic fragmentation is very gentle, and will retain the overall structure of the CNT network so that the collapse is avoided. The voids that will be created by enzymatic treatment can be filled with nanoparticles that can be deposited using soluble components, or with the premade nanoparticles. These nanoparticles should be electrically active in supercapacitor function. Nonlimiting examples include iron phosphate, magnetite, Prussian Blue, cadmium sulfide, lanthanum fluoride, cobalt oxide, tin oxide, titanium oxide, or lithium titanate. Cobalt oxide is very convenient, because it can be electrochemically deposited that guarantees that the deposition happens on the surface of CNTs.

[0149] Paper or formatted pieces can be compressed under pressure, between 2 and 100 bar, in order to make pieces thinner and harder. Heating will further assist compactification.

Functionalization

[0150] In some cases the starting material may be functionalized, for example, it can be carboxymethyl cellulose, acetyl cellulose, nitrocellulose, glycidyl cellulose, hydroxyethyl cellulose, or PEG-cellulose. Degree of functionalization is especially important for the microbial or enzymatic hydrolysis. High degree of functionalization may prevent hydrolysis. On the other hand optimal functionalization will allow limited hydrolysis so that long fragments will be obtained that are resistant to further hydrolysis.

[0151] Cellulose fragment can be functionalized by any method known in-the-art after they have been fabricated. Because they are more easily detached from other fragments than cellulose molecules from cellulose fibers, functionalization of fragments is often relatively straightforward. Especially the interaction with solid particles, such as nanoparticles and CNTs is fast and might require minimal amount of solvent, such as water.

[0152] Cellulose fragment can bind nanoparticles with covalent, ion, coordination, or hydrogen bond (FIG. 5). Hydroxyl groups bind with many metal ions with coordination bonds. Nonlimiting examples are aluminum, magnesium, calcium, and titanium ions. Large number of bonds makes the interaction very strong. This has important implications for the fabrication of high modulus materials. Silica and alumina form hydrogen bonds with cellulose fragments. Carboxymethyl functionalized cellulose fragments will form ion bonds with metal ions, and metal ion containing particles. Strong bond is formed with aluminum, copper, zinc, and tin ions. These are nonlimiting examples. Covalent bonds require a chemical coupling reaction, for example, amide bond formation between amino functionalized CNT and carboxymethyl functionalized cellulose fragment using carbodiimide as a coupling reagent. Glycidyl cellulose fragments will bind spontaneously with amino groups.

Supercapacitors

[0153] The capacitance is

$$C = \frac{Q}{V} = \frac{A\epsilon}{d} \quad (1)$$

where Q is the charge, V is the potential, $\epsilon = \epsilon_0 \epsilon_r$, in which ϵ_0 is the permittivity of empty space and ϵ_r of the medium and d is the thickness of the electric double layer, which is about 0.3 nm almost independently of the materials involved. Dielectric constant (permittivity) of solution is dictated by the solvent that is water or some other polar solvent in electrolyte capacitors. In the table 1 are some solvents and their dielectric constants.

TABLE 1

| Permittivities of some solvents that can be used in supercapacitors of the present invention. | |
|---|--------------|
| Liquid | Permittivity |
| Methanol | 33 |
| Acetonitrile | 36 |
| Glycerol | 47 |
| Water | 80 |
| Ethylene carbonate | 90 |
| Formamide | 111 |
| N-methylacetamide | 179 |
| N-methylformamide | 189 |

[0154] Electrolytes dissolve also better into the solvents that have high permittivity. Solvents should be electrochemically as inert as possible. Water is perhaps most reactive solvent that is listed in Table 1. In organic solvents tetramethyl-lammonium tetrafluoroborate or an ionic liquid can be used as an electrolyte.

[0155] The electrically conducting surface area is linearly correlated with the capacitance. One way to further increase

the active surface area is to adsorb or couple conducting particles 902 with the HNTs 901 (FIG. 9). Spherical particle has a fourfold area compared to the area 903 that it covers. Moreover, most of the covered area is still active. In the ideal case the active area can be increased fivefold. This increase is independent of the radius of the particles. Thus, it is advantageous to use as small nanoparticles as possible, because overall mass and volume will increase minimally. Porosity or roughness of the particle 902 will increase the area even more.

[0156] The conductivity of the nanoparticles is not of prime concern. Because cellulose-HNT network conducts electricity well, the nanoparticles that are in contact with HNTs will be charged even, if they are poor electrical conductors. Nanoparticles should be resistant to corrosion under electrical potential. nanoparticle 1001 may be coated with a thin layer 1002 that is chemically and physically very stable (FIG. 10). Example is coating of magnetite, or Prussian Blue particle with iron phosphate, plumbate, or silicate, or cobalt oxide with cobalt phosphate. Coating may be dielectric, if it is very thin, almost atomic layer, but will still increase stability. Thin phosphate coating may be done by dipping CNT-cellulose-nanoparticle nanocomposite into dilute phosphoric acid or sodium phosphate solution.

[0157] In addition of the surface area the capacitance depends on the ratio ϵ/d . Because in water the distance of ions from the surface of HNTs is about 0.3 nm, this ratio is about 267 ($=80/0.3$). If HNTs are coated with a 3 nm layer that has $\epsilon_r > 800$, the capacitance will increase. One such material is barium titanate that has $\epsilon_r \approx 10,000$. The capacitance will increase 12-fold in ideal case. Because of defects in the coating, the increase in the capacitance will be less, for example, 4-fold. HNTs are now coated with electrically insulating layer, and potential of the HNTs can be increased many fold, up to 3-fold, without electrolysis of water. Total charge will be 12-fold as compared the same system without any coating of HNTs. Power density in this example will be 36-fold (3×12). In general the energy of a capacitor is:

$$W = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} CV^2$$

[0158] Because continuous coating with a highly polarizable dielectric can increase both capacitance (C) and potential (V), the increase in the stored energy can be very large.

[0159] The present invention provides one additional advantage over conventional supercapacitors. Traditionally only a thin layer of active material, such as carbon black is compressed onto an electrode, such as aluminum foil. Because HNT network is fairly well conducting, much thicker electroactive layers can be used. This is especially true, when the contact between HNTs has been improved, for example, by partial graphene connectors (FIG. 16).

[0160] CNT-cellulose-nanoparticle layers can be dried so that they are easy to handle. Thickness of the layers can be between 1 μm and 1 cm, advantageously between 0.1 mm and 1 mm. Pulp-like mass can be deposited directly onto a grid that can be made, for example, of copper. Grid can be coated with a thin layer of gold or platinum. This process resembles the conventional papermaking. In this case the composite layer and grid will not be separated. Alternatively the grid can be made of plastic. Then the grid is separated and replaced with a copper grid. The latter method is preferred, because the holes in the grid can be much bigger, i.e., the mesh number

can be smaller. Currently, the mesh number about four is preferred. Layers will be stacked and the grids will be electrically connected with each other within a stack. The stack will be connected also with one electrode. Two stacks will be placed into a container so that they will be separated with a semipermeable membrane. When copper grid is used, the liquid is preferably an organic solvent. Grid can also be made of some other material, such as aluminum, stainless steel, chromium, copper, silver, or graphite. It can be also coated so that it is not corroded on water. Coating material can be, for example, gold, platinum, polyaniline, polythiophene, or silver or HNT containing epoxy. There is virtually no size limit for this kind of supercapacitor. Instead of stacking of layers, the HNT-cellulose nanoparticle composite can be rolled with the grid into a cylinder. Other constructions are equally possible.

[0161] In many applications it is preferable to have a capacitor that is essentially one piece (FIG. 15). This can be accomplished, if the semipermeable membrane 1503 is made of cellulose, or modified cellulose. Very wide range of cellulose derivatives may be used. First, paper of CNT-cellulose fragment gel is fabricated, but dried only partially. On top of this CNT containing paper 1502 is fabricated a layer of non-conducting paper 1503, and the two-layer paper will be partially dried. CNT-cellulose fragment gel is added on top of the non-conducting paper so that a seamless structure (FIG. 15) will be obtained.

[0162] Especially, when supercapacitor is one piece, it is desirable that the electrolyte is solid. Electrolyte can be ionic liquid, such as methyl ethyl imidazole tetrafluoroborate, absorbed into polymer that can be cellulose or some other polymer. Electrolyte can be also be any commonly used salt in polyethylene glycol (PEG) or poly(ethylene carbonate). These kinds of supercapacitors can be printed, and in any case they require minimal casing.

[0163] In another analogous embodiment a three-layered hard board will be fabricated, two CNT-cellulose fragment gel layers on both sides and cellulose or modified cellulose layer in the middle. Hard boards are manufactured by compressing pulp between one grid and plate or two grids using high pressure, between 2 and 40 bar. Aluminum foils or other similar electrodes will optionally be glued on both sides so that electrical contact is created. Electrodes may be in several layers inside the hard board. If water is used as a solvent for electrolyte, then graphite electrodes, such as graphite fiber, will be preferred.

[0164] An alternative embodiment does not have semipermeable membrane, but instead ion selective membrane. The ion selective membrane will allow noncompatible electrolytes in anodic and cathodic compartments. Examples are sodium sulfate or potassium phosphate in anodic compartment, and magnesium or calcium chloride in cathodic compartment. If semipermeable membrane is used in these cases, a precipitate would be formed and the supercapacitor would be clogged.

[0165] Still another advantage of the ion selective membrane is that electrochemically active ions or particles can be more advantageously used. For example, magnetite, lead(II, II, IV)oxide, Prussian blue, or cuprous iodide can all be oxidized and reduced. Nickel and cobalt analogues of magnetite and Prussian blue can be equally well be used. Prussian Blue contains both ferro (ironII) and ferri (ironIII) ions, and can be oxidized or reduced. Some metal ions can be both oxidized and reduced. These include Cr³⁺, and Mn⁴⁺. In general, par-

ticles that can be oxidized or reduced are applicable within the scope of this invention. These particles add both capacitance and pseudocapacitance that is electrochemical process. Using these kind of particles will increase the capacitance more than Eq. 1 implies, because of the space charge also volume of the particle is important.

[0166] The electrochemical products would gradually diffuse through a semipermeable membrane and the supercapacitor would be discharged. The ion selective membrane retains the electroactive species in their compartments. In addition to the actual capacitance, these electroactive species contribute to so called pseudocapacitance that is very efficient way to increase the apparent capacitance. While conventional capacitance relays on the surface charge, the pseudocapacitance utilizes space charge, i.e., particles are charged also inside. Because this process requires only movement of electrons inside the particles, and particles are not consumed, unlike the electrodes in batteries, the lifetime of the supercapacitor can still be very long. In other words, there is no material removal and consequent reassembly of electrodes as is the case in batteries. In FIG. 12 is a TEM image of CNT-cellulose-Prussian Blue material. The sample was dispersed into water by ultrasonic vibration. TEM grid was dipped into a very dilute dispersion. TEM grid had holes that appear as light large oval shapes in FIG. 12. CNTs 1202 and Prussian Blue nanoparticles 1201 are clearly visible. While most nanoparticles are attached with CNTs, the ultrasonic vibration separated some nanoparticles from CNTs.

[0167] Ion selective membranes can be made of many materials including ion exchange plastics, glass, ceramics, such as zeolites. Superionic conductors are one currently one preferred class of materials for ion selective membranes. Polyethylene glycol is sodium and lithium ion conductor. Many ion selective membranes have ion exchange properties, and in addition well defined very small pore size. Zeolites are a prime example of such materials.

[0168] Graphene is one currently preferred nanomaterial for the increasing the surface area, and connecting HNTs 1600 and 1601 electrically FIG. 16. Cellulose 1602 will also separate graphite sheets 1604 from each other so that flat sheets do not collapse back together. Another method to prevent collapse of graphite sheets is to coat them with nanoparticles 1603, such as silica, alumina, carbon, gold, silver, chromium, cadmium sulfide, tin oxide, magnetite, Prussian blue, lithium titanate, lanthanide fluoride, or iron phosphate that will act as spacers. Advantageously, these nanoparticles are also electrically conducting so that their surface will contribute also to supercapacitor function. If they are electrochemically active they act as pseudocapacitors.

Continuous Coating of CNTs

[0169] Eq. 1 implies that increase of the dielectric constant will increase the capacitance linearly. Dielectric constant can be increased by proper choice of solvent, and also by some high dielectric constant coating. While the choice of a solvent is well known in-the-art, the coating is a subject of the present invention.

[0170] In one currently preferred embodiment CNTs are first suspended into water using either CMC, or cellulose fragment gel. Water is replaced by 2-propanol. A mixture of barium i-propoxide and titanium i-propoxide in 2-propanol is added. When potassium hydroxide water solution is added barium titanate is formed. Polarity may be affected by applying electrical potential during the deposition. Preprepared

barium titanate nanoparticles may be added before the deposition of barium titanate from alcoholates so that these barium titanate nanoparticles will be glued by in situ deposited barium titanate with CNTs. Chemical vapor deposition (CVD) or atomic layer deposition (ALD) provide good quality layers. Especially ALD allows atomic precision in growing of the coating layer. These methods are well known in the art.

[0171] Although the distance of ions from CNT (d in Eq. 1) will increase, the dielectric constant will increase much more, and capacitance will be much bigger, for instance 10 times bigger. The increased surface charge density will increase conductivity. Thus, during charging the conductivity should increase, and no additional electrodes will be needed. In supercapacitors the density of electrons (in cathode) or holes (in anode) increases and electric wire having supercapacitor structure can be fabricated. Conductivity can increase substantially, if the temperature is lowered so that electrons form Cooper pairs.

EMI Protection

[0172] Structures that provide electromagnetic shield can be made from CNT-cellulose-MP materials. The electromagnetic noise will penetrate poorly through most CNT-cellulose-MP materials.

[0173] HNT-cellulose-nanoparticle material may additionally contain magnetic or paramagnetic particles for ideal EMI protection. Paramagnetic particles are advantageously ferrite particles, for example magnetite particles. Particle size can be between 5 nm and 50 μm . Particle concentration should be advantageously such that percolation threshold will be exceeded. Magnetic particles and paramagnetic particles are simply called magnetic particles in this disclosure, and denoted as MP.

[0174] CNT(1701)-cellulose (1702) composite and magnetic particles (1703) can be in the same layer 1704 (FIG. 17 A), or in separate layers 1705 and 1706 (FIG. 17 B). MPs are advantageously coated with silica or aluminum oxide layer (See FIG. 10). This is accomplished by dipping into tetraethyl silicate or aluminum isopropoxide solution, for example in 2-propanol.

[0175] Currently dual layer structure is preferred for EMI protection, mainly because the density of electrically and magnetically active particles can be higher than in one layer containing both. It must be noted that dual layer structure can contain layers, which contain both CNTs and magnetic particles. In this case one layer contains more CNTs and the other more magnetic particles.

[0176] Triple layer structure is even more efficient than single layer or dual layer. In this structure electrically conducting layers are outside, and magnetically active particles or even an inert layer is in the middle. Triple layer is several orders more effective even, if the total amount of active materials is the same as in the single layer structure. The efficacy is partially due to multiple reflections between layers so that interference destroys most of the incoming electromagnetic radiation. Another reason for the increased efficacy is that the node of the radiation can not be coincident with both layers simultaneously.

[0177] When paramagnetic particles are deposited on solid surface, for example, by spraying, a magnetic field be applied. The first magnetic field is advantageously parallel with the surface. Another layer may be deposited so that the second magnetic field is still parallel with the surface, but perpen-

dicular to the direction of the first magnetic field. If multiple layers (FIG. 18) will be deposited the magnetic field direction can be different every time. Single layer structures can be fabricated so that MPs are mixed simultaneously with cellulose and CNTs, or they are added afterwards. They can be added as premade particles, or synthesized in situ. In dual layer structures the MP layer can be fabricated with known methods. Also then cellulose and functionalized cellulose can be used as binding agents.

[0178] In most applications the EMI protective paper will be impregnated with plastic, such as polypropylene, polyacrylate, or polycarbonate or resin, such as epoxy or polyurethane. Plastic prevents the release of CNTs in consumer products. It also helps the attachment of shield into an electronic device by hot pressing, gluing or by some other commonly used dealing method.

[0179] Applications are plentiful, including all electronics, including computers, mobile devices, wireless link stations, electric motors, and electrical wires.

Further Processing

[0180] Paper and paper-like products can be fabricated with the same methods that conventional paper is fabricated. CNT-molecular cellulose-nanoparticle nanocomposite is a gel in water, and retains water very well. Water must largely be removed during the fabrication of paper. Coagulants, such as copolymer of acrylic amide and acrylic acid or other well known coagulants, can be used. These materials can also be used instead of cellulose to wrap graphitic materials according to this invention. We have found that freezing of the gel before paper fabrication will decrease the filtration time considerably. Thus, the fabrication of paper either in sheet format or roll format can be done by conventional methods. Supercapacitors and EMI protection materials can be layered structures. These can also be made by modified methods, in which the first layer is filtered so that most of the water is removed, and on top of the first layer is added a second layer, and so on. Various layers form one continuous paper-like structure, in which the layers are firmly connected with each other.

[0181] Especially a three-layer structure can be formed by coating a premade paper or plastic on both sides with a CNT-molecular cellulose-nanoparticle nanocomposite gel or ink. All kinds of surfaces and shapes can be coated with wet material. After drying the surface is partially or totally covered with cellulose-HNT material.

[0182] The materials of the present invention can be mixed with other composite or hybride materials. These include thermoplastics, resins, ceramic, and even metals.

[0183] HNT-cellulose and HNT-cellulose-MP materials can be mixed with melted thermoplastics or with monomers that will be polymerized after the mixing, cellulose, HNTs, or both can be functionalized so that they will bind chemically with the matrix. For instance, cellulose acrylate may be mixed with the acrylate monomer. HNTs may be added into this mixture, and the mixture is polymerized. In this case there is no need for prefabrication of HNT-cellulose nanocomposite. Also HNTs may be functionalized with acrylates in this specific example. Similarly, cellulose-HNT can be incorporated in polycarbonate, silicone, nylon, Kevlar, polystyrene, polyethylene, polypropylene, and polyvinylchloride.

[0184] Carboxymethyl cellulose (CMC) is currently preferred with MPs. Carboxylates bind strongly with MPs, and

will disperse them. Additional ferro, ferri, copper, tin, aluminum, or several other salts will cross-link CMC, and create strong structure.

[0185] In one currently preferred method a concentrated mixture of the HNTs and cellulose acetate propionate (CAP) is fabricated first, and this mixture is then mixed with a thermoplastic. The advantage of this process is that CAP can be melted without decomposition, and no solvent is required in the fabrication process. Once HNTs are dispersed into the CAP, they can be easily mixed with the thermoplastic. The HNT-CAP and thermoplastic can be mixed as powders and heated so that both of them will be melted. The good mechanical mixing is sufficient for the dispersion of HNT-CAP into the thermoplastic, although optionally ultrasonic vibration may be used.

[0186] CAP may be partially hydrolyzed with a base, so that some or all of the hydroxyl groups of cellulose are released. The purpose of this hydrolysis is to make the composite more polar or hydrophilic, and also more porous. This can be important in some applications, such as capacitors, in which ions must be able to move.

[0187] If covalent coupling with the matrix is not essential, the mixing of the cellulose-HNT with a polymer melt is preferred over copolymerization. In several cases mixing is easier, if proper cellulose derivative is used. Often cellulose acetate is preferred. For polystyrene, cellulose benzoate is adequate, while for polypropylene cellulose butyrate or palmitate is a better fit.

[0188] Thermoset plastics and resins are typically fabricated from two components, which are mixed shortly before the use. Cellulose, HNTs and MPs can be mixed with one of these components or both. For example, cellulose glycidyl ether-HNT nanocomposite may be mixed with bisphenol A bisglycidyl ether. When this epoxy is mixed with a hardener before the use, HNT-cellulose nanocomposite is chemically coupled with the epoxy matrix via cellulose. Coupling may be assisted by addition of alumina nanoparticles into HNT-cellulose-nanoparticle nanocomposite. Other alternative is to soak nanocomposite into aluminum i-propoxide solution in i-propanol. Aluminum ion will catalyze the reaction between hydroxyl groups and epoxy groups leading into a covalent linkage between epoxy matrix and cellulose and similarly between epoxy matrix and HNTs. If HNTs are functionalized with epoxy groups, also HNTs and cellulose will be chemically coupled. Similarly, HNT-cellulose may be mixed with urethanes. The hydroxyl groups of cellulose react with isocyanate groups, and cellulose serves as a hardener. Other resins include phenol-formaldehyde, in which can represent phenol-formaldehyde resin. HNT-cellulose-nanoparticle paper can be used to reinforce plastics and resins similarly as glass or carbon fiber. Because CNT or HNT content can be very high the effect will be significant.

[0189] Many ceramics can be fabricated by mixing the components first in water. Also water-alcohol mixtures can be used. These are suitable for the mixing of cellulose and CNTs.

[0190] Thus, all components can be mixed simultaneously. For example, compounds like calcium hydroxide, aluminum hydroxide, copper chloride, and iron chloride can be mixed with cellulose-NT slurry, and sodium hydroxide can be added, when applicable. The mixture is heated at about 110° C., dried, and calcinated at relatively low temperature of about 250° C. under nitrogen. If silicic acid is added, glass-

like product will be obtained. If pyrolysis of cellulose backbone is desired, the temperature can be much higher, up to 800° C.

[0191] Sol-gel method is amenable for the fabrication of HNT-cellulose nanocomposites. This method is closely related to the fabrication of ceramics. In the sol-gel method the solvent is preferably alcohol, and additional gel forming component, such as tetraethyl silicate, is part of the mixture. When small amount of water is added, tetraethyl silicate is hydrolyzed, and silica gel is formed. Silicon atom may be connected with one or two alkyl or aryl groups like methyl, or phenyl groups, which may also have functional groups, such as hydroxyl, amino, or carboxylic groups. Metal alcoholates are hydrolyzed by water into metal hydroxides, which often transform into corresponding oxides either spontaneously, or after heating. In order to neutralize the hydroxide ions, the water may contain acid, such as hydrochloric, hydrobromic, nitric, perchloric, sulfuric, formic, trifluoroacetic, or an easily hydrolysable ester like methyl formate. If the water phase contains anions, such as halogenides, sulfide, selenide, telluride, carbonate, sulfate, phosphate, arsenide, and oxalate a corresponding salt is formed. The solution may contain several different alcoholates, and tetramethoxy or tetraethoxy silicate. Either composite nanoparticle, or metal silicate nanoparticles are formed in this case. Typical metal alcoholates or related compounds include barium(II)isopropoxide, zinc(II)methoxy ethoxide, aluminum(III)isopropoxide, iron (III)isopropoxide, nickel(II)methoxy-ethoxide, holmium(III) iso-propoxide, yttrium(III)iso-propoxide, europium(III)-D-3-trifluoro-acetylcamphorate, tin(IV)iso-propoxide, titanium (IV)isopropoxide, titanium(IV)iso-butoxide, tungsten(V) ethoxide, tungsten(VI)isopropoxide, bismuth(III)methoxy-2-methyl-2-propoxide, hafnium(IV)tert-butoxide, hafnium tri-isopropoxy tetramethylheptane-dionate, zirconium(IV) tert-butoxide, niobium(V)iso-propoxide, vanadium(V)tri-isopropoxide oxide, aluminium cobalt isopropoxide, lead(II) titanium(IV)isopropoxide, lead zirconium ethylhexano-isopropoxide, and SrTa₂(OEt)₁₀(dmae)₂. Almost any ceramic nanocomposite can be prepared using alcoholates. Examples are lead zirconium titanate, barium titanate, and strontium bismuth thallium oxide containing nanocomposites, which are piezo electric materials, and yttrium barium copper oxide that is a high temperature superconducting material. Barium titanate has very high dielectric constant, and is useful in supercapacitors. Barium and strontium titanates are examples of ferroelectric materials. Another example is potassium tantalum niobate.

[0192] Silylamides are another class of soluble metal compounds that are hydrolyzed by water. These include tris[N,N-bis(trimethylsilyl)amide]-cerium(III), and analogous compounds of erbium(III), europium(III), gadolinium(III), holmium(III), lanthanum(III), lutetium(III), neodium(III), praseodymium(III), samarium(III), scandium(III), terbium (III), thulium(III), ytterbium(III), and yttrium(III). These metal cations are lanthanides, and form fluorescent nanocomposites. Some other metals can be coprecipitated in order to change absorption or emission properties, or simply to reduce the cost.

[0193] Cellulose-HNT aerogels are made from the compounds mentioned above by replacing alcohol with supercritical carbon dioxide, and slowly evaporating carbon dioxide.

[0194] Thermal instability of cellulose prevents the incorporation of HNT-cellulose into any metal that has melting

point above 260° C. However, there are other methods that are applicable. These include compression of nano- or micropowders, electrochemical deposition of metals, and flash cooling of evaporated metals so that amorphous metals are formed around HNT-cellulose at a low temperature. Again, if pyrolysis is desired, it can be performed before mixing the HNT-amorphous carbon-nanoparticle nanocomposite with metal. Then the temperature limit can be much higher, up to 800° C. The pyrolysis can also be combined with mixing the cellulose-HNT-nanoparticle-nanocomposite with hot metal.

EXPERIMENTAL DETAILS

[0195] While this invention has been described in detail with reference to certain examples and illustrations of the invention, it should be appreciated that the present invention is not limited to the precise examples. Rather, in view of the present disclosure, many modifications and variations would present themselves to those skilled in the art without departing from the scope and spirit of this invention. The examples provided are set forth to aid in an understanding of the invention but are not intended to, and should not be construed to limit in any way the present invention.

[0196] In all examples starting materials, and the produced nanocomposites are slightly or sparingly soluble in the solvent that is used.

Example 1

[0197] One gram of CNTs, and two gram of cellulose, two grams of calcium carbonate nanoparticles were suspended into 100 ml of 0.2% CMC solution in water by using 400 W ultrasonic vibration 1 h. Similarly, one gram of CNPs were dissolved into 100 ml of 0.2% of CMC solution. These two dispersions were mixed, and the mixture was further sonicated 1 h. The mixture was made slightly acidic by 2 M hydrochloric acid. Paper sheet was fabricated by conventional paper making process, so that the thickness of the paper was about 150 µm after compression. Paper was heated between a stainless steel grid and a glass plate 2 h at 280° C. The weight loss was 36%. The specific resistance of the paper was 0.6 Ωcm, and specific capacitance 212 F/g.

[0198] When the heating was done in a microwave oven the specific capacitance was 112 F/g.

Example 2

[0199] One gram of enzymatically fragmented cellulose, and one gram of calcium carbonate nanoparticles were suspended into 50 ml of 2-propanol, and 500 mg of HNTs were added. The mixture was sonicated 60 minutes with tip sonicator, power 400 W. Paper was prepared by conventional methods. After drying the paper was dipped into 0.5 M CuCl₂ solution. After drying the paper was dipped into 0.5 M KI solution, and immediately into methanol in order to remove iodine. This paper had specific capacitance 260 F/g.

Example 3

[0200] Two grams of cellulose fragment gel, two grams of calcium carbonate, and one gram of CNTs were suspended into 50 ml of water using ultrasonic vibration (500 W, one hour). The mixture was filtered. A specific capacitance of this material was 90 F/g.

Example 4

[0201] Two grams of microcrystalline cellulose, two grams calcium carbonate nanoparticles and one gram of CNTs and hundred milligrams of amorphous carbon nanoparticles were suspended into 50 ml of water using ultrasonic vibration (500 W, one hour). The mixture was filtered. A specific capacitance of this material was 97 F/g. When the microcrystalline cellulose was partially pyrolyzed at 300° C., the specific capacitance increased to 115 F/g.

Example 5

[0202] Instead of pyrolysis of cellulose, calcium carbonate was removed by addition of 2 M HCl on the paper that was prepared by filtration. Paper was washed neutral by water. Into the paper was added 0.5 M CuCl₂ solution and 0.5 M KI solution. The mixture was filtered and washed with methanol. The specific capacitance of this material was 265 F/g.

Example 6

[0203] Two grams of cellulose fragment gel and one gram of CNTs and hundred milligrams of amorphous carbon nanoparticles and hundred milligrams of graphene were suspended into 50 ml of water using ultrasonic vibration (500 W, one hour). The mixture was filtered. A specific capacitance of this material was 272 F/g.

Example 7

[0204] 3 g of mechanically and enzymatically processed molecular cellulose that is coordinated with 3 g calcium of carbonate nanoparticles is first dispersed into 200 ml of water. Carbon nanotubes are treated with HCl in order to make the dispersion process easier. The treatment removes unwanted residues from the manufacturing process. First 100 grams of carbon nanotubes are put in a closed container. Then 300 ml of HCl is added on top of the carbon nanotubes. The container is then shaken and let stand for 2 hours. After this the carbon nanotubes are washed with distilled water until their pH is neutral. Washed tubes are dried in oven at 120 degrees of Celsius for over night. After drying they are mechanically ground using planetary mill.

[0205] 200 ml of the molecular cellulose pulp and calcium carbonate dispersion is mixed with 1.3 grams of dry carbon nanotubes in a beaker. The mixture has now 30% weight/weight carbon nanotubes. The mixture is stirred shortly with spoon and then the mixture is treated with tip ultra-sonicator. Sonication time is 10 minutes at power of 750 watts. The dispersion is treated with HCl to remove inorganic salts. HCl is added until calcium carbonate is solubilized, and no carbon dioxide evolution is observed. After this the mass is washed with distilled water until the filtrate is neutral.

[0206] Desired amount of pulp is filtered through metal mesh or plastic netting sieve. Quite often 80 g/m² square weight is preferred. Two pieces of filter paper are put on top of filtered paper. Paper is then pressed with heavy rolling pin until it is detached from the mesh. The sample paper is now put between four filter papers and further pressed with hydraulic press while heating at 90° C. After this sample is dried in paper dryer for 2 hrs. EMI shielding efficacy of the paper was 25-30 dB.

Example 8

[0207] Procedure of example 7 was repeated expect that double walled carbon nanotubes were used instead of MWNTs. EMI shielding efficacy was measured by self constructed ASTM coaxial EMI SE tester and Anritsu 37369D VNA. Results are displayed in FIG. 19.

Example 9

[0208] Carbon nanotubes (1 g Baytubes, Bayer, Germany), 1 g microcrystalline cellulose, 0.2 g cellulose, 1 g of calcium carbonate, and carboxymethyl cellulose (0.2 g) were dispersed into 100 ml of water using ultrasonic vibration. Onto this solution was added ferric chloride and sodium sulfite solution. After careful mixing, ammonia solution was added. The CNT-cellulose-magnetite nanocomposite was separated with a permanent magnet. Soluble salts were removed by washing with water, and finally with alcohol. The alcohol suspension was mixed with reactive diluent. The nanocomposite was mixed with diglycidylether of bisphenol A (100 g). Tall oil based hardener (30 g, Arizona Chemicals Inc.) was added, and mixed well. After curing the epoxy resin was electrically conductive ($25 \Omega\text{m}$) and paramagnetic.

Example 10

[0209] One gram of HCl treated carbon nanotubes and 1 gram of microcrystalline cellulose is first ground dry in mortar. Then 200 ml of purified water is added and sample is sonicated with 750 W sonicator 30 minutes. From this sample 20 ml is taken to be mixed with 400 mg of fibrous cellulose.

[0210] This fibrous cellulose is first prepared as following. Starting point is as received cellulose sheet from the pulp factory. The cellulose is shredded dry into even sized small pieces and put in beaker with 200 ml of water. First the pulp is vigorously mixed with magnet stirrer for 12 hrs and then sonicated while mixed at 750 W for 30 minutes.

[0211] A mixture of carbon nanotubes, microcrystalline cellulose and fibrous cellulose is sonicated at 750 W power for 30 minutes. Paper sheets are then prepared. Resistance of 80 g/m^2 paper is less than 10 ohms with two point measurement and less than 1 ohm with 4 point measurement. Shielding efficiency of such paper was 25 dB at 10 GHz.

[0212] Additional modifications and advantages will readily occur to those skilled in the art. Therefore the invention in its broader aspects is not limited to the specific details, and representative materials and devices shown and described. Accordingly, various modifications may be made without departing from the spirit and scope of the general inventive concept as described in the disclosure and defined by the claims and their equivalents.

1. A method for the fabrication of nanocomposite from the first material and the second material, known for the use of liquid medium, into which both the first material and the second material are slightly or sparingly soluble, and using soluble material, such as hemicellulose to assist dissolution of the first material and the second material and use of power source to provide kinetic energy for the partial or total separation of molecular components from the first material and the second material so that the said nanocomposite will be formed and deposited, while the said kinetic energy is provided into the mixture.

2. A method of claim 1 for the fabrication of a nanocomposite, known for the use of first nano-, or microparticles in order to distribute kinetic energy unevenly at molecular scale

for the separation of molecular components from the said first material and the said second material so that the said molecular components will form the said nanocomposite.

3. A method of claim 1, in which the said first material is a graphitic material.

4. A method of claim 1, in which the said second material is a cellulosic material, or polyacrylate derivative.

5. A method of claim 3, in which the said graphitic material consists of carbon nanotubes or functionalized carbon nanotubes

6. A method of claim 5, in which the said carbon nanotubes consists more than 90% of double walled carbon nanotubes or functionalized double walled carbon nanotubes

7. A method of claim 3, in which the said graphitic material consists of graphite or graphene or combination of carbon nanotubes and graphene.

8. A method of claim 4, in which the said cellulosic material consists of cellulose, or biochemically, biologically, or chemically modified cellulose.

9.-13. (canceled)

14. A method of claim 2, in which the said first nano- or microparticles are alumina, silica, calcium carbonate, calcium sulfate, barium sulfate, barium oxalate, strontium sulfate, barium or strontium titanate, titanium oxide, tin oxide, lead oxide, iron oxide, iron phosphate, nickel, cobalt, silver, or gold particles.

15.-16. (canceled)

17. A method of claim 1, in which the said kinetic energy is produced mechanically, or hydrodynamically.

18. A method of claim 17, in which the said hydrodynamic kinetic energy is in the form of high pressure liquid jets, or ultrasonic vibration.

19. A method of claim 1, in which the second nanoparticles, that are electromagnetically active, are included in the fabrication of nanocomposite or hybride material.

20. A method of claim 2, in which the second nanoparticles, that are electromagnetically active, are included in the fabrication of nanocomposite or hybride material.

21. A method of claim 20, in which the said second nanoparticle is cuprous iodide, Prussian blue, magnetite, iron phosphate, cobalt oxide, manganese oxide, tin oxide, zinc oxide, titanium oxide, barium titanate, or strontium titanate.

22. A method of claim 20, in which the said second nanoparticle is covered with a thin layer of metal phosphate, sulfate, or silicate.

23.-24. (canceled)

25. A material that is fabricated by the method of claim 3.

26. A material that is fabricated by the method of claim 4.

27. A material that is fabricated by the method of claim 5.

28. A material that is fabricated by the method of claim 6.

29. A material that is fabricated by the method of claim 7.

30. A material that is fabricated by the method of claim 8.

31. A material that is fabricated by the method of claim 20.

32. A material that is fabricated by the method of claim 21.

33. A material that is fabricated by the method of claim 22.

34. (canceled)

35. A hybride material that is fabricated from the material of claim 2 by chemical cross-linking.

36. (canceled)

37. A hybride material that is fabricated from the material of claim 30 by chemical cross-linking.

38.-39. (canceled)

40. Use of the material of the claim 25 in a supercapacitor.

41. Use of the material of the claim 26 in a supercapacitor.

- 42.** Use of the material of the claim **27** in a supercapacitor.
43. Use of the material of the claim **28** in a supercapacitor.
44. Use of the material of the claim **29** in a supercapacitor.
45. Use of the material of the claim **30** in a supercapacitor.
46. Use of the material of the claim **31** in a supercapacitor.
47. Use of the material of the claim **32** in a supercapacitor.
48. Use of the material of the claim **33** in a supercapacitor.
49.-50. (canceled)
51. Use of the material of claim **25** for the protection against electromagnetic interference.
52. Use of the material of claim **26** for the protection against electromagnetic interference.
53. Use of the material of claim **27** for the protection against electromagnetic interference.
54. Use of the material of claim **28** for the protection against electromagnetic interference.
55. Use of the material of claim **29** for the protection against electromagnetic interference.
56. Use of the material of claim **30** for the protection against electromagnetic interference.
- 57.** Use of the material of claim **31** for the protection against electromagnetic interference.
58. Use of the material of claim **32** for the protection against electromagnetic interference.
59. Use of the material of claim **33** for the protection against electromagnetic interference.
60. A layered structure containing at least two layers known for the first layer that is made of the material of claim **29**, and the second layer contains magnetically active particles.
61. A layered structure containing at least three layers known for the first layer that is made of the material of claim **29**, and the second dielectric layer between the first and third layer, and the third layer that is made of the material of claim **29**.
62. (canceled)
63. A supercapacitor that is electrically connected with two potential sources.

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(54) Title: NANOCRYSTALLINE CELLULOSE (NCC) IN TAPE JOINT COMPOUND (JC)

(57) Abstract: A joint compound with improved crack resistance is formed by combining water, a filler such as calcium carbonate, a latex emulsion binder, a thickening system such as methyl hydroxyethyl cellulose, and nanocrystalline cellulose. The nanocrystalline cellulose is provided in an amount effective to reduce the crack formation during drying.

NANOCRYSTALLINE CELLULOSE (NCC) IN TAPE JOINT COMPOUND (JC)

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit under 35 U.S.C. 119 (e) of U.S. Provisional Patent Application Serial No. 61/602,671, filed February 24, 2012, the entire content of which is hereby expressly incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Disclosed and Claimed Inventive Concepts

[0002] The presently disclosed and claimed inventive concept(s) relates generally to a joint compound that can totally eliminate cracking in various thicknesses of the joint compound and thick coatings. Specifically, the joint compound comprises nanocrystalline cellulose, water, a filler, a binder and a thickener.

2. Background and Applicable Aspects of the Presently Disclosed and Claimed Inventive Concept(s)

[0003] Wallboard is generally installed in large panels, which are nailed, screwed, or glued to the studding of walls of buildings. The joints where sections of the wallboard are butted together are covered with a joint compound and then a fiberglass or paper reinforcing tape is embedded within the joint compound and then permitted to dry. When the joint compound is dry, a second application of the joint compound is applied over the joint and is permitted to dry. A coating of the joint compound is also applied to cover nail heads or screws or any cracks in the wall board and let dry. After the joint compound dries, the joint and covering of the nails or screws are lightly sanded and the wall is then finished with decorating material such as paint.

[0004] Typically, tape joint compositions, which are normally referred to as joint compounds, contain a binder, a thickener system, a filler, water, a biocide, clay and mica. This joint composition is a ready-mix, drying type composition that is normally sold in five-gallon cans or corrugated boxes. The water and filler are the ingredients that comprise the largest weight percentage in the joint composition. Joint compounds are either regular weight compounds that are the traditional type or lightweight compounds.

[0005] Optimally, a joint compound will not alter its dimensions as it dries. However, when a relatively thick coating of the joint compound is applied to a surface, it can crack as it dries. The thicker the coating is the more likely the cracking and the more severe the

cracking. This requires additional applications to fill in the voids in the cracks, increasing the cost of finishing a wall surface.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. 1 is a photograph showing a thick coating of dried joint compound which does not include nanocrystalline cellulose.

[0007] FIG. 2 is a photograph showing a thick coating of dried joint compound which includes nanocrystalline cellulose.

[0008] FIG. 3 is a photograph of the compound shown in FIG. 1 without nanocrystalline cellulose.

[0009] FIG. 4 is a photograph of the compound shown in FIG. 2 with nanocrystalline cellulose.

DETAILED DESCRIPTION

[0010] Before explaining at least one embodiment of the inventive concept(s) in detail by way of exemplary drawings, experimentation, results, and laboratory procedures, it is to be understood that the inventive concept(s) is not limited in its application to the details of construction and the arrangement of the components set forth in the following description or illustrated in the drawings, experimentation and/or results. The inventive concept(s) is capable of other embodiments or of being practiced or carried out in various ways. As such, the language used herein is intended to be given the broadest possible scope and meaning; and the embodiments are meant to be exemplary - not exhaustive. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

[0011] Unless otherwise defined herein, scientific and technical terms used in connection with the presently disclosed and claimed inventive concept(s) shall have the meanings that are commonly understood by those of ordinary skill in the art. Further, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular. Generally, nomenclatures utilized in connection with, and techniques of chemistry described herein are those well known and commonly used in the art. Reactions and purification techniques are performed according to manufacturer's specifications or as commonly accomplished in the art or as described herein. The nomenclatures utilized in connection with, and the laboratory procedures and techniques of, analytical chemistry, synthetic organic chemistry, and medicinal and pharmaceutical chemistry described herein are those well known and commonly used in the art. Standard techniques are used for

chemical syntheses, chemical analysis, pharmaceutical preparation, formulation, and delivery, and treatment of patients.

[0012] All patents, published patent applications, and non-patent publications mentioned in the specification are indicative of the level of skill of those skilled in the art to which this presently disclosed and claimed inventive concept(s) pertains. All patents, published patent applications, and non-patent publications referenced in any portion of this application are herein expressly incorporated by reference in their entirety to the same extent as if each individual patent or publication was specifically and individually indicated to be incorporated by reference.

[0013] All of the compositions and/or methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the inventive concept(s) as defined by the appended claims.

[0014] As utilized in accordance with the present disclosure, the following terms, unless otherwise indicated, shall be understood to have the following meanings:

[0015] The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims and/or the specification may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.” The use of the term “or” in the claims is used to mean “and/or” unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and “and/or.” Throughout this application, the term “about” is used to indicate that a value includes the inherent variation of error for the device, the method being employed to determine the value, and/or the variation that exists among the study subjects. The use of the term “at least one” will be understood to include one as well as any quantity more than one, including but not limited to, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 100, etc. The term “at least one” may extend up to 100 or 1000 or more, depending on the term to which it is attached; in addition, the quantities of 100/1000 are not to be considered limiting, as higher limits may also produce satisfactory results. In addition, the use of the term “at least one of X, Y and Z” will be understood to include X alone, Y alone, and Z alone, as well as any combination of X, Y and Z.

[0016] As used in this specification and claim(s), the words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as

"have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0017] The term "or combinations thereof" as used herein refers to all permutations and combinations of the listed items preceding the term. For example, "A, B, C, or combinations thereof" is intended to include at least one of: A, B, C, AB, AC, BC, or ABC, and if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB.

Continuing with this example, expressly included are combinations that contain repeats of one or more item or term, such as BB, AAA, MB, BBC, AAABCCCC, CBBAAA, CABABB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context.

[0018] In accordance with the presently disclosed and claimed inventive concept(s), a joint compound comprises nanocrystalline cellulose, a binder, a thickener, a filler, water, a biocide and clay. Additional components that are commonly used in joint compounds are perlite, mica, preservatives, wetting agents, defoamers, and plasticizers. With the exception of perlite and mica, these additional components are normally used in minor amounts generally ranging from about 0.05 to about 1.0% by weight based on the total dry weight of the compound.

[0019] Nanocrystalline cellulose is a crystalline portion of cellulose which can be formed by acid hydrolysis of cellulose combined with mechanical treatment. These nanometer size cellulose particles are crystalline in nature, insoluble in water, stable, chemically inactive and physiologically inert with attractive binding properties.

[0020] Cellulose is one of the most abundant biopolymers on earth, occurring in wood, cotton, hemp and other plant-based material and serving as the dominant reinforcing phase in plant structures. Cellulose can also be synthesized by algae, tunicates, and some bacteria. It is a homopolymer of glucose repeating units which are connected by 1-4 β -glycosidic linkages. The 1-4 β -linkages form cellulose in linear chains, which interact strongly with each other through hydrogen bonds. Because of their regular structure and strong hydrogen bonds, cellulose polymers are highly crystalline and aggregate to form substructures and microfibrils. Microfibrils, in turn aggregate to form cellulosic fibers.

[0021] Purified cellulose from wood or agricultural biomass can be extensively disintegrated or produced by bacterial processes. If the cellulosic material is composed of nanosized fibers, and the properties of the material are determined by its nanofiber structure, these polymers are described as nanocelluloses or nanocrystalline cellulose. The terms are used interchangeably herein.

[0022] In general, nanocelluloses are rod shaped fibrils with a length/diameter ratio of approximately 20 to 200. In one non-limiting embodiment, the nanocelluloses have a diameter less than about 60 nm. In another non-limiting embodiment, the nanocelluloses have a diameter between about 4 nm to about 15 nm, and a length of about 150 nm to about 350 nm. The size and shape of the crystals vary with their origins. For example, but not by way of limitation, nanocrystalline cellulose from wood can be about 3 to about 5 nm in width and about 20 to about 200 nm in length. Other nanocrystalline cellulose obtained from other sources such as cotton may have slightly different dimensions.

[0023] The nanocrystalline cellulose has high stiffness, large specific surface area, high aspect ratio, low density and reactive surfaces that can facilitate chemical grafting and modification. At the same time, the material is inert to many organic and inorganic substances.

[0024] The production of nanocrystalline cellulose by fibrillation of cellulose fibers into nano-scale elements requires intensive mechanical treatment. However, depending upon the raw material and the degree of processing, chemical treatments may be applied prior to mechanical fibrillation. Generally preparation of nanocrystalline cellulose can be described by two methods, acid hydrolysis and mechanical defibrillation. In the first method, nanocellulose can be prepared from the chemical pulp of wood or agricultural fiber mainly by acid hydrolysis to remove the amorphous regions, which then produce nano-size fibrils. The hydrolysis conditions are known to affect the properties of the resulting nanocrystals. Different acids also affect the suspension properties. Nanocrystal size, dimensions, and shape can also be determined to a certain extent by the nature of the cellulose source.

[0025] The acid hydrolysis can be conducted using a strong acid under strictly controlled conditions of temperature, agitation and time. The nature of the acid and the acid-to-cellulosic ratio are also important parameters that affect the preparation of nanocellulose. Examples of the acids can include, but are not limited to, sulfuric acid, hydrochloric acid, phosphoric acid and hydrobromic acid. The hydrolysis temperature can range from room temperature up to about 70 °C and the corresponding hydrolysis time can be varied from about 30 minutes to about 12 hours depending on the temperatures. Immediately following hydrolysis, suspension can be diluted to stop the reaction.

[0026] In one non-limiting embodiment, the suspension can be diluted from about five-fold to about ten-fold to stop the reaction. Then the suspension can be centrifuged, washed once with water and re-centrifuged and washed again. This process can be repeated for about four to five times to reduce the acid content. Regenerated cellulose dialysis tubes or Spectrum Spectra/Pro regenerated cellulose dialysis membrane having a molecular cutoff of about 12,000-14,000 can be used to dialyze the suspension against distilled water for

several days until the water pH reach a constant value, for example but not by way of limitation, a pH value of about 7.0.

[0027] To further disperse and reduce the size of the cellulose crystals, the suspensions of cellulose crystals can be processed by either sonicating or passing through a high shear micro fluidizer. This kind of prepared material is referred to as nanocellulose, nanocrystalline cellulose (NCC), cellulose nanocrystals, cellulose nanofibres or cellulose whiskers.

[0028] The second method is primarily a physical treatment. Bundles of microfibrils called cellulose microfibril or microfibrillated cellulose with diameters from tens of nanometers (nm) to micrometers (μm) are generated by using high pressure homogenizing and grinding treatments. A novel process using high-intensity ultrasonication has also been used to isolate fibrils from natural cellulose fibers. High intensity ultrasound can produce very strong mechanical oscillating power, so the separation of cellulose fibrils from biomass is possible by the action of hydrodynamic forces of ultrasound. This method can produce a microfibrillated cellulose with a diameter with a diameter less than about 60 nm. In one non-limiting embodiment, a microfibrillated cellulose between about 4 nm to about 15 nm, and a length less than 1000 nm. The microfibrillated cellulose can optionally further undergo chemical, enzymatic and/or mechanical treatment. Both methods for preparing nanocrystalline cellulose are described in U.S. Patent No. 8,105,430, the entire disclosure of which is hereby incorporated by reference.

[0029] Generally, about 0.05% to about 0.5% by weight of nanocrystalline cellulose can be used. In one non-limiting embodiment, about 0.05 to about 0.15% by weight can be incorporated into the joint compound.

[0030] The binder is typically a latex emulsion, for example, but not by way of limitation, polyvinyl alcohol, ethylene vinyl acetate latex, or poly(vinyl acetate) latex. The binder is a coalescent agent that upon drying of the compound forms a thin matrix to hold the compound. In other words, the binder is the matrix that holds the other components in their proper places so as to form the desired product. Hence, the binder is an essential ingredient in the joint compound. Other materials that can be used as binder can include, but are not limited to, starch, casein, polyacrylamide, and copolymers of acrylamide and acrylic acid. In general, the binder ranges from a lower limit of about 1% to an upper limit of about 3%, by weight based on the total weight of the compound. In one non-limiting embodiment, the upper limit can be about 2.5 weight % by weight, based on the total weight of the compound.

[0031] The thickener of the presently disclosed and claimed inventive concept(s) can be, for example, but by no way of limitation, ethylhydroxyethyl cellulose (EHEC), hydroxyethyl cellulose (HEC), hydrophobically modified hydroxyethyl cellulose,

hydroxypropyl methylcellulose (HPMC), methylhydroxyethyl cellulose (MHEC), carboxymethyl cellulose (CMC), hydroxypropyl guar, and underivatized guar.

[0032] The amount of the thickener in the joint compound can have a lower limit of about 0.01 weight % based on the total dry weight of the joint compound (excluding the water present in the joint compound). In one non-limiting embodiment, the lower limit can be about 0.3 weight % based on the total dry weight of the joint compound. The upper limit of the thickener system can be about 0.6 weight%. In one non-limiting embodiment, the upper limit can be about 0.5 weight %.

[0033] Fillers are an important component in joint compounds. They serve the purpose of adding body to the joint compound, making the compound economical, and controlling the pH of the compound. Conventional fillers that can be used either alone or in combination in the presently disclosed and inventive concept(s) can include, but are not limited to, calcium carbonate, calcium sulfate dihydrate (gypsum), and dolomitic limestone. Calcium sulfate hemihydrate (plaster of Paris) may be used as a minor component in the presence of other fillers in order to better control open time and cracking and other joint compound properties.

[0034] In one non-limiting embodiment, the filler can be finely ground calcium carbonate. The filler can be a dry powder, which usually comprises at least about 45 weight % based on the weight of the joint compound. In one non-limiting embodiment, the filler comprises at least 50 weight %, based on the weight of the joint compound. Generally, the filter can fall within the range of about 45 to an upper limit of about 65% by weight. In order to achieve the desired pH of the compound of 8 to 10, the filler is the principal alkaline ingredient and therefore, is the main ingredient that controls the pH. If necessary, a pH modifier may be also added to increase the alkalinity of the compound.

[0035] Water can be added to the dry ingredients of the joint compound to provide the viscosity of the joint compound composition generally in the range of from about 300 to about 700 Brabender units.

[0036] Biocides increase the shelf life of the joint compound and prevent the composition from spoiling. In other words, biocides prevent microorganisms, such as mold, bacteria, and fungi, from growing in the compound and also on the walls of the building structure in which it is used. Examples of two efficient industry-accepted biocides can be Mergal® 174, 2[(hydroxymethyl)amino]ethanol, a broad spectrum biocide, manufactured by Troy Chemical Corp; and Proxel™ GXL product, 1,2-benzisothiazolin-3-one, an all purpose biocide, manufactured by Arch Chemicals, Inc.

[0037] Other biocides can include, but are not limited to, copper oxine, zinc stearate, calcium borate, zinc borate, barium borate, zinc omadine, zinc omadine/zinc oxide mix, 2,5-dimethyl-1, 3, 5-thiadiazinane-2-thione (Thione), 2-n-octyl-4-isothiazolin-3-one (octhilinone),

5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, hexahydro-1,3,5-triethyl-2-triazine, 5-bromo-5-nitro-1,3-dioxane, 2-(hydroxymethyl)amino-ethanol, 2-(hydroxymethyl)amino-2-methylpropanol, α -benzoyl- α -chloroformaldoxime, benzylbromoacetate, p-chloro-m-xylenol, bis-(2-hydroxy-5-chlorophenyl)sulfide, p-tolydiiodomethylsulfone, 3-iodo-2-propynylbutylcarbamate, bis-(2-hydroxy-5-chlorophenyl)methylene, dipropylamine ether, dodecylamine, and 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride.

[0038] The biocide should generally be present in the amount ranging from a lower limit of about 0.05 to an upper limit of about 1.0% by weight based on the total weight of the compound.

[0039] In accordance with the presently disclosed and claimed inventive concept(s), suitable clays for use in a joint compound can be any of the natural earthy, fine-grained, largely crystalline substances of hydrous aluminum silicates usually containing alkalis, alkaline earth, and iron that make up the group of clay materials. Included in this group can be, but are not limited to, sepiolite, montmorillonite, bentonite, illite, kaolin, and attapulgite. In one non-limiting embodiment, the clay is attapulgite. Attapulgite can typically be used at levels ranging from about 1.5 to about 3.5% of the total weight of the joint compound.

[0040] If a lightweight drying type joint compound having improved crack resistance is desired, the lightweight property can be provided by incorporating specially treated expanded perlite into the formulation. It is well known in the art that the expanded perlite should have a particle size that can pass through a 100-mesh screen, if it is to be incorporated into a joint compound. The expanded perlite can be a very lightweight material which can contain many fine cracks and fissures which may be penetrated by water and could thereby destroy its ability to render the joint compound lightweight. As a result, the expanded perlite is often treated to render it water-insensitive. The preferred method is to treat the expanded perlite with a silicone compound but other materials may be used to render it water-insensitive. The specially treated expanded perlite is commercially available from suppliers such as Silbriko Corporation. If non-treated perlite is used, care is taken to prevent undue water absorption during manufacture and over the expected shelf life of the joint compound. The lightweight examples illustrated herein were prepared using Silbriko's SiiCell® 3534 product, a surface treated perlite that is commonly used in the industry. The perlite can be used in amounts having an upper limit of about 8.5 weight percent. In one non-limiting embodiment, the upper limit can be 6.0 weight percent.

[0041] Depending on local preferences, other ingredients may be used in the joint compound formulations. These can include, but are not limited to, air entraining agents,

surfactants, humectants, pH buffering salts, defoamers, and mixtures thereof.

[0042] Normally, joint compounds can be prepared by combining all of the wet ingredients and mixing for one minute to homogenize. A blend of all the solids is then added to the mixing bowl, with continuing mixing. The entire mass is blended for a total of up to about 20 minutes. Different manufacturers may modify this procedure. In general, the higher the concentration of clay, the greater the required mixing time. Hence, the use of the reduced levels of clay described herein may in many cases permit the reduction of said mix time, with increase in total plant output.

[0043] The following examples illustrate the presently disclosed and claimed inventive concept(s), parts and percentages being by weight, unless otherwise indicated. Each example is provided by way of explanation of the presently disclosed and claimed inventive concept(s), not limitation of the presently disclosed and claimed inventive concept(s). In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the presently disclosed and claimed inventive concept(s) without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the presently disclosed and claimed inventive concept(s) covers such modifications and variations as come within the scope of the appended claims and their equivalents.

EXAMPLES

Preparation of Nanocrystalline Cellulose

[0044] Nanocrystalline cellulose (NCC) was prepared using the procedure similar to D. G. Gray et al, Langmuir, V.12, p. 2076-2082 (1996), which is incorporated herein by reference in its entirety. The details of the procedure are given below.

[0045] Prior to acid hydrolysis, the pulp was fluffed using a grinder. The fluffed pulp was hydrolysed in about 65% of sulfuric acid at about 45 °C for about 2 hrs. The solid content of the reaction was about 10%. First, the fluffed pulp was added into acid in a water bath with mechanical mixing and allowed to hydrolyze. After hydrolysis, the cellulose suspension was diluted with deionized (DI) water (~10 times volumes of the acid solution) and centrifuged twice to remove the acid. 2% sodium carbonate solution was then added to neutralize the residue acid. The suspension was dialyzed with DI water to remove the salt. The purified suspension was dried to determine the yield.

Evaluations

[0046] In order to evaluate the initial crack formation of the joint compound of the presently disclosed and claimed inventive concept(s), the following joint compound formulation was prepared:

Water—31.5 weight percent
30 micron CaCO₃—60.9 weight percent
Attapulgite clay—2 weight percent
Mica—3 weight percent
PVA latex (55%)—2 weight percent
MHEC—0.4 weight percent

[0047] This is a standard joint compound formulation. A formulation utilizing the presently disclosed and claimed inventive concept(s) was prepared using the same components listed above. However, the percentage of MHEC was reduced to 0.3 weight percent and 0.1 weight percent of nanocrystalline cellulose was added.

[0048] Quarter-inch thick layers of each of the above joint compounds were applied to a surface at a thickness of 1/4 inch, and allowed to dry. The images of the dried joint compound layers are shown in Figs. 1 and 2. Fig. 1 shows the joint compound with 0.4% MHEC, the joint compound shown in Fig. 2 has 0.3% MHEC and 0.1% NCC. The crack formation in Fig. 1, without the nanocrystalline cellulose, is significantly larger and more developed than that with the nanocrystalline cellulose in Fig. 2.

[0049] To further test this, the same compounds were tested at varying thicknesses from 1/32 of an inch up to 1/4 of an inch. The disk on the lower right of Figs. 3 and 4, being 1/32, with the disk on the upper left being 1/4 inch. The thickness of the two disks at the bottom of each column varied from the thickness of the two disks at the top of each column by 1/32 of an inch. The sample with 0.4% MHEC, Fig. 3, shows a significant crack at 1/8 of an inch, whereas, the sample with the 0.1% NCC, Fig. 4, shows crack formation at about 5/32 of an inch and significantly less crack formation.

[0050] This evidence demonstrates that by including a small percentage of nanocrystalline cellulose into joint compound formulations, crack formation can be significantly reduced. At the same time, this permits reduction in the amount of thickener added to the composition.

[0051] It is, of course, not possible to describe every conceivable combination of the components or methodologies for purpose of describing the disclosed information, but one of ordinary skill in the art can recognize that many further combinations and permutations of the disclosed information are possible. Accordingly, the disclosed information is intended to embrace all such alternations, modifications and variations that fall within the spirit and scope of the appended claims.

WHAT IS CLAIMED IS:

1. A joint compound comprising nanocrystalline cellulose, water, a filler, a binder and a thickener, wherein the amount of the nanocrystalline cellulose is effective to improve crack resistance of the joint compound upon drying.
2. The joint compound of claim 1, wherein the nanocrystalline cellulose is present in an amount of from about 0.05 to about 0.5 percent by weight based on the total weight of the compound.
3. The joint compound of claim 1, wherein the filler is selected from the group consisting of calcium carbonate, calcium sulfate dihydrate, limestone, calcium sulfate hemihydrate, and combinations thereof.
4. The joint compound of claim 3, wherein the filler comprises calcium carbonate.
5. The joint compound of claim 4, wherein the filler is present in an amount of from about 45 to about 65 percent by weight based on the total weight of the compound.
6. The joint compound of claim 1, wherein the binder is selected from the group consisting of polyvinyl alcohol, ethylene vinyl acetate latex, poly(vinyl acetate) latex, starch, casein, polyacrylamide, copolymers of acrylamide and acrylic acid, and combinations thereof.
7. The joint compound of claim 6, wherein the binder is present in an amount of from about 1 to about 2.5 percent by weight based on the total weight of the compound.
8. The joint compound of claim 1, wherein the thickener is selected from the group consisting of carboxymethyl cellulose, ethylhydroxyethyl cellulose, hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, hydroxypropylmethyl cellulose, methylhydroxyethyl cellulose, methylcarboxycellulose, hydroxypropyl guar, underivatized guar, and combinations thereof.
9. The joint compound of claim 8, wherein the thicker is present in an amount of from about 0.3 to about 0.5 percent by weight based on the total weight of the compound.
10. The joint compound of claim 8, wherein the thickener is methylhydroxyethyl cellulose.

11. The joint compound of claim 1 further comprising perlite.
12. The joint compound of claim 1 further comprising a biocide.
13. The joint compound of claim 12, wherein the biocide is present in an amount ranging from about 0.05 to about 1.0% by weight based on the total weight of the compound.
14. The joint compound of claim 1 further comprising about 1.5 to about 3.5 percent by weight of clay based on the total weight of the compound.
15. The joint compound of claimn14, wherein the clay comprises attapulgite clay.
16. The joint compound of claim 1 further comprising mica.
17. The joint compound of claim 1, wherein the nanocrystalline cellulose is present in an amount of about 0.05 to about 0.1 % by weight and the thicker is present in an amount of from about 0.3 to 0.5% by weight based on the total weight of the compound.

Enhanced crack formation in 14 inch
JC control (No NCC added)
0.4% MHEC

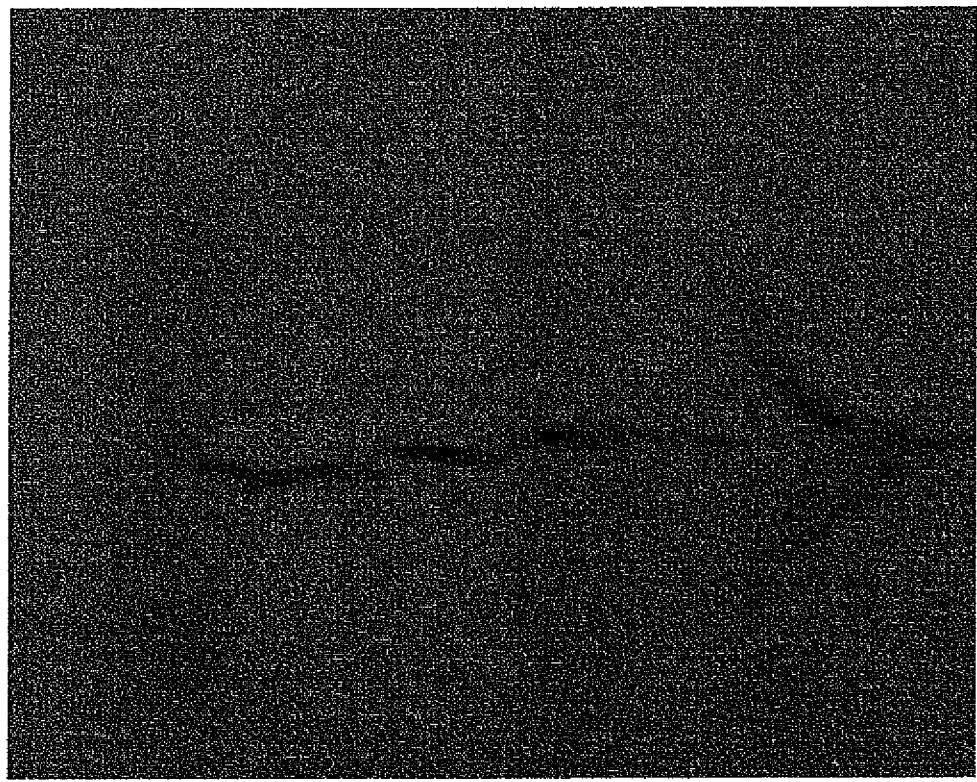


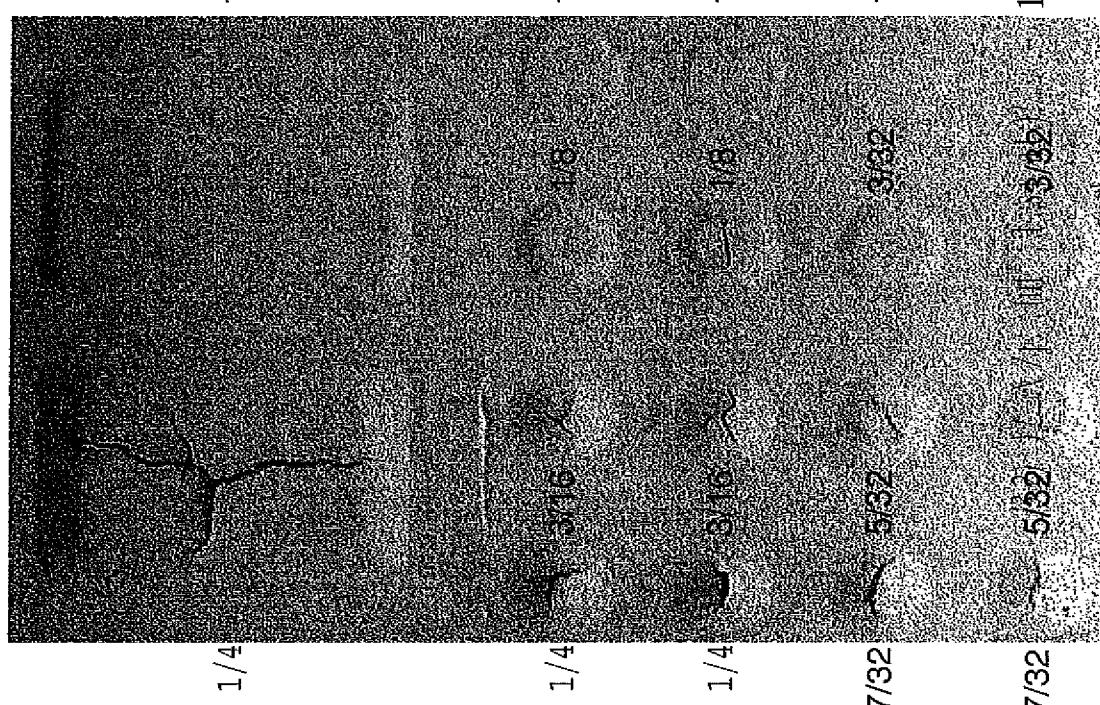
FIG. 1

Suppressed crack formation with
added NCC
0.3% MHEC + 0.1% NCC

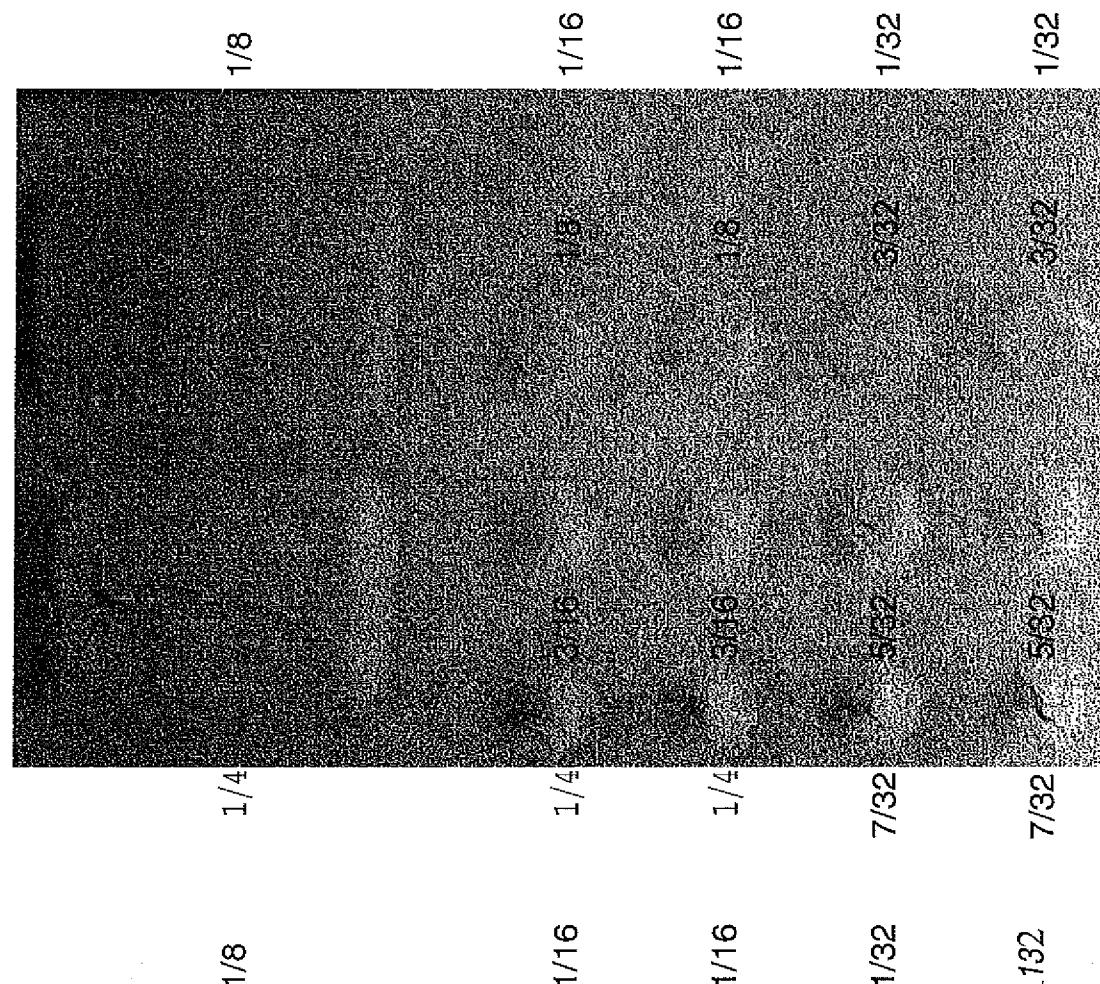


FIG. 2

0.4% MHEC



0.3% MHEC + 0.1% NCC



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FIG. 3

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/026640

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|-------------------------------------|-----------|-----------|-----------|-----------|
| A. CLASSIFICATION OF SUBJECT MATTER | | | | |
| INV. C04B26/04 | C04B26/06 | C04B26/28 | C04B26/02 | C04B28/14 |
| ADD. | | | | |

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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| Date of the actual completion of the international search | Date of mailing of the international search report |
| 29 July 2013 | 06/08/2013 |
| Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3046 | Authorized officer Gattinger, Irene |

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US007867358B2

(12) **United States Patent**
Medoff(10) **Patent No.:** US 7,867,358 B2
(45) **Date of Patent:** Jan. 11, 2011(54) **PAPER PRODUCTS AND METHODS AND SYSTEMS FOR MANUFACTURING SUCH PRODUCTS**7,026,635 B2 4/2006 Rangwalla et al.
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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(21) Appl. No.: **12/417,707**(22) Filed: **Apr. 3, 2009**

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(65) **Prior Publication Data**

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Related U.S. Application Data

(60) Provisional application No. 61/049,391, filed on Apr. 30, 2008.

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(51) **Int. Cl.****D21C 5/00** (2006.01)*Primary Examiner*—Eric Hug(52) **U.S. Cl.** **162/50**; 162/9; 162/158;
162/192*Assistant Examiner*—Jacob Thomas Minskey(74) *Attorney, Agent, or Firm*—Celia H. Leber(58) **Field of Classification Search** 162/50,
162/9, 158, 192**ABSTRACT**

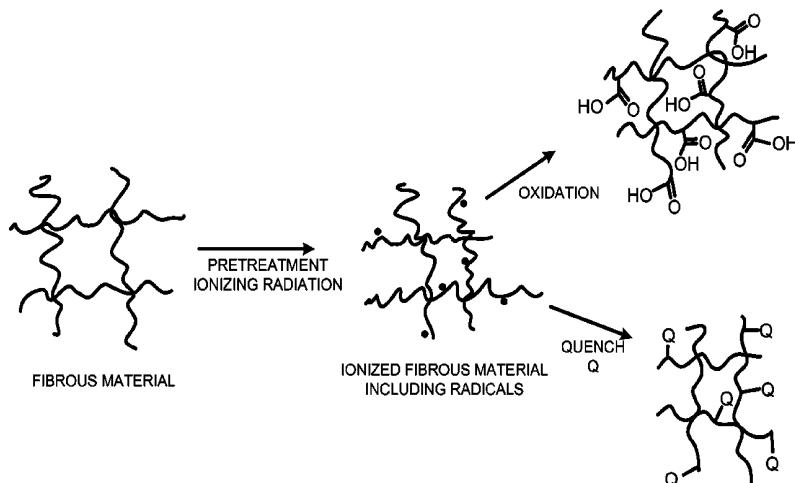
See application file for complete search history.

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Methods of producing cellulosic or lignocellulosic materials for use in papermaking include treating a cellulosic or lignocellulosic dry feedstock having a first average molecular weight with ionizing radiation, and controlling the dose of ionizing radiation such that the average molecular weight of the feedstock is reduced to a predetermined level. A method of producing an irradiated paper product includes treating a paper product including a first carbohydrate-containing material having a first molecular weight with ionizing radiation, and controlling the dose of ionizing radiation so as to provide an irradiated paper product with a second carbohydrate-containing material having a second molecular weight higher than the first molecular weight. Pulp and paper products are produced.

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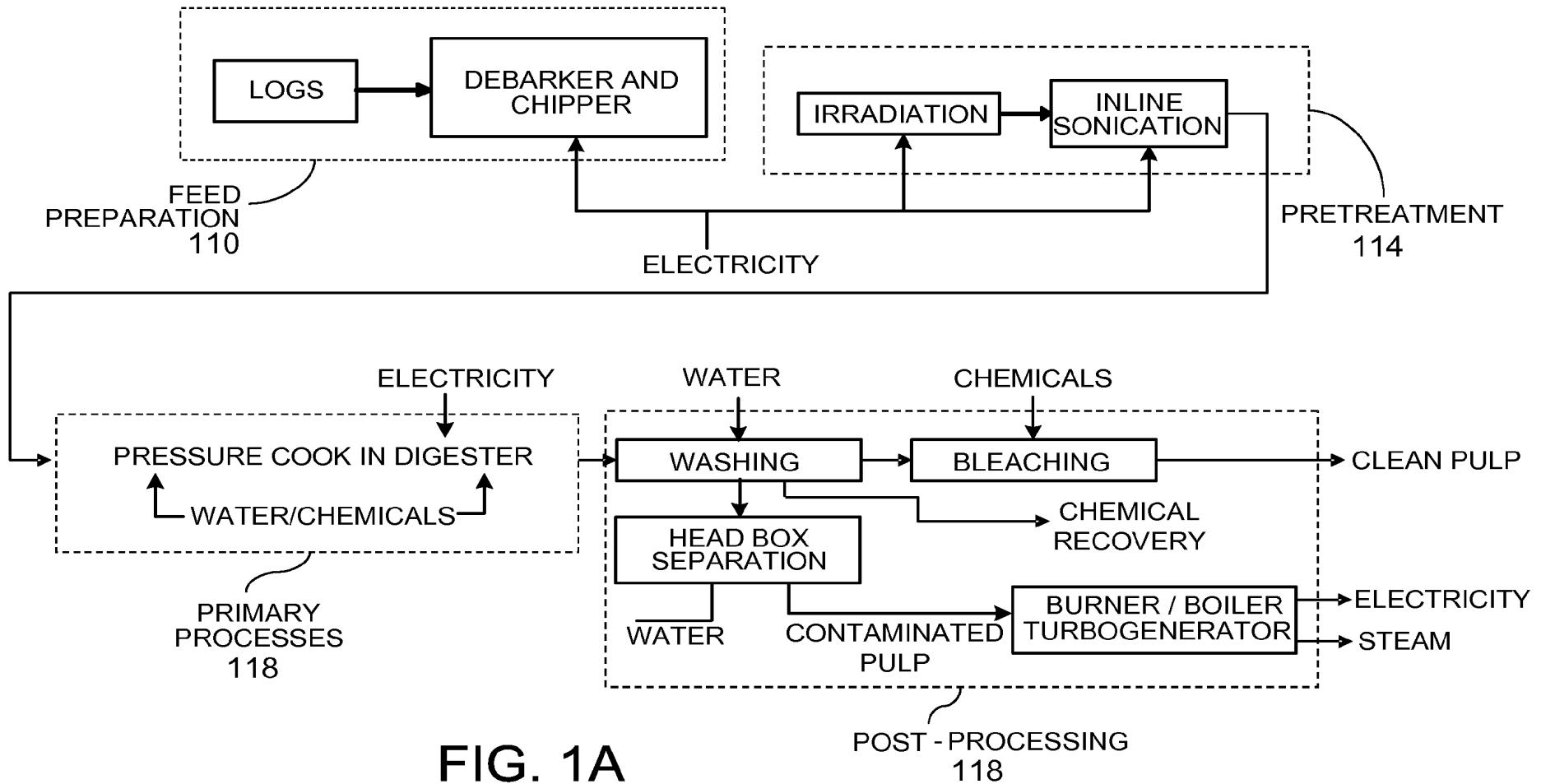
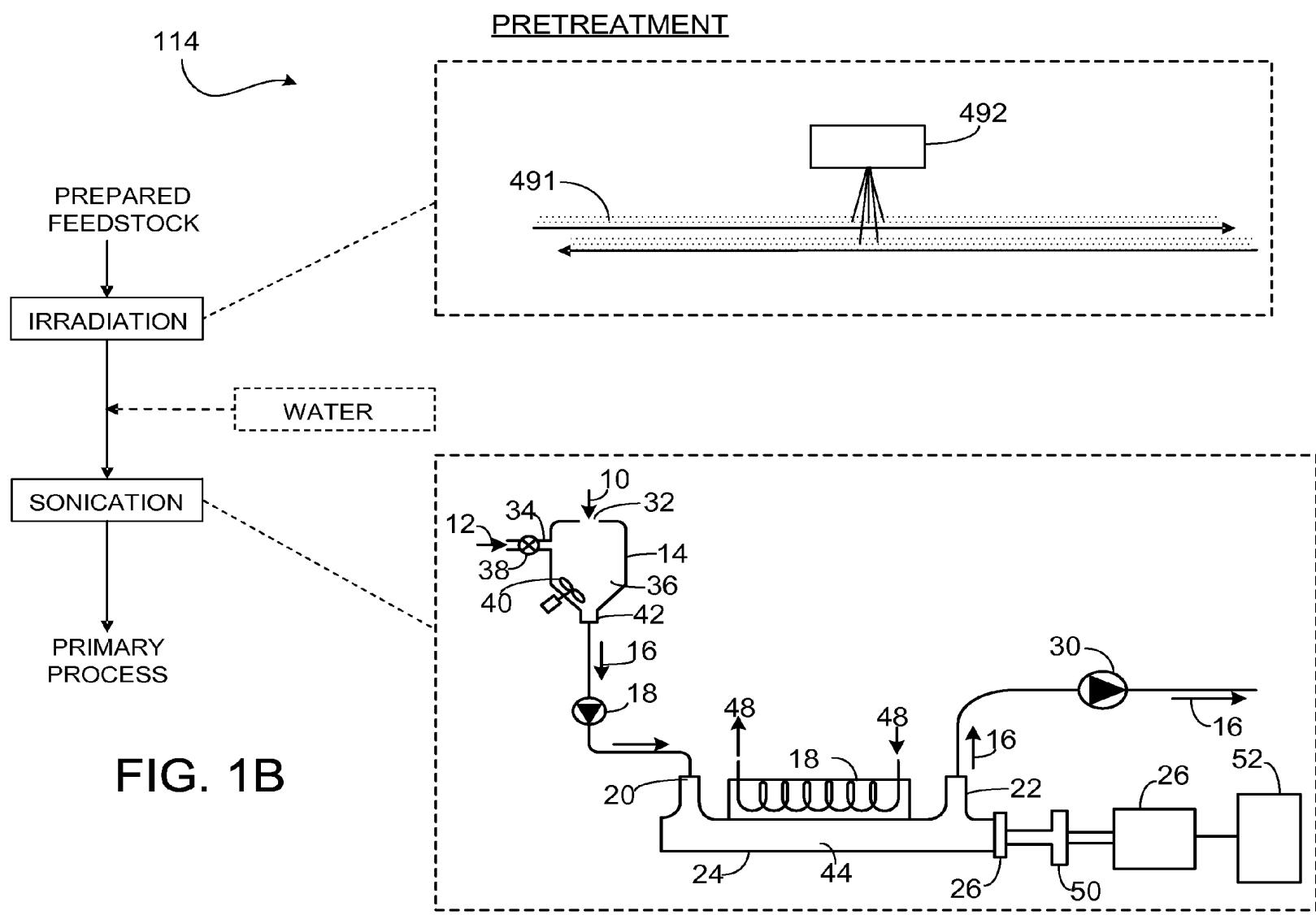


FIG. 1A



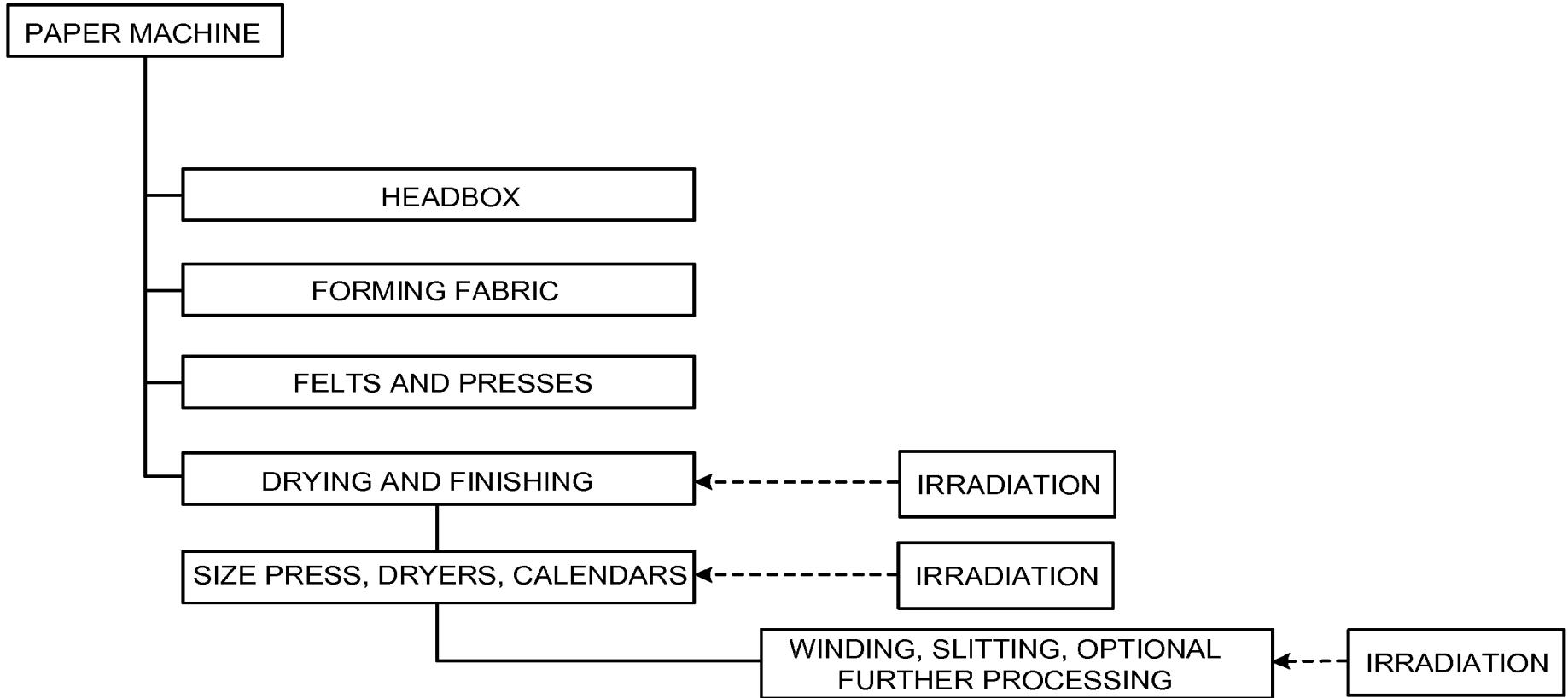


FIG. 2

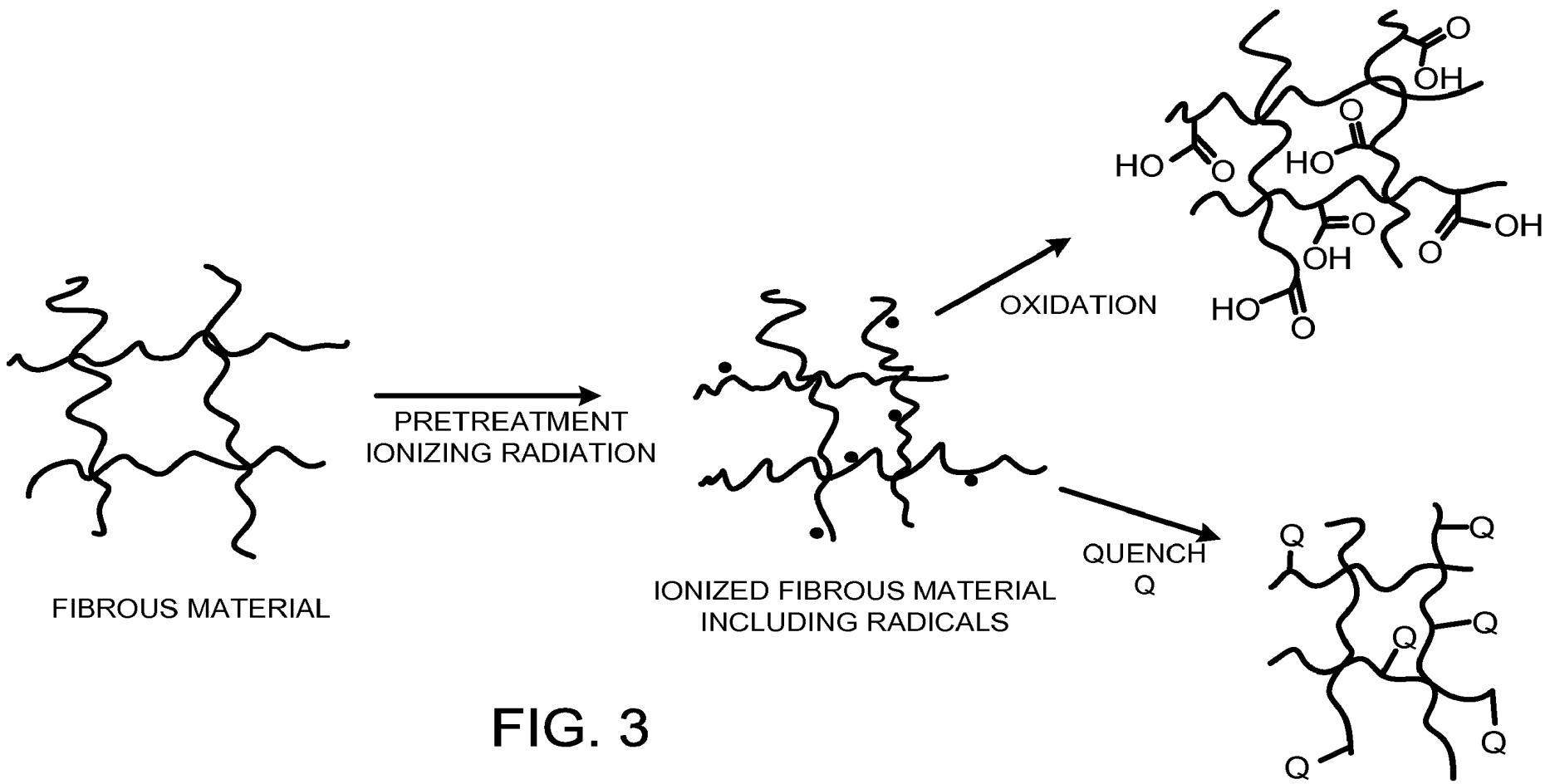
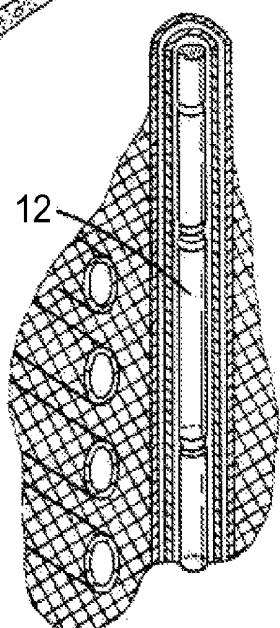
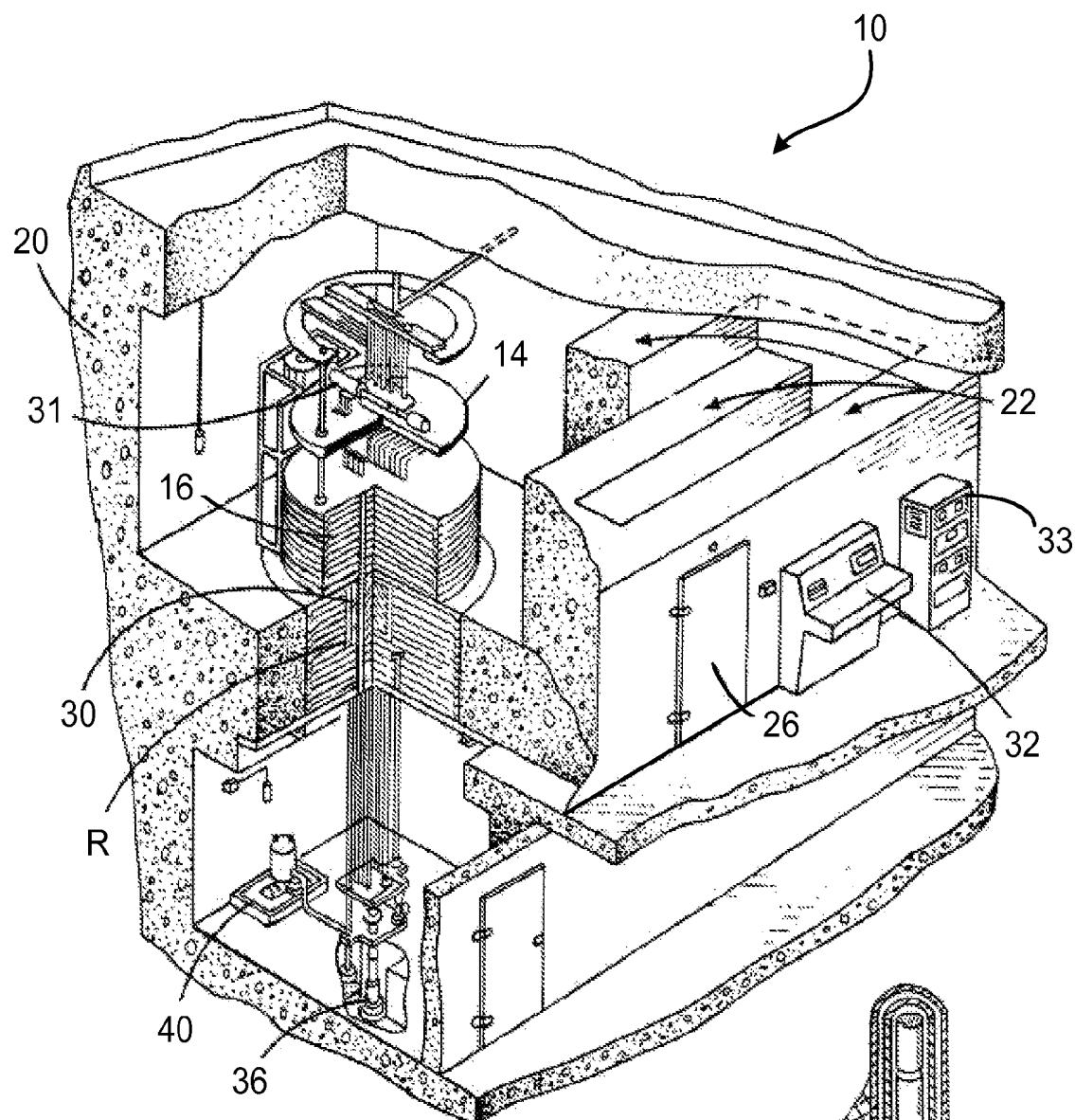


FIG. 3



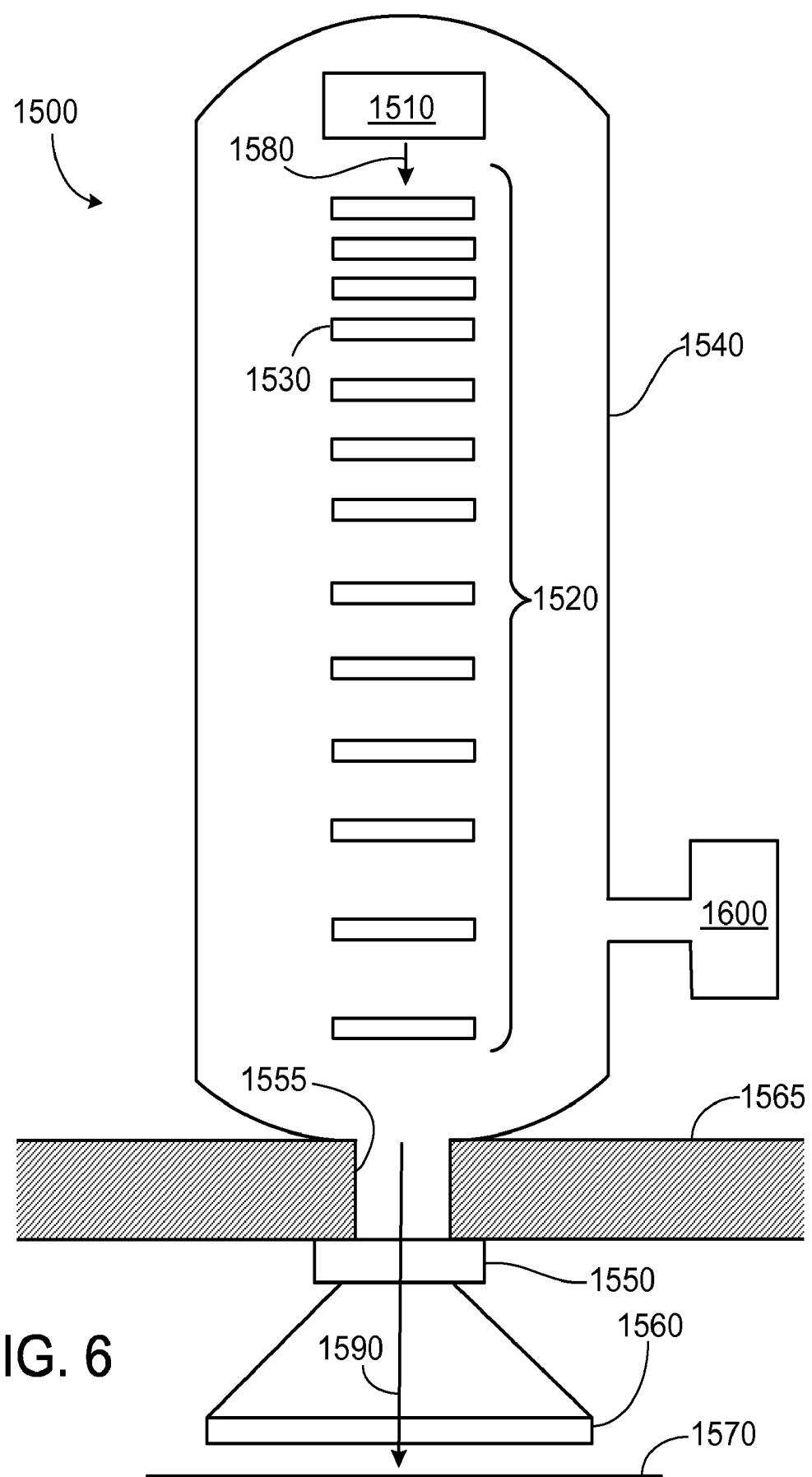


FIG. 6

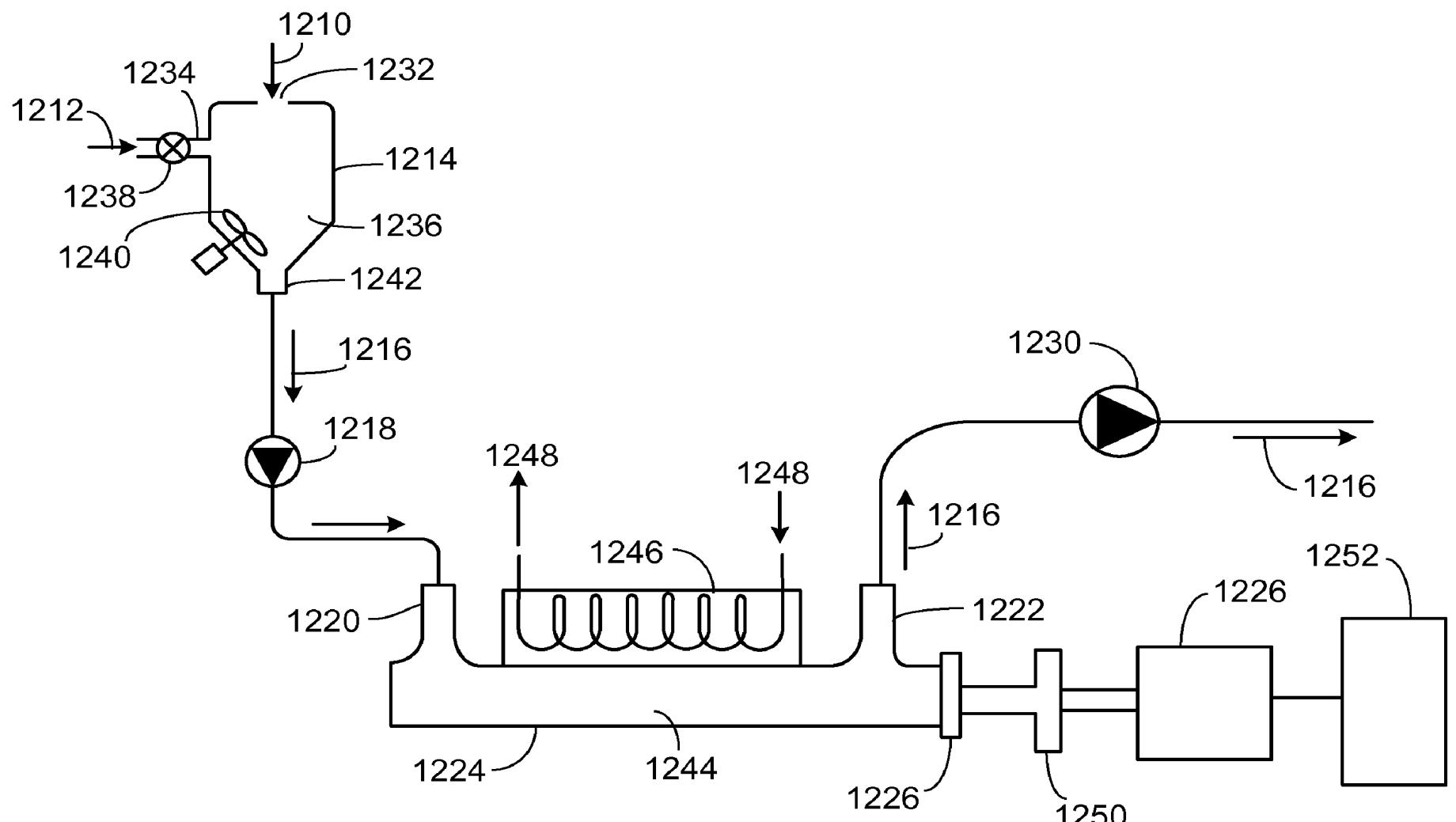


FIG. 7

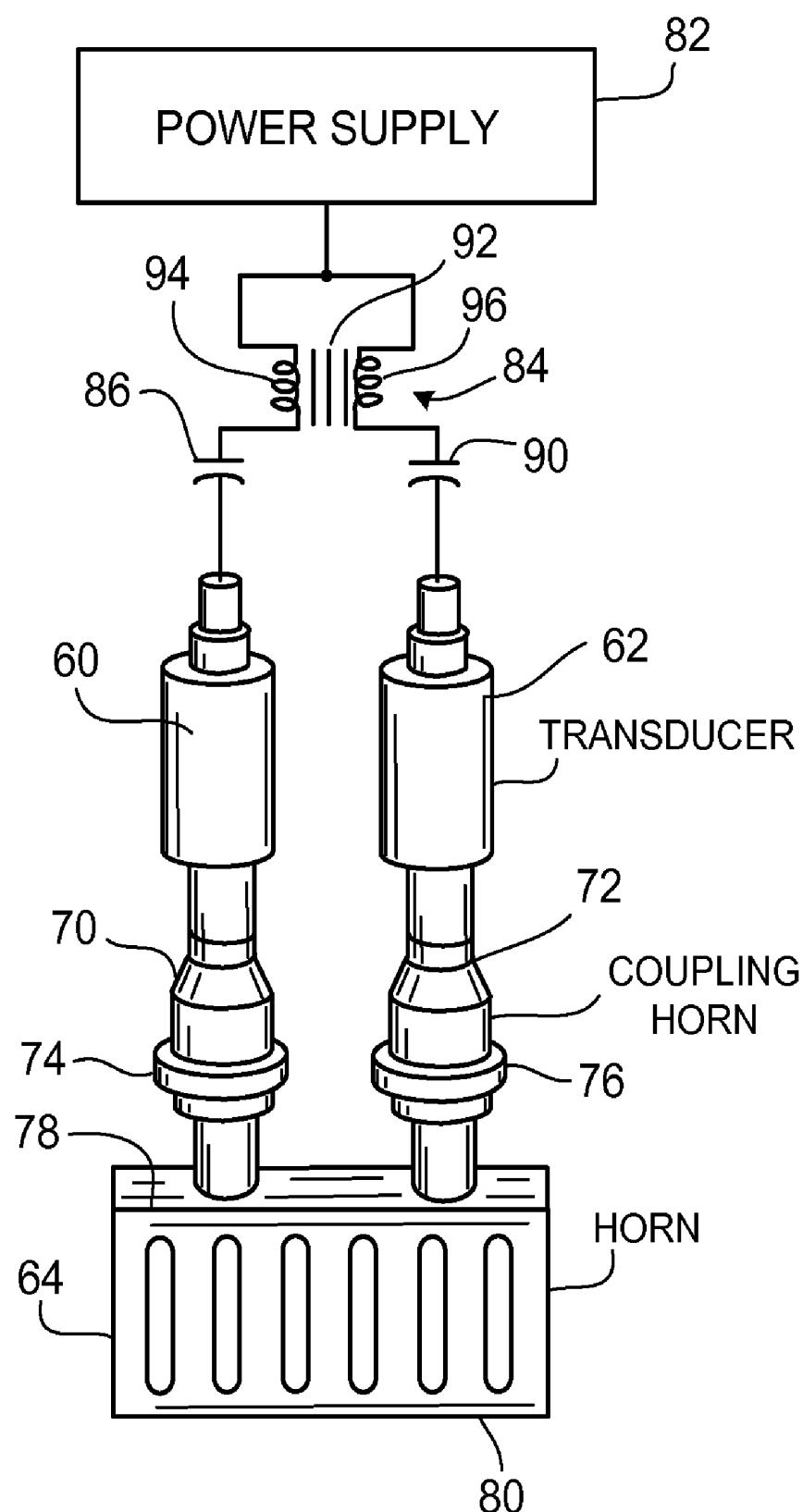


FIG. 8

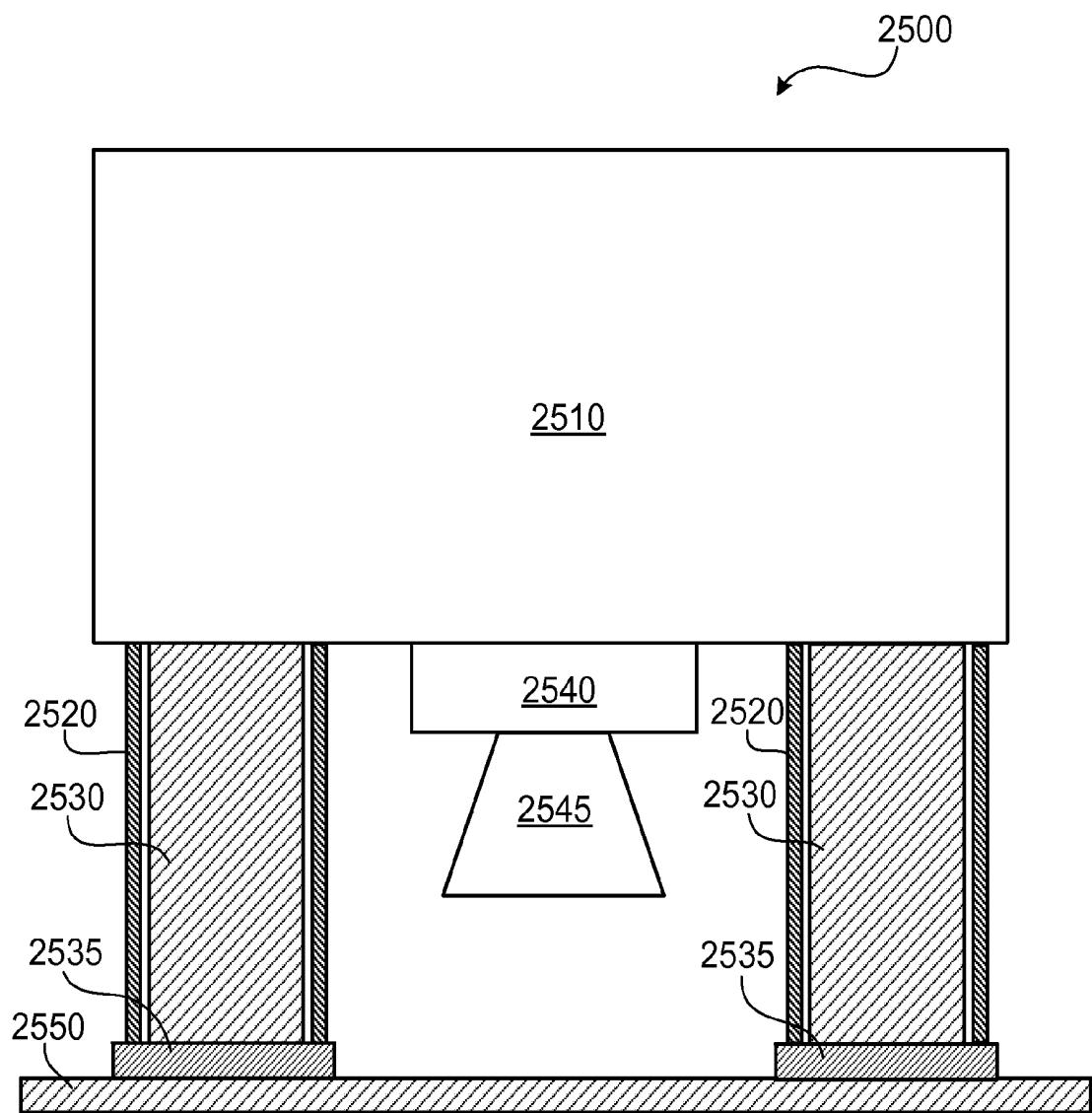


FIG. 9

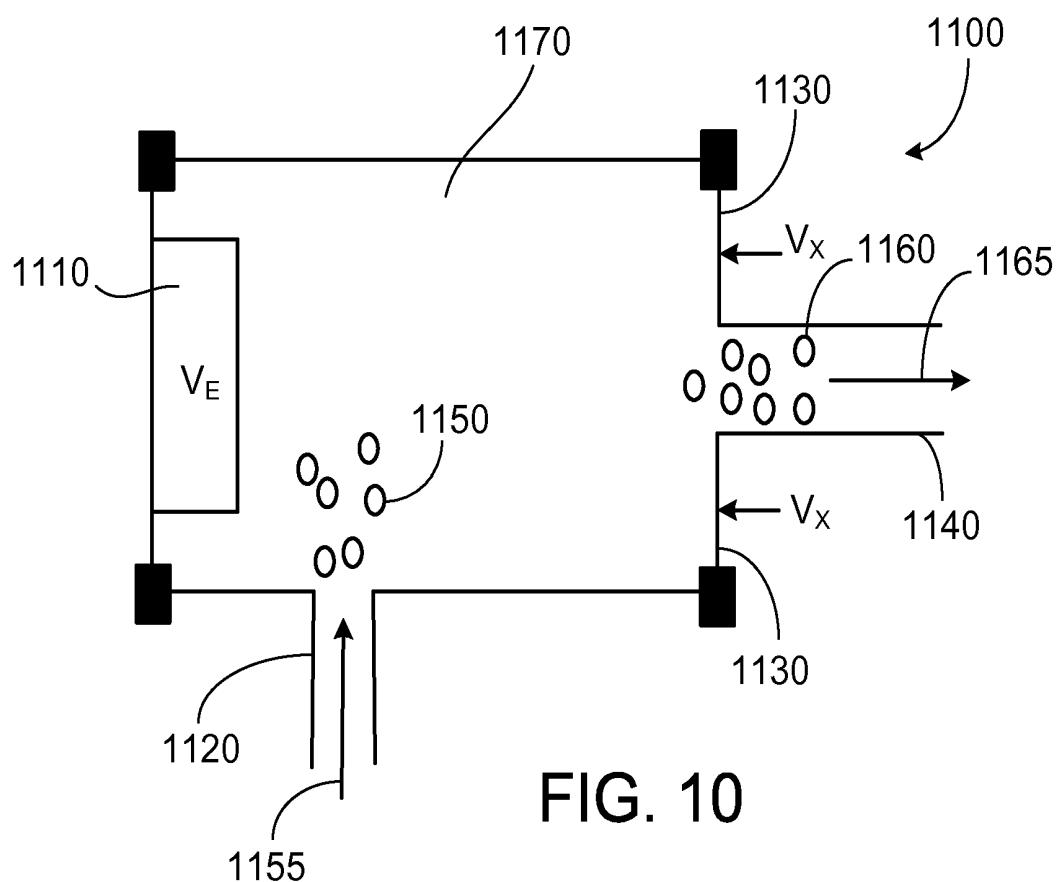


FIG. 10

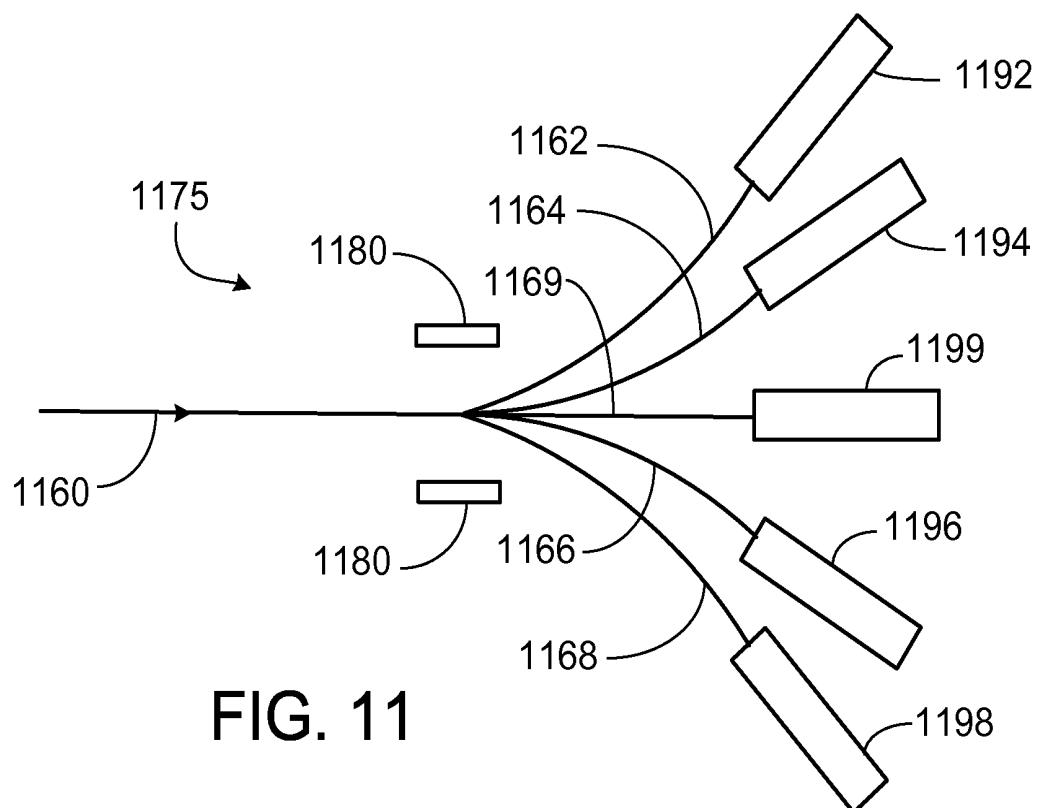


FIG. 11

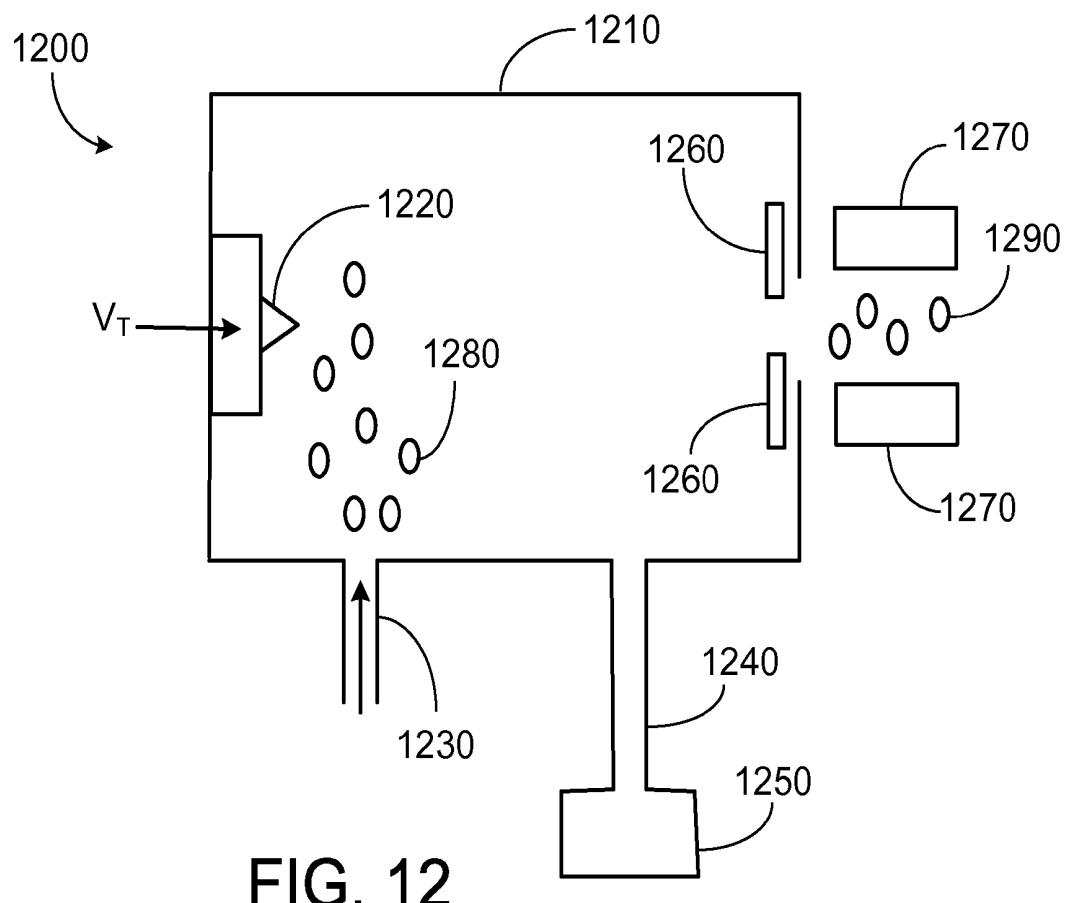


FIG. 12

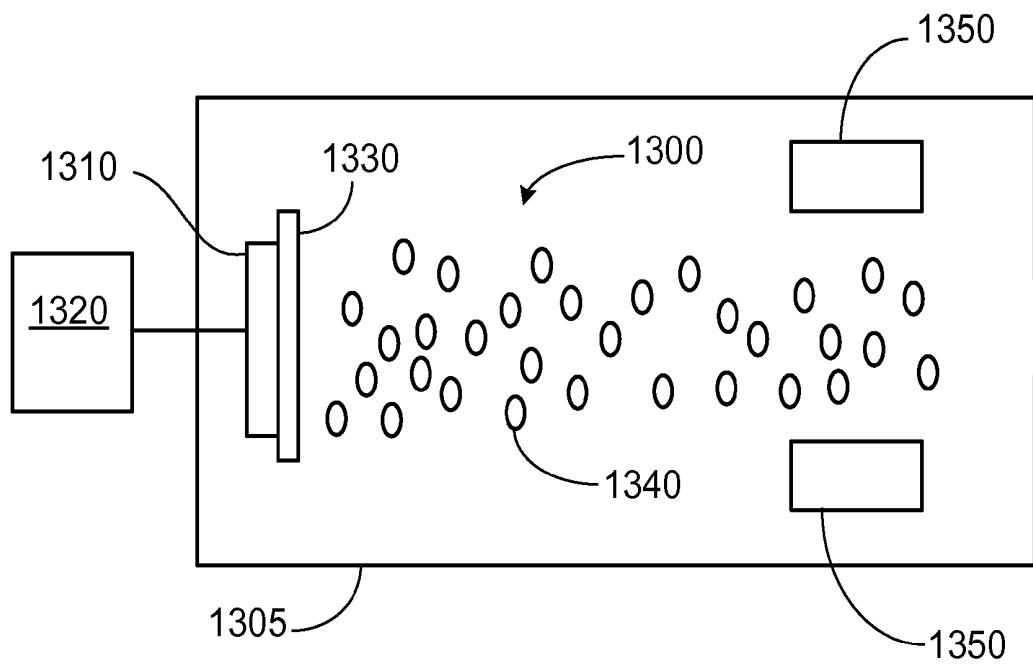


FIG. 13

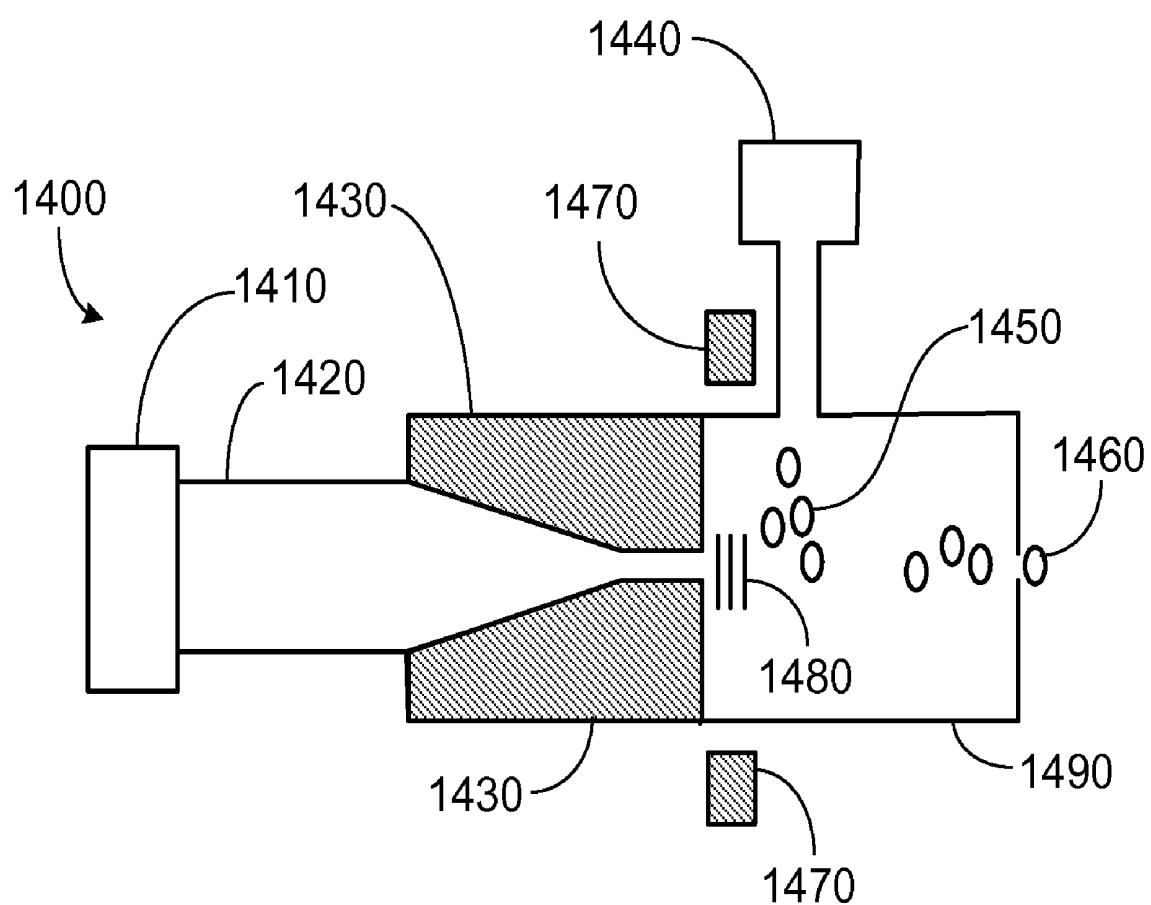


FIG. 14

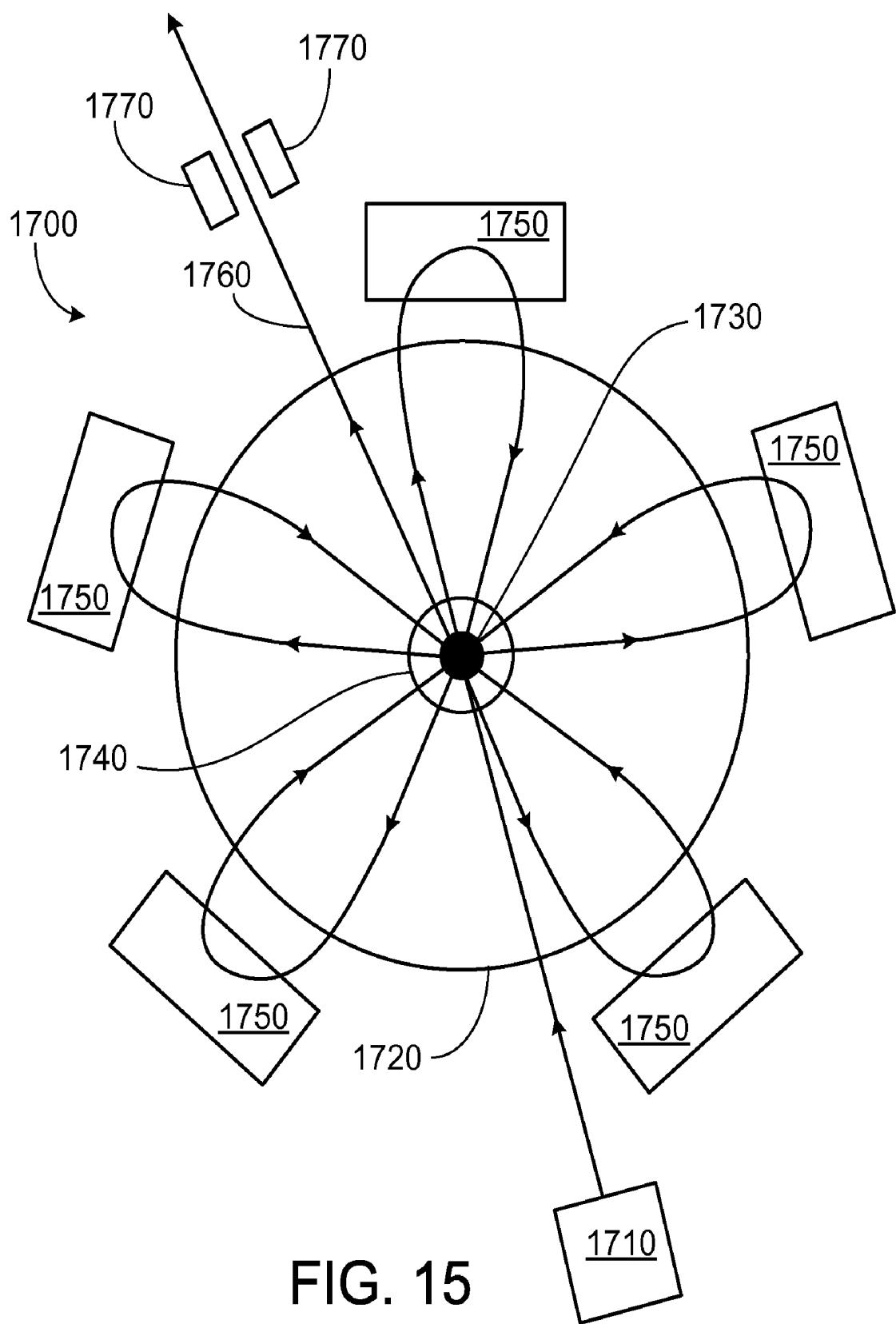


FIG. 15

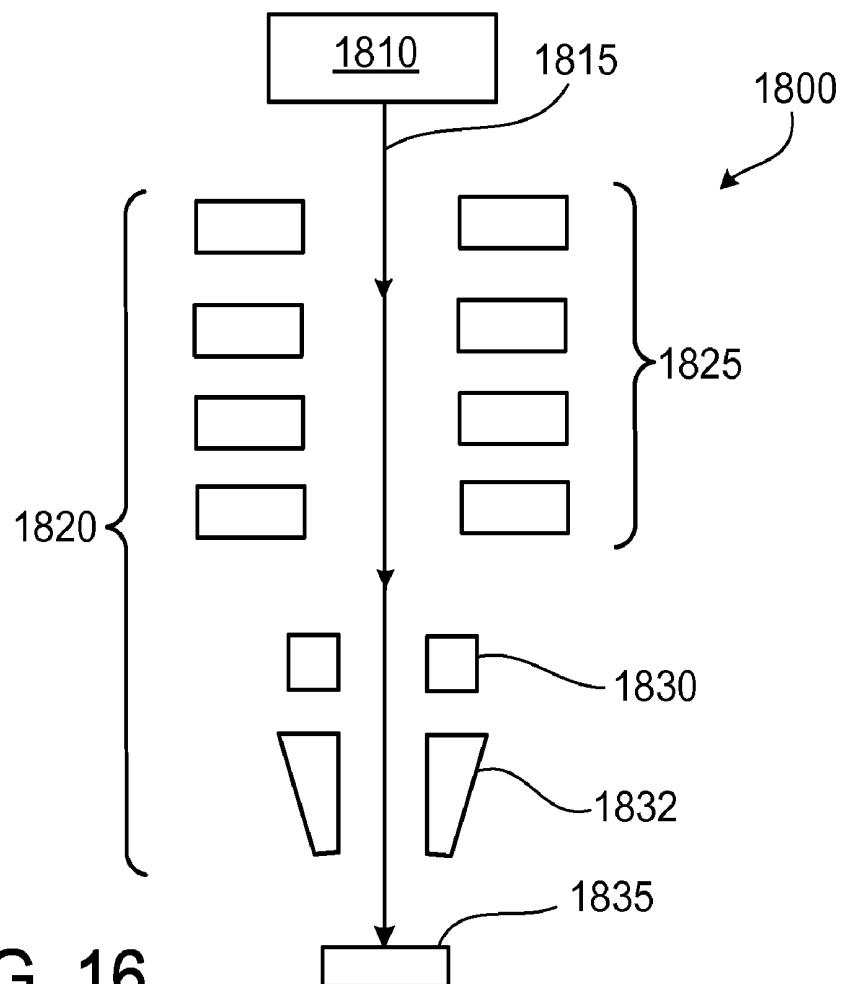


FIG. 16

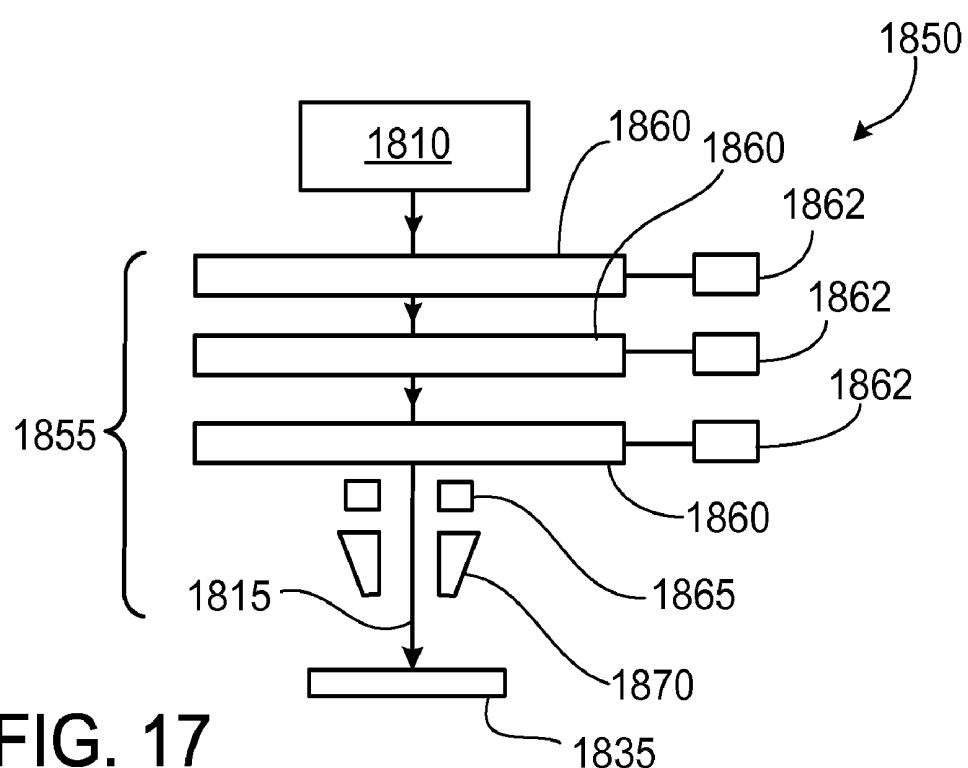
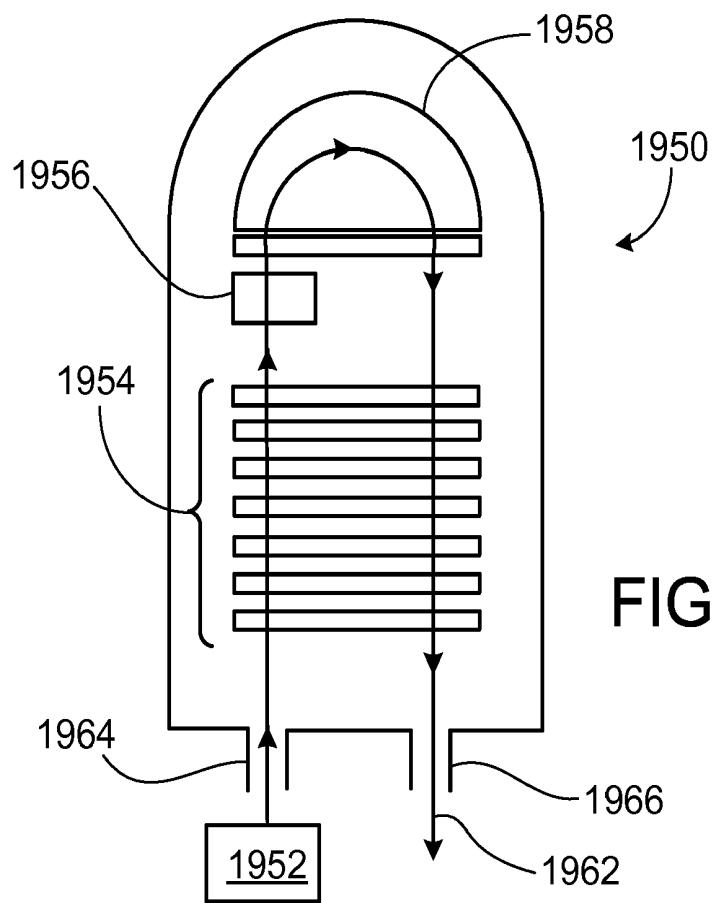
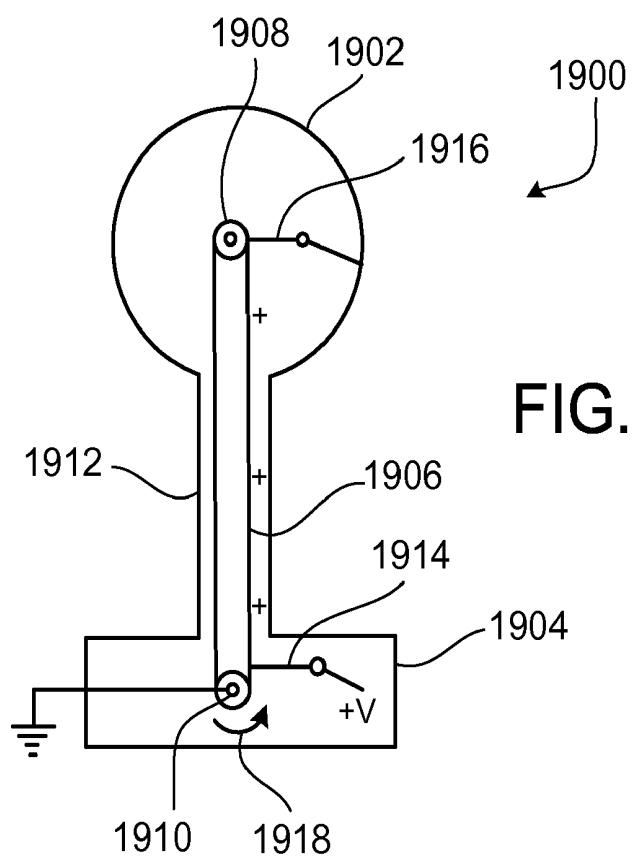


FIG. 17



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**PAPER PRODUCTS AND METHODS AND
SYSTEMS FOR MANUFACTURING SUCH
PRODUCTS**

RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application Ser. No. 61/049,391, filed Apr. 30, 2008. The complete disclosure of the provisional application is hereby incorporated by reference herein.

TECHNICAL FIELD

This invention relates to methods and systems for preparing paper products, and products produced by such methods and systems.

BACKGROUND

Paper, as that term is used herein, refers to the wide variety of cellulose-based sheet materials used for writing, printing, packaging, and other applications. Paper may be used, for example, but without limitation, in the following applications: as paper money, bank notes, stock and bond certificates, checks, and the like; in books, magazines, newspapers, and art; for packaging, e.g., paper board, corrugated cardboard, paper bags, envelopes, wrapping tissue, boxes; in household products such as toilet paper, tissues, paper towels and paper napkins; paper honeycomb, used as a core material in composite materials; building materials; construction paper; disposable clothing; and in various industrial uses including emery paper, sandpaper, blotting paper, litmus paper, universal indicator paper, paper chromatography, battery separators, and capacitor dielectrics.

Paper is generally produced by pulping a cellulosic material to form a pulp containing cellulosic fibers, amalgamating the cellulosic fibers to form a wet web, and drying the wet web. In the finished paper, the fibers are held together by mechanical interlocking and hydrogen bonding. Pulping may be accomplished in a number of ways, for example: using a chemical process (e.g., the Kraft process), a mechanical process (groundwood), or thermomechanical process (TMP). The amalgamating and drying steps are generally performed using a high speed paper machine.

The most common source of cellulosic fibers is wood pulp from trees. Pulp is also derived from recovered ("recycled") paper. Vegetable fiber materials, such as cotton, hemp, linen, and rice, are also used. Other non-wood fiber sources include, but are not limited to, sugarcane, bagasse, straw, bamboo, kenaf, jute, flax, and cotton. A wide variety of synthetic fibers, such as polypropylene and polyethylene, as well as other ingredients such as inorganic fillers, may be incorporated into paper as a means for imparting desirable physical properties.

For many applications, it is desirable that paper have high strength and tear resistance, even in very thin sheets, for example, when the paper is used in packaging, in industrial applications, as money, and in other applications that require strength and durability. It is also generally desirable that paper exhibit good printability characteristics, with the particular characteristics depending to some extent on the printing process in which the paper will be used.

SUMMARY

The invention is based, in part, on the discovery that by irradiating fibrous materials at appropriate levels, the physical characteristics of the fibrous material can be favorably

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altered. For example, the molecular weight, level of crosslinking, grafting sites, and/or functional groups of at least the cellulosic portions of the materials can be altered. Moreover, physical properties such as the tensile strength and shear strength of the fibrous material can be favorably affected. Relatively high doses of ionizing radiation can be used to reduce the molecular weight of at least the cellulosic portions of the fibrous material, assisting with transformation of a fibrous material to a pulp that is suitable for use in papermaking. Relatively lower doses of ionizing radiation can be used to increase the molecular weight of a paper product, enhancing its tensile strength and other mechanical properties. Ionizing radiation can also be used to control the functionalization of the fibrous material, i.e., the functional groups that are present on or within the material.

In one aspect, the invention features methods of producing a cellulosic or lignocellulosic material for use in papermaking. Some methods include treating a cellulosic or lignocellulosic dry feedstock having a first average molecular weight with at least 2.5 MRad of ionizing radiation to reduce the average molecular weight of the feedstock to a predetermined level.

Some implementations include one or more of the following features. The predetermined level is selected so that the treated feedstock is suitable for use as, or in forming, a pulp in a papermaking process. The methods further include subjecting the treated feedstock to a pulping process. The methods further include subjecting the treated feedstock to a mechanical disintegrating process. The methods can further include applying acoustic energy to the treated feedstock.

In some embodiments, the feedstock can include wood chips, and the dose of ionizing radiation can be about 2.5 to about 10 MRad. Treating can include irradiating with gamma radiation and/or irradiating with electron beam radiation. In certain embodiments, the electrons in the electron beam can have an energy of at least 0.25 MeV.

In another aspect, the invention features methods of making an irradiated paper product. Some methods include treating a paper product including a first carbohydrate-containing material having a first molecular weight with ionizing radiation to provide an irradiated paper product including a second carbohydrate-containing material having a second molecular weight higher than the first molecular weight.

Some implementations include one or more of the following features. The dose of ionizing radiation can be at least 0.10 MRad, e.g., at least 0.25 MRad. The dose of ionizing radiation can be controlled to a level of about 0.25 to about 5 MRad. Treating can include irradiating with gamma radiation, and/or with electron beam radiation. Electrons in the electron beam can have an energy of at least 0.25 MeV, e.g., from about 0.25 MeV to about 7.5 MeV. The methods can further include quenching the treated paper product. For example, quenching can be performed in the presence of a gas selected to react with radicals present in the treated paper product.

In yet a further aspect, the invention features methods of making an irradiated paper product that include treating a carbohydrate-containing pulp material with ionizing radiation such that the average molecular weight of the carbohydrate-containing pulp material is increased.

Some implementations of these methods can include one or more of the following features. Treating can occur during formation of the paper product. Forming can include amalgamating the pulp material into a wet paper web. Treating can be performed on the wet paper web or prior to formation of the wet paper web. Forming can further include drying the wet paper web, and treating can occur after drying.

In a further aspect, the invention features a paper, the paper comprising an irradiated lignocellulosic material, wherein the irradiated lignocellulosic material includes at least about 2 percent by weight lignin, such as at least about 2.5, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 or at least about 10.0 percent by weight lignin.

In some cases, the irradiated lignocellulosic material includes crosslinks, and the crosslinks occur in at least the lignin portion of the irradiated lignocellulosic material.

The invention also features a method of making a paper, the method including combining a cellulosic or lignocellulosic material with lignin and forming a paper from the combination.

In some cases the cellulosic or lignocellulosic material has been irradiated, and/or the combination is irradiated and then formed into a paper, and/or the formed paper is irradiated.

The invention also features pulp and paper products formed by irradiating cellulosic and lignocellulosic materials, e.g., using the methods described herein.

In one aspect, the invention features pulp materials including a treated cellulosic or lignocellulosic fibrous material having an average molecular weight of less than 500,000 and containing functional groups not present in a naturally occurring cellulosic or lignocellulosic fibrous materials from which the treated material was obtained. For example, in some embodiments, the functional groups include enol groups and/or carboxylic acid groups or salts or esters thereof. The functional groups can also be selected from the group consisting of aldehyde groups, nitroso groups, nitrile groups, nitro groups, ketone groups, amino groups, alkyl amino groups, alkyl groups, chloroalkyl groups, chlorofluoroalkyl groups, and carboxylic acid groups. In some cases the naturally occurring cellulosic or lignocellulosic fibrous materials can include wood chips.

In another aspect, the invention features paper products that include a treated cellulosic or lignocellulosic fibrous material, the treated cellulosic or lignocellulosic fibrous material containing functional groups not present in a naturally occurring cellulosic or lignocellulosic fibrous material from which the treated material was obtained.

The cellulosic or lignocellulosic material can be selected from the group consisting of paper waste, wood, particle board, sawdust, silage, grasses, rice hulls, bagasse, cotton, jute, hemp, flax, bamboo, sisal, abaca, straw, corn cobs, corn stover, switchgrass, alfalfa, hay, rice hulls, coconut hair, cotton, seaweed, algae, and mixtures thereof.

The term "dry feedstock" as used herein refers to a feedstock (e.g., woodchips or other cellulosic or lignocellulosic fibrous material) having a moisture content of less than 25%.

The full disclosures of each of the following U.S. Patent Applications, which are being filed concurrently herewith, are hereby incorporated by reference herein: Ser. Nos. 12/417,720, 12/417,699, 12/417,840, 12/417,731, 12/417,900, 12/417,800, 12,417,723, 12/417,786, and 12/417,904.

In any of the methods disclosed herein, radiation may be applied from a device that is in a vault.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All mentioned publications, patent applications, patents, and other references are incorporated herein by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In

addition, the materials, methods and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

DESCRIPTION OF DRAWINGS

FIG. 1A is a diagrammatic view of a pulping system.

FIG. 1B is a diagrammatic view of the pretreatment subsystem of the pulping system shown in FIG. 1A.

FIG. 2 is a diagrammatic view of a paper making system.

FIG. 3 is a diagram that illustrates changing a molecular and/or a supramolecular structure of a fibrous material.

FIG. 4 is a perspective, cut-away view of a gamma irradiator housed in a concrete vault.

FIG. 5 is an enlarged perspective view of region, R, of FIG. 4.

FIG. 6 is a schematic diagram of a DC accelerator.

FIG. 7 is a schematic view of a system for sonicating a process stream of cellulosic material in a liquid medium.

FIG. 8 is a schematic view of a sonicator having two transducers coupled to a single horn.

FIG. 9 is a schematic cross-sectional side view of a hybrid electron beam/sonication device.

FIG. 10 is a schematic diagram of a field ionization source.

FIG. 11 is a schematic diagram of an electrostatic ion separator.

FIG. 12 is a schematic diagram of a field ionization generator.

FIG. 13 is a schematic diagram of a thermionic emission source.

FIG. 14 is a schematic diagram of a microwave discharge ion source.

FIG. 15 is a schematic diagram of a recirculating accelerator.

FIG. 16 is a schematic diagram of a static accelerator.

FIG. 17 is a schematic diagram of a dynamic linear accelerator.

FIG. 18 is a schematic diagram of a van de Graaff accelerator.

FIG. 19 is a schematic diagram of a folded tandem accelerator.

DETAILED DESCRIPTION

As discussed above, the invention is based, in part, on the discovery that by irradiating fibrous materials, i.e., cellulosic and lignocellulosic materials, at appropriate levels, the molecular structure of at least a cellulosic portion of the fibrous material can be changed. For example, the change in molecular structure can include a change in any one or more of an average molecular weight, average crystallinity, surface area, polymerization, porosity, branching, grafting, and domain size of the cellulosic portion. These changes in molecular structure can in turn result in favorable alterations of the physical characteristics exhibited by the fibrous materials. Moreover, the functional groups of the fibrous material can be favorably altered.

For example, the following properties can be increased by 10, 20, 30, 40, 50, 75, or even 100% relative to the same properties prior to irradiation:

TAPPI T494 om-06 Tensile Properties of Paper and Paperboard (Using Constant Rate of Elongation Apparatus), including tensile strength and breaking length;

TAPPI Method T 414 om-04 Internal tearing resistance of paper (Elmendorf-type Method);

TAPPI Method T 403 om-02 Bursting strength of paper; and

TAPPI Method T 451 cm-84 Flexural properties of paper (Clark Stiffness).

Various cellulosic and lignocellulosic materials, their uses, and applications have been described in U.S. Pat. Nos. 7,307,108, 7,074,918, 6,448,307, 6,258,876, 6,207,729, 5,973,035 and 5,952,105; and in various patent applications, including "FIBROUS MATERIALS AND COMPOSITES," PCT/US2006/010648, filed on Mar. 23, 2006, and "FIBROUS MATERIALS AND COMPOSITES," U.S. Patent Application Publication No. 2007/0045456. The aforementioned documents are all incorporated by reference herein in their entireties. The cellulosic or lignocellulosic material can include, for example, paper waste, wood, particle board, sawdust, silage, grasses, rice hulls, bagasse, cotton, jute, hemp, flax, bamboo, sisal, abaca, straw, corn cobs, corn stover, switchgrass, alfalfa, hay, rice hulls, coconut hair, cotton, seaweed, algae, and mixtures thereof.

Relatively high doses of ionizing radiation can be used to reduce the molecular weight of the fibrous material, assisting with transformation of fibrous material to pulp that is suitable for use in papermaking. Thus, irradiation can be used to pre-treat a feedstock and thus facilitate a chemical, mechanical, or thermo-mechanical pulping process, or in some cases can be used to replace at least a portion of a conventional pulping process. Relatively high doses can also be applied to selected areas of a paper product or a precursor (e.g., a wet paper web) to form predetermined regions in which the paper is weakened, e.g., to create tear zones.

Relatively lower doses of ionizing radiation can be applied, at one or more stages of a papermaking process and/or to a finished paper product, to increase the molecular weight and the level of crosslinking of a paper product.

Ionizing radiation can also be used to control the functionalization of the fibrous material, i.e., the functional groups that are present on or within the material, which can increase solubility and/or dispersibility during pulping, and can favorably affect the surface properties of a paper product, e.g., the receptivity of the surface to coatings, inks and dyes.

Each of these processes will be discussed in detail below.

The irradiating steps discussed above can be combined in many ways. Some examples of processes including irradiation include the following:

(a) Irradiating only with a high dose of ionizing radiation, to reduce molecular weight and facilitate pulping. Irradiation can be performed prior to or during pulping.

(b) Irradiating only with a low dose of ionizing radiation, to increase molecular weight, and pulping conventionally. Irradiation can be performed at any stage of the papermaking process, or on the finished paper.

(c) Irradiating with a high dose of ionizing radiation, to break down molecular weight and facilitate pulping, followed by irradiation with a low dose of radiation, to increase molecular weight.

(d) Irradiating under conditions that favorably alter the functional groups present in the material. This can be accomplished during one of the steps discussed above, or as a separate step, as will be discussed in detail below.

(e) Irradiating selected areas of paper or a paper precursor with a relatively high dose of radiation to form predetermined weakened areas. This step can be performed alone, or in combination with any of the steps discussed in (a)-(d) above.

(f) Irradiating multiple times to achieve a given final dose, e.g., delivering a dose of 1 MRad repeated 10 times, to pro-

vide a final dose of 10 MRad. This may prevent overheating of the irradiated material, particularly if the material is cooled between doses.

Irradiating to Reduce Molecular Weight

Ionizing radiation can be applied to a cellulosic or lignocellulosic fibrous material that is suitable for use in making paper (e.g., wood chips) prior to or during pulping, at a dose that is sufficient to convert the starting material to pulp. In other words, irradiation with a dose of ionizing radiation that is selected to convert or to aid in converting the starting material to pulp can be used in place of conventional pulping processes such as chemical, mechanical, and thermomechanical pulping.

In this case, the dose is selected so that the molecular weight of the starting material is reduced to an extent similar to the extent by which molecular weight is reduced by conventional pulping. For example, in the case of converting wood chips to pulp, the dose would generally be selected to reduce the molecular weight from the starting molecular weight (1 million or greater) to about 20,000 to 500,000. The optimal dose will depend on the feedstock used, but will generally be in the range of 10 MRad to 1000 MRad, e.g., 25 MRad to 500 MRad, for conventional paper feedstocks such as wood-based materials.

Advantageously, in some implementations it is not necessary to remove lignin from the pulp, as is conventionally done during the pulping process. This is the case, for example, if the paper is irradiated with a low, molecular weight increasing, dose of ionizing radiation during or after the paper making process, as will be discussed below. In this case, the residual lignin may actually be useful, as the lignin acts as a filler, effectively reducing the amount of cellulosic material needed, and may be cross-linked by the low dose radiation.

In other implementations, instead of replacing conventional pulping with irradiation, ionizing radiation can be applied prior to or during a conventional pulping process, to facilitate or enhance the pulping process. For example, wood chips can be irradiated with a relatively high dose of ionizing radiation prior to the start of the pulping process. If desired, after irradiation, the wood chips can be subjected to a mechanical process prior to chemical pulping, such as further chipping, shearing, or pulverizing. Irradiating and, optionally, mechanically pulping of the irradiated feedstock, can initiate breakdown of the feedstock, in some cases allowing chemical pulping to be performed under less harsh conditions, e.g., using fewer chemicals, less energy, and/or less water.

Ionizing radiation can also be used in a paper recycling process, to re-pulp waste paper for use as starting material in recycled paper production. In this case, the dose of ionizing radiation delivered is selected to be sufficient to break down the hydrogen and mechanical bonding in the paper without deleteriously affecting the cellulosic and/or lignocellulosic fibers in the paper. The dose of ionizing radiation can, for example, be about 20% to 30% less than the dose used when the starting material is wood chips.

FIG. 1A shows a system 100 for converting cellulosic or lignocellulosic starting material, wood logs in the example shown, into pulp suitable for use in papermaking. System 100 includes a feed preparation subsystem 110, a pretreatment subsystem 114, a primary process subsystem 118, and a post-processing subsystem 122. Feed preparation subsystem 110 receives the starting material in its raw form (e.g., logs), and physically prepares the starting material for the downstream processes (e.g., reduces the size of the material and begins to homogenize the material). In the example shown, this is

accomplished by debarking and chipping the logs. Starting materials with significant cellulosic and lignocellulosic components can have a high average molecular weight and crystallinity that can make pulping difficult.

Pretreatment subsystem 114 receives feedstock (e.g., wood chips) from the feed preparation subsystem 110 and prepares the feedstock for use in primary production processes by, for example, reducing the average molecular weight and crystallinity, and changing the kind and degree of functionalization of the feedstock. This is accomplished, in the example shown, by irradiation with a relatively high dose of ionizing radiation, followed by an inline sonication (acoustic) process. Sonication will be discussed in detail below. A conveyor belt carries the feedstock from the feed preparation subsystem 110 to the pretreatment subsystem 114.

As shown in FIG. 1B, in the pretreatment subsystem 114, the feedstock is irradiated, e.g., using electron beam emitters 492, mixed with water to form a slurry, and subjected to the application of ultrasonic energy. As discussed above, irradiation of the feedstock changes the molecular structure (e.g., reduces the average molecular weight and the crystallinity) of the feedstock. Mixing the irradiated feedstock into a slurry and applying ultrasonic energy to the slurry further changes the molecular structure of the feedstock. Application of radiation and sonication in sequence can have synergistic effects in that the combination of techniques appears to achieve greater changes to the molecular structure (e.g., reduction of the average molecular weight and the crystallinity) than either technique can efficiently achieve on its own. Without wishing to be bound by theory, in addition to reducing the polymerization of the feedstock by breaking intramolecular bonds between segments of cellulosic and lignocellulosic components of the feedstock, the irradiation can make the overall physical structure of the feedstock more brittle. After the brittle feedstock is mixed into a slurry, the application of ultrasonic energy further changes the molecular structure (e.g., reduces the average molecular weight and the crystallinity) and also can reduce the particle size of the feedstock.

The conveyor belt 491 carrying the feedstock into the pretreatment subsystem distributes the feedstock into multiple feed streams (e.g., fifty feed streams), each leading to separate electron beam emitters 492. Preferably, the feedstock is irradiated while it is dry. For example, the feedstock may have a moisture content of less than 25%, preferably less than 20%, less than 15% or less than 10%. Each feed stream is carried on a separate conveyor belt to an associated electron beam emitter. Each irradiation feed conveyor belt can be approximately one meter wide. Before reaching the electron beam emitter, a localized vibration can be induced in each conveyor belt to evenly distribute the dry feedstock over the cross-sectional width of the conveyor belt.

Electron beam emitter 492 (e.g., electron beam irradiation devices commercially available from Titan Corporation, San Diego, Calif.) is, in one example, configured to apply a 100 kilo-Gray dose of electrons at a power of 300 kW. The electron beam emitters are scanning beam devices with a sweep width of 1 meter to correspond to the width of the conveyor belt. In some embodiments, electron beam emitters with large, fixed beam widths are used. A number of factors, including belt/beam width, desired dose, feedstock density, and power applied, govern the number of electron beam emitters required for the plant to process 2,000 tons per day of dry feedstock.

In some embodiments, sonication is omitted from the pretreatment system. In some embodiments, further mechanical processing, e.g., further chipping, replaces or is used in addition to sonication.

In some cases, the output of primary process subsystem 118 is directly useful as pulp, but in other cases, the output requires further processing, which is provided by post-processing subsystem 122. Post-processing subsystem 122 provides chemical pulping of the output of the primary process subsystem (e.g., pressure cooking and digestion, in the example shown). If the paper to be produced with the pulp is bleached, for example if the paper is bleached printing paper, a bleaching step is performed. This step can be omitted for pulp to be used for unbleached paper. In some embodiments, post-processing subsystem 122 utilizes other pulping processes, such as thermomechanical pulping, instead of chemical pulping. As shown, in some cases post-processing subsystem 122 can produce treated water to be recycled for use as process water in other subsystems, and/or can produce burnable waste that can be used as fuel for boilers producing steam and/or electricity.

Irradiating to Increase Molecular Weight

Relatively low doses of ionizing radiation can crosslink, graft, or otherwise increase the molecular weight of a carbohydrate-containing material, such as a cellulosic or lignocellulosic material (e.g., cellulose). In some embodiments, the starting number average molecular weight (prior to irradiation) of a paper product or a precursor to a paper product is from about 20,000 to about 500,000, e.g., from about 25,000 to about 100,000. The number average molecular weight after irradiation is greater than the starting number average molecular weight, for example by at least about 10%, 25%, 50%, 75%, 100%, 150%, 200%, 300%, or as much as 500%. For example, if the starting number average molecular weight is in the range of about 20,000 to about 100,000, the number average molecular weight after irradiation is, in some instances, from about 40,000 to about 200,000.

The new methods can be used to favorably alter properties of cellulose-based papers by applying radiation at one or more selected stages of the papermaking process. In some cases, irradiation will improve the strength and tear resistance of the paper, by increasing the strength of the cellulosic fibers of which the paper is made. In addition, treating the cellulosic material with radiation can sterilize the material, which may reduce the tendency of the paper to promote the growth of mold, mildew of the like. Irradiation is generally performed in a controlled and predetermined manner to provide optimal properties for a particular application, such as strength, by selecting the type or types of radiation employed and/or dose or doses of radiation applied.

A low dose of ionizing radiation can be applied to increase molecular weight, e.g., after pulping and before amalgamation of the pulped fibers into a web; to the wet fiber web; to the paper web during or after drying; or to the dried paper web, e.g., before, during, or after subsequent processing steps such as sizing, coating, and calendering. It is generally preferred that radiation be applied to the web when it has a relatively low moisture content. In the example shown in FIG. 2, irradiation can be performed during drying and finishing, e.g., between sizing, drying, pressing and calendering operations, or during post-processing, e.g., to the finished paper in roll, slit roll or sheet form.

As noted above, in some embodiments radiation is applied at more than one point during the manufacturing process. For example, ionizing radiation can be used at a relatively high dose to form or to help form the pulp, and then later at a relatively lower dose to increase the molecular weight of the fibers in the paper. As will be discussed in further detail below, radiation can also be applied to the finished paper in a manner so as to favorably affect the functional groups present within

and/or on the surface of the paper. High dose radiation can be applied to the finished paper at selected areas of the paper web to create locally weakened areas, e.g., to provide tear zones.

As a practical matter, using existing technology, it is generally most desirable to integrate the irradiation step into the papermaking process either after pulping and prior to introduction of the pulp to the papermaking machine, or after the web has exited the papermaking machine, typically after drying and sizing. However, as noted above, irradiation may be performed at any desired stage in the process.

If desired, various cross-linking additives can be added to the pulp to enhance cross-linking in response to irradiation. Such additives include materials that are cross-linkable themselves and materials that will assist with cross-linking. Cross-linking additives include, but are not limited to, lignin, starch, diacrylates, divinyl compounds, and polyethylene. In some implementations, such additives are included in concentrations of about 0.25% to about 2.5%, e.g., about 0.5% to about 1.0%.

Irradiating to Affect Material Functional Groups

After treatment with one or more ionizing radiations, such as photonic radiation (e.g., X-rays or gamma-rays), e-beam radiation or irradiation with particles heavier than electrons that are positively or negatively charged (e.g., protons or carbon ions), any of the carbohydrate-containing materials or mixtures described herein become ionized; that is, they include radicals at levels that are detectable, for example, with an electron spin resonance spectrometer. After ionization, any material that has been ionized can be quenched to reduce the level of radicals in the ionized material, e.g., such that the radicals are no longer detectable with the electron spin resonance spectrometer. For example, the radicals can be quenched by the application of sufficient pressure to the ionized material and/or by contacting the ionized material with a fluid, such as a gas or liquid, that reacts with (quenches) the radicals. Various gases, for example nitrogen or oxygen, or liquids, can be used to at least aid in the quenching of the radicals and to functionalize the ionized material with desired functional groups. Thus, irradiation followed by quenching can be used to provide pulp or paper with desired functional groups, including, for example, one or more of the following: aldehyde groups, enol groups, nitroso groups, nitrile groups, nitro groups, ketone groups, amino groups, alkyl amino groups, alkyl groups, chloroalkyl groups, chlorofluoroalkyl groups, and/or carboxylic acid groups. These groups increase the hydrophilicity of the region of the material where they are present. In some implementations, the paper web is irradiated and quenched, before or after processing steps such as coating and calendering, to affect the functionality within and/or at the surface of the paper and thereby affect the ink receptivity and other properties of the paper. In other implementations, the paper feedstock is irradiated with a relatively high dose of ionizing radiation, to facilitate pulping, and then later quenched to improve the stability of the ionized material in the pulp.

FIG. 3 illustrates changing a molecular and/or a supramolecular structure of fibrous material, such as paper feedstock, paper precursor (e.g., a wet paper web), or paper, by pretreating the fibrous material with ionizing radiation, such as with electrons or ions of sufficient energy to ionize the material, to provide a first level of radicals. As shown in FIG. 3, if the ionized material remains in the atmosphere, it will be oxidized, e.g., to an extent that carboxylic acid groups are generated by reaction with the atmospheric oxygen. In some instances, with some materials, such oxidation is desired, because it can aid in further breakdown in molecular weight

of the carbohydrate-containing material (for example, if irradiation is being used to facilitate pulping). However, since the radicals can "live" for some time after irradiation, e.g., longer than 1 day, 5 days, 30 days, 3 months, 6 months, or even longer than 1 year, material properties can continue to change over time, which in some instances can be undesirable.

Detecting radicals in irradiated samples by electron spin resonance spectroscopy and radical lifetimes in such samples is discussed in Bartolotta et al., Physics in Medicine and Biology, 46 (2001), 461-471 and in Bartolotta et al., Radiation Protection Dosimetry, Vol. 84, Nos. 1-4, pp. 293-296 (1999). As shown in FIG. 3, the ionized material can be quenched to functionalize and/or to stabilize the ionized material.

In some embodiments, quenching includes application of pressure to the ionized material, such as by mechanically deforming the material, e.g., directly mechanically compressing the material in one, two, or three dimensions, or applying pressure to fluid in which the material is immersed, e.g., isostatic pressing. In the case of paper that has been ionized, pressure may be applied, e.g., by passing the paper through a nip. In such instances, the deformation of the material itself brings radicals, which are often trapped in crystalline domains, into proximity close enough for the radicals to recombine, or react with another group. In some instances, pressure is applied together with application of heat, e.g. a quantity of heat sufficient to elevate the temperature of the material to above a melting point or softening point of a component of the ionized material, such as lignin, cellulose or hemicellulose. Heat can improve molecular mobility in the material, which can aid in quenching of radicals. When pressure is utilized to quench, the pressure can be greater than about 1000 psi, such as greater than about 1250 psi, 1450 psi, 3625 psi, 5075 psi, 7250 psi, 10000 psi, or even greater than 15000 psi.

In some embodiments, quenching includes contacting the ionized material with fluid, such as liquid or gas, e.g., a gas capable of reacting with the radicals, such as acetylene or a mixture of acetylene in nitrogen, ethylene, chlorinated ethylenes or chlorofluoroethylenes, propylene or mixtures of these gases. In other particular embodiments, quenching includes contacting the ionized material with liquid, e.g., a liquid soluble in, or at least capable of penetrating into, the ionized material and reacting with the radicals, such as a diene, such as 1,5-cyclooctadiene. In some specific embodiments, the quenching includes contacting the ionized material with an antioxidant, such as Vitamin E. If desired, the material can include an antioxidant dispersed therein, and quenching can come from contacting the antioxidant dispersed in the material with the radicals.

Other methods for quenching are possible. For example, any method for quenching radicals in polymeric materials described in Muratoglu et al., U.S. Patent Publication No. 2008/0067724 and Muratoglu et al., U.S. Pat. No. 7,166,650, the disclosures of which are incorporated herein by reference in their entireties, can be utilized for quenching any ionized material described herein. Furthermore, any quenching agent (described as a "sensitizing agent" in the above-noted Muratoglu disclosures) and/or any antioxidant described in either Muratoglu reference, can be utilized to quench any ionized material.

Functionalization can be enhanced by utilizing heavy charged ions, such as any of the heavier ions described herein. For example, if it is desired to enhance oxidation, charged oxygen ions can be utilized for the irradiation. If nitrogen functional groups are desired, nitrogen ions or any ion that

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includes nitrogen can be utilized. Likewise, if sulfur or phosphorus groups are desired, sulfur or phosphorus ions can be used in the irradiation.

In some embodiments, after quenching, any of the quenched ionized materials described herein can be further treated with one or more further doses of radiation, such as ionizing or non-ionizing radiation, sonication, pyrolysis, and oxidation for additional molecular and/or supramolecular structure change.

In some embodiments, the fibrous material is irradiated under a blanket of inert gas, e.g., helium or argon, prior to quenching.

The location of the functional groups can be controlled, e.g., by selecting a particular type and dose of ionizing particles. For example, gamma radiation tends to affect the functionality of molecules within paper, while electron beam radiation tends to preferentially affect the functionality of molecules at the surface.

In some cases, functionalization of the material can occur simultaneously with irradiation, rather than as a result of a separate quenching step. In this case, the type of functional groups and degree of oxidation can be affected in various ways, for example by controlling the gas blanketing the material to be irradiated, through which the irradiating beam passes. Suitable gases include nitrogen, oxygen, air, ozone, nitrogen dioxide, sulfur dioxide and chlorine.

In some embodiments, functionalization results in formation of enol groups in the fibrous material. When the fibrous material is paper, this can enhance receptivity of the paper to inks, adhesives, coatings, and the like, and can provide grafting sites. Enol groups can help break down molecular weight, especially in the presence of added base or acid. Thus, the presence of such groups can assist with pulping. In the finished paper product, generally the pH is close enough to neutral that these groups will not cause a deleterious decrease in molecular weight.

Particle Beam Exposure in Fluids

In some cases, the cellulosic or lignocellulosic materials can be exposed to a particle beam in the presence of one or more additional fluids (e.g., gases and/or liquids). Exposure of a material to a particle beam in the presence of one or more additional fluids can increase the efficiency of the treatment.

In some embodiments, the material is exposed to a particle beam in the presence of a fluid such as air. Particles accelerated in any one or more of the types of accelerators disclosed herein (or another type of accelerator) are coupled out of the accelerator via an output port (e.g., a thin membrane such as a metal foil), pass through a volume of space occupied by the fluid, and are then incident on the material. In addition to directly treating the material, some of the particles generate additional chemical species by interacting with fluid particles (e.g., ions and/or radicals generated from various constituents of air, such as ozone and oxides of nitrogen). These generated chemical species can also interact with the material, and can act as initiators for a variety of different chemical bond-breaking reactions in the material. For example, any oxidant produced can oxidize the material, which can result in molecular weight reduction.

In certain embodiments, additional fluids can be selectively introduced into the path of a particle beam before the beam is incident on the material. As discussed above, reactions between the particles of the beam and the particles of the introduced fluids can generate additional chemical species, which react with the material and can assist in functionalizing the material, and/or otherwise selectively altering certain properties of the material. The one or more additional fluids

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can be directed into the path of the beam from a supply tube, for example. The direction and flow rate of the fluid(s) that is/are introduced can be selected according to a desired exposure rate and/or direction to control the efficiency of the overall treatment, including effects that result from both particle-based treatment and effects that are due to the interaction of dynamically generated species from the introduced fluid with the material. In addition to air, exemplary fluids that can be introduced into the ion beam include oxygen, nitrogen, one or more noble gases, one or more halogens, and hydrogen.

Cooling Irradiated Materials

During treatment of the materials discussed above with ionizing radiation, especially at high dose rates, such as at rates greater than 0.15 Mrad per second, e.g., 0.25 Mrad/s, 0.35 Mrad/s, 0.5 Mrad/s, 0.75 Mrad/s or even greater than 1 Mrad/sec, the materials can retain significant quantities of heat so that the temperature of the material becomes elevated. While higher temperatures can, in some embodiments, be advantageous, e.g., when a faster reaction rate is desired, it is advantageous to control the heating to retain control over the chemical reactions initiated by the ionizing radiation, such as crosslinking, chain scission and/or grafting, e.g., to maintain process control.

For example, in one method, the material is irradiated at a first temperature with ionizing radiation, such as photons, electrons or ions (e.g., singularly or multiply charged cations or anions), for a sufficient time and/or a sufficient dose to elevate the material to a second temperature higher than the first temperature. The irradiated material is then cooled to a third temperature below the second temperature. If desired, the cooled material can be treated one or more times with radiation, e.g., with ionizing radiation. If desired, cooling can be applied to the material after and/or during each radiation treatment.

Cooling can in some cases include contacting the material with a fluid, such as a gas, at a temperature below the first or second temperature, such as gaseous nitrogen at or about 77 K. Even water, such as water at a temperature below nominal room temperature (e.g., 25 degrees Celsius) can be utilized in some implementations.

Types of Radiation

The radiation can be provided, e.g., by: 1) heavy charged particles, such as alpha particles; 2) electrons, produced, for example, in beta decay or electron beam accelerators; or 3) electromagnetic radiation, e.g., gamma rays, x-rays or ultraviolet rays. Different forms of radiation ionize the cellulosic or lignocellulosic material via particular interactions, as determined by the energy of the radiation.

Heavy charged particles primarily ionize matter via Coulomb scattering; furthermore, these interactions produce energetic electrons that can further ionize matter. Alpha particles are identical to the nucleus of a helium atom and are produced by alpha decay of various radioactive nuclei, such as isotopes of bismuth, polonium, astatine, radon, francium, radium, several actinides, such as actinium, thorium, uranium, neptunium, curium, californium, americium and plutonium.

Electrons interact via Coulomb scattering and bremsstrahlung radiation produced by changes in the velocity of electrons. Electrons can be produced by radioactive nuclei that undergo beta decay, such as isotopes of iodine, cesium, technetium and iridium. Alternatively, an electron gun can be used as an electron source via thermionic emission.

Electromagnetic radiation interacts via three processes: photoelectric absorption, Compton scattering and pair production. The dominating interaction is determined by the

energy of incident radiation and the atomic number of the material. The summation of interactions contributing to the absorbed radiation in cellulosic material can be expressed by the mass absorption coefficient.

Electromagnetic radiation is subclassified as gamma rays, x-rays, ultraviolet rays, infrared rays, microwaves or radio waves, depending on its wavelength.

For example, gamma radiation can be employed to irradiate the materials. Referring to FIGS. 4 and 5 (an enlarged view of region R), a gamma irradiator 10 includes gamma radiation sources 408, e.g., ^{60}Co pellets, a working table 14 for holding the materials to be irradiated and storage 16, e.g., made of a plurality iron plates, all of which are housed in a concrete containment chamber (vault) 20 that includes a maze entranceway 22 beyond a lead-lined door 26. Storage 16 defines a plurality of channels 30, e.g., sixteen or more channels, allowing the gamma radiation sources to pass through storage on their way proximate the working table.

In operation, the sample to be irradiated is placed on a working table. The irradiator is configured to deliver the desired dose rate and monitoring equipment is connected to an experimental block 31. The operator then leaves the containment chamber, passing through the maze entranceway and through the lead-lined door. The operator mans a control panel 32, instructing a computer 33 to lift the radiation sources 12 into working position using cylinder 36 attached to hydraulic pump 40.

Gamma radiation has the advantage of significant penetration depth into a variety of materials in the sample. Sources of gamma rays include radioactive nuclei, such as isotopes of cobalt, calcium, technetium, chromium, gallium, indium, iodine, iron, krypton, samarium, selenium, sodium, thallium and xenon.

Sources of x-rays include electron beam collision with metal targets, such as tungsten or molybdenum or alloys, or compact light sources, such as those produced commercially by Lyncean Technologies, Inc., of Palo Alto, Calif.

Sources for ultraviolet radiation include deuterium or cadmium lamps.

Sources for infrared radiation include sapphire, zinc or selenide window ceramic lamps.

Sources for microwaves include klystrons, Slevin type RF sources or atom beam sources that employ hydrogen, oxygen or nitrogen gases.

In some embodiments, a beam of electrons is used as the radiation source. A beam of electrons has the advantages of high dose rates (e.g., 1, 5, or even 10 MRad per second), high throughput, less containment and less confinement equipment. Electrons can also be more efficient at causing chain scission. In addition, electrons having energies of 4-10 MeV can have penetration depths of 5 to 30 mm or more, such as 40 mm.

Electron beams can be generated, e.g., by electrostatic generators, cascade generators, transformer generators, low energy accelerators with a scanning system, low energy accelerators with a linear cathode, linear accelerators, and pulsed accelerators. Electrons as an ionizing radiation source can be useful, e.g., for relatively thin materials, e.g., less than 0.5 inch, e.g., less than 0.4 inch, 0.3 inch, 0.2 inch, or less than 0.1 inch. In some embodiments, the energy of each electron of the electron beam is from about 0.25 MeV to about 7.5 MeV (million electron volts), e.g., from about 0.5 MeV to about 5.0 MeV, or from about 0.7 MeV to about 2.0 MeV. Electron beam irradiation devices may be procured commercially from Ion Beam Applications, Louvain-la-Neuve, Belgium or from Titan Corporation, San Diego, Calif. Typical electron energies can be 1, 2, 4.5, 7.5, or 10 MeV. Typical electron

beam irradiation device power can be 1, 5, 10, 20, 50, 100, 250, or 500 kW. Typical doses may take values of 1, 5, 10, 20, 50, 100, or 200 kGy.

Tradeoffs in considering electron beam irradiation device power specifications include operating costs, capital costs, depreciation and device footprint. Tradeoffs in considering exposure dose levels of electron beam irradiation would be energy costs and environment, safety, and health (ESH) concerns. Generators are typically housed in a vault, e.g., of lead or concrete.

The electron beam irradiation device can produce either a fixed beam or a scanning beam. A scanning beam may be advantageous with large scan sweep length and high scan speeds, as this would effectively replace a large, fixed beam width. Further, available sweep widths of 0.5 m, 1 m, 2 m or more are available.

In embodiments in which the irradiating is performed with electromagnetic radiation, the electromagnetic radiation can have an energy per photon (in electron volts) of, e.g., greater than 10^2 eV, e.g., greater than 10^3 , 10^4 , 10^5 , 10^6 or even greater than 10^7 eV. In some embodiments, the electromagnetic radiation has energy per photon of between 10^4 and 10^7 , e.g., between 10^5 and 10^6 eV. The electromagnetic radiation can have a frequency of, e.g., greater than 10^{16} Hz, greater than 10^{17} Hz, 10^{18} , 10^{19} , 10^{20} or even greater than 10^{21} Hz. In some embodiments, the electromagnetic radiation has a frequency of between 10^{18} and 10^{22} Hz, e.g., between 10^{19} to 10^{21} Hz.

One type of accelerator that can be used to accelerate ions produced using the sources discussed above is a Dynamitron® (available, for example, from Radiation Dynamics Inc., now a unit of IBA, Louvain-la-Neuve, Belgium). A schematic diagram of a Dynamitron® accelerator 1500 is shown in FIG. 6. Accelerator 1500 includes an injector 1510 (which includes an ion source) and an accelerating column 1520 that includes a plurality of annular electrodes 1530. Injector 1510 and column 1520 are housed within an enclosure 1540 that is evacuated by a vacuum pump 1600.

Injector 1510 produces a beam of ions 1580, and introduces beam 1580 into accelerating column 1520. The annular electrodes 1530 are maintained at different electric potentials, so that ions are accelerated as they pass through gaps between the electrodes (e.g., the ions are accelerated in the gaps, but not within the electrodes, where the electric potentials are uniform). As the ions travel from the top of column 1520 toward the bottom in FIG. 6, the average speed of the ions increases. The spacing between subsequent annular electrodes 1530 typically increases, therefore, to accommodate the higher average ion speed.

After the accelerated ions have traversed the length of column 1520, the accelerated ion beam 1590 is coupled out of enclosure 1540 through delivery tube 1555. The length of delivery tube 1555 is selected to permit adequate shielding (e.g., concrete shielding) to be positioned adjacent to column 1520, isolating the column. After passing through tube 1555, ion beam 1590 passes through scan magnet 1550. Scan magnet 1550, which is controlled by an external logic unit (not shown), can sweep accelerated ion beam 1590 in controlled fashion across a two-dimensional plane oriented perpendicular to a central axis of column 1520. As shown in FIG. 6, ion beam 1590 passes through window 1560 (e.g., a metal foil window or screen) and then is directed to impinge on selected regions of a sample 1570 by scan magnet 1550.

In some embodiments, the electric potentials applied to electrodes 1530 are static potentials, generated, e.g., by DC potential sources. In certain embodiments, some or all of the electric potentials applied to electrodes 1530 are variable

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potentials generated by variable potential sources. Suitable variable sources of large electric potentials include amplified field sources, e.g., such as klystrons. Accordingly, depending upon the nature of the potentials applied to electrodes 1530, accelerator 1500 can operate in either pulsed or continuous mode.

To achieve a selected accelerated ion energy at the output end of column 1520, the length of column 1520 and the potentials applied to electrodes 1530 are chosen based on considerations well-known in the art. However, it is notable that to reduce the length of column 1520, multiply-charged ions can be used in place of singly-charged ions. That is, the accelerating effect of a selected electric potential difference between two electrodes is greater for an ion bearing a charge of magnitude 2 or more than for an ion bearing a charge of magnitude 1. Thus, an arbitrary ion X^{2+} can be accelerated to final energy E over a shorter length than a corresponding arbitrary ion X^+ . Triply- and quadruply-charged ions (e.g., X^{3+} and X^{4+}) can be accelerated to final energy E over even shorter distances. Therefore, the length of column 1520 can be significantly reduced when ion beam 1580 includes primarily multiply-charged ion species.

To accelerate positively-charged ions, the potential differences between electrodes 1530 of column 1520 are selected so that the direction of increasing field strength in FIG. 6 is downward (e.g., toward the bottom of column 1520). Conversely, when accelerator 1500 is used to accelerate negatively-charged ions, the electric potential differences between electrodes 1530 are reversed in column 1520, and the direction of increasing field strength in FIG. 6 is upward (e.g., toward the top of column 1520). Reconfiguring the electric potentials applied to electrodes 1530 is a straightforward procedure, so that accelerator 1500 can be converted relatively rapidly from accelerating positive ions to accelerating negative ions, or vice versa. Similarly, accelerator 1500 can be converted rapidly from accelerating singly-charged ions to accelerating multiply-charged ions, and vice versa.

Doses

In some embodiments, the high dose irradiating, to reduce molecular weight (with any radiation source or a combination of sources), is performed until the material receives a dose of at least 2.5 MRad, e.g., at least 5.0, 7.5, 10.0, 100, or 500 MRad. In some embodiments, the irradiating is performed until the material receives a dose of between 3.0 MRad and 100 MRad, e.g., between 10 MRad and 100 MRad or between 25 MRad and 75 MRad. If gamma radiation is used, the dose will generally be towards the higher end of these ranges, while if electron beam radiation is used, the dose may, in some embodiments, be towards the lower end. Dosage rates will also be towards the lower end for some cellulosic materials which already have relatively low molecular weight, e.g., recycled paper.

In some embodiments, the low dose irradiating, to increase molecular weight (with any radiation source or a combination of sources), is performed until the material receives a dose of at least 0.05 MRad, e.g., at least 0.1, 0.25, 1.0, 2.5, or 5.0 MRad. In some embodiments, irradiating is performed until the material receives a dose of between 0.1 and 2.5 MRad. Other suitable ranges include between 0.25 MRad and 4.0 MRad, between 0.5 MRad and 3.0 MRad, and between 1.0 MRad and 2.5 MRad.

The doses discussed above, both high and low, are also suitable for functionalization of the material, with the degree of functionalization generally being higher the higher the dose.

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In some embodiments, the irradiating is performed at a dose rate of between 5.0 and 1500.0 kilorads/hour, e.g., between 10.0 and 750.0 kilorads/hour or between 50.0 and 350.0 kilorads/hours. When high throughput is desired, e.g., in a high speed papermaking process, radiation can be applied at, e.g., 0.5 to 3.0 MRad/sec, or even faster, using cooling to avoid overheating the irradiated material.

In some embodiments in which coated paper is irradiated, the paper coating includes resin that is cross-linkable, e.g., 10 diacrylate or polyethylene. As such, the resin crosslinks as the carbohydrate-containing material is irradiated to increase its molecular weight, which can provide a synergistic effect to optimize the scuff resistance and other surface properties of the paper. In these embodiments, the dose of radiation is 15 selected to be sufficiently high so as to increase the molecular weight of the cellulosic fibers, i.e., at least about 0.25 to about 2.5 MRad, depending on the material, while being sufficiently low so as to avoid deleteriously affecting the paper coating. The upper limit on the dose will vary depending on 20 the composition of the coating, but in some embodiments the preferred dose is less than about 5 MRad.

In some embodiments, two or more radiation sources are used, such as two or more ionizing radiations. For example, samples can be treated, in any order, with a beam of electrons, 25 followed by gamma radiation and/or UV light having wavelengths from about 100 nm to about 280 nm. In some embodiments, samples are treated with three ionizing radiation sources, such as a beam of electrons, gamma radiation, and energetic UV light.

30 Acoustic Energy

Radiation may be used in combination with acoustic energy, e.g., sonic or ultrasonic energy, to improve material throughput and/or characteristics, and/or to minimize energy usage. For example, acoustic energy can be used in combination with high dose radiation to enhance the pulping process.

Referring again to FIG. 1A, in the pretreatment system 114, a starting material that will be used to form the pulp, e.g., wood chips, can be subjected to an inline sonication step using acoustic energy.

FIG. 7 shows a general system in which cellulosic material stream 1210 (e.g., feedstock to make pulp) is mixed with water stream 1212 in reservoir 1214 to form process stream 1216. A first pump 1218 draws process stream 1216 from reservoir 1214 and toward flow cell 1224. Ultrasonic transducer 1226 transmits ultrasonic energy into process stream 1216 as the process stream flows through flow cell 1224. A second pump 1230 draws process stream 1216 from flow cell 1224 and toward subsequent processing.

Reservoir 1214 includes first intake 1232 and second intake 1234 in fluid communication with volume 1236. A conveyor (not shown) delivers cellulosic material stream 1210 to reservoir 1214 through first intake 1232. Water stream 1212 enters reservoir 1214 through second intake 1234. In some embodiments, water stream 1212 enters volume 1236 along a tangent establishing swirling flow within volume 1236. In certain embodiments, cellulosic material stream 1210 and water stream 1212 are introduced into volume 1236 along opposing axes to enhance mixing within the volume.

Valve 1238 controls the flow of water stream 1212 through second intake 1232 to produce a desired ratio of cellulosic material to water (e.g., approximately 10% cellulosic material, weight by volume). For example, 2000 tons/day of cellulosic material can be combined with 1 million to 1.5 million gallons/day, e.g., 1.25 million gallons/day, of water.

Mixing of cellulosic material and water in reservoir 1214 is controlled by the size of volume 1236 and the flow rates of cellulosic material and water into the volume. In some embodiments, volume 1236 is sized to create a minimum mixing residence time for the cellulosic material and water. For example, when 2000 tons/day of cellulosic material and 1.25 million gallons/day of water are flowing through reservoir 1214, volume 1236 can be about 32,000 gallons to produce a minimum mixing residence time of about 15 minutes.

Reservoir 1214 includes a mixer 1240 in fluid communication with volume 1236. Mixer 1240 agitates the contents of volume 1236 to disperse cellulosic material throughout the water in the volume. For example, mixer 1240 can be a rotating vane disposed in reservoir 1214. In some embodiments, mixer 1240 disperses the cellulosic material substantially uniformly throughout the water.

Reservoir 1214 further includes an exit 1242 in fluid communication with volume 1236 and process stream 1216. The mixture of cellulosic material and water in volume 1236 flows out of reservoir 1214 via exit 1242. Exit 1242 is arranged near the bottom of reservoir 1214 to allow gravity to pull the mixture of cellulosic material and water out of reservoir 1214 and into process stream 1216.

First pump 1218 (e.g., any of several recessed impeller vortex pumps made by Essco Pumps & Controls, of Los Angeles, Calif.) moves the contents of process stream 1216 toward flow cell 1224. In some embodiments, first pump 1218 agitates the contents of process stream 1216 such that the mixture of cellulosic material and water is substantially uniform at inlet 1220 of flow cell 1224. For example, first pump 1218 agitates process stream 1216 to create a turbulent flow that persists along the process stream between the first pump and inlet 1220 of flow cell 1224.

Flow cell 1224 includes a reactor volume 1244 in fluid communication with inlet 1220 and outlet 1222. In some embodiments, reactor volume 1244 is a stainless steel tube capable of withstanding elevated pressures (e.g., 10 bars). In addition or in the alternative, reactor volume 1244 defines a rectangular cross section.

Flow cell 1224 further includes a heat exchanger 1246 in thermal communication with at least a portion of reactor volume 1244. Cooling fluid 1248 (e.g., water) flows into heat exchanger 1246 and absorbs heat generated when process stream 1216 is sonicated in reactor volume 1244. In some embodiments, the flow rate and/or the temperature of cooling fluid 1248 into heat exchanger 1246 is controlled to maintain an approximately constant temperature in reactor volume 1244. In some embodiments, the temperature of reactor volume 1244 is maintained at 20 to 50° C., e.g., 25, 30, 35, 40 or 45° C. Additionally or alternatively, heat transferred to cooling fluid 1248 from reactor volume 1244 can be used in other parts of the overall process.

An adapter section 1226 creates fluid communication between reactor volume 1244 and booster 1250 coupled (e.g., mechanically coupled using a flange) to ultrasonic transducer 1226. For example, adapter section 1226 can include a flange and O-ring assembly arranged to create a leak tight connection between reactor volume 1244 and booster 1250. In some embodiments, ultrasonic transducer 1226 is a high-powered ultrasonic transducer made by Hielscher Ultrasonics, of Teltow, Germany.

In operation, generator 1252 delivers electricity to ultrasonic transducer 1252. Ultrasonic transducer 1226 includes a piezoelectric element that converts electrical energy into sound in the ultrasonic range. In some embodiments, the materials are sonicated using sound having a frequency of from about 16 kHz to about 110 kHz, e.g., from about 18 kHz

to about 75 kHz or from about 20 kHz to about 40 kHz (e.g., sound having a frequency of 20 kHz to 40 kHz). The ultrasonic energy is delivered to the working medium through booster 1248. Ultrasonic energy traveling through booster 1248 in reactor volume 1244 creates a series of compressions and rarefactions in process stream 1216 with intensity sufficient to create cavitation in process stream 1216. Cavitation disaggregates the cellulosic material dispersed in process stream 1216. Cavitation also produces free radicals in the water of process stream 1216. These free radicals act to further break down the cellulosic material in process stream 1216.

In general, 5 to 4000 MJ/m³, e.g., 10, 25, 50, 100, 250, 500, 750, 1000, 2000 or 3000 MJ/m³, of ultrasonic energy is applied to process stream 16 flowing at a rate of about 0.2 m³/s (about 3200 gallons/min). After exposure to ultrasonic energy in reactor volume 1244, process stream 1216 exits flow cell 1224 through outlet 1222. Second pump 1230 moves process stream 1216 to subsequent processing (e.g., any of several recessed impeller vortex pumps made by Essco Pumps & Controls, Los Angeles, Calif.).

While certain embodiments have been described, other embodiments are possible.

As an example, while process stream 1216 has been described as a single flow path, other arrangements are possible. In some embodiments, e.g., process stream 1216 includes multiple parallel flow paths (e.g., flowing at a rate of 10 gallon/min). In addition or in the alternative, the multiple parallel flow paths of process stream 1216 flow into separate flow cells and are sonicated in parallel (e.g., using a plurality of 16 kW ultrasonic transducers).

As another example, while a single ultrasonic transducer 1226 has been described as being coupled to flow cell 1224, other arrangements are possible. In some embodiments, a plurality of ultrasonic transducers 1226 are arranged in flow cell 1224 (e.g., ten ultrasonic transducers can be arranged in flow cell 1224). In some embodiments, the sound waves generated by each of the plurality of ultrasonic transducers 1226 are timed (e.g., synchronized out of phase with one another) to enhance cavitation acting upon process stream 1216.

As another example, while a single flow cell 1224 has been described, other arrangements are possible. In some embodiments, second pump 1230 moves process stream to a second flow cell where a second booster and ultrasonic transducer further sonicate process stream 1216.

As still another example, while reactor volume 1244 has been described as a closed volume, reactor volume 1244 is open to ambient conditions in certain embodiments. In such embodiments, sonication pretreatment can be performed substantially simultaneously with other pretreatment techniques. For example, ultrasonic energy can be applied to process stream 1216 in reactor volume 1244 while electron beams are simultaneously introduced into process stream 1216.

As another example, while a flow-through process has been described, other arrangements are possible. In some embodiments, sonication can be performed in a batch process. For example, a volume can be filled with a 10% (weight by volume) mixture of cellulosic material in water and exposed to sound with intensity from about 50 W/cm² to about 600 W/cm², e.g., from about 75 W/cm² to about 300 W/cm² or from about 95 W/cm² to about 200 W/cm². Additionally or alternatively, the mixture in the volume can be sonicated for about 1 hour to about 24 hours, e.g., for about 1.5 hours to about 12 hours or for about 2 hours to about 10 hours. In certain embodiments, the material is sonicated for a

pre-determined time, and then allowed to stand for a second predetermined time before sonicating again.

Referring now to FIG. 8, in some embodiments, two electroacoustic transducers are mechanically coupled to a single horn. As shown, a pair of piezoelectric transducers **60** and **62** is coupled to slotted bar horn **64** by respective intermediate coupling horns **70** and **72**, the latter also being known as booster horns. The mechanical vibrations provided by the transducers, responsive to high frequency electrical energy applied thereto, are transmitted to the respective coupling horns, which may be constructed to provide a mechanical gain, such as a ratio of 1 to 1.2. The horns are provided with a respective mounting flange **74** and **76** for supporting the transducer and horn assembly in a stationary housing.

The vibrations transmitted from the transducers through the coupling or booster horns are coupled to the input surface **78** of the horn and are transmitted through the horn to the oppositely disposed output surface **80**, which, during operation, is in forced engagement with a workpiece (not shown) to which the vibrations are applied.

The high frequency electrical energy provided by the power supply **82** is fed to each of the transducers, electrically connected in parallel, via a balancing transformer **84** and a respective series connected capacitor **86** and **90**, one capacitor connected in series with the electrical connection to each of the transducers. The balancing transformer is known also as "balun" standing for "balancing unit." The balancing transformer includes a magnetic core **92** and a pair of identical windings **94** and **96**, also termed the primary winding and secondary winding, respectively.

In some embodiments, the transducers include commercially available piezoelectric transducers, such as Branson Ultrasonics Corporation models 105 or 502, each designed for operation at 20 kHz and a maximum power rating of 3 kW. The energizing voltage for providing maximum motional excursion at the output surface of the transducer is 930 volt rms. The current flow through a transducer may vary between zero and 3.5 ampere depending on the load impedance. At 930 volt rms the output motion is approximately 20 microns. The maximum difference in terminal voltage for the same motional amplitude, therefore, can be 186 volt. Such a voltage difference can give rise to large circulating currents flowing between the transducers. The balancing unit **430** assures a balanced condition by providing equal current flow through the transducers, hence eliminating the possibility of circulating currents. The wire size of the windings must be selected for the full load current noted above and the maximum voltage appearing across a winding input is 93 volt.

As an alternative to using ultrasonic energy, high-frequency, rotor-stator devices can be utilized. This type of device produces high-shear, microcavitation forces that can disintegrate materials in contact with such forces. Two commercially available high-frequency, rotor-stator dispersion devices are the Supraton™ devices manufactured by Krupp Industrietechnik GmbH and marketed by Dorr-Oliver Deutschland GmbH of Connecticut, and the Dispax™ devices manufactured and marketed by Ika-Works, Inc. of Cincinnati, Ohio. Operation of such a microcavitation device is discussed in Stuart, U.S. Pat. No. 5,370,999.

While ultrasonic transducer **1226** has been described as including one or more piezoelectric active elements to create ultrasonic energy, other arrangements are possible. In some embodiments, ultrasonic transducer **1226** includes active elements made of other types of magnetostrictive materials (e.g., ferrous metals). Design and operation of such a high-powered ultrasonic transducer is discussed in Hansen et al., U.S. Pat.

No. 6,624,539. In some embodiments, ultrasonic energy is transferred to process stream **16** through an electrohydraulic system.

While ultrasonic transducer **1226** has been described as using the electromagnetic response of magnetostriuctive materials to produce ultrasonic energy, other arrangements are possible. In some embodiments, acoustic energy in the form of an intense shock wave can be applied directly to process stream **16** using an underwater spark. In some embodiments, ultrasonic energy is transferred to process stream **16** through a thermohydraulic system. For example, acoustic waves of high energy density can be produced by applying power across an enclosed volume of electrolyte, thereby heating the enclosed volume and producing a pressure rise that is subsequently transmitted through a sound propagation medium (e.g., process stream **1216**). Design and operation of such a thermohydraulic transducer is discussed in Hartmann et al., U.S. Pat. No. 6,383,152.

In some embodiments, it may be advantageous to combine irradiation and sonication devices into a single hybrid machine. For such a hybrid machine, multiple processes may be performed in close juxtaposition or even simultaneously, with the benefit of increasing pretreatment throughput and potential cost savings.

For example, consider the electron beam irradiation and sonication processes. Each separate process is effective in lowering the mean molecular weight of cellulosic material by an order of magnitude or more, and by several orders of magnitude when performed serially.

Both irradiation and sonication processes can be applied using a hybrid electron beam/sonication device as is illustrated in FIG. 8. Hybrid electron beam/sonication device **2500** is pictured above a shallow pool (depth 3-5 cm) of a slurry of cellulosic material **2550** dispersed in an aqueous, oxidant medium, such as hydrogen peroxide or carbamide peroxide. Hybrid device **2500** has an energy source **2510**, which powers both electron beam emitter **2540** and sonication horns **2530**.

Electron beam emitter **2540** generates electron beams that pass though an electron beam aiming device **2545** to impact the slurry **2550** containing cellulosic material. The electron beam aiming device can be a scanner that sweeps a beam over a range of up to about 6 feet in a direction approximately parallel to the surface of the slurry **2550**.

On either side of the electron beam emitter **2540** are sonication horns **2530**, which deliver ultrasonic wave energy to the slurry **2550**. The sonication horns **2530** end in a detachable endpiece **2535** that is in contact with the slurry **2550**.

The sonication horns **2530** are at risk of damage from long-term residual exposure to the electron beam radiation. Thus, the horns can be protected with a standard shield **2520**, e.g., made of lead or a heavy-metal-containing alloy such as Lipowitz metal, which is impervious to electron beam radiation. Precautions must be taken, however, to ensure that the ultrasonic energy is not affected by the presence of the shield. The detachable endpieces **2535**, are constructed of the same material and attached to the horns **2530**, are used to be in contact with the cellulosic material **2550** and are expected to be damaged. Accordingly, the detachable endpieces **2535** are constructed to be easily replaceable.

A further benefit of such a simultaneous electron beam and ultrasound process is that the two processes have complementary results. With electron beam irradiation alone, an insufficient dose may result in cross-linking of some of the polymers in the cellulosic material, which lowers the efficiency of the overall depolymerization process. Lower doses of electron beam irradiation and/or ultrasound radiation may also be used

to achieve a similar degree of depolymerization as that achieved using electron beam irradiation and sonication separately.

An electron beam device can also be combined with one or more of high-frequency, rotor-stator devices, which can be used as an alternative to ultrasonic energy devices, and performs a similar function.

Further combinations of devices are also possible. For example, an ionizing radiation device that produces gamma radiation emitted from, e.g., ^{60}Co pellets, can be combined with an electron beam source and/or an ultrasonic wave source. Shielding requirements may be more stringent in this case.

Ion Generation

Various methods may be used for the generation of ions suitable for ion beams which may be used in treating the cellulosic or lignocellulosic materials. After the ions have been generated, they are typically accelerated in one or more of various types of accelerators, and then directed to impinge on the cellulosic or lignocellulosic materials.

(i) Hydrogen Ions

Hydrogen ions can be generated using a variety of different methods in an ion source. Typically, hydrogen ions are introduced into an ionizing chamber of an ion source, and ions are produced by supplying energy to gas molecules. During operation, such chambers can produce large ion currents suitable for seeding a downstream ion accelerator.

In some embodiments, hydrogen ions are produced via field ionization of hydrogen gas. A schematic diagram of a field ionization source is shown in FIG. 10. Field ionization source 1100 includes a chamber 1170 where ionization of gas molecules (e.g., hydrogen gas molecules) occurs. Gas molecules 1150 enter chamber 1170 by flowing along direction 1155 in supply tube 1120. Field ionization source 1100 includes an ionization electrode 1110. During operation, a large potential V_E (relative to a common system ground potential) is applied to electrode 1110. Molecules 1150 that circulate within a region adjacent to electrode 1110 are ionized by the electric field that results from potential V_E . Also during operation, an extraction potential V_X is applied to extractors 1130. The newly-formed ions migrate towards extractors 1130 under the influence of the electric fields of potentials V_E and V_X . In effect, the newly-formed ions experience repulsive forces relative to ionization electrode 1110, and attractive forces relative to extractors 1130. As a result, certain of the newly-formed ions enter discharge tube 1140, and propagate along direction 1165 under the influence of potentials V_E and V_X .

Depending upon the sign of potential V_E (relative to the common ground potential), both positively and negatively charged ions can be formed. For example, in some embodiments, a positive potential can be applied to electrode 1110 and a negative potential can be applied to extractors 1130. Positively charged hydrogen ions (e.g., protons H^+) that are generated in chamber 1170 are repelled away from electrode 1110 and toward extractors 1130. As a result, discharged particle stream 1160 includes positively charged hydrogen ions that are transported to an injector system.

In certain embodiments, a negative potential can be applied to electrode 1110 and a positive potential can be applied to extractors 1130. Negatively charged hydrogen ions (e.g., hydride ions H^-) that are generated in chamber 1170 are repelled away from electrode 1110 and toward extractors 1130. Discharged particle stream 1160 includes negatively charged hydrogen ions, which are then transported to an injector system.

In some embodiments, both positive and negative hydrogen ions can be produced via direct thermal heating of hydrogen gas. For example, hydrogen gas can be directed to enter a heating chamber that is evacuated to remove residual oxygen and other gases. The hydrogen gas can then be heated via a heating element to produce ionic species. Suitable heating elements include, for example, arc discharge electrodes, heating filaments, heating coils, and a variety of other thermal transfer elements.

In certain embodiments, when hydrogen ions are produced via either field emission or thermal heating, various hydrogen ion species can be produced, including both positively and negatively charged ion species, and singly- and multiply-charged ion species. The various ion species can be separated from one another via one or more electrostatic and/or magnetic separators. FIG. 11 shows a schematic diagram of an electrostatic separator 1175 that is configured to separate a plurality of hydrogen ion species from one another. Electrostatic separator 1175 includes a pair of parallel electrodes 1180 to which a potential V_S is applied by a voltage source (not shown). Particle stream 1160, propagating in the direction indicated by the arrow, includes a variety of positively- and negatively-charged, and singly- and multiply-charged, ion species. As the various ion species pass through electrodes 1180, the electric field between the electrodes deflects the ion trajectories according to the magnitude and sign of the ion species. In FIG. 11, for example, the electric field points from the lower electrode toward the upper electrode in the region between electrodes 1180. As a result, positively-charged ions are deflected along an upward trajectory in FIG. 11, and negatively-charged ions are deflected along a downward trajectory. Ion beams 1162 and 1164 each correspond to positively-charged ion species, with the ion species in ion beam 1162 having a larger positive charge than the ion species in beam 1164 (e.g., due to the larger positive charge of the ions in beam 1162, the beam is deflected to a greater extent).

Similarly, ion beams 1166 and 1168 each correspond to negatively-charged ion species, with the ion species in ion beam 1168 having a larger negative charge than the ion species in ion beam 1166 (and thereby being deflected to a larger extent by the electric field between electrodes 1180). Beam 1169 includes neutral particles originally present in particle stream 1160; the neutral particles are largely unaffected by the electric field between electrodes 1180, and therefore pass undeflected through the electrodes. Each of the separated particle streams enters one of delivery tubes 1192, 1194, 1196, 1198, and 1199, and can be delivered to an injector system for subsequent acceleration of the particles, or steered to be incident directly on the cellulosic or lignocellulosic material. Alternatively, or in addition, any or all of the separated particle streams can be blocked to prevent ion and/or atomic species from reaching cellulosic or lignocellulosic material. As yet another alternative, certain particle streams can be combined and then directed to an injector system and/or steered to be incident directly on the cellulosic or lignocellulosic material using known techniques.

In general, particle beam separators can also use magnetic fields in addition to, or rather than, electric fields for deflecting charged particles. In some embodiments, particle beam separators include multiple pairs of electrodes, where each pair of electrodes generates an electric field that deflects particles passing therethrough. Alternatively, or in addition, particle beam separators can include one or more magnetic deflectors that are configured to deflect charged particles according to magnitude and sign of the particle charges.

(ii) Noble Gas Ions

Noble gas atoms (e.g., helium atoms, neon atoms, argon atoms) form positively-charged ions when acted upon by relatively strong electric fields. Methods for generating noble gas ions therefore typically include generating a high-intensity electric field, and then introducing noble gas atoms into the field region to cause field ionization of the gas atoms. A schematic diagram of a field ionization generator for noble gas ions (and also for other types of ions) is shown in FIG. 12. Field ionization generator 1200 includes a tapered electrode 1220 positioned within a chamber 1210. A vacuum pump 1250 is in fluid communication with the interior of chamber 1210 via inlet 1240, and reduces the pressure of background gases within chamber 1210 during operation. One or more noble gas atoms 1280 are admitted to chamber 1210 via inlet tube 1230.

During operation, a relatively high positive potential V_T (e.g., positive relative to a common external ground) is applied to tapered electrode 1220. Noble gas atoms 1280 that enter a region of space surrounding the tip of electrode 1220 are ionized by the strong electric field extending from the tip; the gas atoms lose an electron to the tip, and form positively charged noble gas ions.

The positively charged noble gas ions are accelerated away from the tip, and a certain fraction of the gas ions 1290 pass through extractor 1260 and exit chamber 1210, into an ion optical column that includes lens 1270, which further deflects and/or focuses the ions.

Electrode 1220 is tapered to increase the magnitude of the local electric field in the region near the apex of the tip. Depending upon the sharpness of the taper and the magnitude of potential V_T , the region of space in chamber 1210 within which ionization of noble gas atoms occurs can be relatively tightly controlled. As a result, a relatively well collimated beam of noble gas ions 1290 can be obtained following extractor 1260.

As discussed above in connection with hydrogen ions, the resulting beam of noble gas ions 1290 can be transported through a charged particle optical column that includes various particle optical elements for deflecting and/or focusing the noble gas ion beam. The noble gas ion beam can also pass through an electrostatic and/or magnetic separator, as discussed above in connection with FIG. 11.

Noble gas ions that can be produced in field ionization generator 1200 include helium ions, neon ions, argon ions, and krypton ions. In addition, field ionization generator 1200 can be used to generate ions of other gaseous chemical species, including hydrogen, nitrogen, and oxygen.

Noble gas ions may have particular advantages relative to other ion species when treating cellulosic or lignocellulosic material. For example, while noble gas ions can react with cellulosic or lignocellulosic materials, neutralized noble gas ions (e.g., noble gas atoms) that are produced from such reactions are generally inert, and do not further react with the cellulosic or lignocellulosic material. Moreover, neutral noble gas atoms do not remain embedded in the cellulosic or lignocellulosic material, but instead diffuse out of the material. Noble gases are non-toxic and can be used in large quantities without adverse consequences to either human health or the environment.

(iii) Carbon, Oxygen, and Nitrogen Ions

Ions of carbon, oxygen, and nitrogen can typically be produced by field ionization in a system such as field ionization source 1100 or field ionization generator 1200. For example, oxygen gas molecules and/or oxygen atoms (e.g., produced by heating oxygen gas) can be introduced into a chamber,

where the oxygen molecules and/or atoms are field ionized to produce oxygen ions. Depending upon the sign of the potential applied to the field ionization electrode, positively- and/or negatively-charged oxygen ions can be produced. The desired ion species can be preferentially selected from among various ion species and neutral atoms and molecules by an electrostatic and/or magnetic particle selector, as shown in FIG. 11.

As another example, nitrogen gas molecules can be introduced into the chamber of either field ionization source 1100 or field ionization generator 1200, and ionized to form positively- and/or negatively-charged nitrogen ions by the relatively strong electric field within the chamber. The desired ion species can then be separated from other ionic and neutral species via an electrostatic and/or magnetic separator, as shown in FIG. 11.

To form carbon ions, carbon atoms can be supplied to the chamber of either field ionization source 1100 or field ionization generator 1200, wherein the carbon atoms can be ionized to form either positively- and/or negatively-charged carbon ions. The desired ion species can then be separated from other ionic and neutral species via an electrostatic and/or magnetic separator, as shown in FIG. 11. The carbon atoms that are supplied to the chamber of either field ionization source 1100 or field ionization generator 1200 can be produced by heating a carbon-based target (e.g., a graphite target) to cause thermal emission of carbon atoms from the target. The target can be placed in relatively close proximity to the chamber, so that emitted carbon atoms enter the chamber directly following emission.

(iv) Heavier Ions

Ions of heavier atoms such as sodium and iron can be produced via a number of methods. For example, in some embodiments, heavy ions such as sodium and/or iron ions are produced via thermionic emission from a target material that includes sodium and/or iron, respectively. Suitable target materials include materials such as sodium silicates and/or iron silicates. The target materials typically include other inert materials such as beta-alumina. Some target materials are zeolite materials, and include channels formed therein to permit escape of ions from the target material.

FIG. 13 shows a thermionic emission source 1300 that includes a heating element 1310 that contacts a target material 1330, both of which are positioned inside an evacuated chamber 1305. Heating element 1310 is controlled by controller 1320, which regulates the temperature of heating element 1310 to control the ion current generated from target material 1330. When sufficient heat is supplied to target material 1330, thermionic emission from the target material generates a stream of ions 1340. Ions 1340 can include positively-charged ions of materials such as sodium, iron, and other relatively heavy atomic species (e.g., other metal ions). Ions 1340 can then be collimated, focused, and/or otherwise deflected by electrostatic and/or magnetic electrodes 1350, which can also deliver ions 1340 to an injector.

Thermionic emission to form ions of relatively heavy atomic species is also discussed, for example, in U.S. Pat. No. 4,928,033, entitled "Thermionic Ionization Sourced," the entire contents of which are incorporated herein by reference.

In certain embodiments, relatively heavy ions such as sodium ions and/or iron ions can be produced by microwave discharge. FIG. 14 shows a schematic diagram of a microwave discharge source 1400 that produces ions from relatively heavy atoms such as sodium and iron. Discharge source 1400 includes a microwave field generator 1410, a waveguide tube 1420, a field concentrator 1430, and an ionization chamber 1490. During operation, field generator 1410 produces a

microwave field which propagates through waveguide 1420 and concentrator 1430; concentrator 1430 increases the field strength by spatially confining the field, as shown in FIG. 14. The microwave field enters ionization chamber 1490. In a first region inside chamber 1490, a solenoid 1470 produces a strong magnetic field 1480 in a region of space that also includes the microwave field. Source 1440 delivers atoms 1450 to this region of space. The concentrated microwave field ionizes atoms 1450, and the magnetic field 1480 generated by solenoid 1470 confines the ionized atoms to form a localized plasma. A portion of the plasma exits chamber 1490 as ions 1460. Ions 1460 can then be deflected and/or focused by one or more electrostatic and/or magnetic elements, and delivered to an injector.

Atoms 1450 of materials such as sodium and/or iron can be generated by thermal emission from a target material, for example. Suitable target materials include materials such as silicates and other stable salts, including zeolite-based materials. Suitable target materials can also include metals (e.g., iron), which can be coated on an inert base material such as a glass material.

Microwave discharge sources are also discussed, for example, in the following U.S. Patents: U.S. Pat. No. 4,409,520, entitled "Microwave Discharge Ion Source," and U.S. Pat. No. 6,396,211, entitled "Microwave Discharge Type Electrostatic Accelerator Having Upstream and Downstream Acceleration Electrodes." The entire contents of each of the foregoing patents are incorporated herein by reference.

Particle Beam Sources

Particle beam sources that generate beams for use in irradiating cellulosic or lignocellulosic material typically include three component groups: an injector, which generates or receives ions and introduces the ions into an accelerator; an accelerator, which receives ions from the injector and increases the kinetic energy of the ions; and output coupling elements, which manipulate the beam of accelerated ions.

(i) Injectors

Injectors can include, for example, any of the ion sources discussed in the preceding sections above, which supply a stream of ions for subsequent acceleration. Injectors can also include various types of electrostatic and/or magnetic particle optical elements, including lenses, deflectors, collimators, filters, and other such elements. These elements can be used to condition the ion beam prior to entering the accelerator; that is, these elements can be used to control the propagation characteristics of the ions that enter the accelerator. Injectors can also include pre-accelerating electrostatic and/or magnetic elements that accelerate charged particles to a selected energy threshold prior to entering the accelerator. An example of an injector is shown in Iwata, Y. et al.

(ii) Accelerators

One type of accelerator that can be used to accelerate ions produced using the sources discussed above is a Dynamitron® (available, for example, from Radiation Dynamics Inc., now a unit of IBA, Louvain-la-Neuve, Belgium). A schematic diagram of a Dynamitron® accelerator 1500 is shown in FIG. 6 and discussed above.

Another type of accelerator that can be used to accelerate ions for treatment of cellulosic or lignocellulosic-based material is a Rhodotron® accelerator (available, for example, from IBA, Louvain-la-Neuve, Belgium). In general, Rhodotron-type accelerators include a single recirculating cavity through which ions that are being accelerated make multiple passes. As a result, Rhodotron® accelerators can be operated in continuous mode at relatively high continuous ion currents.

FIG. 15 shows a schematic diagram of a Rhodotron® accelerator 1700. Accelerator 1700 includes an injector 1710, which introduces accelerated ions into recirculating cavity 1720. An electric field source 1730 is positioned within an inner chamber 1740 of cavity 1720, and generates an oscillating radial electric field. The oscillation frequency of the radial field is selected to match the transit time of injected ions across one pass of recirculating cavity 1720. For example, a positively-charged ion is injected into cavity 1720 by injector 1710 when the radial electric field in the cavity has zero amplitude. As the ion propagates toward chamber 1740, the amplitude of the radial field in chamber 1740 increases to a maximum value, and then decreases again. The radial field points inward toward chamber 1740, and the ion is accelerated by the radial field. The ion passes through a hole in the wall of inner chamber 1740, crosses the geometrical center of cavity 1720, and passes out through another hole in the wall of inner chamber 1740. When the ion is positioned at the center of cavity 1720, the electric field amplitude inside cavity 1720 has been reduced to zero (or nearly zero). As the ion emerges from inner chamber 1740, the electric field amplitude in cavity 1720 begins to increase again, but the field is now oriented radially outward. The field magnitude during the second half of the ion's pass through cavity 1720 again reaches a maximum and then begins to diminish. As a result, the positive ion is again accelerated by the electric field as the ion completes the second half of a first pass through cavity 1720.

Upon reaching the wall of cavity 1720, the magnitude of the electric field in cavity 1720 is zero (or nearly zero) and the ion passes through an aperture in the wall and encounters one of beam deflection magnets 1750. The beam deflection magnets essentially reverse the trajectory of the ion, as shown in FIG. 15, directing the ion to re-enter cavity 1720 through another aperture in the wall of the chamber. When the ion re-enters cavity 1720, the electric field therein begins to increase in amplitude again, but is now once more oriented radially inward. The second and subsequent passes of the ion through cavity 1720 follow a similar pattern, so that the orientation of the electric field always matches the direction of motion of the ion, and the ion is accelerated on every pass (and every half-pass) through cavity 1720.

As shown in FIG. 15, after six passes through cavity 1720, the accelerated ion is coupled out of cavity 1720 as a portion of accelerated ion beam 1760. The accelerated ion beam passes through one or more electrostatic and/or magnetic particle optical elements 1770, which can include lenses, collimators, beam deflectors, filters, and other optical elements. For example, under control of an external logic unit, elements 1770 can include an electrostatic and/or magnetic deflector that sweeps accelerated beam 1760 across a two-dimensional planar region oriented perpendicular to the direction of propagation of beam 1760.

Ions that are injected into cavity 1720 are accelerated on each pass through cavity 1720. In general, therefore, to obtain accelerated beams having different average ion energies, accelerator 1700 can include more than one output coupling. For example, in some embodiments, one or more of deflection magnets 1750 can be modified to allow a portion of the ions reaching the magnets to be coupled out of accelerator 1700, and a portion of the ions to be returned to chamber 1720. Multiple accelerated output beams can therefore be obtained from accelerator 1700, each beam corresponding to an average ion energy that is related to the number of passes through cavity 1720 for the ions in the beam.

Accelerator 1700 includes 5 deflection magnets 1750, and ions injected into cavity 1720 make 6 passes through the

cavity. In general, however, accelerator **1700** can include any number of deflection magnets, and ions injected into cavity **1720** can make any corresponding number of passes through the cavity. For example, in some embodiments, accelerator **1700** can include at least 6 deflection magnets and ions can make at least 7 passes through the cavity (e.g., at least 7 deflection magnets and 8 passes through the cavity, at least 8 deflection magnets and 9 passes through the cavity, at least 9 deflection magnets and 10 passes through the cavity, at least 10 deflection magnets and 11 passes through the cavity).

Typically, the electric field generated by field source **1730** provides a single-cavity-pass gain of about 1 MeV to an injected ion. In general, however, higher single-pass gains are possible by providing a higher-amplitude electric field within cavity **1720**. In some embodiments, for example, the single-cavity-pass gain is about 1.2 MeV or more (e.g., 1.3 MeV or more, 1.4 MeV or more, 1.5 MeV or more, 1.6 MeV or more, 1.8 MeV or more, 2.0 MeV or more, 2.5 MeV or more).

The single-cavity-pass gain also depends upon the magnitude of the charge carried by the injected ion. For example, ions bearing multiple charges will experience higher single-pass-cavity gain than ions bearing single charges, for the same electric field within cavity. As a result, the single-pass-cavity gain of accelerator **1700** can be further increased by injecting ions having multiple charges.

In the foregoing description of accelerator **1700**, a positively-charged ion was injected into cavity **1720**. Accelerator **1700** can also accelerate negatively charged ions. To do so, the negatively charged ions are injected so that the direction of their trajectories is out of phase with the radial electric field direction. That is, the negatively charged ions are injected so that on each half pass through cavity **1720**, the direction of the trajectory of each ion is opposite to the direction of the radial electric field. Achieving this involves simply adjusting the time at which negatively-charged ions are injected into cavity **1720**. Accordingly, accelerator **1700** is capable of simultaneously accelerating ions having the same approximate mass, but opposite charges. More generally, accelerator **1700** is capable of simultaneously accelerating different types of both positively- and negatively-charged (and both singly- and multiply-charged) ions, provided that the transit times of the ions across cavity **1720** are relatively similar. In some embodiments, accelerator **1700** can include multiple output couplings, providing different types of accelerated ion beams having similar or different energies.

Other types of accelerators can also be used to accelerate ions for irradiation of cellulosic or lignocellulosic material. For example, in some embodiments, ions can be accelerated to relatively high average energies in cyclotron- and/or synchrotron-based accelerators. The construction and operation of such accelerators is well-known in the art. As another example, in some embodiments, Penning-type ion sources can be used to generate and/or accelerate ions for treating cellulosic or lignocellulosic-based material. The design of Penning-type sources is discussed in section 7.2.1 of Prelec (1997).

Static and/or dynamic accelerators of various types can also generally be used to accelerate ions. Static accelerators typically include a plurality of electrostatic lenses that are maintained at different DC voltages. By selecting appropriate values of the voltages applied to each of the lens elements, ions introduced into the accelerator can be accelerated to a selected final energy. FIG. 16 shows a simplified schematic diagram of a static accelerator **1800** that is configured to accelerate ions to treat cellulosic or lignocellulosic material **1835**. Accelerator **1800** includes an ion source **1810** that produces ions and introduces the ions into an ion column

1820. Ion column **1820** includes a plurality of electrostatic lenses **1825** that accelerate the ions generated by ion source **1810** to produce an ion beam **1815**. DC voltages are applied to lenses **1825**; the potentials of the lenses remain approximately constant during operation. Generally, the electrical potential within each lens is constant, and the ions of ion beam **1815** are accelerated in the gaps between the various lenses **1825**. Ion column **1820** also includes a deflection lens **1830** and a collimation lens **1832**. These two lenses operate to direct ion beam **1815** to a selected position on cellulosic or lignocellulosic material **1835**, and to focus ion beam **1815** onto the cellulosic or lignocellulosic material.

Although FIG. 16 shows a particular embodiment of a static accelerator, many other variations are possible and suitable for treating cellulosic or lignocellulosic material. In some embodiments, for example, the relative positions of deflection lens **1830** and collimation lens **1832** along ion column **1820** can be exchanged. Additional electrostatic lenses can also be present in ion column **1820**, and ion column **1820** can further include magnetostatic optical elements. In certain embodiments, a wide variety of additional elements can be present in ion column **1820**, including deflectors (e.g., quadrupole, hexapole, and/or octopole deflectors), filtering elements such as apertures to remove undesired species (e.g., neutrals and/or certain ionic species) from ion beam **1815**, extractors (e.g., to establish a spatial profile for ion beam **1815**), and other electrostatic and/or magnetostatic elements.

Dynamic linear accelerators—often referred to as LINACS—can also be used to generate an ion beam that can be used to treat cellulosic or lignocellulosic material. Typically, dynamic linear accelerators include an ion column with a linear series of radiofrequency cavities, each of which produces an intense, oscillating radiofrequency (RF) field that is timed to coincide with injection and propagation of ions into the ion column. As an example, devices such as klystrons can be used to generate the RF fields in the cavities. By matching the field oscillations to the injection times of ions, the RF cavities can accelerate ions to high energies without having to maintain peak potentials for long periods of time. As a result, LINACS typically do not have the same shielding requirements as DC accelerators, and are typically shorter in length. LINACS typically operate at frequencies of 3 GHz (S-band, typically limited to relatively low power) and 1 GHz (L-band, capable of significantly higher power operation). Typical LINACS have an overall length of 2-4 meters.

A schematic diagram of a dynamic linear accelerator **1850** (e.g., a LINAC) is shown in FIG. 17. LINAC **1850** includes an ion source **1810** and an ion column **1855** that includes three acceleration cavities **1860**, a deflector **1865**, and a focusing lens **1870**. Deflector **1865** and focusing lens **1870** function to steer and focus ion beam **1815** onto cellulosic or lignocellulosic material **1835** following acceleration, as discussed above. Acceleration cavities **1860** are formed of a conductive material such as copper, and function as a waveguide for the accelerated ions. Klystrons **1862**, connected to each of cavities **1860**, generate the dynamic RF fields that accelerate the ions within the cavities. Klystrons **1862** are individually configured to produce RF fields that, together, accelerate the ions in ion beam **1815** to a final, selected energy prior to being incident on cellulosic or lignocellulosic material **1835**.

As discussed above in connection with static accelerators, many variations of dynamic accelerator **1850** are possible and can be used to produce an ion beam for treating cellulosic or lignocellulosic material. For example, in some embodiments, additional electrostatic lenses can also be present in ion column **1855**, and ion column **1855** can further include magnetostatic optical elements. In certain embodiments, a wide

variety of additional elements can be present in ion column 1855, including deflectors (e.g., quadrupole, hexapole, and/or octopole deflectors), filtering elements such as apertures to remove undesired species (e.g., neutrals and/or certain ionic species) from ion beam 1815, extractors (e.g., to establish a spatial profile for ion beam 1815), and other electrostatic and/or magnetostatic elements. In addition to the specific static and dynamic accelerators discussed above, other suitable accelerator systems include, for example: DC insulated core transformer (ICT) type systems, available from Nissin High Voltage, Japan; S-band LINACS, available from L3-PSD (USA), Linac Systems (France), Mevex (Canada), and Mitsubishi Heavy Industries (Japan); L-band LINACS, available from Iotron Industries (Canada); and ILU-based accelerators, available from Budker Laboratories (Russia).

In some embodiments, van de Graaff-based accelerators can be used to produce and/or accelerate ions for subsequent treatment of cellulosic or lignocellulosic material. FIG. 18 shows an embodiment of a van de Graaff accelerator 1900 that includes a spherical shell electrode 1902 and an insulating belt 1906 that recirculates between electrode 1902 and a base 1904 of accelerator 1900. During operation, insulating belt 1906 travels over pulleys 1910 and 1908 in the direction shown by arrow 1918, and carries charge into electrode 1902. Charge is removed from belt 1906 and transferred to electrode 1902, so that the magnitude of the electrical potential on electrode 1902 increases until electrode 1902 is discharged by a spark (or, alternatively, until the charging current is balanced by a load current).

Pulley 1910 is grounded, as shown in FIG. 18. A corona discharge is maintained between a series of points or a fine wire on one side of belt 1906. Wire 1914 is configured to maintain the corona discharge in accelerator 1900. Wire 1914 is maintained at a positive potential, so that belt 1906 intercepts positive ions moving from wire 1914 to pulley 1910. As belt 1906 moves in the direction of arrow 1918, the intercepted charges are carried into electrode 1902, where they are removed from belt 1906 by a needle point 1916 and transferred to electrode 1902. As a result, positive charges accumulate on the surface of electrode 1902; these charges can be discharged from the surface of electrode 1902 and used to treat cellulosic or lignocellulosic material. In some embodiments, accelerator 1900 can be configured to provide negatively charged ions by operating wire 1914 and needle point 1916 at a negative potential with respect to grounded pulley 1910.

In general, accelerator 1900 can be configured to provide a wide variety of different types of positive and negative charges for treating cellulosic or lignocellulosic material. Exemplary types of charges include electrons, protons, hydrogen ions, carbon ions, oxygen ions, halogen ions, metal ions, and other types of ions.

In certain embodiments, tandem accelerators (including folded tandem accelerators) can be used to generate ion beams for treatment of cellulosic or lignocellulosic material. An example of a folded tandem accelerator 1950 is shown in FIG. 19. Accelerator 1950 includes an accelerating column 1954, a charge stripper 1956, a beam deflector 1958, and an ion source 1952.

During operation, ion source 1952 produces a beam 1960 of negatively charged ions, which is directed to enter accelerator 1950 through input port 1964. In general, ion source 1952 can be any type of ion source that produces negatively charged ions. For example, suitable ion sources include a source of negative ions by cesium sputtering (SNICS) source, a RF-charge exchange ion source, or a toroidal volume ion source (TORVIS). Each of the foregoing exemplary ion

sources is available, for example, from National Electrostatics Corporation (Middleton, Wis.).

Once inside accelerator 1950, the negative ions in beam 1960 are accelerated by accelerating column 1954. Typically, accelerating column 1954 includes a plurality of accelerating elements such as electrostatic lenses. The potential difference applied in column 1954 to accelerate the negative ions can be generated using various types of devices. For example, in some embodiments, (e.g., Pelletron® accelerators), the potential is generated using a Pelletron® charging device. Pelletron® devices include a charge-carrying belt that is formed from a plurality of metal (e.g., steel) chain links or pellets that are bridged by insulating connectors (e.g., formed from a material such as nylon). During operation, the belt 15 recirculates between a pair of pulleys, one of which is maintained at ground potential. As the belt moves between the grounded pulley and the opposite pulley (e.g., the terminal pulley), the metal pellets are positively charged by induction. Upon reaching the terminal pulley, the positive charge that has accumulated on the belt is removed, and the pellets are 20 negatively charged as they leave the terminal pulley and return to the ground pulley.

The Pelletron® device generates a large positive potential within column 1954 that is used to accelerate the negative ions of beam 1960. After undergoing acceleration in column 1954, beam 1960 passes through charge stripper 1956. Charge stripper 1956 can be implemented as a thin metal foil and/or a tube containing a gas that strips electrons from the negative ions, for example. The negatively charged ions are thereby converted to positively charged ions, which emerge from charge stripper 1956. The trajectories of the emerging positively charged ions are altered so that the positively charged ions travel back through accelerating column 1954, undergoing a second acceleration in the column before 35 emerging as positively charged ion beam 1962 from output port 1966. Positively charged ion beam 1962 can then be used to treat cellulosic or lignocellulosic material according to the various methods disclosed herein.

Due to the folded geometry of accelerator 1950, ions are 40 accelerated to a kinetic energy that corresponds to twice the potential difference generated by the Pelletron® charging device. For example, in a 2 MV Pelletron® accelerator, hydride ions that are introduced by ion source 1952 will be accelerated to an intermediate energy of 2 MeV during the first pass through column 1954, converted to positive ions (e.g., protons), and accelerated to a final energy of 4 MeV during the second pass through column 1954.

In certain embodiments, column 1954 can include elements in addition to, or as alternatives to, the Pelletron® charging device. For example, column 1954 can include static accelerating elements (e.g., DC electrodes) and/or dynamic acceleration cavities (e.g., LINAC-type cavities with pulse RF field generators for particle acceleration). Potentials applied to the various accelerating devices are selected to 50 accelerate the negatively charged ions of beam 1960.

Exemplary tandem accelerators, including both folded and non-folded accelerators, are available from National Electrostatics Corporation (Middleton, Wis.), for example.

In some embodiments, combinations of two or more of the 60 various types of accelerators can be used to produce ion beams that are suitable for treating cellulosic or lignocellulosic material. For example, a folded tandem accelerator can be used in combination with a linear accelerator, a Rhodotron® accelerator, a Dynamitron®, a static accelerator, or any other type of accelerator to produce ion beams. Accelerators can be used in series, with the output ion beam from one type of accelerator directed to enter another type of accelerator for

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additional acceleration. Alternatively, multiple accelerators can be used in parallel to generate multiple ion beams. In certain embodiments, multiple accelerators of the same type can be used in parallel and/or in series to generate accelerated ion beams.

In some embodiments, multiple similar and/or different accelerators can be used to generate ion beams having different compositions. For example, a first accelerator can be used to generate one type of ion beam, while a second accelerator can be used to generate a second type of ion beam. The two ion beams can then each be further accelerated in another accelerator, or can be used to treat cellulosic or lignocellulosic material.

Further, in certain embodiments, a single accelerator can be used to generate multiple ion beams for treating cellulosic or lignocellulosic material. For example, any of the accelerators discussed herein (and other types of accelerators as well) can be modified to produce multiple output ion beams by sub-dividing an initial ion current introduced into the accelerator from an ion source. Alternatively, or in addition, any one ion beam produced by any of the accelerators disclosed herein can include only a single type of ion, or multiple different types of ions.

In general, where multiple different accelerators are used to produce one or more ion beams for treatment of cellulosic or lignocellulosic material, the multiple different accelerators can be positioned in any order with respect to one another. This provides for great flexibility in producing one or more ion beams, each of which has carefully selected properties for treating cellulosic or lignocellulosic material (e.g., for treating different components in cellulosic or lignocellulosic material).

The ion accelerators disclosed herein can also be used in combination with any of the other treatment steps disclosed herein. For example, in some embodiments, electrons and ions can be used in combination to treat cellulosic or lignocellulosic material. The electrons and ions can be produced and/or accelerated separately, and used to treat cellulosic or lignocellulosic material sequentially (in any order) and/or simultaneously. In certain embodiments, electron and ion beams can be produced in a common accelerator and used to treat cellulosic or lignocellulosic material. For example, many of the ion accelerators disclosed herein can be configured to produce electron beams as an alternative to, or in addition to, ion beams. For example, Dynamitron® accelerators, Rhodotron® accelerators, and LINACs can be configured to produce electron beams for treatment of cellulosic or lignocellulosic material.

Moreover, treatment of cellulosic or lignocellulosic material with ion beams can be combined with other techniques such as sonication. In general, sonication-based treatment can occur before, during, or after ion-based treatment. Other treatments such as electron beam treatment can also occur in any combination and/or order with ultrasonic treatment and ion beam treatment.

Paper Additives

Any of the many additives and coatings used in the paper-making industry can be added to or applied to the fibrous materials, papers, or any other materials and products described herein. Additives include fillers such as calcium carbonate, plastic pigments, graphite, wollastonite, mica, glass, fiber glass, silica, and talc; inorganic flame retardants such as alumina trihydrate or magnesium hydroxide; organic flame retardants such as chlorinated or brominated organic compounds; carbon fibers; and metal fibers or powders (e.g., aluminum, stainless steel). These additives can reinforce,

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extend, or change electrical or mechanical properties, compatibility properties, or other properties. Other additives include starch, lignin, fragrances, coupling agents, antioxidants, opacifiers, heat stabilizers, colorants such as dyes and 5 pigments, polymers, e.g., degradable polymers, photostabilizers, and biocides. Representative degradable polymers include polyhydroxy acids, e.g., polylactides, polyglycolides and copolymers of lactic acid and glycolic acid, poly(hydroxybutyric acid), poly(hydroxyvaleric acid), poly[lactide-co-(*e*-caprolactone)], poly[glycolide-*co*-(*e*-caprolactone)], polycarbonates, poly(amino acids), poly(hydroxyalkanoate)s, polyanhydrides, polyorthoesters and blends of these polymers.

When additives are included, they can be present in 15 amounts, calculated on a dry weight basis, of from below about 1 percent to as high as about 80 percent, based on total weight of the fibrous material. More typically, amounts range from between about 0.5 percent to about 50 percent by weight, e.g., from about 0.5 percent to about 5 percent, 10 percent, 20 percent, 30 percent or more, e.g., 40 percent.

Any additives described herein can be encapsulated, e.g., spray dried or microencapsulated, e.g., to protect the additives from heat or moisture during handling.

Suitable coatings include any of the many coatings used in 25 the paper industry to provide specific surface characteristics, including performance characteristics required for particular printing applications.

As mentioned above, various fillers can be included in the 30 paper. For example, inorganic fillers such as calcium carbonate (e.g., precipitated calcium carbonate or natural calcium carbonate), aragonite clay, orthorhombic clays, calcite clay, rhombohedral clays, kaolin clay, bentonite clay, dicalcium phosphate, tricalcium phosphate, calcium pyrophosphate, insoluble sodium metaphosphate, precipitated calcium carbonate, magnesium orthophosphate, trimagnesium phosphate, hydroxyapatites, synthetic apatites, alumina, silica xerogel, metal aluminosilicate complexes, sodium aluminum silicates, zirconium silicate, silicon dioxide or combinations of the inorganic additives may be used. The fillers can have, 35 e.g., a particle size of greater than 1 micron, e.g., greater than 2, 5, 10, or 25 microns or even greater than 35 microns.

Nanometer scale fillers can also be used alone, or in combination with fibrous materials of any size and/or shape. The 40 fillers can be in the form of, e.g., particles, plates or fibers. For example, nanometer sized clays, silicon and carbon nanotubes, and silicon and carbon nanowires can be used. The fillers can have a transverse dimension less than 1000 nm, e.g., less than 900, 800, 750, 600, 500, 350, 300, 250, 200, or 100 nm, or even less than 50 nm.

50 In some embodiments, the nano-clay is a montmorillonite. Such clays are available from Nanocor, Inc. and Southern Clay products, and have been described in U.S. Pat. Nos. 6,849,680 and 6,737,464. The clays can be surface treated before mixing into, e.g., a resin or a fibrous material. For 55 example, the clay can be surface treated so that its surface is ionic in nature, e.g., cationic or anionic.

Aggregated or agglomerated nanometer scale fillers, or 60 nanometer scale fillers that are assembled into supramolecular structures, e.g., self-assembled supramolecular structures can also be used. The aggregated or supramolecular fillers can be open or closed in structure, and can have a variety of shapes, e.g., cage, tube or spherical.

Lignin Content

Paper can contain lignin, for example up to 1, 2, 3, 4, 5, 7.5, 65 10, 15, 20, or even 25% by weight of lignin.

This lignin content can be the result of the lignin present in the lignocellulosic material(s) used to manufacture the paper.

Alternatively, or in addition, lignin can be added to the paper as an additive, as mentioned above. In this case, the lignin can be added as a solid, e.g., as a powder or other particulate material, or can be dissolved or dispersed and added in liquid form. In the latter case, the lignin can be dissolved in solvent or a solvent system. The solvent or solvent system can be in the form of a single phase or two or more phases. Solvent systems for cellulosic and lignocellulosic materials include DMSO-salt systems. Such systems include, for example, DMSO in combination with a lithium, magnesium, potassium, sodium or zinc salt. Lithium salts include LiCl, LiBr, LiI, lithium perchlorate and lithium nitrate. Magnesium salts include magnesium nitrate and magnesium chloride. Potassium salts include potassium iodide and nitrate. Examples of sodium salts include sodium iodide and nitrate. Examples of zinc salts include zinc chloride and nitrate. Any salt can be anhydrous or hydrated. Typical loadings of the salt in the DMSO are between about 1 and about 50 percent, e.g., between about 2 and 25, between about 3 and 15 or between about 4 and 12.5 percent by weight.

In some cases, lignin will cross-link in the paper during irradiation, further enhancing the physical properties of the paper.

Paper Types

Paper is often characterized by weight. The weight assigned to a paper is the weight of a ream, 500 sheets, of varying "basic sizes," before the paper is cut into the size as sold to end customers. For example, a ream of 20 lb, 8½×11" paper weighs 5 pounds, because it has been cut from a larger sheet into four pieces. In the United States, printing paper is generally 20 lb, 24 lb, or 32 lb at most. Cover stock is generally 68 lb, and 110 lb or more.

In Europe the weight is expressed in grams per square meter (gsm or just g). Printing paper is generally between 60 g and 120 g. Anything heavier than 160 g is considered card stock. The weight of a ream therefore depends on the dimensions of the paper, e.g., one ream of A4 (210 mm×297 mm) size (approx 8.27"×11.7") weighs 2.5 kilograms (approx 5.5 pounds).

The density of paper ranges from 250 kg/m³ (16 lb/ft³) for tissue paper to 1500 kg/m³ (94 lb/ft³) for some specialty paper. In some cases the density of printing paper is about 800 kg/m³ (50 lb/ft³).

The processes described herein are suitable for use with all of these grades of paper, as well as other types of paper such as corrugated cardboard, paper board, and other paper products. The processes described herein may be used to treat paper that is used, for example, in any of the following applications: as stamps; as paper money, bank notes, securities, checks, and the like; in books, magazines, newspapers, and art; for packaging, e.g., paper board, corrugated cardboard, paper bags, envelopes, wrapping tissue, boxes; in household products such as toilet paper, tissues, paper towel sand paper napkins; paper honeycomb, used as a core material in composite materials; building materials; construction paper; disposable clothing; and in various industrial uses including emery paper, sandpaper, blotting paper, litmus paper, universal indicator paper, paper chromatography, battery separators, and capacitor dielectrics. The paper may be single or multi-layered paper.

The paper may be made of any desired type of fiber, including fiber derived from wood and recycled paper, as well as fiber derived from other sources. Vegetable fiber materials, such as cotton, hemp, linen, and rice, can be used alone or in combination with each other or with wood-derived fibers. Other non-wood fiber sources include, but are not limited to,

sugarcane, bagasse, straw, bamboo, kenaf, jute, flax, and cotton. A wide variety of synthetic fibers, such as polypropylene and polyethylene, as well as other ingredients such as inorganic fillers, may be incorporated into paper as a means for imparting desirable physical properties. It may be desirable to include these non-wood fibers in paper used in special application such as for paper money, fine stationary, art paper and other applications requiring particular strength or aesthetic characteristics.

The paper may be irradiated before or after printing. Radiation may be used to mark the paper, for example by increasing the number of carboxylic acid groups in the irradiated area. This may be useful, for example, in marking currency.

Process Water

In the processes disclosed herein, whenever water is used in any process, it may be grey water, e.g., municipal grey water, or black water. In some embodiments, the grey or black water is sterilized prior to use. Sterilization may be accomplished by any desired technique, for example by irradiation, steam, or chemical sterilization.

EXAMPLES

The following examples are not intended to limit the inventions recited in the claims.

Example 1

Methods of Determining Molecular Weight of Cellulosic and Lignocellulosic Materials by Gel Permeation Chromatography

This example illustrates how molecular weight is determined for the materials discussed herein. Cellulosic and lignocellulosic materials for analysis were treated as follows:

A 1500 pound skid of virgin bleached white Kraft board having a bulk density of 30 lb/ft³ was obtained from International Paper. The material was folded flat, and then fed into a 3 hp Flinch Baugh shredder at a rate of approximately 15 to 20 pounds per hour. The shredder was equipped with two 12 inch rotary blades, two fixed blades and a 0.30 inch discharge screen. The gap between the rotary and fixed blades was adjusted to 0.10 inch. The output from the shredder resembled confetti (as above). The confetti-like material was fed to a Munson rotary knife cutter, Model SC30. The discharge screen had ½ inch openings. The gap between the rotary and fixed blades was set to approximately 0.020 inch. The rotary knife cutter sheared the confetti-like pieces across the knife-edges. The material resulting from the first shearing was fed back into the same setup and the screen was replaced with a ¼ inch screen. This material was sheared. The material resulting from the second shearing was fed back into the same setup and the screen was replaced with a ⅓ inch screen. This material was sheared. The resulting fibrous material had a BET surface area of 1.6897 m²/g+/-0.0155 m²/g, a porosity of 87.7163 percent and a bulk density (@0.53 psia) of 0.1448 g/mL. An average length of the fibers was 0.824 mm and an average width of the fibers was 0.0262 mm, giving an average L/D of 32:1.

Sample materials presented in the following Tables 1 and 2 include Kraft paper (P), wheat straw (WS), alfalfa (A), and switchgrass (SG). The number "132" of the Sample ID refers to the particle size of the material after shearing through a ⅓ inch screen. The number after the dash refers to the dosage of radiation (MRad) and "US" refers to ultrasonic treatment. For

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example, a sample ID “P132-10” refers to Kraft paper that has been sheared to a particle size of 132 mesh and has been irradiated with 10 MRad.

TABLE 1

| Peak Average Molecular Weight of Irradiated Kraft Paper | | | | |
|---|-----------|----------------------------|-------------------------|-----------------------|
| Sample Source | Sample ID | Dosage ¹ (MRad) | Ultrasound ² | Average MW ± Std Dev. |
| Kraft Paper | P132 | 0 | No | 32853 ± 10006 |
| | P132-10 | 10 | " | 61398 ± 2468** |
| | P132-100 | 100 | " | 8444 ± 580 |
| | P132-181 | 181 | " | 6668 ± 77 |
| | P132-US | 0 | Yes | 3095 ± 1013 |

**Low doses of radiation appear to increase the molecular weight of some materials

¹Dosage Rate = 1 MRad/hour

²Treatment for 30 minutes with 20 kHz ultrasound using a 1000 W horn under re-circulating conditions with the material dispersed in water.

TABLE 2

| Peak Average Molecular Weight of Irradiated Materials | | | | |
|---|--------|----------------------------|-------------------------|-----------------------|
| Sample ID | Peak # | Dosage ¹ (MRad) | Ultrasound ² | Average MW ± Std Dev. |
| WS132 | 1 | 0 | No | 1407411 ± 175191 |
| | 2 | " | " | 39145 ± 3425 |
| | 3 | " | " | 2886 ± 177 |
| WS132-10* | 1 | 10 | " | 26040 ± 3240 |
| WS132-100* | 1 | 100 | " | 23620 ± 453 |
| A132 | 1 | 0 | " | 1604886 ± 151701 |
| | 2 | " | " | 37525 ± 3751 |
| | 3 | " | " | 2853 ± 490 |
| A132-10* | 1 | 10 | " | 50853 ± 1665 |
| | 2 | " | " | 2461 ± 17 |
| A132-100* | 1 | 100 | " | 38291 ± 2235 |
| | 2 | " | " | 2487 ± 15 |
| SG132 | 1 | 0 | " | 1557360 ± 83693 |
| | 2 | " | " | 42594 ± 4414 |
| | 3 | " | " | 3268 ± 249 |
| SG132-10* | 1 | 10 | " | 60888 ± 9131 |
| SG132-100* | 1 | 100 | " | 22345 ± 3797 |
| SG132-10-US | 1 | 10 | Yes | 86086 ± 43518 |
| | 2 | " | " | 2247 ± 468 |
| SG132-100-US | 1 | 100 | " | 4696 ± 1465 |

*Peaks coalesce after treatment

**Low doses of radiation appear to increase the molecular weight of some materials

¹Dosage Rate = 1 MRad/hour

²Treatment for 30 minutes with 20 kHz ultrasound using a 1000 W horn under re-circulating conditions with the material dispersed in water.

Gel Permeation Chromatography (GPC) is used to determine the molecular weight distribution of polymers. During GPC analysis, a solution of the polymer sample is passed through a column packed with a porous gel trapping small molecules. The sample is separated based on molecular size with larger molecules eluting sooner than smaller molecules. The retention time of each component is most often detected by refractive index (RI), evaporative light scattering (ELS), or ultraviolet (UV) and compared to a calibration curve. The resulting data is then used to calculate the molecular weight distribution for the sample.

A distribution of molecular weights rather than a unique molecular weight is used to characterize synthetic polymers. To characterize this distribution, statistical averages are utilized. The most common of these averages are the “number average molecular weight” (M_n) and the “weight average molecular weight” (M_w). Methods of calculating these values are described in the art, e.g., in Example 9 of WO 2008/073186.

The polydispersity index or PI is defined as the ratio of M_w/M_n . The larger the PI, the broader or more disperse the

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distribution. The lowest value that a PI can be is 1. This represents a monodisperse sample; that is, a polymer with all of the molecules in the distribution being the same molecular weight.

5 The peak molecular weight value (M_P) is another descriptor defined as the mode of the molecular weight distribution. It signifies the molecular weight that is most abundant in the distribution. This value also gives insight to the molecular weight distribution.

10 Most GPC measurements are made relative to a different polymer standard. The accuracy of the results depends on how closely the characteristics of the polymer being analyzed match those of the standard used. The expected error in reproducibility between different series of determinations, calibrated separately, is about 5-10% and is characteristic to the limited precision of GPC determinations. Therefore, GPC results are most useful when a comparison between the molecular weight distribution of different samples is made during the same series of determinations.

15 The lignocellulosic samples required sample preparation prior to GPC analysis. First, a saturated solution (8.4% by weight) of lithium chloride (LiCl) was prepared in dimethyl acetamide (DMAc). Approximately 100 mg of the sample was added to approximately 10 g of a freshly prepared saturated LiCl/DMAc solution, and the mixture was heated to approximately 150° C.-170° C. with stirring for 1 hour. The resulting solutions were generally light- to dark-yellow in color. The temperature of the solutions were decreased to approximately 100° C. and heated for an additional 2 hours. The temperature of the solutions were then decreased to approximately 50° C. and the sample solution was heated for approximately 48 to 60 hours. Of note, samples irradiated at 100 MRad were more easily solubilized as compared to their untreated counterpart. Additionally, the sheared samples (denoted by the number 132) had slightly lower average molecular weights as compared with uncut samples.

20 The resulting sample solutions were diluted 1:1 using DMAc as solvent and were filtered through a 0.45 µm PTFE filter. The filtered sample solutions were then analyzed by GPC. The peak average molecular weight (M_p) of the samples, as determined by Gel Permeation Chromatography (GPC), are summarized in Tables 1 and 2, above. Each sample was prepared in duplicate and each preparation of the sample was analyzed in duplicate (two injections) for a total of four injections per sample. The EasiCal® polystyrene standards PS1A and PS1B were used to generate a calibration curve for the molecular weight scale from about 580 to 7,500,00 Dalton. GPC analysis conditions are recited in Table 3, below.

TABLE 3

| GPC Analysis Conditions | |
|------------------------------|---|
| Instrument: | Waters Alliance GPC 2000 |
| Columns (3): | Pfgel 10µ Mixed-B |
| | S/N's: 10M-MB-148-83; 10M-MB-148-84; 10M-MB-174-129 |
| Mobile Phase (solvent): | 0.5% LiCl in DMAc (1.0 mL/min.) |
| Column/Detector Temperature: | 70° C. |
| Injector Temperature: | 70° C. |
| Sample Loop Size: | 323.5 µL |

Example 2

Electron Beam Processing Cardboard Samples

Brown cardboard samples 0.050 inches thick were treated with a beam of electrons using a vaulted Rhodotron® TT200 continuous wave accelerator delivering 5 MeV electrons at 80 kW output power. Table 4 describes the nominal parameters for the TT200. Table 5 reports the nominal doses (in MRad) and actual doses (in kgy) delivered to the samples.

TABLE 4

| Rhodotron ® TT 200 Parameters | |
|---|---|
| Beam | |
| Beam Produced: | Accelerated electrons |
| Beam energy: | Nominal (maximum): 10 MeV (+0 keV-250 keV) |
| Energy dispersion at 10 Mev: | Full width half maximum (FWHM) 300 keV |
| Beam power at 10 MeV: | Guaranteed Operating Range 1 to 80 kW |
| Power Consumption | |
| Stand-by condition (vacuum and cooling ON): | <15 kW |
| At 50 kW beam power: | <210 kW |
| At 80 kW beam power: | <260 kW |
| RF System | |
| Frequency: | 107.5 ± 1 MHz |
| Tetrode type: | Thomson TH781 |
| | Scanning Horn |
| Nominal Scanning Length (measured at 25-35 cm from window): | |
| Scanning Range: | From 30% to 100% of Nominal Scanning Length |
| Nominal Scanning Frequency (at max. scanning length): | 100 Hz ± 5% |
| Scanning Uniformity (across 90% of Nominal Scanning Length) | ±5% |

TABLE 5

| Dosages Delivered to Samples | |
|---|--------------------------------------|
| Total Dosage (MRad) (Number Associated with Sample ID) | Delivered Dose (kgy) ¹ |
| 1 | 9.9 |
| 3 | 29.0 |
| 5 | 50.4 |
| 7 | 69.2 |
| 10 | 100.0 |
| 15 | 150.3 |
| 20 | 198.3 |
| 30 | 330.9 |
| 50 | 529.0 |
| 70 | 695.9 |
| 100 | 993.6 |

¹For example, 9.9 kgy was delivered in 11 seconds at a beam current of 5 mA and a line speed of 12.9 feet/minute. Cool time between 1 MRad treatments was about 2 minutes.

The cardboard samples treated below 7 MRad were stiffer to the touch than untreated controls, but otherwise appeared visibly identical to the controls. Samples treated at about 10 MRad were of comparable stiffness to the controls to the touch, while those treated with higher doses were more flexible under manipulation. Extensive material degradation was visibly apparent for samples treated above 50 Mrad.

Other Embodiments

It is to be understood that while the invention has been described in conjunction with the detailed description

thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

What is claimed is:

1. A method of making an irradiated paper product, the method comprising
 - treating a paper product comprising a carbohydrate-containing material with from about 0.25 to about 10 MRad of ionizing radiation having an energy of from about 0.25 to 7.5 MeV, without the addition of cross-linking additives, so as to self-crosslink the carbohydrate-containing material and thereby increase the molecular weight of the carbohydrate-containing material, providing an irradiated paper product.
 2. The method of claim 1 wherein the dose of ionizing radiation is from about 0.25 to about 2.5 MRad.
 3. The method of claim 1 wherein treating comprises irradiating with gamma radiation.
 4. The method of claim 1 wherein treating comprises irradiating with electron beam radiation.
 5. The method of claim 1 further comprising quenching the treated paper product.
 6. The method of claim 5 wherein quenching is performed in the presence of a gas selected to react with radicals present in the treated paper product.
 7. The method of claim 1 wherein the dose of ionizing radiation is from about 0.25 to about 5 MRad.

* * * * *

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(54) Title: A METHOD FOR PRODUCING MODIFIED CELLULOSE

(57) Abstract: The present invention provides a method for producing modified nanofibrillated cellulose characterized by bringing cellulosic material into a fiber suspension, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto fibers in said fiber suspension under special conditions and subjecting the obtained fiber suspension derivative to mechanical disintegration. A modified nanofibrillated cellulose obtainable by a method of the present invention is provided. Furthermore, the invention relates to the use of said modified nanofibrillated cellulose.

A METHOD FOR PRODUCING MODIFIED CELLULOSE

FIELD OF THE INVENTION

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The present invention relates to a method for producing modified nanofibrillated cellulose characterized by steps of preparing a suspension containing fibers from cellulosic material, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under special conditions and subjecting 10 the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration. The invention also relates to modified nanofibrillated cellulose obtainable by a method of the present invention. The invention provides a paper containing the modified nanofibrillated cellulose and method and use thereof. Furthermore, the invention relates to the use of said 15 modified nanofibrillated cellulose in paper, food products, composite materials, concrete, oil drilling products, coatings, cosmetic products and pharmaceutical products. The invention also provides a use of the present method for producing modified nanofibrillated cellulose energy efficiently.

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BACKGROUND OF THE INVENTION

Cellulose-based nano-sized fibrils provide new possibilities for producing light and strong materials. For example increasing environmental requirements promote more 25 extensive utilization of new natural fiber based biomaterials in the future. Nanosized materials can provide properties which can not be achieved with larger sized particles. The smaller the particle, the larger the surface area is and more possibilities for desired interactions with other materials exist.

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Cellulose fibers (width 30-40 µm, length 2-3 mm) can be dismantled into nanosized structures (width about 5-30 nm, length several µms). Microfibrillated cellulose (MFC) has been produced by combining enzymatic or chemical treatments to mechanical treatments. Microfibrils provide even in minor proportion conventional paper products increased toughness and strength. International patent publication WO 2007/091942 35 discloses a method for manufacturing microfibrillated cellulose using enzymatic treatment.

Properties of the cellulose fibers used for producing paper can be modified by adding polymers to the fiber suspension. Suitable additive polymers include for example starch-based polymers, such as cationized starch, or synthetic polymers such as polyacryl polymers, polyamineamide-, polyamine- and acrylamino-epichlorohydrine polymers, cellulose derivatives or anionic polymers containing carboxyl groups or carboxylate ions in the form of alkali metals of ammonium salts, for example carboxymethyl polysaccharides, such as carboxymethyl cellulose (CMC). International patent publications WO 01/66600 and WO 00/47628 disclose derivatized microfibrillar polysaccharides, such as cellulose and production methods thereof.

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CMC or sodium carboxymethyl cellulose is a water-soluble anionic polymer achieved by introducing carboxymethyl groups along the cellulose chain. The functional properties of CMC depend on the degree of substitution on the cellulose structure (i.e. how many of the hydroxyl groups have taken part in the substitution reaction), and 15 also on the chain length of the cellulose backbone. The degree of substitution (DS) of CMC is usually in the range from 0.6 to 0.95 derivatives per monomer unit.

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CMC can be used as an additive during the grinding of paper pulp (B. T. Hofreiter in "Pulp and Paper Chemistry and Chemical Technology", Chapter 14, Volume III, 3rd. edition, New York, 1981; W. F. Reynolds in "Dry strength additives", Atlanta 1980; D. Eklund and T. Lindström in "Paper Chemistry - an introduction", Grankulla, Finland 1991; J. C. Roberts in "Paper Chemistry"; Glasgow and London 1991).

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CMC has a low affinity for cellulose fibers, since both are anionically charged. CMC can still be attached irreversibly to pulp fibres and it increases the surface charge density of pulp fibres.

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US patents 5,061,346 and 5,316,623 disclose the addition of CMC to pulp in paper making processes. Publications WO 2004/055268 and WO 2004/055267 present fiber suspensions comprising cellulose enzyme-treated microfibrillar sulphate pulp (eMFC) and carboxymethyl cellulose (CMC) as raw material for packages and for surface application in paperboard and paper production, respectively.

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CMC is used as thickener to modify the rheology. CMC has also been used as a dispersion agent. Furthermore, CMC has been used as binder. US patent US 5,487,419 discloses CMC as dispersion agent. US patent US 6,224,663 discloses use of CMC as an additive in a cellulose composition. Publication WO 95/02966 discloses the use of

CMC to modify microcrystalline cellulose and in some cases microfibrillated MCC by mixing the two components and the use of this mixture in food compositions.

CMC sorption is known in the art. US Patent 6,958,108 and international patent publication WO 99/57370 disclose a method for producing a fiber product, wherein alkali soluble CMC is added to the pulp under alkali conditions. International patent publication WO 01/021890 discloses a method for modifying cellulose fibers with a cellulose derivative such as CMC. Publication WO 2009/126106 relates to attachment of amphoteric CMC polymers to cellulose fibres before homogenization.

The following articles by Laine et al. disclose modification of cellulosic fibers with CMC: Nord Pulp Pap Res J, 15:520-526 (2000); Nord Pulp Pap Res J, 17:50-56 (2002); Nord Pulp Pap Res J, 17:57-60 (2002); Nord Pulp Pap Res J, 18:316-325 (2003); Nord Pulp Pap Res J, 18:325-332 (2003).

Despite the ongoing research and development in the manufacturing of microfibrillated cellulose there is still a continuing need in the industry to improve the processes. One problem is high energy consumption and thus there is a need for an energy efficient method. There is also a need for a process, wherein the properties of paper are improved. The present invention provides a method for overcoming the problems associated with the prior art.

SUMMARY OF THE INVENTION

The present invention relates to a method for producing modified nanofibrillated cellulose. The method comprises preparing a suspension containing fibers from cellulosic material, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under special conditions and subjecting the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration to obtain modified nanofibrillated cellulose modified with said cellulose derivative or polysaccharide or polysaccharide derivative. The present invention also relates to modified nanofibrillated cellulose obtainable by the method of the present invention and characterized by that a diameter of modified nanofibrillated cellulose is less than 1 μm .

A significant advance of the present invention is reduced consumption of refining energy compared to the prior art methods. A novel and efficient method for producing modified nanofibrillated cellulose energy efficiently is thus provided.

- 5 Additives such as cellulose derivatives or polysaccharides or polysaccharide derivatives are usually added to already fibrillated material i.e. by addition to suspension after mechanical disintegration.

- In the present invention the cellulose derivative or polysaccharide or polysaccharide derivative is added prior and/or during mechanical disintegration. This results in the decreased consumption of energy and better fibrillation. In the present invention a cellulose derivative or polysaccharide or polysaccharide derivative is used in a novel way while adsorbed to cellulosic material under special conditions. Cellulosic material is brought into a fiber suspension and a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed to said fiber suspension. The fiber suspension containing the adsorbed cellulose derivative or polysaccharide or polysaccharide derivative is then subjected to mechanical disintegration. The cellulose derivative or polysaccharide or polysaccharide derivative is anionic or non-ionic.
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- The present invention further relates to a paper comprising the modified nanofibrillated cellulose prepared according to the method of the present invention.

One of the advantages of the invention is an improvement of the paper properties.

- 25 The present invention further relates to the use of said nanofibrillated cellulose in paper, food products, composite materials, concrete, oil drilling products, coatings, cosmetic products or pharmaceutical products.

- 30 The present invention further relates to use of a method for producing nanofibrillated cellulose energy efficiently and use of a method for producing paper with improved properties.

BRIEF DESCRIPTION OF THE DRAWINGS

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Figure 1 shows the Scott Bond (J/m^2) i.e. the internal strength of a paper sheet, measured on Scott Bond Tester as a function of drainage time, measured using a

dynamic drainage analyzer. From this figure it is evident that by adding the nanofibrillated cellulose (NFC) prepared according to this invention (10 min + CS + CMC modified NFC, filled sphere) to only slightly refined pulp almost fivefold increase in internal strength is achieved without severe loss in dewatering efficiency.

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Soft wood (pine) pulp was refined for 10 minutes and the pulp was washed to sodium form. A cationic starch (CS; Raisamyl 50021, DS =0.035, Ciba Specialty Chemicals) was used as an additive in some of the cases (10 min + CS + CMC modified NFC, filled sphere; 10 min + CS + unmodified NFC open sphere). The NFC was dispersed with 10 ultrasound microtip sonication prior to use. All experiments were done in a solution of deionised water containing 1 mM NaHCO₃ and 9 mM NaCl.

Pulp was first mixed with cationic starch (CS, 25 mg/g dry pulp) for 15 min, then the dispersed nanofibrillated cellulose (NFC, 30 mg/g dry pulp) was added and the 15 suspension was mixed for another 15 min. In the cases where no CS was used (10 min + unmodified NFC; triangle) only NFC (30 mg/g) was added and the suspension was mixed for 15 min before sheet making. The sheets were prepared in laboratory sheet former (SCAN-C26:76) and dried under restrain. For comparison the effect of refining is shown by the black squares. In this series the pulp has been refined for 10, 20 15, 20 and 30 minutes, respectively, as shown by black squares. The CMC modified NFC in this example was prepared by sorption of Finnfix WRM CMC and 3 passes through the friction grinder with addition of the same CMC before the second and third pass. Abbreviations: CS, cationic starch; NFC, nanofibrillated cellulose; CMC, Carboxy methyl cellulose.

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Figure 2 depicts optical microscopy images of CMC modified nanofibrillated cellulose. CMC (Finnfix WRM, high molecular weight CMC) was added during fibrillation in fluidizer. **Figure 2a** shows modified nanofibrillated cellulose after 1+1 passes through the fluidizer. **Figure 2b** shows modified nanofibrillated cellulose after 1+2 passes through the fluidizer. **Figure 2c** shows modified nanofibrillated cellulose after 1+3 passes through the fluidizer. The decrease in the amount of large particles can be observed.

Figure 3 depicts optical microscopy images of samples after 1+3 passes through the fluidizer. **Figure 3a** shows the image of unmodified nanofibrillated cellulose (NFC). **Figure 3b** shows the image of NFC modified according to this invention by addition of 10 mg/g dry pulp Finnfix, WRM high molecular weight CMC before each pass (a total

of 40 mg/g after 1+3 passes). **Figure 3c** shows the image of NFC modified according to this invention by addition of 10 mg/g dry pulp Finnfix, BW low molecular weight CMC before each pass (a total of 40 mg/g after 1+3 passes).

- 5 **Figure 4a** depicts a schematic diagram of CMC pre-sorption onto the fibre prior to mechanical disintegration. **Figure 4b** depicts a schematic diagram of CMC addition to the pulp suspension prior to and/or during mechanical disintegration. In contrast to the method shown in Figure 4a CMC is allowed to adsorb during the whole disintegration process.

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Figure 5 shows the Scott Bond as a function of passes through Masuko or Fluidizer. The corresponding microscopy images are of the Fluidizer samples after 2, 3 and 4 passes through the fluidizer, respectively.

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DETAILED DESCRIPTION OF THE INVENTION

- The present invention provides a method for producing modified nanofibrillated cellulose by adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto fibers in a fiber suspension under special conditions and subjecting the fiber suspension comprising a cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration. By combining the adsorption of a cellulose derivative or polysaccharide or polysaccharide derivative onto fibers under special conditions and mechanical disintegration the number of passes through a disintegration device needed to refine the pulp is reduced and the energy demanded is decreased. Special conditions according to the present invention include temperature, presence of monovalent or polyvalent cations, adsorption time and/or mixing. It has surprisingly been found that the amount of refining energy needed in the process is decreased. The present invention provides significant advances compared to the prior art by decreasing the energy consumption during fibrillation. The modification of nanofibrillated cellulose with a cellulose derivative or polysaccharide or polysaccharide derivative prior to and/or during the mechanical disintegration surprisingly increases the processing efficiency.
- 30 Furthermore, the modified nanofibrillated cellulose improves the paper properties more than unmodified nanofibrillated cellulose. None of the prior art methods results in the similar strength properties for paper when compared to modified nanofibrillated

cellulose according to the present invention. Nanofibrillated cellulose modified with a cellulose derivative or polysaccharide or polysaccharide derivative contains up to five times more nanofibrils than the unmodified nanocellulose prepared from the same pulp. The strength of paper produced from the modified nanofibrillated cellulose using the special conditions of the present invention is already after the initial pass through the friction grinder considerably increased as compared to unmodified fibrils. Thus, mechanical treatment to obtain modified nanofibrillated cellulose can be reduced to one fifth, while still achieving considerably improved paper qualities. Nanofibrillated cellulose together with a modification by a cellulose derivative or polysaccharide or polysaccharide derivative under special conditions provides a synergistic effect, which can be utilized in paper produced from said modified nanocellulose.

Unless otherwise specified, the terms, which are used in the specification and claims, have the meanings commonly used in the pulp and paper industry. Specifically, the following terms have the meanings indicated below:

The term "nanofibrillated cellulose" or NFC" refers to very refined cellulose where most of the fibrils have been fully liberated from the fibers and occur as individual threads, which are 5 nm – 1 µm thick and several µms long. Conventionally the fibrils having a diameter of less than 1 µm are called nanofibrils and fibrils having a diameter of more than 1 µm and length of several micrometers are called microfibrils.

The term "mechanical disintegration" or "fibrillation" or "grinding" in the present invention relates to producing nanofibrillated cellulose from larger fiber material.

Mechanical disintegration includes also for example refining, beating and homogenization. Mechanical disintegration can be carried out with suitable equipment such as a refiner, grinder, homogenizer, colloider, friction grinder, fluidizer such as microfluidizer, macrofluidizer or fluidizer-type homogenizer.

The term "cellulosic material" refers to nonwoody and wood cellulosic materials used. As cellulosic material for the method and process of the present invention almost any kind of cellulosic raw materials is suitable, as described below.

The term "special conditions" in the present invention refers to a specified temperature, presence of monovalent or polyvalent cations, adsorption time and/or mixing which are defined according to the present invention.

The term "chemical pulp" refers to all types of chemical wood-based pulps, such as bleached, half-bleached and unbleached sulphite, sulphate and soda pulps, kraft pulps together with unbleached, half-bleached and bleached chemical pulps and mixtures thereof.

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The term "paper", as used herein, includes not only paper and production thereof, but also other web-like products, such as nonwoven, board and paperboard, and the production thereof.

- 10 The present invention provides a method for producing modified nanofibrillated cellulose wherein the method comprises steps of preparing a suspension containing fibers from cellulosic material, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under specified conditions and subjecting the fiber suspension comprising said cellulose derivative or
15 polysaccharide or polysaccharide derivative to mechanical disintegration to obtain modified nanofibrillated cellulose modified with said cellulose derivative or polysaccharide or polysaccharide derivative.

According to an embodiment of the present invention a cellulose derivative or
20 polysaccharide or polysaccharide derivative is adsorbed onto the fibers either prior to mechanical disintegration (sorption) or by adding a cellulose derivative or polysaccharide or polysaccharide derivative during the mechanical disintegration (addition) under special conditions. In still another embodiment of the invention the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the
25 fibers both prior to and during the mechanical disintegration.

In a preferred embodiment of the invention as cellulosic material for the method of the present invention almost any kind of cellulosic raw materials is suitable. The cellulosic material which is used in the present invention includes pulp such as a chemical pulp,
30 mechanical pulp, thermo mechanical pulp (TMP) or chemi-thermo mechanical pulp (CTMB) produced from wood, non-wood material or recycled fibers. Wood can be from softwood tree such as spruce, pine, fir, larch, douglas-fir or hemlock, or from hardwood tree such as birch, aspen, poplar, alder, eucalyptus or acacia, or from a mixture of softwoods and hardwoods. Non-wood material can be from agricultural residues, grasses or other plant substances such as straw, leaves, bark, seeds, hulls, flowers, vegetables or fruits from cotton, corn, wheat, oat, rye, barley, rice, flax,

hemp, manila hemp, sisal hemp, jute, ramie, kenaf, bagasse, bamboo or reed. Non-wood material can also be from algae or fungi or of bacterial origin.

In a preferred embodiment of the invention as a cellulose derivative for the purposes
5 of the present invention almost any kind of cellulose derivative is suitable. A cellulose derivative can be carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, ethylhydroxyethyl cellulose, carboxymethylcellulose, carboxymethylhydroxyethyl cellulose, hydroxypropylhydroxyethyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose, carboxymethylmethyl cellulose, or hydrophobically modified variants thereof, or cellulose acetate, cellulose sulfate, cellulose phosphate, cellulose phosphonate, cellulose vinyl sulfate, or nitrocellulose or other derivatives known by the person skilled in the art can be applied. The present invention is exemplified by using carboxymethyl cellulose (CMC) for producing modified nanofibrillated cellulose. Preferably anionic CMC is used. Even
10 though CMC represents a preferred embodiment, it should be noted, that other cellulose derivatives known by the person skilled in the art can be used.
15

In a preferred embodiment of the invention a polysaccharide or polysaccharide derivative can be selected from guar gums, chitins, chitosans, galactans, glucans,
20 xantan gums, mannans or dextrans ,which are given here by the way of examples. It should be noted, that other polysaccharides or polysaccharide derivatives known by the person skilled in the art can be used.

The amount of added cellulose derivative or polysaccharide or polysaccharide derivative is at least 5 mg/g of fiber suspension, preferably from 10 to 50 mg/g of fiber suspension, more preferably about 15 mg/g, 20 mg/g, 25mg/g, 30 mg/g, 35 mg/g or 40 mg/g of fiber suspension, the upper limit being 1000 mg/g of fiber suspension, preferably the upper limit is 100 mg/g of fiber suspension.
25

30 In an embodiment where CMC is used as the cellulose derivative, different commercially available CMC grades having a suitable degree of substitution and molar mass can be used for carrying out the invention. Typically high molecular weight CMC has suitable characteristics for mechanical disintegration or fibrillation and typically low molecular weight CMC can penetrate the fiber wall, which also increases the
35 amount of adsorbed CMC.

In a preferred embodiment of the invention a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers at a temperature of at least 5°C, preferably at a temperature of at least 20°C, the upper limit being 180°C. In a more preferred embodiment of the invention temperature is from 75°C to 80°C.

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In a preferred embodiment of the invention a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers for at least 1 minute, preferably for at least 1 hour, preferably for 2 hours. Preferably the adsorption is aided by sufficient mixing.

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In a preferred embodiment of the present invention the absorption is made in the presence of monovalent or polyvalent cations such as aluminium, calcium and/or sodium salts containing Al³⁺, Ca²⁺ and/or Na⁺, respectively, preferably for example CaCl₂. High valencies are advantageous for the adsorption. Generally a higher concentration of electrolyte and a higher valence of the cation increase the affinity of an anionic cellulose derivative, such as CMC, to the pulp. Generally, however, an optimum exists. The preferred concentration interval for salts with divalent cations such as CaCl₂ is between 0 and 1 M, preferably about 0.05 M.

15

In a preferred embodiment of the invention the pH value of the fiber suspension is at least pH 2, preferably from about pH 7.5 to 8, the upper limit being pH 12. A suitable base or acid is used for setting the pH. The pH value is dependent on the origin of the fibers in the mass.

20

The sorption at specified conditions ensures that a cellulose derivative or polysaccharide or polysaccharide derivative is irreversibly attached to the pulp prior to disintegration. The addition at low temperature during disintegration does not facilitate sorption but indicates the effect of a cellulose derivative or polysaccharide or polysaccharide derivative in solution on fibrillation efficiency.

25

The present invention comprises a step of mechanical disintegration. In a preferred embodiment of the invention the mechanical disintegration is carried out with a refiner, grinder, homogenizer, colloider such as a supermass colloid, friction grinder, fluidizer such as microfluidizer, macrofluidizer or any fluidizer-type homogenizer known by the person skilled in the art without, however, not limiting to these examples. Typically the fiber suspension is passed through mechanical disintegration at least once, preferably 1, 2, 3, 4 or 5 times.

This enables the reduction of mechanical treatment by up to one fifth, while at the same time considerable improvement for example in paper quality is achieved. It is shown in the Examples that the energy consumption during friction grinding of pulp modified with a cellulose derivative, such as CMC, is lower compared to friction grinding of same pulp without a cellulose derivative, such as CMC adsorbed. The energy consumption of producing the modified nanocellulose of the present invention is lower compared to unmodified pulp. The energy needed to obtain roughly the same amount of nanofibrillated material is halved.

10

In a preferred embodiment of the invention the fiber suspension containing the cellulose derivative or polysaccharide or polysaccharide derivative is redispersed in water to a concentration of at least 0,1%, preferably at least 1%, more preferably at least 2%, 3%, 4% or 5%, up to 10% prior to mechanical disintegration. In a preferred embodiment using the friction grinder for the mechanical disintegration the fiber suspension containing the cellulose derivative or polysaccharide or polysaccharide derivative is redispersed in water to 3% consistency. Preferably 1-5 passes are run.

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The present invention also relates to nanofibrillated cellulose prepared according to the method of any of the claims.

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In nanosized structure the surface area of cellulose is maximized and the structure has more chemically functional groups than cellulose in general. This means that nanocellulose fibers attach strongly to surrounding substances. This provides the paper produced from the nanocellulose with good strength properties. Using the modified nanocellulose according to the present invention even higher strength properties than with unmodified nanocellulose are obtained.

30

The present invention relates to the use of modified nanofibrillated cellulose according to the present invention in paper. The present invention also relates to a paper containing the modified nanofibrillated cellulose of the present invention. In a preferred embodiment the amount of modified nanofibrillated cellulose is at least 0,2%, preferably at least 1%, 2%, 3%, 4% or 5%, up to 20% by weight of the paper. Other ingredients in paper are such that are known to the person skilled in the art. The paper is prepared using the standard methods used in the field and known by the person skilled in the art. The technical paper properties of both fibril sheets of the present invention and paper sheets containing modified nanofibrillated cellulose of the

present invention are tested using standard methods known by the person skilled in the art.

Adsorbed cellulose derivative or polysaccharide or polysaccharide derivative of the present invention is used in a novel way. Combining the adsorption of the cellulose derivative or polysaccharide or polysaccharide derivative and mechanical disintegration provides novel and surprising advantages. It is noted that in the present process, energy savings are achieved. Another advantage of the modification is the new properties of the modified fibrils that can be used for example to improve the properties of paper. The strength of the paper produced from the modified nanofibrillated cellulose of the present invention is already after the initial pass through the refiner considerably increased as compared to unmodified fibrils. Thus, mechanical treatment can be reduced to up to one fifth, while at the same time considerable improvement for example in paper quality is achieved.

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The efficiency of the mechanical disintegration or fibrillation is determined by gravimetrically measuring the amount of nano-size particles after each pass through the homogenizing device.

20

Application areas for the modified nanofibrillated cellulose of the present invention include, but are not restricted to paper, food products, composite materials, concrete, oil drilling products, coatings, cosmetic products and pharmaceutical products. Other possible application areas of the modified nanocellulose of the present invention include for example the use as a thickener, use in composites for vehicles, consumables and furniture, in new materials for electronics and use in moldable light weight and high strength materials.

25

The following example is given to further illustrate the invention and is not intended to limit the scope thereof. Based on the above description, a person skilled in the art will be able to modify the invention in many ways.

Examples

Example 1

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Materials

Pulp

Bleached, never-dried kraft birch pulps provided by UPM-Kymmene Oyj were used.

CMC

Two different CMC grades were used: the high molecular weight Finnfix WRM or low
5 molecular weight Finnfix BW (DS 0.52-0.51) (CP Kelco, Äänekoski, Finland).

CMC adsorption was carried out with two strategies: either treating the pulp prior to fibrillation with CMC in specific conditions (sorption) or adding the CMC during the fibrillation (addition). The third strategy was to adsorb CMC both prior to fibrillation
10 and during fibrillation.

CMC sorption

The pulp (never dried hardwood) was first washed with deionised water prior to sorption. A slurry with pulp consistency of 30 g/l containing 0.05 M CaCl₂ and 0.01 M
15 NaHCO₃ was prepared and heated to 75-80°C. 20 mg carboxymethyl cellulose (CMC) was added per gram of pulp (o.d). The pH was adjusted to pH 7.5-8 with 1M NaOH. The slurry was mixed for 2h at 75-80°C. After sorption the pulp was washed with deionised water, excess water was removed by filtration and the moist pulp cakes were stored in cold room until fibrillation. Batches corresponding to about 20-25 l of
20 3% CMC sorbed pulp were prepared for fibrillation with friction grinder and batches of about 5 l of 3% CMC sorbed pulp were prepared for fluidizer runs. Sorption is presented in Figure 4a.

CMC addition

25 The CMC was dissolved carefully the day before fibrillation into 2% consistency. After dispersing the pulp the addition was done before each pass by adding the CMC solution calculated as 10 mg per dry gram of fibre for one pass. One to four additions corresponding to total additions of 10-40 mg/g were performed. Between the additions the slurry was mixed 15 minutes without heating. In this case the cellulose derivative adsorption was going on during fibrillation.
30

Fibrillation

Fibrillation was done with either friction grinder (Masuko Supermass colloider, Masuko Sangyo, Japan) or a laboratory scale fluidizer (Microfluidics M110Y, Microfluidics Corp.,
35 USA).

Friction grinding

In friction grinding the CMC sorbed pulp was redispersed in water to 3% consistency using the grinder with 200µm gap. Subsequently 1 to 5 passes were run through the friction grinder with a gap of roughly 100-160 µm and power around 3 kW and samples were taken after each pass. In the cases where CMC was also added during fibrillation, the slurry was heated to 60-80°C for 30 min and mixed for 10 min after CMC addition prior to passing through the colloider.

The following experiments were carried out with friction grinder:

1. Reference, unmodified pulp was passed five times through the friction grinder.
- 10 2. High molecular weight CMC (WRM) was sorbed onto pulp, the pulp was washed prior to refining and one to five passes were run through the friction grinder.
3. High molecular weight CMC (WRM) was sorbed onto pulp, the pulp was washed prior to refining. 20 mg/g CMC (WRM) was added to suspension (adsorption) before each pass through the friction grinder. The pulp was run one to three times through the refiner.
- 15 4. Low molecular weight CMC (BW) was sorbed to the pulp and the pulp was washed prior to refining, one to five passes were run through the friction grinder.

20 The concentration of nanofibrils in each of the above listed experiments are presented in the upper part of Table 2, "Masuko Supermass Colloider".

Fluidizer

In the experiments carried out with the fluidizer the well beaten pulp (hardwood pulp) was diluted to 2% consistency and pre-dispersed with a Polytron mixer before first run through the fluidizer. The sample was first passed through the wider chamber pair with diameters of 400 and 200µm at 950 bar and then 1 to 3 times through the smaller chamber pair with diameters of 200 and 100µm at 1350 bar.

30 The following experiments were carried out with a fluidizer:

1. Reference: unmodified pulp – only fibrillation.
2. Presorption of CMC (high molecular weight, WRM or low molecular weight, BW) prior to fibrillation
3. Presorption of CMC (high molecular weight, WRM or low molecular weight, BW) prior to fibrillation + addition (adsorption) of CMC during fibrillation.
- 35 4. Addition (adsorption) of CMC during fibrillation only (WRM or BW).

The concentrations of nanofibrils in each of the above listed experiments are presented in the lower part of Table 2, "Microfluidics fluidizer".

Amount of nanosized material

- 5 The proportion of nanosized material in the nanofibrillated cellulose (NFC) was estimated by centrifugation. The more there were unsettled fibrils in the supernatant after centrifugation the more efficient the fibrillation had been. Solids content was determined gravimetrically after drying the samples before and after drying them in oven (105°C). Based on the value, the samples are diluted into constant (ca. 1.7
10 g/ml) consistency and dispersed with ultrasound microtip (Branson Digital Sonifier D-450) for 10 min, 25 % amplitude setting. After sonification, samples are centrifuged (Beckman Coulter L-90K) for 45 min at 10 000 G. From clear supernatant, 5 ml is carefully taken with a pipette. Two parallel measurements (10 ml) are combined for gravimetric analysis and results are given as an average value for two measurements.

15

Optical microscopy imaging

- Fibrous material was stained with 1% Congo red (Merck L431640) in order to improve contrast in light microscopy. Staining liquid was centrifuged (13 00 rpm, 2 min) prior to use to remove insoluble material. For microscopical examination a fibre sample
20 (150µl) was mixed with Congo red solution at a ratio of 1:1 in an eppendorf tube and about 100 µl of stained fibre slurry was spread with 50 µl of distilled water on microscope slide and covered with a cover slip. The samples were examined using bright field settings under Olympus BX61 microscope equipped with ColorView 12 camera (Olympus). Images were taken with magnifications of 40 x and 100 x using
25 Analysis Pro 3.1 image processing program (Soft Imaging System GmbH).

Preparation of fibril sheets

- To demonstrate the efficiency of the present invention sheets containing 85% NFC and 15 % unrefined soft wood pulp were prepared according to the standard method using
30 a normal laboratory sheet former (SCAN-C26:76).

Preparation of paper sheets with fibrils as additives

- Softwood pulp was refined for 10 minutes, and the pulp was washed to sodium form. A cationic starch (Raisamyl 50021, DS =0.035, Ciba Specialty Chemicals) was used as
35 an additive. A 2 g/l starch stock solution was prepared fresh every day. The NFC was dispersed with ultrasound microtip sonication prior to use. All experiments were done in a solution of deionised water containing 1 mM NaHCO₃ and 9 mM NaCl.

Pulp was first mixed with cationic starch (CS) for 15 min and then the dispersed nanofibrillated cellulose (NFC) was added and the suspension was mixed for another 15 min. The sheets were prepared in laboratory sheet former (SCAN-C26:76) and
5 dried under restrain.

The paper technical properties of both fibril sheets and paper sheets containing modified NFC were tested using standard methods.

10 Results

Energy consumption during production

The energy consumption during friction grinding of CMC sorbed pulp is illustrated in Table 1. Furthermore, average solids content after fibrillation and estimated amount of
15 nanosized material are presented.

Table 1. Energy consumption for the fibrillation of pulp after CMC sorption using friction grinder.

| Sample | Passes | Cumulative total refining energy (MW*h/t) | Average solids content [%] | Nanomaterial (upper phase) [g/l] |
|--------------|--------|---|----------------------------|----------------------------------|
| Reference | 1 | 1.84 | | Too low to determine |
| Reference | 3 | 6.63 | | Too low to determine |
| Reference | 5 | 12.75 | | 0.099 |
| WRM sorption | 1 | 1.59 | 2.74 | 0.164 |
| WRM sorption | 2 | 3.16 | 2.44 | 0.110 |
| WRM sorption | 3 | 5.30 | 2.04 | 0.117 |
| WRM sorption | 4 | 7.95 | | Not determined |
| WRM sorption | 5 | 11.06 | 1.75 | 0.110 |

Effect of CMC modification on amount of nanosized material**Table 2.** Concentration of nanofibrils in upper phase after centrifugation.

| sample ID | Nanomaterial conc (g/l) |
|--|----------------------------|
| Masuko supermass colloider | |
| unmodified hardwood, 5 pass | 0.099 |
| CMC (WRM) sorption only prior to fibrillation, 1 pass | 0.16 |
| CMC (WRM) sorption only prior to fibrillation, 3 pass | 0.12 |
| CMC (WRM) sorption only prior to fibrillation, 5 pass | 0.11 |
| CMC (WRM) sorption + addition during fibrillation, 2 pass | 0.18 |
| CMC (WRM) sorption + addition during fibrillation, 3 pass | 0.17 |
| CMC (BW) sorption only prior to fibrillation, 1 pass | 0.015 |
| CMC (BW) sorption only prior to fibrillation, 3 pass | not determined |
| CMC (BW) sorption only prior to fibrillation, 5 pass | 0.035 |
| Microfluidics Fluidizer | |
| Unmodified hard wood, 1 + 1 pass | 0.339 |
| Unmodified hard wood, 1 + 2 pass | 0.348 |
| Unmodified hard wood, 1 + 3 pass | 0.452 |
| CMC (BW) sorption only prior to fibrillation, 1 + 1 pass | 0.154 |
| CMC (BW) sorption only prior to fibrillation, 1 + 2 pass | 0.169 |
| CMC (BW) sorption only prior to fibrillation, 1 + 3 pass | 0.218 |
| CMC (BW) addition during fibrillation, 1 + 1 pass | 0.322 |
| CMC (BW) addition during fibrillation, 1 + 2 pass | 0.343 |
| CMC (BW) addition during fibrillation, 1 + 3 pass | 0.415 |
| CMC (BW) sorption + addition during fibrillation, 1 + 1 pass | 0.218 |
| CMC (BW) sorption + addition during fibrillation, 1 + 2 pass | 0.290 |
| CMC (BW) sorption + addition during fibrillation, 1 + 3 pass | 0.196 |
| CMC (WRM) sorption only prior to fibrillation, 1 + 1 pass | 0.129 |

| | |
|---|-------|
| CMC (WRM) sorption only prior to fibrillation, 1 + 2 pass | 0.124 |
| CMC (WRM) sorption only prior to fibrillation, 1 + 3 pass | 0.123 |
| CMC (WRM) addition during fibrillation, 1 + 1 pass | 0.418 |
| CMC (WRM) addition during fibrillation, 1 + 2 pass | 0.407 |
| CMC (WRM) addition during fibrillation, 1 + 3 pass | 0.492 |
| CMC (WRM) sorption + addition during fibrillation, 1 + 1 pass | 0.112 |
| CMC (WRM) sorption + addition during fibrillation, 1 + 2 pass | 0.184 |
| CMC (WRM) sorption + addition during fibrillation, 1 + 3 pass | 0.179 |

Abbreviations: CMC, carboxymethyl cellulose;

BW, low molecular weight CMC (Finnfix BW, CP Kelco, Äänekoski, Finland, DS 0.51);

WRM, high molecular weight CMC (Finnfix WRM, CP Kelco, Äänekoski, Finland)

5

CMC sorption increases the efficiency of the fibrillation (Table 2). Tests using friction grinding indicates that sorption prior to fibrillation in combination with addition during fibrillation gives the highest concentration of fibrils in upper phase after centrifugation. In these cases the total amount of CMC used is also highest, since 20 mg/g was added
10 three times i.e. in total of 60 mg.

However, when fluidizer was used an effective way was to add CMC only during the disintegration.

15 It was thus observed that the upper phase of the CMC modified nanofibrillated cellulose sample contained five times more nanofibrils than the unmodified nanofibrillated cellulose prepared from the same mass.

Effect of CMC modification on strength of test sheets

20 The potential of the modified nanofibrillated cellulose (NFC) as a strength additive is illustrated below. In Table 3 the paper properties of test sheets containing 85% NFC and 15% long fibers are compared. A clear increase in paper strength was observed using the modified NFC as compared to unmodified NFC (reference hardwood). Noteworthy is that the density of the paper produced using modified NFC did not
25 increase although the tensile strength was clearly higher than for unmodified NFC. Satisfying results were obtained already after 1 pass through the friction grinder (Masuko colloider).

Table 3. NFC Paper Sheet Characteristics.

| | TestPoint | Grammage g/m² | Apparent density kg/m³ | Tensile strength kNm/kg | Tear Index Jm/kg | Bending stiffness mNm |
|-------------|------------------|---|--|--|-----------------------------------|--|
| CMC-treated | WRM sorpt. 1p | 66.1 | 991 | 93.17 | 4.51 | 0.104 |
| | WRM sorpt. 3p | 66.2 | 999 | 84.40 | 3.29 | 0.112 |
| | WRM sorpt. 5p | 66.5 | 987 | 84.89 | 2.99 | 0.126 |
| | BW sorpt. 1p | 66.2 | 991 | 86.11 | 3.69 | 0.115 |
| | BW sorpt. 2p | 66.1 | 1000 | 88.04 | 3.20 | 0.107 |
| | BW sorpt. 3p | 67 | 1030 | 84.89 | 2.70 | 0.125 |
| Ref. | hardwood 5p | 67.4 | 1010 | 64.84 | 3.75 | 0.089 |

Abbreviations:

- 5 WRM sorpt., nanofibril sample modified with high molecular weight CMC (WRM);
 BW sorpt., nanofibril sample modified with low molecular weight CMC (BW);
 1p, 2p, 3p and 5p, the amount of the passes through the refiner (refining cycles);
 Ref., hardwood 5p, the corresponding unmodified fiber suspension from hardwood
 passed five times through the friction grinder.
- 10 It was found that the strength of the paper produced from the modified NFC already
 after the initial pass through the refiner, was considerably increased as compared to
 unmodified fibrils. Thus, mechanical treatment can be reduced to one fifth, while still
 achieving considerably improved paper qualities (Table 3).
- 15 The effect of NFC on sheet properties was also studied using NFC as an additive. The
 results are shown in Table 4 and in Figure 1. In these experiments cationic starch (CS,
 25 mg/g) was added to fractionated softwood pulp and adsorbed for 15 minutes,
 whereupon either unmodified or modified NFC was added (30 mg/g) and adsorbed for
 20 15 minutes and sheets were made. Scott Bond is a measure of the internal strength of
 the sheet, measured on Scott Bond Tester, expressed in J/m². In Table 4 the paper
 properties achieved using NFC prepared according to the present method using
 Masuko Mass colloider are shown.
- 25 **Table 4.** Paper Technical paper properties of sheets made from pulp, cationic starch
 (CS) and nanofibrillated cellulose (NFC) at constant ionic strength, pH and after fines

have been removed. NFC was modified using friction grinder (Masuko super colloider). Reference sample contained pulp only or pulp and cationic starch.

| Sample | | NFC | CS + NFC | NFC | CS + NFC |
|-------------------------------|--------|----------------------|----------------------|--------------------------------|--------------------------------|
| | Passes | Tensile index (Nm/g) | Tensile index (Nm/g) | Scott Bond (J/m ²) | Scott Bond (J/m ²) |
| Reference | 5 | 64.6 | 83.37 | 194 | 320 |
| CMC sorption (WRM) | 1 | 70.15 | 90.2 | 180 | 405 |
| CMC sorption (WRM) | 3 | 68.97 | 84.16 | 193 | 531 |
| CMC sorption (WRM) | 5 | 68.26 | 89.49 | 204 | 400 |
| CMC sorption + addition (WRM) | 1 | 67.77 | 85.08 | 211 | 446 |
| CMC sorption + addition (WRM) | 3 | 66.42 | 86.76 | 190 | 559 |

5 Abbreviations:

CS, cationic starch; NFC, nanofibrillated cellulose; CMC, carboxymethyl cellulose; WRM, high molecular weight CMC; BW, low molecular weight CMC

The efficiency of the fibrillation

10

The efficiency of the fibrillation made according to this invention is illustrated by optical microscopy images in Figures 2 and 3. The scale bars in the figures are 500 µm. The decrease in the amount of dark thick fibers shows the efficiency of fibrillation. The finest nanosized material is obviously not visible in optical microscopy.

15

CMC (Finnfix WRM, high molecular weight CMC) was added during fibrillation in fluidizer. In Figure 2 the samples after different amount of passes, 1+1, 1+2 and 1+3 passes, respectively, through the fluidizer are compared, (Figures 2a, 2b and 2c). The decrease in the amount of large particles can be observed.

20

In Figure 3 CMC-modified samples (Figure 3b and 3c) are compared to a sample of unmodified nanofibrillated cellulose (Figure 3a) after 1 + 3 passes through the fluidizer. NFC was modified according to this invention by addition of 10 mg/g dry pulp Finnfix, WRM high molecular weight CMC before each pass (a total of 40 mg/g after 25 1+3 passes) (Figure 3b). The image of NFC modified according to this invention by

addition of 10 mg/g dry pulp Finnfix, BW low molecular weight CMC before each pass (a total of 40 mg/g after 1+3 passes) is shown in Figure 3c. Clearly there are much less large particles left in the samples modified according to this invention than in an unmodified sample.

5

Example 2

Materials

10 Pulps

Bleached softwood kraft pulp made from Scots Pine (*Pinus sylvestris*) was acquired from UPM-Kymmene Oyj, Kaukas pulp mill in air dry sheets. The dry pulp samples were swollen in deionized water and beaten in a Valley beater according to standard 15 SCAN-C 25:76. Unless otherwise stated the beating time was 10 min. Thereafter any remaining metal ions were removed by acid treatment, and the fibres were washed into their Na-form according to method described by Swerin et al. (1990). Finally the samples were dewatered and stored in a refrigerator at ca. 20 % consistency. Prior to 20 use the samples were diluted to desired consistency and cold disintegrated according to standard SCAN-C 18:65. The salt concentration of the suspensions was adjusted to 9 mM NaCl and 1 mM NaHCO₃, and the pH was adjusted to 8.0.

Polyelectrolytes

Two different CMC (carboxymethyl cellulose) grades from CP Kelco Oy (Äänekoski, 25 Finland) were used for preparation of modified NFC. They are hereafter referred to as WRM (high molecular weight) CMC and BW (low molecular weight) CMC.

In sheet preparation and dewatering experiments cationic starch (CS, Raisamyl 50021 from Ciba Specialty Chemicals Ltd), of which degree of substitution (D.S.) ca 0.035, 30 and charge density of ca. 0.2 meq/g was used to enhance the retention of the NFC on the fibres.

Nanofibrillar cellulose

Different grades of modified NFC were used. The NFC was prepared from never dried 35 birch pulp, obtained from UPM-Pietarsaari and grinded to SR 90. NFC samples were prepared either using the Masuko Mass Colloider (Masuko Sangyo Co., Kawaguchi,

Japan) or the laboratory scale fluidizer (M-110Y, Microfluidics Corp.). As a reference a sample prepared by passing the pulp 5 times through the Masuko colloider was used.

Electrolytes (NaCl and NaHCO₃) were of analytical grade and dissolved in deionized

5 water. Analytical grade HCl and NaOH solutions were used for pH adjustments. The used water was deionized.

Methods

10 Sheet forming

The pH and electrolyte concentration of the fibre suspension was kept constant using 1 mM NaHCO₃ and 9 mM NaCl. Polyelectrolyte (cationic starch or PDADMAC) was first added to the fibre suspension and the suspension was vigorously mixed for 15 min.

15 The NFC was dispersed using ultrasound, added to polyelectrolyte treated pulp and the suspension was mixed for another 15 min. Sheets were formed in a laboratory sheet former, Lorentzen & Wettre AB, Sweden (ISO 5269-1) with a 100 mesh wire. The grammage of sheets was adjusted to about 60 g/m² by dilution of the suspension when necessary. The sheets were wet pressed under 4.2 bars for 4 minutes and dried

20 in a frame to avoid shrinkage during drying (105°C for 3 minutes). The samples were conditioned over night in 50% humidity and 20°C according to the standard SCAN_P 2:75 before testing.

Sheet testing

25 All the sheet properties were measured according to SCAN or ISO standards. Grammage (ISO 536:1995(E)), thickness and bulk were determined with Lorentzen & Wettre micrometer (ISO 534:2005(E)). The Scott Bond was determined using Huygen Internal bond tester) and Tensile strength, fracture toughness index and TEA were measured with Lorentzen & Wettre tearing tester (SE009 Elmendorf, SCAN-P 11:73).

30

Results

Strength of sheets

35 In Tables 5 and 6 the sheet properties of sheets made using NFC prepared with Masuko supermass colloider (Table 5) or microfluidics fluidizer (Table 6) are summarized. Cationic starch, CS, Raisamyl 50021 was used in the experiments presented in table 5 and 6.

Table 5. Sheet properties of sheets made from pulp, cationic starch (CS, 25 mg/g)) and nanofibrillated cellulose (NFC, 30 mg/g). NFC was prepared with Masuko supermass colloider. Reference sample contains only pulp.

| NFC grade | Passes | Grammage (g/m ²) | Density (kg/m ³) | Tensile index (Nm/g) | Scott Bond (J/m ²) |
|-------------------------|--------|------------------------------|------------------------------|----------------------|--------------------------------|
| Reference | No NFC | 60,8 | 558 | 58,35 | 132 |
| WRM sorption | 1 | 58 | 579 | 90,2 | 405 |
| WRM sorption | 3 | 58,3 | 599 | 84,16 | 531 |
| WRM sorption | 5 | 56,4 | 573 | 89,49 | 400 |
| WRM sorption + addition | 1 | 59 | 584 | 85,08 | 446 |
| WRM sorption + addition | 3 | 61,4 | 608 | 86,76 | 559 |
| BW sorption | 1 | 59 | 564 | 76,26 | 347 |
| BW sorption | 3 | 59,5 | 582 | 84,62 | 426 |
| BW sorption | 5 | 59,8 | 603 | 85,77 | 470 |

5

Abbreviations: WRM, high molecular weight CMC; BW, low molecular weight CMC

Table 6. Sheet properties of sheets made from pulp, cationic starch (CS, 25 mg/g)) and nanofibrillated cellulose (NFC, 30 mg/g). NFC was prepared with microfluidics fluidizer. Reference sample contains pulp, cationic starch (CS) and unmodified NFC.

| NFC grade | Passes | Grammage (g/m ²) | Density (kg/m ³) | Tensile index (Nm/g) | Scott Bond (J/m ²) |
|-------------------------|--------|------------------------------|------------------------------|----------------------|--------------------------------|
| BW sorption | 4 | 62,4 | 575 | 79,26 | 383 |
| BW addition | 4 | 62,8 | 597 | 85,16 | 520 |
| WRM addition | 4 | 62,6 | 589 | 82,68 | 427 |
| WRM sorption | 4 | 62,8 | 592 | 79,91 | 520 |
| REF no CMC | 4 | 62,3 | 572 | 82,97 | 411 |
| BW sorption + addition | 2 | 65,1 | 589 | 74,21 | 480 |
| BW sorption + addition | 3 | 63,5 | 583 | 78,1 | 446 |
| BW sorption + addition | 4 | 66 | 608 | 84,59 | 517 |
| WRM sorption + addition | 2 | 62,9 | 574 | 84,63 | 380 |
| WRM sorption + addition | 3 | 62,6 | 593 | 82,65 | 434 |
| WRM sorption + addition | 4 | 63,3 | 608 | 83,1 | 561 |

Abbreviations: WRM, high molecular weight CMC; BW, low molecular weight CMC

In Figure 5 both the way of preparing NFC and the effect of passes through the Fluidizer are compared. The corresponding microscopy images show that the fibril size is decreasing with the passes through the Fluidizer. No clear difference between

5 Masuko and Fluidizer samples are found in this case. Compared to the reference at 132 J/m², the Scott Bond increases clearly and also compared to unmodified NFC (411 J/m² after 4 passes) CMC modified NFC gives higher Scott Bond.

The present invention has been described herein with reference to specific
10 embodiments. It is, however clear to a person skilled in the art that the process(es) may be varied within the bounds of the claims.

CLAIMS

1. A method for producing modified nanofibrillated cellulose, **characterized** by the steps of
 - 5 - preparing a suspension containing fibers from cellulosic material;
 - adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under special conditions; and
 - subjecting the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration;
 - 10 to obtain modified nanofibrillated cellulose modified with said cellulose derivative or polysaccharide or polysaccharide derivative.
2. The method according to claim 1, **characterized** in that the cellulosic material is a pulp such as a chemical pulp, mechanical pulp, thermo mechanical pulp or chemi-
 - 15 thermo mechanical pulp produced from wood, non-wood material or recycled fibers.
3. The method according to claim 2, **characterized** in that wood is from softwood tree, hardwood tree, or a mixture of softwoods and hardwoods.
- 20 4. The method according to any of the preceding claims, **characterized** in that the cellulose derivative is carboxymethyl cellulose.
5. The method according to claims 1 to 4, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers
 - 25 prior to or during mechanical disintegration.
6. The method according to claims 1 to 5, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers both prior to and during mechanical disintegration.
- 30 7. The method according to any of the preceding claims, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers at a temperature of at least 5°C, preferably at a temperature of at least 20°C, the upper limit being 180°C.

8. The method according to any of the preceding claims, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers at a temperature of 75°C - 80°C.

5 9. The method according to any of the preceding claims, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers for at least 1 minute, preferably for at least 1 hour, preferably for 2 hours.

10 10. The method according to any of the preceding claims, **characterized** in that the method takes place in the presence of monovalent or polyvalent cations such as aluminium, calcium and/or sodium salts, preferably CaCl₂.

15 11. The method according to any of the preceding claims, **characterized** in that the pH value of the fiber suspension is at least pH 2, preferably from pH 7.5 to 8, the upper limit being pH 12.

20 12. The method according to any of the preceding claims, **characterized** in that the amount of added cellulose derivative or polysaccharide or polysaccharide derivative is at least 5 mg/g of fiber suspension, preferably from 10 to 50 mg/g, preferably 20 mg/g, the upper limit being 1000 mg/g of fiber suspension.

25 13. The method according to any of the preceding claims, **characterized** in that mechanical disintegration is carried out with a refiner, grinder, homogenizer, colloider, friction grinder, fluidizer such as microfluidizer, macrofluidizer or fluidizer-type homogenizer.

30 14. The method according to any of the preceding claims, **characterized** in that the fiber suspension is passed through mechanical disintegration at least once, preferably 2, 3, 4 or 5 times.

35 15. The method according to any of the preceding claims, **characterized** in that the fiber suspension containing the cellulose derivative or polysaccharide or polysaccharide derivative is redispersed in water to a concentration of at least 0,1%, preferably at least 1%, more preferably at least 2%, 3%, 4% or 5%, up to 10% prior to mechanical disintegration.

16. A modified nanofibrillated cellulose obtainable by a method according to any of claims 1 to 15 and characterized by that a diameter of nanofibrillated cellulose is less than 1 μm .

5 17. Use of modified nanofibrillated cellulose according to claim 16 in food products, composite materials, concrete, oil drilling products, coatings, cosmetic products, pharmaceutical products or paper.

18. A paper containing the modified nanofibrillated cellulose of claim 16.

10 19. A paper according to claim 18, **characterized** in that the amount of modified nanofibrillated cellulose is at least 0,2%, preferably at least 1%, 2%, 3%, 4% or 5%, up to 20% by weight of the paper.

15 20. Use of a method according to claims 1 to 15 for producing modified nanofibrillated cellulose energy efficiently.

21. Use of a method according to claims 1 to 15 for producing paper with improved properties.

20 22. A method for manufacturing paper with improved properties **characterized** by the steps of
- preparing a fiber suspension from cellulosic material; and
- adding modified nanofibrillated cellulose according to claim 16 to the fiber
25 suspension.

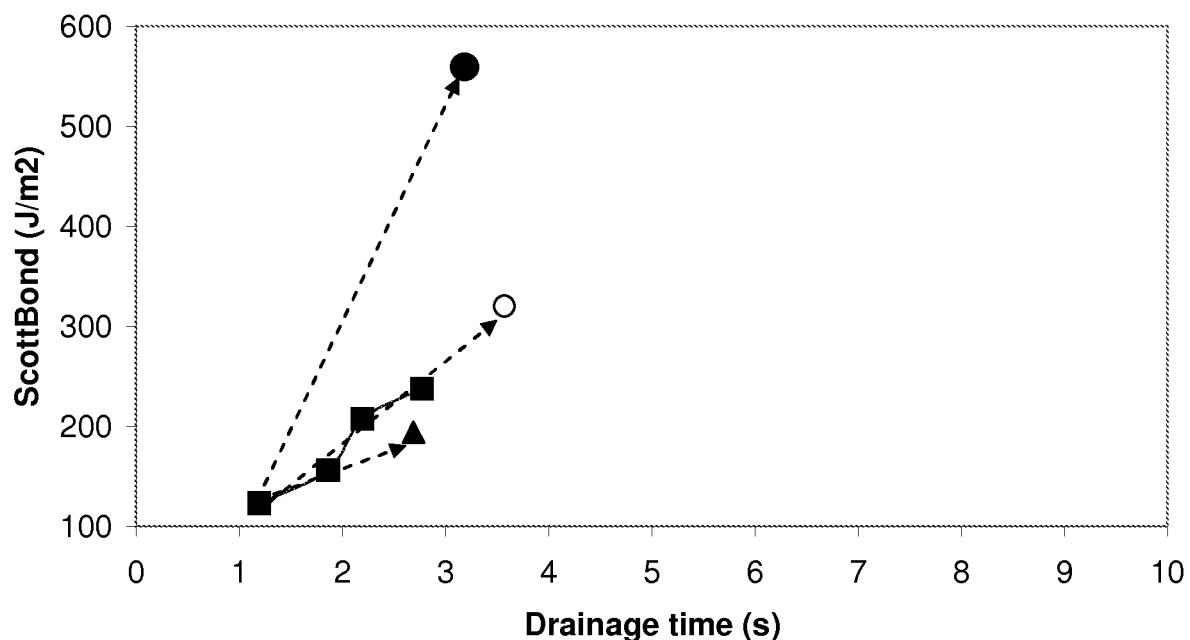


Fig. 1

2 / 5



2c



2b



2a

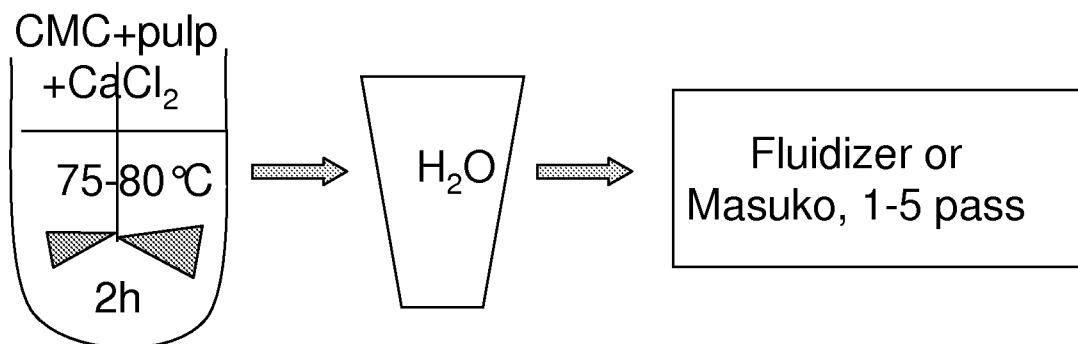
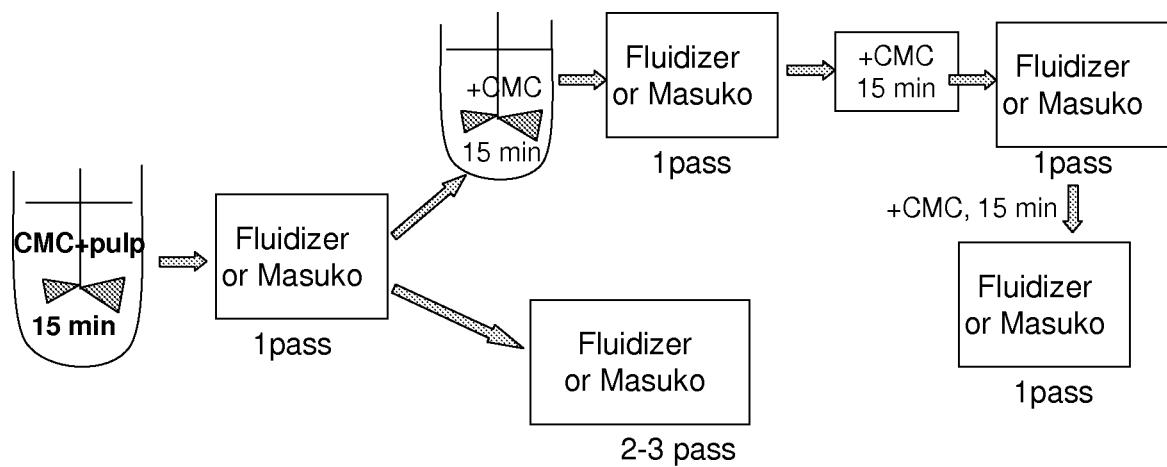
Fig. 2

3 / 5



Fig. 3

4 / 5

**Fig. 4 A****Fig. 4 B**

5 / 5

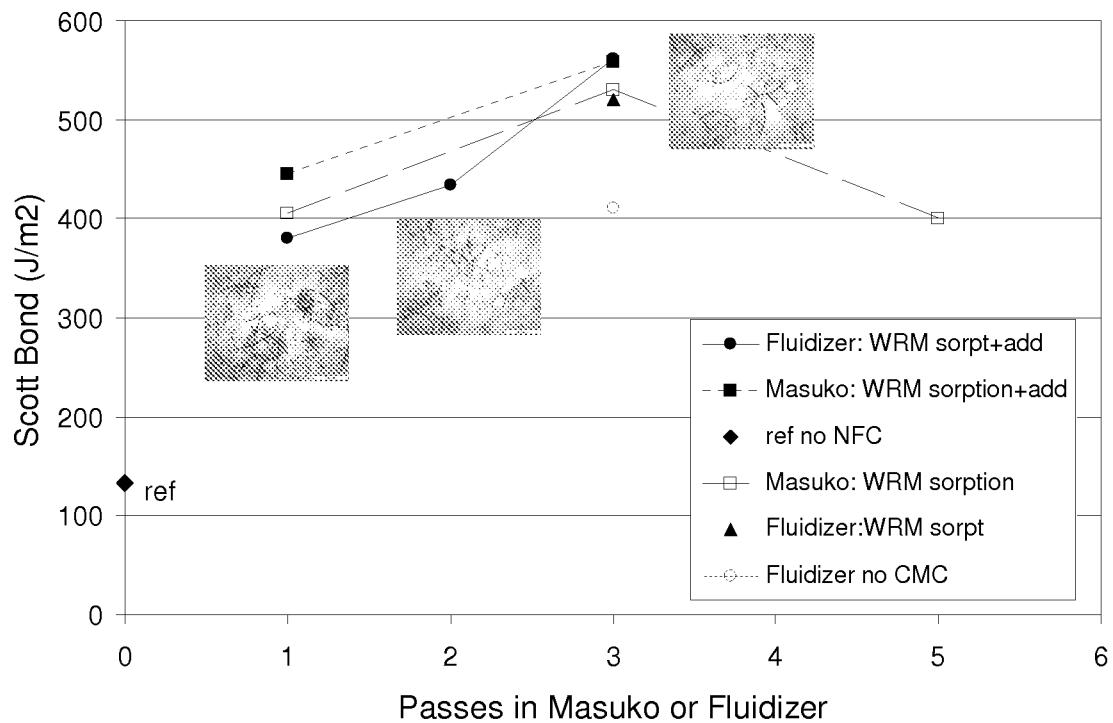


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2010/050096

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: D21H, D21D, D21C, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI, XPESP

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | US 2005272836 A1 (YAGINUMA YOSHIHITO et al.) 08 December 2005 (08.12.2005) claims 10-13, paragraphs [0012]-[0034], [0049], [0047], [0070], [0078], [0083] | 1-17 |
| A | WO 2007001229 A1 (AKZO NOBEL NV et al.) 04 January 2007 (04.01.2007) page 1, line 28 - page 2, line 29; page 3, line 33 - page 4, line 34; example 3 | |
| E | WO 2009126106 A1 (STFI PACKFORSK AB et al.) 15 October 2009 (15.10.2009) the whole document | 1-5, 7-18, 20, 21 |

 Further documents are listed in the continuation of Box C. See patent family annex.

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| | |
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| Date of the actual completion of the international search 17 June 2010 (17.06.2010) | Date of mailing of the international search report 22 June 2010 (22.06.2010) |
| Name and mailing address of the ISA/FI National Board of Patents and Registration of Finland P.O. Box 1160, FI-00101 HELSINKI, Finland Facsimile No. +358 9 6939 5328 | Authorized officer Heimo Koskinen Telephone No. +358 9 6939 500 |

INTERNATIONAL SEARCH REPORT

| |
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| International application No. PCT/FI2010/050096 |
|---|

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PCT/FI2010/050096

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(54) Title: STABILIZED MICROFIBRILLAR CELLULOSE

(57) Abstract: A derivatized microfibrillar cellulose, derivatized to contain a substituent that provides cationic charge. A method for producing a derivatized microfibrillar cellulose to include a substituent that provides cationic charge, which may include derivatizing a microfibrillar cellulose to obtain a derivatized microfibrillar cellulose, microfibrillizing a derivatized non-microfibrillar cellulose to produce a derivatized microfibrillar cellulose, or microfibrillizing and derivatizing a non-microfibrillar cellulose substantially simultaneously. A method of modifying the rheological properties of a composition of matter using derivatized microfibrillar cellulose. Methods of improving coatings, paper manufacture, and the stability of emulsions, dispersions, and foams using a derivatized microfibrillar cellulose. Compositions that include derivatized microfibrillar cellulose, including paper compositions, comestible compositions, non-comestible spreadable compositions, and emulsions, dispersion, and foams.

DescriptionSTABILIZED MICROFIBRILLAR CELLULOSEFIELD OF THE INVENTION

5 The present invention relates to stabilized microfibrillar cellulose. More specifically, the present invention relates to microfibrillar cellulose that is electrostatically stabilized by cationic groups.

BACKGROUND OF THE INVENTION

10 Polysaccharides are often found in nature in forms having fibrous morphology. Polysaccharides which are not found in nature in fibrous form can often be transformed into fibrous morphologies using fiber-spinning techniques. Whether the fibrous morphology is of natural or artificial origin, the polysaccharide will often be present in such a form that the fibers can be reduced to fibrillar and microfibrillar sub-morphologies through the application of energy.

15 Fibrillar and microfibrillar cellulose obtained in this manner have been considered for use in applications, including use as additives to aqueous-based systems in order to affect rheological properties, such as viscosity. The use level of these materials in aqueous systems is often on the order of about 2% by weight, below which these materials have a tendency to poorly occupy volume,

20 and to exhibit gross inhomogeneities in distribution.

Microfibrillated cellulose and its manufacture are discussed in U.S. Patent Nos. 4,500,546; 4,487,634; 4,483,743; 4,481,077; 4,481,076; 4,464,287; 4,452,722; 4,452,721; 4,378,381; 4,374,702; and 4,341,807, the disclosures of which are hereby incorporated by reference thereto. These documents, in part, purport to describe microfibrillated cellulose in stable, homogenous suspensions, characterized as useful in end use products including foods, cosmetics, pharmaceuticals, paints, and drilling muds.

Cellulose nanofibrils are characterized in WO 98/02486 (PCT/FR97/01290), WO 98/02487 (PCT/FR97/01291), and WO 98/02499 (PCT/FR97/01297), the disclosures of which are hereby incorporated by

reference. Nanofibrils are characterized as having diameters in the range of about 2 to about 10 nanometers.

EP 845495 discusses cationic cellulose particulate which is characterized as insoluble, positively charged, and used in water treatment, specifically to treat water in a paper manufacturing plant. In papermaking this cationic particulate is said to remove anionic trash from the water. The particles are obtained by milling, which is stated to reduce particle size uniformly such that particles are typically round as described by a length/diameter ratio of approximately 1.

Particle size is stated to be 0.001 mm (i.e., 1 μm), and preferably 0.01 mm (10 μm).

EP 859011 ("EP '011") is directed to a process for obtaining cationic cellulose microfibrils or their soluble derivatives. The process is described as including making a cationic cellulose derivative and processing the derivative through a high-pressure homogenizer to form transparent gels. The product can be dehydrated and rehydrated. Viscosity measurements are reported on the product at a concentration of 2% in water. EP '011 indicates that the degree of substitution ("DS") of the cellulose can range from 0.1 to 0.7, with a DS of between 0.2 and 0.7, 0.3 and 0.6, and 0.5 and 0.6 characterized as representing increasing orders of preference. The examples show cellulose with a DS ranging from a low of 0.24 up to 0.72. Gelling is reported to occur above a microfibril concentration of 10 g/L, or above 1%, in water. EP '011 defines gelling as occurring when $G' > G''$, where G' is the dynamic storage modulus and G'' is the dynamic loss modulus.

Microfibrillated chitosan is reported to form uniplanar, oriented sheets upon drying by H. Yokata, J. Polymer Sci., Part C: Polymer Letters, **24**:423-425 (1986). This article mentions that at a level of 4% chitosan in water, a gel is formed having a viscosity of 26,600 cps (Brookfield, 20° C, rotor #7, 10rpm). The microfibrillated chitosan is made by homogenization of commercial chitosan flakes in a Gaulin homogenizer. The commercial chitosan is deacetylated using sodium hydroxide.

JP 59 [1984]-84938 discusses a method for producing a chitosan suspension. Commercial chitosan separated and purified from crabs and lobsters is pulverized to pieces having maximum length of about 1-2 mm. The pieces are then suspended in water at up to 15% chitosan, and are run in multiple passes

5 through a high-pressure homogenizer at between 3,000 and 8,000 psi.

It would be desirable to obtain microfibrillar cellulose capable of forming a gel at concentrations of 1% or less, thereby providing economy and ease of formulation, while still providing necessary rheological behavior and homogeneity of distribution.

10 In addition, there is a continuing need in industry to improve the stability of commercial emulsions, such as paper sizing emulsions. At present, one method for stabilizing such emulsions is the addition of charged materials, such as cationic starches, which may be added in amounts equal to 10-20% by weight of the size component. Interaction with anionic components, such as sulfonates, can

15 also improve stability. However, emulsion failure still takes place in such emulsions, either through density-driven separation, also referred to as creaming, or through gellation. It would accordingly be desirable to develop a material that could be added to emulsions to provide long-term stability.

SUMMARY OF THE INVENTION

20 The present invention is directed to a derivatized microfibrillar cellulose which is derivatized to include a substituent that provides cationic charge and is capable of forming a gel in water at a concentration of less than 1%. The cellulose used to prepare the derivatized microfibrillar cellulose may be obtained from any suitable source, including but not limited to chemical pulps, mechanical

25 pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.

Preferably the cellulose is obtained from purified, optionally bleached wood

pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; or vegetables.

The substituent which provides cationic charge to the derivatized microfibrillar cellulose may be, or include, an amine. A quaternary amine is
5 particularly preferred.

The derivatized microfibrillar cellulose may form a gel in water throughout the concentration range of between about 0.01 % and about 100%, or throughout the concentration range of between about 0.01 % and about 50 %, in water.

Moreover, the derivatized microfibrillar cellulose may form a gel at a
10 concentration of less than about 1% in water, and preferably forms a gel at least one point in the concentration range of from about 0.05 % up to about 0.99% in water.

The derivatized microfibrillar cellulose of the present invention may include a solvent in which the derivatized microfibrillar cellulose is substantially
15 insoluble. Suitable solvents include water, alcohol, or oil, with water being preferred.

The derivatized microfibrillar cellulose may have a degree of substitution of less than about 0.5, or of less than about 0.35, or of less than about 0.2, or of less than about 0.18, or of less than about 1.15. Preferably the degree of substitution
20 is between about 0.02 and about 0.5, and more preferably between about 0.05 and about 0.2.

A particularly preferred embodiment of the present invention is microfibrillar 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose having a degree of substitution of less than about 2.0, preferably of less than
25 about 0.35, more preferably of between about 0.02 and about 0.20, and most preferably between about 0.1 and about 0.2.

The derivatized microfibrillar cellulose may form part of a comestible composition of matter, including but not limited to a low fat, reduced fat, or fat-free mayonnaise, or a salad dressing. When it forms part of a comestible
30 composition of matter, the derivatized microfibrillar cellulose may include a

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Description

STABILIZED MICROFIBRILLAR CELLULOSE

FIELD OF THE INVENTION

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15 Fibrillar and microfibrillar cellulose obtained in this manner have been considered for use in applications, including use as additives to aqueous-based systems in order to affect rheological properties, such as viscosity. The use level of these materials in aqueous systems is often on the order of about 2% by weight, below which these materials have a tendency to poorly occupy volume,

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25 purport to describe microfibrillated cellulose in stable, homogenous suspensions, characterized as useful in end use products including foods, cosmetics, pharmaceuticals, paints, and drilling muds.

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pharmaceutically active ingredient, and may at least partially provide for the controlled, sustained, or delayed release of the pharmaceutically active ingredient.

Alternatively, the derivatized microfibrillar cellulose may form part of a

5 non-comestible composition of matter, such as, by way of non-limiting example, a wound care product. Suitable wound care products include, without limitation, wound dressings and ostomy rings. In another embodiment, the non-comestible composition of matter may be a skin care lotion or cream, a sunscreen lotion or cream, or an oral care composition, such as a toothpaste.

10 The non-comestible composition of matter may further be or include an agricultural composition, such as a fertilizer, herbicide, fungicide, or pesticide. The derivatized microfibrillar cellulose may provide at least partially for the controlled, sustained, or delayed release of the fertilizer, herbicide, or pesticide.

15 In an alternative embodiment, the non-comestible composition of matter may be a drilling fluid.

In another embodiment, the present invention is directed to a paper composition which contains the derivatized microfibrillar cellulose described herein.

20 The present invention further includes a method for producing the derivatized microfibrillar cellulose described herein, which involves at least one of the following steps:

- (a) a derivatizing step of treating a microfibrillar cellulose to obtain a derivatized microfibrillar cellulose;
- (b) a microfibrillizing step of treating a derivatized non-microfibrillar cellulose to produce a derivatized microfibrillar cellulose; or,
- (c) microfibrillizing and derivatizing a non-microfibrillar cellulose substantially simultaneously.

25 In the above method, the derivatized microfibrillar cellulose is derivatized to include a substituent that contains cationic charge, as for example by the

presence of amine groups. Preferably the derivatizing step involves derivatizing the cellulose with a quaternary amine reagent, such that the derivatized microfibrillar cellulose includes quaternary amine functionalized cellulose.

The derivatizing step of the above method may include contacting a non-
5 microfibrillar cellulose with a swelling agent. This contact may occur under alkaline conditions, and the swelling agent may be an anionic reagent. Moreover, the alkaline conditions may include contacting the cellulose with the anionic reagent in the presence of an alkaline reagent which is at least one of sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an
10 alkali silicate, an alkali aluminate, an alkali carbonate, an amine, ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof. The derivatizing step may further take place at high solids.

In a preferred method, the derivatized microfibrillar cellulose is obtained by:

- 15 (a) derivatizing cellulose with 3-chloro-2-hydroxypropyl trimethylammonium chloride under alkaline conditions to produce 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose;
- (b) suspending the 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose in water to form a suspension; and
- 20 (c) homogenizing the suspension to produce microfibrillated 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose.

The microfibrillizing step of the above method may include applying energy to the cellulose under conditions sufficient to produce microfibrillar cellulose, and the cellulose may be treated with enzyme prior to microfibrillizing.

25 Any suitable approach may be used to apply sufficient energy to the cellulose to obtain microfibrillar cellulose, including, without limitation, one or more of homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, and milling. Use of a homogenizer is preferred, and preferred homogenization
30 conditions include passing the non-microfibrillar cellulose through a pressure

differential of at least about 3,000 psi, and more preferably passing the non-microfibrillar cellulose through the homogenizer at least three times.

Preferably, the derivatized microfibrillar cellulose obtained by the above methods forms a gel throughout a concentration range of from about 0.01 % to 5 about 100% in water, and more preferably throughout a concentration range of between about 0.01 % and about 50 % in water. Alternatively, the derivatized microfibrillar cellulose should form a gel at at least one point in the concentration range of from about 0.05 % to about 0.99% in water. In a particularly preferred embodiment, the derivatized microfibrillar cellulose forms a gel at a 10 concentration of about 0.9% in water.

The present invention extends to derivatized microfibrillar cellulose produced by the above-described method, including it's the described variations of the method.

In yet another embodiment, the present invention includes a method of 15 modifying the rheological properties of a composition of matter by incorporating the derivatized microfibrillar cellulose into the composition of matter, which may be a liquid, such as water. The derivatized microfibrillar cellulose may be used in an amount which is effective to provide scale control and/or corrosion control.

Alternatively, the derivatized microfibrillar cellulose may be used to modify one 20 or more of the viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention of the composition of matter. Compositions whose rheological properties may be modified in this manner include foods, pharmaceuticals, neutraceuticals, personal care products, fibers, papers, paints, coatings, and construction compositions. More 25 specifically, possible compositions include oral care products; creams or lotions for epidermal application, including moisturizing, night, anti-age, or sunscreen creams or lotions; food spreads, including reduced fat, low fat, or fat free food spreads (for example, mayonnaise); and drilling fluids.

Alternatively, the derivatized microfibrillar cellulose may be incorporated 30 into a coating composition in order to improve its physical and/or mechanical

properties. Those properties may include one or more of film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

The derivatized microfibrillar cellulose may further be incorporated into the manufacture of paper and paper products in order to improve at least one of sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, absorbency, film formation, membrane formation, and polyelectrolyte complexation during manufacture. Microfibrillated quaternary amine functionalized cellulose is particularly preferred for use in this method.

In one embodiment of this method, the microfibrillated quaternary amine functionalized cellulose may be used to increase the rate of drainage and/or dewatering during paper manufacture. In another embodiment, the microfibrillated quaternary amine functionalized cellulose may be used for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture. Representative dispersed particles which may be retained in this manner include pulp fines, fillers, sizing agents, pigments, clays, detrimental organic particulate materials, detrimental inorganic particulate materials, and combinations thereof. In a yet further embodiment, the microfibrillated quaternary amine functionalized cellulose may be used in a papermaking machine to improve the uniformity of formation of a sheet of paper during its manufacture. Additionally, the microfibrillated quaternary amine functionalized cellulose may be used in a papermaking machine to improve the strength of a sheet of paper produced on a paper machine.

In each of the embodiments described in the above paragraph, the microfibrillated quaternary amine functionalized cellulose may be used in the presence of one or more of the following: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.

The derivatized microfibrillar cellulose may further be used in a method for improving the stability of an emulsion, dispersion, or foam system, by including the derivatized microfibrillar cellulose in the system. Where the system being treated is an emulsion, the emulsion may be produced by processing of an emulsion formulation, in which case the derivatized microfibrillar cellulose may be added to the emulsion formulation prior to completion of processing of the emulsion formulation. In one variation, a non-microfibrillated derivatized cellulose is added to the emulsion formulation prior to completion of processing, and the emulsion formulation is then processed under conditions sufficient to 5 microfibrillate the non-microfibrillated derivatized cellulose. In another variation, a microfibrillated non-derivatized cellulose is added to the emulsion formulation prior to completion of processing, and the emulsion formulation is then processed under conditions sufficient to derivatize the microfibrillated non-derivatized cellulose. In yet a third variation, a non-microfibrillated, non-10 derivatized cellulose is added to the emulsion formulation prior to completion of processing, and the emulsion formulation is further processed under conditions sufficient to both microfibrillate and derivatize the non-microfibrillated, non-derivatized cellulose.

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Emulsion systems which may be treated in this manner include water-in-oil 20 and oil-in-water emulsions. The present invention includes the system produced by the above method.

In a yet further embodiment, the present invention extends to a system comprising an emulsion, dispersion, or foam containing a the derivatized microfibrillar cellulose.

25 In another embodiment, the present invention includes a polyelectrolyte complex containing the derivatized microfibrillar cellulose.

The derivatized microfibrillar cellulose of the present invention may also be used in a method for treating wastewater, which includes the step of adding, to the wastewater, a amount of the derivatized microfibrillar cellulose sufficient to 30 treat the wastewater. Materials being treated by this method in the wastewater

may include, by way of non-limiting example only, anionic contaminants and color bodies.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the dynamic mechanical spectra of Sample 1 from Table 4.

5 Fig. 2 shows the dynamic mechanical spectra of Sample 2 from Table 4.

Fig. 3 shows the dynamic mechanical spectra of Sample 3 from Table 4.

Fig. 4 shows the dynamic mechanical spectra of Sample 4 from Table 4.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises stabilized microfibrillar cellulose. Sources

10 of cellulose for use in this invention include the following: (a) wood fibers, such as from chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint; (b) seed fibers, such as from cotton; (c) seed hull fiber, such as from soybean hulls, pea hulls, corn hulls;

(d) bast fibers, such as from flax, hemp, jute, ramie, kenaf; (e) leaf fibers, such as

15 from manila hemp, sisal hemp; (f) stalk or straw fibers, such as from bagasse,

corn, wheat; (g) grass fibers, such as from bamboo; (h) cellulose fibers from

algae, such as velonia; (i) bacteria or fungi; and (j) parenchymal cells, such as

from vegetables and fruits, and in particular sugar beets, and citrus fruits such as

lemons, limes, oranges, grapefruits. Microcrystalline forms of these cellulose

20 materials may also be used. The cellulose may be used as is, or spinning may be used to generate or improve fibrous structure. Preferred cellulose sources are (1) purified, optionally bleached, wood pulps produced from sulfite, kraft (sulfate), or prehydrolyzed kraft pulping processes; (2) purified cotton linters; and, (3)

fruits and vegetables, in particular sugar beets and citrus fruits. The source of the

25 cellulose is not limiting, and any source may be used, including synthetic

cellulose or cellulose analogs.

Cellulose is found in nature in several hierarchical levels of organization and orientation. Cellulose fibers comprise a layered secondary wall structure within which macrofibrils are arranged. Macrofibrils comprise multiple 30 microfibrils which further comprise cellulose molecules arranged in crystalline

and amorphous regions. Cellulose microfibrils range in diameter from about 5 to about 100 nanometers for different species of plant, and are most typically in the range of from about 25 to about 35 nanometers in diameter. The microfibrils are present in bundles which run in parallel within a matrix of amorphous
5 hemicelluloses (specifically xyloglucans), pectinic polysaccharides, lignins, and hydroxyproline rich glycoproteins (includes extensin). Microfibrils are spaced approximately 3-4 nm apart with the space occupied by the matrix compounds listed above. The specific arrangement and location of the matrix materials and how they interact with the cellulose microfibrils is not yet fully known. Further
10 background on the structure, functions, and biogenesis of native cellulose may be found in Haigler, C.H., Cellular Chemistry and Its Applications, Nevell, pp. 30-83 (1985), the entirety of which is hereby incorporated by reference.

For purposes of the present invention microfibrils refer to small diameter, high length-to-diameter ratio substructures which are comparable in dimensions
15 to those of cellulose microfibrils occurring in nature. By way of non-limiting example, cellulose microfibrils may have diameters in the range of about 5 to about 100 nanometers, combined with lengths providing high aspect ratios, such as in excess of 100, in excess of 500, or in excess of 1,000. While the present specification and claims refer to microfibrils and microfibrillation, the scope of
20 the present invention also includes nanofibrils, and the rheology modification, stabilization, and other properties that may be obtained with microfibrils by practicing the present invention may also be obtained using nanofibrils, either alone or in combination with microfibrils.

The derivatized microfibrillar cellulose of the present invention is
25 characterized by being in microfibrillar form, and by the presence of cationic substituents that provide electrostatic functionality. The amount of substituent present may be quantified by the degree of substitution, or DS. The degree of substitution, which will vary with the molecular weight of the cellulose, is the average number of substituted hydroxyl groups per anhydroglucose unit, while
30 the molar substitution is the average number of substituent groups added per

anhydroglucose unit. The DS determines the solubility of the derivatized cellulose, and may be readily adjusted to obtain a derivatized cellulose that is substantially insoluble in the environment of use, whether aqueous or non-aqueous. While the environment of use will frequently be aqueous, the 5 derivatized microfibrillar cellulose of the present invention has utility in applications having other solvents or liquid carriers, such as paints, coating, lacquers, oil-rich foods, inks (including but not limited to ink-jet inks), and water-in-oil emulsions.

Any suitable method may be used to obtain the derivatized microfibrillar 10 cellulose. In particular, the steps of microfibrillation and derivatization to impart electrostatic functionality to the cellulose may be carried out separately or combined to arrive at the end result. Therefore, a non-microfibrillar cellulose starting material may be derivatized with cationic groups and then microfibrillated, or may first be microfibrillated and then derivatized. 15 Alternatively, if the starting material is microfibrillar cellulose, only the derivatizing step would be necessary, whereas if the starting material is a cellulose that has already been properly derivatized with cationic groups, only the microfibrillation step is required.

The degree of substitution of the cellulose should be sufficiently low so that 20 the derivatized microfibrillar cellulose will be substantially insoluble in the solvent or carrier that is present in the intended environment of use. In many applications the solvent or carrier will be water, and in such applications the degree of substitution should be such that the derivatized microfibrillar cellulose is substantially insoluble in water. However, in other applications a polar solvent 25 or carrier (such as an alcohol) may be used having different solubility characteristics, or a non-polar solvent or carrier (such as an oil) may be used, and in such cases the degree of substitution should be adjusted to obtain a derivatized microfibrillar cellulose that is substantially insoluble in the solvent or carrier used in the application of interest, which, for purposes of convenience, will 30 hereafter be referred to as the "solvent of use". Functionally, the derivatized

microfibrillar cellulose should be sufficiently insoluble in the environment of use to provide the desired properties in the intended application.

The presence of substantially insoluble material may be confirmed by observation of a 1-5% suspension of the material in question in the solvent or carrier of use under a light microscope at sufficient magnification to see insoluble material. A size determination may be made by preparing a suspension of the material under consideration at approximately 0.1-0.01% in a liquid non-solvent which is effective in dispersing microfibrils. This suspension is then dried on a transmission electron microscope (TEM) grid; the sample is coated to protect it from electron beam damage, and examined at sufficient magnification and focus to observe structure in the 1-1000 nanometer range. If microfibrillar elements are present they can be detected under these conditions, and the combination of insolubility under the light microscope and microfibrillar structure under the TEM will indicate the presence of substantially insoluble microfibrillar material.

For purposes of simplicity, unless specifically indicated otherwise the term "substituents" shall be used herein to mean chemical species that provide electrostatic functionality to the cellulose through cationic charge. In addition, "electrostatic" means cationic charge. "Derivatization" refers not only to chemical reactions resulting in covalent bonds, but to any process whereby the substituents become sufficiently associated with the cellulose to provide the rheological and other benefits of the present invention, and may include, for example, adsorption. However, "derivatized" does not include the naturally-occurring, de minimis presence of groups that would only provide the electrostatic functionality required by the present invention at concentrations higher than those found in nature.

The sequence of steps used to arrive at the derivatized microfibrillar cellulose of the present invention is not critical. Therefore, the starting material used to make the derivatized microfibrillar cellulose may be in microfibrillar or non-microfibrillar form. Similarly, the starting material may already be derivatized with electrostatic substituents, or not. If the starting material is non-

microfibrillar, substituents may be placed on the cellulose followed by microfibrillation, or the microfibrillation may be carried out first, followed by the placement of the substituents onto the resulting microfibrils. It is also acceptable to process cellulose into fibrils, place the substituents on the fibrils, and then 5 further process the fibrils into microfibrils. Similarly, any non-microfibrillar form of cellulose which already contains such substituents may be processed into microfibrillar form. Moreover, derivatization and microfibrillation may be carried out simultaneously.

It will be understood that most, if not all, cellulose will contain some 10 quantity of both microfibrillar and non-microfibrillar structure both before and after processing, and that the ratio between the two structures may range from cellulose that is substantially completely microfibrillar, to cellulose that is substantially completely non-microfibrillar. As used herein, the terms "microfibrillar", "microfibrillated", and the like include celluloses that are 15 substantially completely microfibrillated, and those which may be substantially microfibrillated while containing minor but significant amounts of non-microfibrillar structure, provided the cellulose is sufficiently microfibrillated to confer the benefits afforded by the present invention.

Processes which minimize the energy needed to produce microfibrils from 20 non-microfibrillar starting material, and/or which reduce the amount of water extracted during the process or at its end, are preferred. In this regard, it should be noted that while the derivatized microfibrillar cellulose of the present invention can be made by derivatizing a microfibrillated cellulose, the microfibrillation process generally requires less energy, and/or is more efficient, 25 if the cellulose has already been derivatized. Without being bound by theory, this may be because the presence of electrostatic functionalities on the cellulose 'loosens' the structure of fibril bundles.

The ability to use less energy not only offers cost savings, but results in less breakage of the cellulose microfibrils. Therefore, microfibrillating a cellulose 30 that has already been derivatized may result in a derivatized microfibrillar

cellulose with relatively longer microfibrils as compared to effecting derivatization after microfibrillation. This is particularly significant because the energy required for microfibrillation can be significantly reduced by amounts of derivatization which are below the level that would render the resulting

5 derivatized microfibrillar cellulose freely soluble in water. For example, derivatization of cellulose resulting in a DS on the order of 0.1 or 0.2 will 'loosen' the fibril bundles enough to permit microfibrillation using conventional shearing devices such as a homogenizer, impingement mixer, or ultrasonicator. These low DS cellulose microfibrils have diameters on the order of 50 nanometers

10 combined with lengths of up to 500 microns, resulting in aspect ratios in excess of 1,000. While the low DS allows microfibrillation, it is too low to allow the resulting material to be fully soluble in the solvent or carrier of use at the concentrations of interest. Without being bound by theory, the presence of insoluble regions in the fibers may explain the data showing maximum gel

15 formation at low DS's. These gels may be strengthened by weak association of the more hydrophobic unsubstituted regions.

The stabilization or derivatization is accomplished by the generation or placement of substituents onto the fibril and/or microfibril. It appears that the substituents become associated predominantly with the surface regions of the

20 fibrils or microfibrils. Regardless of the precise mechanism, in functional terms microfibril-microfibril contact is inhibited by electrostatic mechanisms or forces. The presence of the substituents also causes the microfibrils to occupy more volume than when they are not derivatized, possibly due to inhibition of contact along at least part of the length of the microfibrils. Rheological performance of

25 the resulting derivatized microfibrillar cellulose is enhanced at low concentration since volume is better occupied and the materials are distributed more homogeneously.

Without being bound by theory, the surfaces of the derivatized microfibrils appear to have some areas free of the substituents such that some limited interaction between microfibrils still takes place. Limited interaction may even

be necessary to facilitate network formation, and may be a cause of the rheological attributes of interest such as yield stress, shear reversible gelation, and insensitivity of the modulus to temperature. It also appears that the length/diameter ratio, or aspect ratio, of the fibrils and microfibrils also
5 contributes to the performance of the materials of the present invention.

Any suitable process may be used to generate or place the substituents on the cellulose. For convenience, the possible processes will generally be referred to collectively as "derivatization" herein; however, within the context of this invention, derivatization is used to mean any process which results in a cellulose
10 (including fibrillar and microfibrillar cellulose) having the substituents sufficiently associated with the cellulose to provide the desired benefit(s), and includes not only chemical reactions resulting in covalent bonding, but also physical adsorption. In addition, the present application will refer both to "derivatization" and to "stabilization". Chemically, both terms refer to the same
15 type of process, namely, the placement or generation of substituents on the cellulosic substrate. Functionally, "derivatization" is generally the broader term, as "stabilization" implies a functionality which is usually observed primarily or exclusively when the cellulose is in microfibrillar form.

Possible derivatization processes include any synthetic method(s) which
20 may be used to associate the substituents with the cellulose. More generally, the stabilization or derivatization step may use any process or combination of processes which promote or cause the placement or generation of the substituents. For example, the conditions for treating non-microfibrillar cellulose should generally include both alkalinity and swelling of the cellulose, in order to
25 make the surface of the fibrils more accessible to the placement or generation of the substituents. Alkalinity and swelling may be provided by separate agents, or the same agent may both provide alkalinity and cause swelling of the cellulose. In particular, alkaline agents often serve multiple purposes, in that they may catalyze the reaction between the cellulose and the substituent, optionally de-

protonate the derivative, and swell open the cellulose structure to allow access of the reagents to carry out the derivatization.

Specific chemical methods which may be used to achieve the present invention include but are not limited to generation of cationic groups, such as quaternary amine and/or amine, on or near the surface of the particulate cellulose. Alkaline conditions are preferably obtained by using sodium hydroxide. Any material that functions as a swelling agent for the cellulose may be used, and alternative alkaline agents include alkali metal or alkaline earth metal oxides or hydroxides; alkali silicates; alkali aluminates; alkali carbonates; amines, including aliphatic hydrocarbon amines, especially tertiary amines; ammonium hydroxide; tetramethyl ammonium hydroxide; lithium chloride; N-methyl morpholine N-oxide; and the like. In addition to catalytic amounts of alkaline agent, swelling agents may be added to increase access for derivatization. Interfibrillar and intercrystalline swelling agents are preferred, particularly swelling agents used at levels which give interfibrillar swelling, such as sodium hydroxide at an appropriately low concentration.

These derivatization reactions, if carried out on the original fibrous cellulose structure, may require specific conditions to maximize the efficiency of location of the derivatization onto the surface of the cellulose. For example, in the case of cellulose from wood pulp the concentration of the swelling agent used appears to have an effect on the performance of the final cellulose. In particular, in using sodium hydroxide it has been determined that the level of the sodium hydroxide can have a significant effect on the rheological performance.

It is preferred that derivatization of these fibrous celluloses be performed in a manner which limits the formation of microfibrils which are soluble in the intended end use composition, as these may not contribute significantly to the desired rheological performance. This typically limits the degree of derivatization which can be made where derivatization at higher levels would make the cellulose soluble in the end use composition. Specific limits may be readily determined based on the application in question, but as a matter of

general guidance it is preferred that the degree of substitution (DS) be below about 0.5, or below about 0.35, or below about 0.2, or below about 0.18, or below about 0.15.

The derivatization may be carried out in any suitable manner, including but
5 not limited to suspension in water; in organic solvent, either alone or in mixtures
with water; in solution; and in high solids, either with water alone or with water
and a minor amount of organic solvent. (For purposes of the present disclosure,
"high solids" refers to a polysaccharide content of greater than about 25%).

Optional derivatizations or functionalities which may also be placed on the
10 cellulose include but are not limited to short chain aliphatic and other
hydrophobic-type substitutions; oligomeric and polymeric substitutions;
uncharged substitutions, as for example short chain ethylene and propylene
glycols; other associative-type functionality; surfactant-like functionality;
methyl; ethyl; propyl; and combinations of these. These substitutions are
15 optional in that they may not be intended for stabilization of the cellulose, and
will instead provide additional functionality such as surface activity,
emulsification power, adsorption characteristics, and the like.

The method for processing a non-microfibrillar form of cellulose into the
microfibrillar form may be carried out before, during, or after the derivatization
20 reaction. The preferred method involves the use of a homogenizer on a dilute
suspension of the non-microfibrillar cellulose in an aqueous medium. The
aqueous medium optionally may have additives such as swelling agents, in
particular interfibrillar and/or intercrystalline swelling agents, for example
sodium hydroxide, to aid in improving the ease of microfibril generation. A
25 more preferred method of microfibrillation involves the use of mechanical energy
on an aqueous suspension of derivatized cellulose which has not been dried.
Other microfibrillation processes include, by way of non-limiting example, use of
an impingement mixer; heat; steam explosion; pressurization-depressurization
cycle; freeze-thaw cycle; impact; grinding (such as a disc grinder); pumping;
30 mixing; ultrasound; microwave explosion; and milling. Combinations of these

may also be used, such as milling followed by homogenization. Essentially any method of reducing particle size may be used, but methods for reducing particle size while preserving a high aspect ratio in the cellulose are preferred. As described previously, the degree of substitution of the cellulose also affects the 5 ease of processing the cellulose to microfibrillar form.

The process to generate the particulate may either be run by the consumer in the final application such that the particulate is generated in situ, or be run as described above in aqueous media, the material dehydrated, and the resulting particulate dried. The dried particulate of this invention, hereafter referred to as 10 the ready-to-gel or RTG form, can be rehydrated readily in polar solvents to obtain the desired rheological attributes. Dehydration can be accomplished by displacing water with less polar solvents and drying.

In terms of general properties, applications where the derivatized 15 microfibrillar celluloses of the present invention have particular utility include those where the desired rheological attributes include at least one of yield stress, shear reversible gelation, and a modulus which is insensitive to temperature. The ability to provide the rheological attributes described herein also makes it possible to provide stabilization of mixtures of liquids and solids having different 20 densities; gel-like properties; pumpable gels; stabilization at elevated temperatures; and, control of hydration and diffusion.

In terms of more specific applications or fields of use, the utility of the 25 present derivatized microfibrillar cellulose includes, without limitation, foods, personal care products, household products, pharmaceuticals, neutraceuticals, paper manufacture and treatment, coating compositions, water and wastewater treatment, drilling fluids, agriculture, construction, and spill control and/or recovery. Use in food applications is also possible, subject to satisfactory resolution of any concern regarding introduction of cationic materials into substances intended for consumption.

In food applications, the derivatized microfibrillar celluloses of the present 30 invention may be useful as rheology modifiers; as stabilizers, such as by

inhibiting creaming or settling in suspensions; and as non-digestible dietary fiber.

They may also be used to control ice crystal growth during, for example, ice cream manufacture and storage.

In personal care products, the derivatized microfibrillar cellulose may be
5 used to stabilize emulsions, dispersions, suspensions, and foams, and may find
use in creams, lotions, gels, and pastes, including those intended for epidermal
application (it should be noted that the derivatized microfibrillar cellulose of the
present invention has substantivity to biological surfaces, including but not
limited to skin, hair, and nails). Representative but not exhaustive examples
10 include sunscreens; moisturizing or anti-aging creams and lotions; cleaning soaps
or gels; antiperspirants and deodorants, including those in stick, pump spray,
aerosol, and roll-on form; fragrance releasing gels; lipsticks, lip glosses, and
liquid makeup products; oral care products, including toothpastes, tooth polishing
and whitening agents, and denture care products such as cleaners and adhesives,
15 and further including use in sorbitol, sorbitol-water mixtures, and glycerol-water
mixtures; products where controlled, sustained, or delayed release of an
ingredient would be desirable; wound care products, such as ointments (including
anesthetic, antiseptic, and antibiotic ointments), dressings, and products such as
ostomy rings where good liquid retention is desirable; and absorbent products,
20 such as diapers. The present invention may have particular utility, not only in
personal care products but in other applications, with products dispersed by a
pumping action. The shear-reversible gelation exhibited by the derivatized
microfibrillar cellulose is well suited for pump dispensing, and may be
advantageously combined with its ability to stabilize emulsions, dispersions, and
25 foams to improve the uniform delivery of product.

In the area of household products, the rheological properties of the present
derivatized microfibrillar celluloses, and their ability to stabilize emulsions,
dispersions, and foams, provide utility in areas such as detergents, shampoos,
cleaners, and air fresheners. Specific examples include, without limitation,
30 laundry products (including detergents, pre-spotting cleaners, and fabric

treatment compositions, such as softeners); rug and upholstery shampoos; toilet bowl cleaners (particularly those dispensed in liquid or gel form); air fresheners; and general purpose cleaning agents, including liquids, gels, pastes, and foams used in cleaning and/or disinfecting household surfaces.

5 In pharmaceutical applications, the derivatized microfibrillar cellulose may have utility in controlled, sustained, or delayed release formulations (including epidermal patches used for slow and/or prolonged release of one or more active ingredients); as disintegrants; as dietary fiber; in wound care, particularly in applications (such as ostomy rings) where liquid-holding ability is important; and
10 as rheology modifiers.

In the area of paper manufacture and treatment, the derivatized microfibrillar cellulose of the present invention has utility in emulsion modification and/or stabilization; sizing; retention; clarification; absorbence; drainage; formation (such as by functioning as a flocculation aid); deposit or
15 scale control (by inhibiting the formation and/or growth of inorganic deposits); water and wastewater treatment; dewatering; film and membrane formation; polyelectrolyte cross-linking; removal of detrimental organic and/or inorganic materials; in paper coatings; and in improving properties such as stiffness, wet strength, absorbancy, softness, toughness, tear resistance, and fold resistance.

20 In the context of paper manufacture, scale control refers to the prevention of calcium carbonate and calcium oxalate deposits forming during the pulping process. Scale control can be achieved by dispersion of salt crystals in the medium to prevent growth and deposition, inhibition of nucleation, or modification of the crystal growth mechanism to prevent the formation of crystal
25 forms that will lead to deposits. The use of derivatized microfibrillar cellulose having micron and smaller particle size, stabilized with appropriate functional groups, would serve to control scale deposit because such microcarriers inhibit the crystal growth which leads to deposition. Moreover, cellulosic materials would be easier to recover from the pulping process due to their organic nature.
30 Preferred functional groups would include amines. Alternative functional groups

and appropriate use levels may be readily determined by those of ordinary skill in the art, based on the particular environment of use.

The derivatized microfibrillar cellulose may also be used in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture; to retain organic and/or inorganic dispersed particles (such as pulp fines, fillers, sizing agents, pigments, and/or clays); to retain detrimental organic and inorganic particulate materials; to improve the uniformity of formation of a sheet of paper; and to improve the strength of a sheet of paper. With particular regard to drainage, drainage aids are additives that increase the rate at which water is removed from a paper slurry on a paper machine. These additives increase machine capacity, and hence profitability, by allowing faster sheet formation. Charged microfibrillar cellulosic derivatives are capable of greatly increasing drainage, either alone or in combination with other charged polymers.

15 The derivatized microfibrillar cellulose of the present invention may also be used in coated papers, where cellulose derivatives may be used to control the rheology of the color coating and to provide water retention, thereby controlling the amount of liquid that permeates into the base sheet.

20 In coating compositions, such as paints and inks, the derivatized microfibrillar cellulose can provide rheology modification, improving properties such as spatter, leveling, sag resistance, flooding, and floating, and may have particular utility in gel paints. It may also improve pigment dispersion and/or stabilization, and function as charge control or flow control agents, including in inks, such as ink jet inks.

25 In the area of water treatment, the derivatized microfibrillar cellulose of the present invention can provide scale control, that is, inhibiting the formation and/or growth of inorganic deposits in aqueous systems; clarification; flocculation; sedimentation; coagulation; charge delivery; and softening.

In drilling fluids, the present derivatized microfibrillar cellulose can provide rheology modification, reduce or prevent fluid loss, and improve secondary oil recovery.

5 In agricultural applications, the derivatized microfibrillar cellulose of the present invention can be used in soil treatment, and may provide moisture retention, erosion resistance, frost resistance, and controlled, sustained, or delayed release of agricultural materials such as fertilizers, pesticides, fungicides, and herbicides. It may also be used for crop protection, such as to minimize or prevent frost damage.

10 In construction, derivatized microfibrillar cellulose can be used in dry wall muds, caulk, water-soluble adhesives, and board manufacture.

15 In other areas, derivatized microfibrillar cellulose can be used for control and cleanup of liquid spills; as absorbents for oil; as stabilizers for emulsions, dispersions, and foams (including but not limited to oil-in-water and water-in-oil emulsions); and for emulsification. Stability of commercial emulsions, such as paper size emulsions, is a recurring issue in industry. Current commercial emulsions include those which generally consist of an oil, waxy, or rosin phase dispersed in water. These dispersions are generally stabilized by the addition of charged materials such as cationic starches, sodium lignin sulfonate, and 20 aluminum sulfate. Such materials are generally added in amounts equal to about 10-20% by weight of the size component. The resulting dispersions are typically 0.2 to 2 micron particles, thought to be stabilized by charge repulsion, for example, with the positively charged starches on particle surfaces repelling each other.

25 One cause of emulsion failure is density-driven separation. This can be limited by increasing viscosity, or internal structure within the fluid. For example, an emulsion which maintains a viscosity of less than about 20 centipoise throughout a standard aging test might have its viscosity increased initially by as much as 100 centipoise through addition of a viscosifier to the

formulation, and still be within acceptable commercial viscosity, provided that the viscosity did not then increase over time to exceed acceptable limits.

One method to accomplish this result would be to use a viscosifying agent that does not cause a substantial increase in viscosity when first added to an emulsion formulation, but which does provide an increase in viscosity during normal processing of the emulsion formulation to produce the emulsion. This can be accomplished by including, as an additive to the emulsion formulation, cellulose that has been derivatized as described herein but not yet microfibrillated. When the emulsion formulation is then subjected to energy, typically high shear, during the processing used to turn the emulsion formulation into an emulsion, the shear will also microfibrillize the derivatized cellulose, resulting in the derivatized microfibrillar cellulose of the present invention, which will be present as part of the emulsion. The gel produced by the derivatized microfibrillar cellulose will then thin under shear stress but re-form when shear stops. Moreover, the insolubility of such low DS cellulose may cause it to concentrate at the oil/water interface of oil-and-water emulsions, rather than the aqueous bulk phase, which may be desirable.

Effectively the same result may be achieved by adding the derivatized microfibrillar cellulose of the present invention to an emulsion formulation, or to the final emulsion, or at any point during production of the emulsion. Further variations would include introducing derivatized cellulose that is only partially microfibrillated into the emulsion-making process at a point where subsequent processing would provide sufficient energy to complete the microfibrillation. It may also be possible to accomplish some or all of the derivatization as part of the emulsion production process; for example, the emulsion formulation may include a charged species that will adsorb onto the cellulose microfibrils, or such a species may be added during processing of the emulsion formulation, separately or in combination with the cellulose. Therefore, the derivatized microfibrillar cellulose of the present invention may serve as a stabilizing additive to

emulsions, with several process routes being available to accomplish this end result.

While the choice of method may cause some variation in the properties of the resulting emulsion, the basic benefit of improved emulsion stability should be achieved by any procedure which has, as its final result, the presence of the derivatized microfibrillar cellulose of the present invention in the final emulsion.

Commercially, it may be desirable to supply customers with derivatized, non-microfibrillated cellulose as a powder which, when added to a formulation and subjected to high shear or other appropriate forms of energy, will microfibrillate and yield the derivatized microfibrillar cellulose of the present invention.

This improved emulsion stability may enable use of emulsion formulations which would not perform satisfactorily in the absence of the derivatized microfibrillar cellulose. Other benefits may include improved retention in paper, improved drainage of water from paper systems due to association of fillers and pulp fines with the retained microfibrils, and resistance to emulsion breakage in the presence of high salt concentrations.

The subject electrostatically derivatized materials of this invention have also been discovered to provide rheology to aqueous systems over a wide range of pH and ionic strength. This insensitivity to pH and ionic strength facilitates use in areas where low pH and high salt conditions exist, such as in personal care creams and lotions, food products, and the like.

In addition to the above, the derivatized microfibrillar cellulose of the present invention represent a vehicle for providing cationic charge to a given environment. This may include utility in water and wastewater treatment, where charged particles may be used to remove color bodies and to flocculate particulates and other contaminants. Thus, by way of non-limiting example, a suitable amount of the derivatized microfibrillar cellulose may be added to water (or to an aqueous system) that is contaminated with anionic material and/or color bodies; allowed to bind or complex with the contaminants, optionally with mixing and/or heating; and physical, chemical, and/or other conventional

separation techniques may then be used to separate the bound or complexed cellulose/contaminant combination from the water. While any amount of derivatized microfibrillar cellulose would facilitate removal of some amount of contaminant from the water, in order to have the most effect the amount of
5 derivatized microfibrillar cellulose should preferably be at least equal to the stoichiometric equivalent necessary to bind or complex with the measured or estimated concentration of the contaminant whose separation or removal is desired.

The following examples indicate various possible methods for making and
10 using the derivatized microfibrillar cellulose of the present invention. These examples are merely illustrative, and are not to be construed as limiting the present invention to particular compounds, processes, conditions, or applications. Throughout this description, "gelling" is defined to occur when $G' > G''$, where G' is the dynamic storage modulus and G'' is the dynamic loss modulus. This is the
15 functional definition used in EP '011; for general background, see Ferry, J.D., Viscoelastic Properties of Polymers, John E. Wiley & Sons, NY, 1980.

The following examples indicate various possible methods for making and
using the derivatized microfibrillar cellulose of present invention. These
examples are merely illustrative, and are not to be construed as limiting the
20 present invention to particular compounds, processes, conditions, or applications.

Example 1

Preparation Of A Quaternary Amine Functionalized Cellulose (QAC).

Isopropanol (IPA) and deionized (DI) water were charged to a nitrogen
25 sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. Bleached sulfate wood pulp (approximately 400 μm length, 5.2% moisture)(Weyerhaeuser Company) was added to the reactor, the mixture slurry was agitated for 10 minutes, after which

the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15°C.

The reactor was then inerted, and aqueous NaOH (50% NaOH) was slowly added to the reactor while maintaining the mixture slurry's temperature at or

5 below 15°C. The slurry was agitated for 1 hour after completion of caustic addition. Dow Quat 188 (3-chloro-2-hydroxypropyl trimethylammonium chloride, Dow Chemical Company, Midland, MI) (65% in water) was slowly added to the reactor by addition funnel while maintaining reaction slurry temperature at 15° C. After Dow Quat addition, the reaction slurry was heated to
10 70° C and held for 1 hour. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80% methanol for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two
15 more times.

The wetcake obtained from the previous three washes was slurried in 1000g of pure methanol using an air driven stirrer and a grounded stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was broken into small particles
20 using a rubber spatula and then dried in a Lab-Line fluidized bed dryer (model number 23852) for 35 minutes. (Air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes). The product was ground using a Retsch Grinding Mill (model 2M1) with a 1mm screen.

25 Table 1: QAC Recipes
(all weights in grams)

| Quaternary Amine Functionalized Cellulose | | | | | | | |
|---|------------------|-------------------------------|---------|----------------------|-------------------|---------------------------------|------|
| Sample # | Cellulose Length | Wt. Cellulose (dry wt. Basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. Dow Quat 188 (65% aq. Soln) | DS |
| 1 | ~400 μm | 65 | 750 | 110 | 18.46 | 58.02 | 0.02 |

| Quaternary Amine Functionalized Cellulose | | | | | | | |
|---|------------------|-------------------------------|---------|----------------------|-------------------|---------------------------------|------|
| Sample # | Cellulose Length | Wt. Cellulose (dry wt. Basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. Dow Quat 188 (65% aq. Soln) | DS |
| 2 | ~400 µm | 65 | 750 | 110 | 13.84 | 43.52 | 0.03 |
| 3 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.03 |
| 4 | ~200 µm | 65 | 750 | 110 | 18.46 | 58.02 | 0.07 |
| 5 | ~200 µm | 65 | 750 | 110 | 18.46 | 58.02 | 0.08 |
| 6 | ~200 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.11 |
| 7 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.11 |
| 8 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.11 |
| 9 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.12 |
| 10 | ~400 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.13 |
| 11 | ~200 µm | 65 | 750 | 110 | 23.07 | 72.53 | 0.14 |
| 12 | ~400 µm | 65 | 750 | 110 | N/A | N/A | 0.25 |

Slurry preparation: An 800 g 1% slurry was made from each Sample in Table 1 using the following materials:

| | | <u>Weight</u> | <u>Weight%</u> |
|----|--|---------------|----------------|
| 5 | QAC | 8.00 grams | 1.0 ± |
| | 0.06% | | |
| | Germaben ® II biocide (Sutton Laboratories, New Jersey) | 4.00 grams | 0.5% |
| | Deionized water | 788.00 grams | 98.5 ± |
| 10 | <u>0.06%</u> | | |
| | Total | 800.00 grams | |

The container was closed and shaken to wet and disperse the QAC solids. The solids will settle if left standing, so the container was shaken just prior to pouring the slurry into the homogenizer.

15 **Homogenization of QAC slurries:** The suspension was processed in the homogenizer equipped with an agitated feed pot as follows: the homogenizer was turned on before the slurry was loaded. An 800-gram slurry was processed for about 20 minutes at about 3000 psi by recycling the discharged stream from the homogenizer to the feed pot. Pressure was monitored and appropriate

adjustments made to the primary stage handwheel to keep the total pressure at about 3000 psi. After the processing was completed, the discharge tube was redirected so that the sample was collected and stored in a capped jar.

Rheological testing of microfibrillated QAC: each microfibrillated QAC sample prepared in Example 1 was then tested for rheological properties. Data was collected on a Bohlin CS Rheometer (Bohlin Instruments, Cranbury, New Jersey). Dynamic mechanical properties were measured including the dynamic storage modulus, the dynamic loss modulus, complex viscosity, and yield stress.

Rheometer Test Conditions

10 **Temperature Sweep:** Measuring System: PP 40; 25° C - 65° C; Shear Stress: automatic; Frequency: 1 Hz; Temperature Ramp Rate: 5° C/60 seconds; Measurement Interval: 20 seconds; Gap: 1 mm.

15 **Yield Stress Test:** Measuring System: CP 4/40; Stress: 6.0E-02 - 1.0E+02; Sweep Time: 60.0 seconds; Number of Steps: 30; Temperature: Manual (25° C); No of measurements: 1; Measurement Interval: 5 seconds.

Stress Sweep Test: Measuring System: PP 40; Temperature: Manual (25 °C); Number of Measurements: 1; Gap: 1 mm; Measurement Interval: 5 seconds; Frequency: 1 Hz.

Table 2: Rheology of Microfibrillated QAC

| Sample # | Cellulose Length | DS of Quat-Cellulose | YIELD STRESS(Pa) | G' @ 5.75 Pa(Pa) | G' @25° C/50° C(Pa) | Homogenizer Processing Time(minutes) |
|----------|------------------|----------------------|------------------|------------------|---------------------|--------------------------------------|
| 1 | ~400 µm | 0.02 | NONE | | | 20 |
| 2 | ~400 µm | 0.03 | NONE | | | 20 |
| 3 | ~400 µm | 0.03 | NONE | | | 20 |
| 4 | ~200 µm | 0.07 | 38.0 | 572 | 619/633 | 25 |
| 5 | ~200 µm | 0.08 | 44.7 | 489 | 468/450 | 30 |
| 6 | ~200 µm | 0.11 | 51.4 | 480 | 505/530 | 25 |
| 7 | ~400 µm | 0.11 | 38.0 | 622 | 621/646 | 15 |
| 8 | ~400 µm | 0.11 | 34.7 | 482 | | 20 |
| 9 | ~400 µm | 0.12 | 68.0 | 500 | 488/487 | 20 |
| 10 | ~400 µm | 0.13 | 18.1 | 420 | | 20 |
| 11 | ~200 µm | 0.14 | 21.4 | 497 | 577/592 | 15 |
| 12 | ~400 µm | 0.25 | 51.4 | 106 | 119/131 | 30 |

Example 2

Ready-To-Gel(RTG) Process For Quaternary Amine Cellulose

- 5 Gels are made as described in the "Slurry preparation" and "Homogenization of QAC Slurries" steps in Example 1. The gels are then processed as follows:

The following description pertains to Sample #1 in the data table. A similar procedure was used for all of the other samples.

- 10 Approximately 2800 ml of IPA was added to a grounded 12-quart stainless steel (SS) beaker. The IPA was stirred at the top speed of an overhead stirrer driven by house air. A SS cowls blade on an SS shaft was used to stir the IPA. Next, approximately 1400 grams of 1% QAC gel was slowly added to the stirring IPA. The material ratio is 2 ml IPA/1 gram gel. The beaker was covered with
15 Saran Wrap and the slurry was stirred for ten minutes.

When ten minutes had passed, the slurry was filtered through a synthetic straining cloth. The slurry was filtered using gravity. The slurry was covered with Saran Wrap during the filtration to reduce IPA evaporation. Occasionally the gel on the cloth was stirred with a plastic spatula to help speed filtration. When it

appeared that the filtration had gone about as far as it could, the wet cake was transferred back to the 12 quart SS beaker.

A fresh amount of approximately 2800 ml IPA was added to the beaker and the slurry was again stirred for ten more minutes with the cowls blade/air stirrer.

5 The slurry was then filtered on a 20 cm Buchner funnel with #415 VWR filter paper. The wet cake was transferred to a glass crystallization dish. The dish containing the wet cake was placed into an 80° C oven under vacuum overnight for drying. The sample was dried to constant weight, and the solids were ground in a Waring Blender.

10 The dehydrated gels were examined by rehydration as follows: a premix of deionized water and Germaben II was prepared.

| | <u>Weight</u> | <u>Weight%</u> |
|---------------------|---------------|----------------|
| Deionized water | 788.00 grams | 99.49% |
| Germaben II biocide | 4.00 grams | 0.51% |

15 The water/Germaben II solution was then weighed into a small Waring blender cup along with the ready-to-gel dry QAC.

| | <u>Weight</u> | <u>Weight%</u> |
|------------------|---------------|----------------|
| water/Germaben | 29.70 grams | 99.0% |
| Ready-to-gel QAC | 0.30 grams | 1.0% |

The blender cup was covered and the sample was mixed until it appeared to be homogeneous. The resulting gel was transferred to a glass jar. It was then shaken on a vortex mixer.

Rheological testing: Same as described in example 1.

25 Table 3: Rheology of RTG QAC

| Sample # | DS of QAC | YIELD STRESS (Pa) | G' @ 5.75 Pa (Pa) |
|-------------|--------------|----------------------|----------------------|
| 1 | 0.09 | 61.4 | 385 |

Rheological properties as a function of concentration: a series of gels were prepared from a 1% QAC (DS 0.09) by diluting with DI water.

Table 4: Rheology of RTG QAC by Concentration

| Sample # | QAC Concentration (wt%) | G' @ 5.75 Pa (Pa) |
|----------|-------------------------|-------------------|
| 1 | 1 | 246 |
| 2 | 0.5 | 35.6 |
| 3 | 0.25 | 0.475 |
| 4 | 0.1 | 0.136 |

G' > G" in all samples (1 - 4); see Figures 1 to 4, respectively.

Stable water/oil emulsions containing QAC: cetyl trimethyl ammonium

- 5 bromide was mixed with deionized water. The CTAB solution was added to 1% quaternary amine (DS=0.15) functionalized microfibrillated cellulose gel prepared as in Example 1. The mixture was stirred in a Waring Blender for 3 minutes on high speed. The sample remained a gel. This gel was processed through a Gaulin homogenizer, 1 pass at 4000 psi. Ten percent (10%) miglyol emulsions were prepared from the gels by adding miglyol and deionized water to the gel and mixing with a rotary mixer for 4 minutes. The resulting emulsions were aged in a 50° C oven.
- 10

Table 5: Stability of Water/Oil Emulsions

| 10% Miglyol Emulsion | Stability at 50° C |
|-----------------------|--------------------|
| 0.45% QAC/0.008% CTAB | > 3 weeks |
| 0.90% QAC/0.016% CTAB | > 3 weeks |

- 15 **Use in paper sizing compositions:** the following examples relate to use of QAC as made in example 1 having a DS of about 0.10 in connection with compositions used in paper sizing.

Example 3

- A 600 ml beaker was used to combine 66.0 grams of Precis® 787 ketene dimer (available from Hercules Incorporated, Wilmington, Delaware; Precis is a registered trademark of Hercules Incorporated), 1.5g of QAC, and 232.5 grams of deionized (DI) water. The mixture was stirred, and then passed through a
- 20

Microfluidics Corporation Model M110 Series impingement mixer (Microfluidics Corp.) with its pressure set at 5000 PSI. The emulsion was collected, and a second pass was made. The second pass product was collected in a clean jar, a stir bar was added, the jar was capped, and then cooled in a 5 to 15° C water bath.

Example 4

Three grams of QAC were dispersed in 465g of DI water for 5 minutes using a Tekmar Ultra-turax SD45 rotor-stator high shear mixer (Tekmar Company, Cincinnati, Ohio) at a power setting of 50. The resulting materials 10 was then given three passes through the impingement mixer at 5000 psi. As in Example 3, 66.0 g of Precis were combined with 234.0 g of QAC in DI water gel, stirred using the high shear mixer at a power setting of 50, then given two passes through the impingement mixer at 5000 psi and cooled in a 5 to 15° C water bath.

Example 5.

15 Four (4.0) grams of QAC was dispersed in 400g of DI water for 5 minutes using the high shear mixer at a power setting of 50, then given three passes through the impingement mixer at 5000 psi to create a gel. A 44% emulsion of Precis ketene dimer was made by combining 176.0 grams of Precis 787 ketene dimer with 224.0 grams of DI water in a wide mouth jar; the pre-mix was sheared 20 in a high shear mixer for 5 minutes at a power setting of 50, the resulting material was quickly poured into the feed chamber of the impingement mixer, and, with mechanical stirring set at about 250 RPM, the premix was passed twice through the impingement mixer set at 5000 psi. Next, 150.0 g of the QAC gel was combined with 150.0 g of the Precis ketene dimer 44% emulsion and stirred for 5 25 minutes using the high shear mixer at a power setting of 50.

The following table provides testing results for the sample emulsions using TAPPI standard Method T560:

Table 6: Surface Sizing of Example 3 through Example 5 Size Emulsions
 (formulation weight in grams)

| | | | (Pre-shear) |
|--------------------------|---|------------|-------------|
| Designation | | (MF gel) | (MF gel) |
| Example | 3 | 4 | 5 |
| Precis 787 | 66.00 | 66.00 | 66.00 |
| QAC | 1.50 | 1.50 | 1.50 |
| DI Water | 232.50 | 232.50 | 232.50 |
| | | | |
| Total | 300.0 | 300.0 | 300.0 |
| | | | |
| Tekmar Shearing cond. | 2 min.@ 50 | 2 min.@ 50 | 2 min.@ 50 |
| Microfluidizer shearing | 2X @ 5kpsi | 2X @ 5kpsi | |
| Tekmar Gel Shearing | | 5 min.@ 50 | 5 min.@ 50 |
| Microfluidizer Gel Shear | | 3X @ 5kpsi | 3X @ 5kpsi |
| | | | |
| Calc. % Actives | 22.00 | 22.00 | 22.00 |
| IRAQ % Actives | NA | 14.9 | NA |
| pH | 2.42 | 2.60 | 2.75 |
| @temp | 20.7 | 21.0 | 26.80 |
| Particle size | 0.75 | 0.97 | Failed |
| Particle size Sonicated | 0.70 | 0.63 | Failed |
| Zeta Potential | -58.3 | -57.9 | Failed |
| Brookfield Visc. | Failed | 119.3 | Failed |
| | "Failed" means emulsion broke prior to testing. | | |

Drainage Aids in Paper Manufacture: the following examples

- 5 demonstrate the effectiveness of derivatized microfibrillar cellulose as a drainage-improvement aid.

Drainage measurements were performed on a Canadian Standard Freeness (CSF) tester, using a bleached kraft pulp consisting of 70% hardwood and 30% softwood. All freeness testing was performed in hard water having a pH of 7.95-10 8.05, alkalinity of 50 ppm (as calcium carbonate), and hardness of 100 ppm (as calcium carbonate) using TAPPI method T 227 om-92. A pulp consistency of 0.3% was used. Higher CSF values indicate better (faster) drainage.

The following results were obtained using microfibrillated quaternary amine cellulose (MFQAC), alone and in combination with microfibrillar

carboxymethyl cellulose (MFCMC). The preparation of MFCMC is described in U.S. patent application serial number 09/248,246, filed February 10, 1999, the disclosure of which is hereby incorporated in its entirety by reference thereto. The MFQAC had a degree of substitution of about 0.09, while the MFCMC had a 5 degree of substitution of about 0.17 charge group per anhydroglucose unit. All loadings are calculated as percent of additive (dry basis) relative to pulp.

Example 6

MFQAC alone.

| | <u>% MFQAC</u> | <u>CSF</u> |
|----|----------------|------------|
| 10 | 0.00 | 211 |
| | 0.05 | 264 |
| | <u>% MFQAC</u> | <u>CSF</u> |
| 15 | 0.10 | 315 |
| | 0.20 | 388 |
| | 0.30 | 451 |
| | 0.40 | 491 |
| | 0.50 | 509 |

Example 7

MFQAC (0.2% loading) with Hercules Reten®1523H anionic polyacrylamide resin:

| | <u>% Reten®1523H</u> | <u>CSF</u> |
|----|----------------------|------------|
| 25 | 0.000 | 464 |
| | 0.003 | 464 |
| | 0.006 | 503 |
| | 0.009 | 513 |
| | 0.012 | 526 |

Example 8

MFQAC with MFCMC

| | % MFQAC <u>(based on pulp)</u> | CSF VALUES | |
|---|-----------------------------------|--------------------|-----------------------|
| | | 0% <u>MFCMC</u> | 0.05% <u>MFCMC</u> |
| 5 | 0.00 | 211 | N/A |
| | 0.10 | 315 | 432 |
| | 0.20 | 388 | 518 |
| | 0.40 | 491 | 612 |

10

In addition to the examples provided above, QAC may be produced with a range of alternative cellulose sources, including Avicel® pH-101NF (-90); Solka® Floc (grade 300 FCC), which may be obtained from Fiber Sales & Development Corp., Urbana, Ohio; and Bleached CTMP (Chemical

15 Thermomechanical Pulp) Fluff, which may be obtained from SCA Graphic Sundsvall AB, Timra, Sweden.

The present invention has of necessity been discussed herein by reference to certain specific methods and materials. The enumeration of these methods and materials was merely illustrative, and in no way constitutes any limitation on the 20 scope of the present invention. It is to be expected that those skilled in the art may discern and practice variations of or alternatives to the specific teachings provided herein, without departing from the scope of the present invention.

WHAT I/WE CLAIM IS:

1. A derivatized microfibrillar cellulose, derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.
2. The derivatized microfibrillar cellulose of claim 1, wherein said cellulose is obtained from at least one of chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.
3. The derivatized microfibrillar cellulose of claim 2, wherein said cellulose is obtained from at least one of purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.
4. The derivatized microfibrillar cellulose of claim 1, wherein said substituent comprises an amine.
5. The derivatized microfibrillar cellulose of claim 4, wherein said substituent comprises a quaternary amine.
6. The derivatized microfibrillar cellulose of claim 1, wherein said derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 100% in water.
7. The derivatized microfibrillar cellulose of claim 6, wherein said derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 50 % in water.
8. The derivatized microfibrillar cellulose of claim 1, wherein said derivatized microfibrillar cellulose forms a gel at a concentration of less than about 1% in water.

9. The derivatized microfibrillar cellulose of claim 8, wherein said derivatized microfibrillar cellulose forms a gel at at least one point in the concentration range of from about 0.05 % up to about 0.99% in water.

10. The derivatized microfibrillar cellulose of claim 1, further
5 comprising a solvent, wherein said derivatized microfibrillar cellulose is substantially insoluble in said solvent.

11. The derivatized microfibrillar cellulose of claim 10, wherein said solvent is water, alcohol, or oil.

12. The derivatized microfibrillar cellulose of claim 11, wherein said
10 solvent is water.

13. The derivatized microfibrillar cellulose of claim 1, having a degree of substitution of less than about 0.5.

14. The derivatized microfibrillar cellulose of claim 13, wherein said degree of substitution is less than about 0.35.

15. The derivatized microfibrillar cellulose of claim 14, wherein said degree of substitution is less than about 0.2.

16. The derivatized microfibrillar cellulose of claim 15, wherein said degree of substitution is less than about 0.18.

17. The derivatized microfibrillar cellulose of claim 16, wherein said
20 degree of substitution is less than about 1.15.

18. The derivatized microfibrillar cellulose of claim 13, wherein said degree of substitution is between about 0.02 and about 0.5.

19. The derivatized microfibrillar cellulose of claim 18, wherein said degree of substitution is between about 0.05 and about 0.2.

25 20. Microfibrillar 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose having a degree of substitution of between about 0.10 and about 0.20.

21. A comestible composition of matter comprising derivatized microfibrillar cellulose derivatized to comprise a substituent that provides

cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

22. The comestible composition of matter of claim 21, in the form of a low fat, reduced fat, or fat-free mayonnaise.

5 23. The comestible composition of matter of claim 22, in the form of a salad dressing.

24. The comestible composition of matter of claim 21, further comprising a pharmaceutically active ingredient.

10 25. The comestible composition of claim 24, wherein said derivatized microfibrillar cellulose at least partially provides controlled, sustained, or delayed release of said pharmaceutically active ingredient.

15 26. A non-comestible composition of matter comprising derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

27. The non-comestible composition of matter of claim 26, in the form of a wound care product.

28. The non-comestible composition of matter of claim 27, wherein said wound care product is a wound dressing.

20 29. The non-comestible composition of matter of claim 27, wherein said wound care product is an ostomy ring.

30. The non-comestible composition of matter of claim 26, in the form of a skin care lotion or cream.

25 31. The non-comestible composition of matter of claim 26, in the form of a sunscreen lotion or cream.

32. The non-comestible composition of matter of claim 26, in the form of an oral care composition.

33. The non-comestible composition of matter of claim 32, wherein said oral care product is a toothpaste.

34. The non-comestible composition of matter of claim 26, in the form of a hair care composition.

35. The non-comestible composition of matter of claim 26, further comprising a fertilizer, herbicide, fungicide, or pesticide.

5 36. The non-comestible composition of matter of claim 35, wherein said derivatized microfibrillar cellulose at least partially provides controlled, sustained, or delayed release of said fertilizer, herbicide, or pesticide.

37. The non-comestible composition of matter of claim 26, in the form of a drilling fluid.

10 38. A paper composition comprising derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 39. The paper composition of claim 38, wherein said derivatized microfibrillar cellulose is microfibrillar 2-hydroxy-3-(trimethylammonium chloride) – propylcellulose.

40. A method for producing derivatized microfibrillar cellulose, said method comprising at least one of the following:

- a) a derivatizing step of treating a microfibrillar cellulose to obtain a derivatized microfibrillar cellulose;
- b) a microfibrillizing step of treating a derivatized non-microfibrillar cellulose to produce a derivatized microfibrillar cellulose; or,
- c) a step of microfibrillizing and derivatizing a non-microfibrillar cellulose substantially simultaneously,

25 wherein said derivatized microfibrillar cellulose is derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

41. The method of claim 40, wherein said cellulose is obtained from 30 at least one of chemical pulps, mechanical pulps, thermal mechanical pulps,

chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.

5 42. The method of claim 41, wherein said cellulose is obtained from at least one of purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.

10 43. The method of claim 40, comprising the steps of:
a) derivatizing cellulose with 3-chloro-2-hydroxypropyl trimethylammonium chloride under alkaline conditions to produce 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose;
b) suspending the 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose in water to form a suspension; and
15 c) homogenizing said suspension to produce microfibrillated 2-hydroxy-3-(trimethylammonium chloride) – propylcellulose.

44. The method of claim 40, wherein said derivatizing step comprises contacting a non-microfibrillar cellulose with a swelling agent.

45. The method of claim 44, further wherein said contacting takes place under alkaline conditions.

46. The method of claim 44, wherein said swelling agent is an anionic reagent.

47. The method of claim 46, further wherein said alkaline conditions comprise contacting the cellulose with said anionic reagent in the presence of an alkaline reagent which is at least one of sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an alkali silicate, an alkali aluminate, an alkali carbonate, an amine, ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof.

48. The method of claim 40, wherein said derivatizing step takes place at high solids.

49. The method of claim 40, wherein said cationic charge comprises the presence of amine groups.

50. The method of claim 40, wherein said derivatizing step comprises derivatizing the cellulose with a quaternary amine reagent.

51. The method of claim 40, wherein said derivatized microfibrillar cellulose comprises quaternary amine cellulose.

52. The method of claim 40, wherein said microfibrillizing step comprises applying energy to said cellulose under conditions sufficient to produce microfibrillar cellulose.

10 53. The method of claim 52, further comprising enzyme-treating said non-microfibrillar cellulose prior to said microfibrillizing step

54. The method of claim 52, comprising applying at least one of homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, and 15 milling to said non-microfibrillar cellulose.

55. The method of claim 54, comprising passing said non-microfibrillar cellulose through a homogenizer under conditions sufficient to produce microfibrillar cellulose.

56. The method of claim 55, wherein said conditions comprise passing 20 said non-microfibrillar cellulose through a pressure differential of at least about 3,000 psi.

57. The method of claim 56, further comprising passing said non-microfibrillar cellulose through said homogenizer at least three times.

58. The method of claim 40, wherein said derivatized microfibrillar 25 cellulose forms a gel throughout a concentration range of from about 0.01 % to about 100% in water.

59. The method of claim 58, wherein said derivatized microfibrillar cellulose forms a gel throughout a concentration range of between about 0.01 % and about 50 % in water.

60. The method of claim 40, wherein said derivatized microfibrillar cellulose forms a gel at at least one point in the concentration range of from about 0.05 % to about 0.99% in water.

5 61. The method of claim 60, wherein said derivatized microfibrillar cellulose forms a gel at a concentration of about 0.9% in water.

62. The method of claim 40, wherein said derivatized microfibrillar cellulose is substantially insoluble in the solvent of use.

63. The method of claim 62, wherein the solvent of use is water.

10 64. The method of claim 63, wherein said derivatized microfibrillar cellulose is derivatized microfibrillar cellulose having a degree of substitution of less than about 0.5.

65. The method of claim 64, wherein said degree of substitution is less than about 0.35.

15 66. The method of claim 65, wherein said degree of substitution is less than about 0.2.

67. The method of claim 66, wherein said degree of substitution is less than about 0.18.

68. The method of claim 67, wherein said degree of substitution is less than about 1.15.

20 69. The method of claim 64, wherein said derivatized microfibrillar cellulose has a degree of substitution of between about 0.02 and about 0.5.

70. The method of claim 69, wherein said degree of substitution is between about 0.05 and about 0.2.

25 71. The method of claim 43, wherein said 2-hydroxy-3-(trimethylammonium chloride) - propylcellulose has a degree of substitution of less than about 2.0.

72. The method of claim 71, wherein said degree of substitution is less than about 0.35.

30 73. The method of claim 72, wherein said degree of substitution is between about 0.02 and about 2.0.

74. The method of claim 73, wherein said degree of substitution is between about 0.1 and about 0.2.

75. Derivatized microfibrillar cellulose produced by the method of claim 40.

5 76. Derivatized microfibrillar cellulose produced by the method of claim 43.

77. The derivatized microfibrillar cellulose of claim 40, wherein said cationic charge comprises the presence of amine groups.

10 78. A method of modifying the rheological properties of a composition of matter, said method comprising the step of incorporating, into said composition of matter, derivatized microfibrillar cellulose that is derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 79. The method of claim 78, wherein said composition comprises a liquid.

80. The method of claim 79, wherein said liquid is water.

20 81. The method of claim 80, comprising using said derivatized microfibrillar cellulose in an amount effective to provide scale control and/or corrosion control.

82. The method of claim 78, wherein said rheological properties are at least one of viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention.

25 83. The method of claim 78, wherein said composition of matter is a food, pharmaceutical, pharmaceutical, personal care, fiber, paper, paint, coating, or construction composition.

84. The method of claim 83, wherein said composition of matter is an oral care product.

30 85. The method of claim 83, wherein said composition of matter is a cream or lotion for epidermal application.

86. The method of claim 85, wherein said composition of matter is moisturizing, night, anti-age, or sunscreen cream or lotion.

87. The method of claim 83, wherein said composition of matter is a food spread.

5 88. The method of claim 87, wherein said food spread is a reduced fat, low fat, or fat free food spread.

89. The method of claim 88, wherein said food spread is a reduced fat, low fat, or fat free mayonnaise.

10 90. The method of claim 83, wherein said composition of matter is a drilling fluid.

91. A method of improving the physical and/or mechanical properties of a coating composition by incorporating, into said coating composition, an effective amount of a derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 92. The method of claim 91, wherein said physical and/or mechanical properties include at least one of film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

20 93. The method of claim 92, wherein said derivatized microfibrillar cellulose complexes, adsorbs, precipitates, or otherwise renders inactive dissolved detrimental substances.

94. A method of improving at least one of sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, adsorbency, 25 film formation, membrane formation, and polyelectrolyte complexation during paper manufacture, said method comprising the step of using a derivatized microfibrillar cellulose during said manufacture, wherein said derivatized microfibrillar cellulose is derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

95. The method of claim 94, wherein said derivatized microfibrillar cellulose is used as a drainage aid and/or as a component of a sizing agent.

96. The method of claim 94, wherein said derivatized microfibrillar cellulose is microfibrillated quaternary amine functionalized cellulose.

5 97. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture.

10 98. The method of claim 97, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.

15 99. The method of claim 97, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

20 100. The method of claim 97, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

25 101. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture

30 102. The method of claim 101, wherein said dispersed particles comprise at least one of pulp fines, fillers, sizing agents, pigments, clays,

detrimental organic particulate materials, detrimental inorganic particulate materials, and combinations thereof.

103. The method of claim 101, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one
5 of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.

10 104. The method of claim 101, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

15 105. The method of claim 101, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

20 106. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine to improve the uniformity of formation of a sheet of paper during its manufacture.

25 107. The method of claim 106, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing carboxylic acid functionality; and combinations thereof.
30

108. The method of claim 106, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or 5 inorganic species; and combinations thereof.

109. The method of claim 106, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or 10 vinylamine; and combinations thereof.

110. The method of claim 96, comprising using said microfibrillated quaternary amine functionalized cellulose in a papermaking machine to improve the strength of a sheet of paper produced on a paper machine.

111. The method of claim 110, further wherein said microfibrillated 15 quaternary amine functionalized cellulose is used in the presence of at least one of: colloidal silica; colloidal aluminum-modified silica; colloidal clay, derivatives of starch containing carboxylic acid functionality; derivatives of guar gum containing carboxylic acid functionality; natural gums or derivatized natural gums containing carboxylic acid functionality; polyacrylamides containing 20 carboxylic acid functionality; and combinations thereof.

112. The method of claim 110, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or 25 inorganic species; and combinations thereof.

113. The method of claim 110, further wherein said microfibrillated quaternary amine functionalized cellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or 30 vinylamine; and combinations thereof.

114. A method for improving the stability of an emulsion, dispersion, or foam system, said method comprising the step of including, in the system, a derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar 5 cellulose is capable of forming a gel in water at a concentration of less than 1%.

115. The method of claim 114, wherein said system comprises an emulsion, further wherein said emulsion is produced by processing of an emulsion formulation.

116. The method of claim 115, further wherein said derivatized 10 microfibrillar cellulose is added to said emulsion formulation prior to completion of processing of said emulsion formulation.

117. The method of claim 115, wherein a non-microfibrillated derivatized cellulose is added to said emulsion formulation prior to completion of processing of said emulsion formulation and said emulsion formulation is 15 processed under conditions sufficient to microfibrillate said non-microfibrillated derivatized cellulose, whereby said derivatized microfibrillar cellulose is produced.

118. The method of claim 115, wherein a microfibrillated non-derivatized cellulose is added to said emulsion formulation prior to completion of 20 processing of said emulsion formulation, and said emulsion formulation is further processed under conditions sufficient to derivatize said microfibrillated non-derivatized cellulose.

119. The method of claim 115, wherein a non-microfibrillated, non-derivatized cellulose is added to said emulsion formulation prior to completion of 25 processing of said emulsion formulation, and said emulsion formulation is further processed under conditions sufficient to microfibrillate and derivatize said non-microfibrillated, non-derivatized cellulose.

120. The method of claim 114, wherein said system is a water-in-oil or oil-in-water emulsion.

30 121. The system produced by the method of claim 114.

122. A system comprising an emulsion, dispersion, or foam containing a derivatized microfibrillar cellulose, wherein said derivatized microfibrillar cellulose is derivatized to comprise a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming 5 a gel in water at a concentration of less than 1%.

123. A polyelectrolyte complex comprising a derivatized microfibrillar cellulose comprising a substituent that provides cationic charge, yet further wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

10 124. A method for treating wastewater comprising the step of adding, to the wastewater, a sufficient amount of a derivatized microfibrillar cellulose derivatized to comprise a substituent that provides cationic charge, wherein said derivatized microfibrillar cellulose is capable of forming a gel in water at a concentration of less than 1%.

15 125. The method of claim 124, wherein said wastewater contains at least one of anionic contaminants and color bodies.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/03458

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08B11/20 C08B11/145

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X | US 5 588 861 A (SHIGERU YAMANAKA ET AL.) 24 September 1996 (1996-09-24) column 3, line 28 - line 32 column 5, line 9 - line 62 example 2; tables 2,3 --- | 1-125 |
| X | EP 0 859 011 A (AGRO INDUSTRIE RECHERCHES ET DEVELOPPEMENTS) 19 August 1998 (1998-08-19) cited in the application page 5, line 1 - line 4 example 29 --- | 1-125 |
| X | US 4 676 904 A (JOBST SCHRÖDER) 30 June 1987 (1987-06-30) column 1, line 55 - line 66 --- | 1-20 -/- |

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INTERNATIONAL SEARCH REPORT

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INTERNATIONAL SEARCH REPORT

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(54) Title: DERIVATIZED MICROFIBRILLAR POLYSACCHARIDE

(57) Abstract

A method for producing derivatized microfibrillar polysaccharide, including but not limited to cellulose, derivatized by steric and/or electrostatic forces, where the electrostatic forces are provided by anionic charge or by a combination of both anionic and cationic charge, by stabilizing and/or microfibrillating a polysaccharide starting material. A method of modifying the rheological properties of a composition of matter using derivatized microfibrillar polysaccharide. Method of improving coatings, paper manufacture, and the stability of emulsions, dispersions, and foams using a derivatized microfibrillar polysaccharide. Compositions that include derivatized microfibrillar polysaccharide, including paper compositions, comestible compositions, non-comestible spreadable compositions, and emulsions, dispersion, and foams.

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DERIVATIZED MICROFIBRILLAR POLYSACCHARIDE

FIELD OF THE INVENTION

5 The present invention relates to derivatized microfibrillar polysaccharide. More specifically, the present invention relates to microfibrillar polysaccharide stabilized by steric and/or electrostatic forces, where the electrostatic forces are provided by anionic charge, or by a combination of both anionic and cationic charge.

BACKGROUND OF THE INVENTION

10 Polysaccharides are often found in nature in forms having fibrous morphology. Polysaccharides which are not found in nature in fibrous form can often be transformed into fibrous morphologies using fiber spinning techniques. Whether the fibrous morphology is of natural or artificial origin, the polysaccharide will often be present such that the fibers can be reduced to fibrillar and microfibrillar sub-morphologies

15 through the application of energy.

Fibrillar and microfibrillar cellulose obtained in this manner have been considered for use in applications, including use as additives to aqueous-based systems in order to affect rheological properties, such as viscosity. The use level of these materials in aqueous systems is often on the order of about 2% by weight, below which these

20 materials have a tendency to poorly occupy volume, and to exhibit gross inhomogeneities in distribution.

Microfibrillated cellulose and its manufacture are discussed in U.S. Patent Nos. 4,500,546; 4,487,634; 4,483,743; 4,481,077; 4,481,076; 4,464,287; 4,452,722; 4,452,721; 4,378,381; 4,374,702; and 4,341,807, the disclosures of which are hereby incorporated by reference thereto. These documents, in part, purport to describe microfibrillated cellulose in stable, homogenous suspensions, characterized as useful in end use products including foods, cosmetics, pharmaceuticals, paints, and drilling muds.

Cellulose nanofibrils are characterized in WO 98/02486 (PCT/FR97/01290), WO 30 98/02487 (PCT/FR97/01291), and WO 98/02499 (PCT/FR97/01297), the disclosures of which are hereby incorporated by reference. Nanofibrils are characterized as having diameters in the range of about 2 to about 10 nanometers.

EP 845495 discusses cationic cellulose particulate which is characterized as insoluble, positively charged, and used in water treatment, specifically to treat water in a paper manufacturing plant. In paper making this cationic particulate is said to remove anionic trash from the water. The particles are obtained by milling, which is stated to 5 reduce particle size uniformly such that particles are typically round as described by a length/diameter ratio of approximately 1. Particle size is stated to be 0.001 mm (i.e., 1 μm), and preferably 0.01 mm (10 μm)

EP 859011 ("EP '011") is directed to a process for obtaining cationic cellulose microfibrils or their soluble derivatives. The process is described as including making a 10 cationic cellulose derivative and processing the derivative through a high pressure homogenizer to form transparent gels. The product can be dehydrated and rehydrated. Viscosity measurements are reported on the product at a concentration of 2% in water. EP '011 indicates that the degree of substitution ("DS") of the cellulose can range from 15 0.1 to 0.7, with a DS of between 0.2 and 0.7, 0.3 and 0.6, and 0.5 and 0.6 characterized as representing increasing orders of preference. The examples show cellulose with a DS ranging from a low of 0.24 up to 0.72. Gelling is reported to occur above a microfibril concentration of 10 g/L, or above 1%, in water. EP '011 defines gelling as occurring when $G' > G''$, where G' is the dynamic storage modulus and G'' is the dynamic loss modulus.

Microfibrillated chitosan is reported to form uniplanar, oriented sheets upon 20 drying by H. Yokata, J. Polymer Sci., Part C: Polymer Letters, 24:423-425 (1986). This article mentions that at a level of 4% chitosan in water, a gel is formed having a viscosity of 26,600 cps (Brookfield, 20° C, rotor #7, 10rpm). The microfibrillated chitosan is made by homogenization of commercial chitosan flakes in a Gaulin 25 homogenizer. The commercial chitosan is deacetylated using sodium hydroxide.

JP 59 [1984]-84938 discusses a method for producing a chitosan suspension. Commercial chitosan separated and purified from crabs and lobsters is pulverized to pieces having maximum length of about 1-2 mm. The pieces are then suspended in water at up to 15% chitosan, and are run in multiple passes through a high pressure 30 homogenizer at between 3,000 and 8,000 psi.

It would be desirable to obtain microfibrillar polysaccharides whose viscosity-affecting properties are achieved without the presence of cationic functionalities, at least

in part because of the general lack of suitability of cationic materials for use in foods. It would also be desirable to obtain microfibrillar polysaccharides that are capable of forming a gel at concentrations of 1% or less, thereby providing economy and ease of formulation, while still providing necessary rheological behavior and homogeneity of distribution.

In addition, there is a continuing need in industry to improve the stability of commercial emulsions, such as paper sizing emulsions. At present, one method for stabilizing such emulsions is the addition of charged materials, such as cationic starches, which may be added in amounts equal to 10-20% by weight of the size component.

Interaction with anionic components, such as sulfonates, can also improve stability. However, emulsion failure still takes place in such emulsions, either through density-driven separation, also referred to as creaming, or through gellation. It would accordingly be desirable to develop a material that could be added to emulsions to provide long-term stability.

15 SUMMARY OF THE INVENTION

The present intention is directed to derivatized microfibrillar polysaccharide, methods for its production, and applications for its use. The derivatized microfibrillar polysaccharides is derivatized to contain substituents that provide electrostatic and/or steric functionality; where electrostatic functionality is present, it includes, but is not necessarily limited to, the presence of anionic charge.

Polysaccharides suitable for use in the present invention include cellulose, hemicellulose, chitin, chitosan, guar gum, pectin, alginate, agar, xanthan, starch, amylose, amylopectin, alternan, gellan, mutan, dextran, pullulan, fructan, locust bean gum, carrageenan, glycogen, glycosaminoglycans, murein, bacterial capsular polysaccharides, and derivatives thereof. Mixtures of these may be employed.

Preferred polysaccharides are cellulose, chitin, chitosan, pectin, agar, starch, carrageenan, and derivatives thereof, used singly or in combination, with cellulose being most preferred. The cellulose may be obtained from any available source, including, by way of example only, chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose,

vegetables, and fruits. Preferred sources of cellulose include purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.

The derivatized microfibrillar polysaccharides that may be obtained using cellulose include, but are not limited to, hydroxyethyl cellulose, ethylhydroxyethyl cellulose, carboxymethylcellulose, carboxymethylhydroxyethyl cellulose, hydroxypropylhydroxyethyl cellulose, methyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose, carboxymethylmethyl cellulose, hydrophobically modified carboxymethylcellulose, hydrophobically modified hydroxyethyl cellulose, hydrophobically modified hydroxypropyl cellulose, hydrophobically modified ethylhydroxyethyl cellulose, hydrophobically modified carboxymethylhydroxyethyl cellulose, hydrophobically modified hydroxypropylhydroxyethyl cellulose, hydrophobically modified methyl cellulose, hydrophobically modified methylhydroxypropyl cellulose, hydrophobically modified methylhydroxyethyl cellulose, hydrophobically modified carboxymethylmethyl cellulose, nitrocellulose, cellulose acetate, cellulose sulfate, cellulose vinyl sulfate, cellulose phosphate, and cellulose phosphonate.

The derivatized microfibrillar cellulose of the present invention may form a gel in water throughout the concentration range of between about 0.01 % and about 100%, or throughout the concentration range of between about 0.01 % and about 50 % in water, or at at least one point in the concentration range of from about 0.05 % up to about 0.99% in water. In an alternative embodiment, the derivatized microfibrillar cellulose of the present invention forms a gel in water at a concentration of about 0.95%.

The derivatized microfibrillar polysaccharide may be used in the presence of a solvent, in which it is substantially insoluble. Examples of solvents include water, alcohol, and oil.

In the case of derivatization with groups that provide electrostatic functionality, the derivatized microfibrillar polysaccharides of the present invention may have a degree of substitution of less than about 0.5, less than about 0.35, less than about 0.2, less than about 0.18, or less than about 0.1. A preferred range for the degree of substitution is between about 0.02 and about 0.5, with a range of between about 0.05 and about 0.2 being more preferred. When the derivatized microfibrillar polysaccharide

is derivatized to comprise substituents that provide electrostatic functionality in the form of anionic charge, the degree of substitution representing those substituents which provide electrostatic functionality in the form of anionic charge is preferably least about 0.05. Anionic charge may be provided, for example, by carboxyl, sulfate, sulfonate, 5 phosphonate, or phosphate groups, or combinations thereof. Where cationic charge is also present, both charges may be provided by the same groups or substituent (i.e., the substituent may be amphoteric or zwitterionic); or, the derivatized microfibrillar polysaccharide may be derivatized to contain both substituents that contain anionic charge and substituents that contain cationic charge. In addition, the derivatized 10 microfibrillar polysaccharides of the present invention may be obtained by blending two or more separate derivatized microfibrillar polysaccharides, where at least one has been derivatized to provide anionic charge, and at least one other has been derivatized to provide anionic charge, cationic charge, or both.

When the derivatized microfibrillar polysaccharide of the present invention is 15 derivatized to contain substituents that provide steric functionality, the derivatized microfibrillar polysaccharides may have a molar substitution of less than about 3.0, or of less than about 1.5, or of less than about 1.0, or of less than about 0.5. The range of molar substitution may be from about 0.5 to about 3.0. Steric functionality may be provided, by way of non-limiting example, by hydroxyethyl groups, hydroxypropyl 20 groups, methyl groups, ethyl groups; straight- or branched-chain alkyl, alkenyl, or alkynyl groups having from about 4 to about 30 carbons; and/or aryl, arylalkyl, arylalkenyl, cyclic, and heterocyclic hydrocarbons having from about 4 to about 30 carbons.

In a preferred embodiment the derivatized microfibrillar polysaccharide contains 25 carboxymethylcellulose, and has a degree of substitution of less than about 0.35, or of less than about 2.0. The range of degree of substitution may be from about 0.02 to about 0.2, with a range of from about 0.10 to about 0.2 being preferred.

The derivatized microfibrillar cellulose of the present invention may form a gel at a concentration of less than about 1% in water.

30 In a further embodiment, the present invention is directed to a comestible composition of matter containing the derivatized microfibrillar polysaccharide of the present invention. The comestible composition of matter may, by way of non-limiting

example, be a low fat, reduced fat, or fat-free food spread, such as a mayonnaise, or a salad dressing. Alternatively, the comestible composition may contain a pharmaceutically active ingredient. The derivatized microfibrillar polysaccharide may be used to provide or improve a controlled, sustained, or delayed release of a component of the comestible composition, including in particular a pharmaceutically active ingredient.

In yet another embodiment, the derivatized microfibrillar polysaccharides of the present invention may be used in non-comestible, spreadable compositions of matter, such as skin care lotions or creams, or sunscreen lotions or creams.

The present invention is further directed to a paper composition containing the derivatized microfibrillar cellulose, and particularly, though not exclusively, microfibrillar carboxymethylcellulose.

The derivatized microfibrillar polysaccharide may be produced by using a derivatizing step to treat a microfibrillar polysaccharide to obtain the derivatized microfibrillar polysaccharide. Alternatively, a derivatized polysaccharide may be microfibrillated to produce the derivatized microfibrillar polysaccharide. In another method, the steps of microfibrillation and derivatization may take place at substantially the same time. In a preferred embodiment, cellulose is first derivatized with monochloroacetic acid or a salt thereof under alkaline conditions to produce carboxymethylcellulose; the carboxymethylcellulose is suspended in water; and the resulting suspension is homogenized to produce microfibrillated carboxymethylcellulose.

The derivatizing step may include contacting a non-microfibrillar polysaccharide with a swelling agent, such as an anionic reagent, and may take place under alkaline conditions. These alkaline conditions may include contacting the cellulose with the anionic reagent in the presence of an alkaline reagent which is sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an alkali silicate, an alkali aluminate, an alkali carbonate, an amine, ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof. The derivatization may take place at high solids.

Microfibrillation may be accomplished by applying energy to a non-microfibrillar polysaccharide under conditions sufficient to produce microfibrillar polysaccharide. The non-microfibrillar may optionally be enzyme-treated before microfibrillizing. More

specifically, microfibrillation may be accomplished using homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, milling, and combinations of these. In a preferred embodiment the non-microfibrillar polysaccharide is passed through a homogenizer under conditions sufficient to produce microfibrillar cellulose; those conditions may include a pressure differential of at least about 3,000 psi, and passing the non-microfibrillar polysaccharide through the homogenizer at least three times.

The method should be conducted to yield a derivatized microfibrillar polysaccharide that is substantially insoluble in the solvent of use. Water is a preferred solvent of use, but other solvents, including but not limited to alcohols and oils, are contemplated for various applications.

The present invention extends to derivatized microfibrillar polysaccharide produced by the above methods.

In an alternative embodiment the present invention is directed to a method of modifying the rheological properties of a liquid composition of matter by incorporating the derivatized microfibrillar polysaccharides of the present invention into the liquid composition of matter.

This may be accomplished by incorporating the derivatized microfibrillar polysaccharide into a water-containing system, where it may be used, for example, to provide scale control and/or corrosion control. The rheological properties which may be modified by the derivatized microfibrillar polysaccharide include viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention.

Liquid compositions which may be rheologically modified include, as non-limiting examples, foods, pharmaceuticals, neutraceuticals, personal care products, fibers, papers, paints, coatings, and construction compositions. These include oral care products; creams or lotions for epidermal application (such as moisturizing, night, anti-age, or sunscreen creams or lotions); food spreads, including reduced fat, low fat, or fat free food spreads (such as mayonnaises); and drilling fluids.

The present invention further extends to a method of improving the physical and/or mechanical properties of a coating composition by incorporating, into the coating composition, an effective amount of the derivatized microfibrillar polysaccharide. The

physical and/or mechanical properties that may be improved in this manner include film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

The present invention has particular utility in the field of paper manufacture and treatment. For example, derivatized microfibrillar cellulose may be used to improve one or more of sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, adsorbency, film formation, membrane formation, and polyelectrolyte complexation during paper manufacture. As a particular example, the derivatized microfibrillar cellulose may be used as a drainage aid and/or as a sizing agent. A polyelectrolyte complex containing the derivatized microfibrillar polysaccharide is also within the scope of the present invention.

Microfibrillated carboxymethylcellulose is a particularly preferred embodiment for use in paper applications. During the process of paper manufacture, the derivatized microfibrillar cellulose may be used, by way of further example, in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture; for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture; to improve the uniformity of formation of a sheet of paper during its manufacture; and to improve the strength of a sheet of paper. The derivatized microfibrillar cellulose may be used in combination with any of the additives and performance enhancers conventionally used in paper manufacture, including cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and, at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof. In the context of retention of organic and/or inorganic dispersed particles, the particles so retained may include one or more of pulp fines, fillers, sizing agents, pigments, clays, detrimental organic particulate materials, and detrimental inorganic particulate materials.

In another embodiment, the stability of an emulsion, dispersion, or foam system may be improved by including, in the system, the derivatized microfibrillar polysaccharide of the present invention. The derivatized microfibrillar polysaccharide may be added to an existing system; added to a formulation which will be processed into such a system; or added during processing of such a formulation. Where addition takes place before completion of processing of a formulation into an emulsion, dispersion, or foam system, the processing conditions used to form the emulsion, dispersion, or foam may be used to produce the derivatized microfibrillar polysaccharide as well. Thus, a derivatized non-microfibrillated polysaccharide (where "non-microfibrillated" includes an incompletely microfibrillated polysaccharide) may be added to a formulation prior to completion of processing, and subsequent processing may then be conducted in a manner that will microfibrillate the polysaccharide. Alternatively, a microfibrillated polysaccharide may be added to the formulation, with subsequent processing conducted so as to derivatize the microfibrillated polysaccharide.

In another variation, both derivatization and microfibrillation may take place during processing. Systems which may be treated in this manner include water-in-oil and oil-in-water emulsions.

The present invention also extends to emulsion, dispersion, and foam systems produced by the above methods; and, to emulsion, dispersion, or foam systems that contain the derivatized microfibrillar polysaccharide of the present invention.

BRIEF DESCRIPTION OF THE FIGURES

- Figure 1 shows the dynamic mechanical spectra of Example 7, Sample 1.
- Figure 2 shows the dynamic mechanical spectra of Example 7, Sample 2.
- Figure 3 shows the dynamic mechanical spectra of Example 7, Sample 3.
- Figure 4 shows the dynamic mechanical spectra of Example 7, Sample 4.
- Figure 5 shows the dynamic mechanical spectra of Example 7, Sample 5.
- Figure 6 shows the dynamic mechanical spectra of Example 13, Sample 1.
- Figure 7 shows the dynamic mechanical spectra of Example 13, Sample 2.
- Figure 8 shows the dynamic mechanical spectra of Example 13, Sample 3.
- Figure 9 is a transmission electron micrograph of a sample microfibrillar carboxymethylcellulose prepared as in example 3 below, with a degree of substitution of about 0.17, negative stained with urinal acetate, at a magnification of 10,000X.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises derivatized microfibrillar polysaccharide.

Suitable polysaccharides for use in the present invention include, without limitation, cellulose, hemicellulose, chitin, chitosan, guar gum, pectin, alginate, agar, xanthan, starch, amylose, amylopectin, alerman, gellan, mutan, dextran, pullulan, fructan, locust bean gum, carrageenan, glycogen, glycosaminoglycans, murein, bacterial capsular polysaccharides, and derivatives thereof, with cellulose being preferred. The polysaccharide may be used as is, or spinning may be used to generate or improve fibrous structure.

Cellulose is a preferred polysaccharide for use in the present invention. Sources of cellulose for use in this invention include the following: (a) wood fibers, such as from chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint; (b) seed fibers, such as from cotton; (c) seed hull fiber, such as from soybean hulls, pea hulls, corn hulls; (d) bast fibers, such as from flax, hemp, jute, ramie, kenaf; (e) leaf fibers, such as from manila hemp, sisal hemp; (f) stalk or straw fibers, such as from bagasse, corn, wheat; (g) grass fibers, such as from bamboo; (h) cellulose fibers from algae, such as velonia; (i) bacteria or fungi; and (j) parenchymal cells, such as from vegetables and fruits, and in particular sugar beets, and citrus fruits such as lemons, limes, oranges, grapefruits. Microcrystalline forms of these cellulose materials may also be used. Preferred cellulose sources are (1) purified, optionally bleached, wood pulps produced from sulfite, kraft (sulfate), or prehydrolyzed kraft pulping processes, (2) purified cotton linters, and (3) fruits and vegetables, in particular sugar beets and citrus fruits. The source of the cellulose is not limiting, and any source may be used, including synthetic cellulose or cellulose analogs.

Cellulose is found in nature in several hierarchical levels of organization and orientation. Cellulose fibers comprise a layered secondary wall structure within which macrofibrils are arranged. Macrofibrils comprise multiple microfibrils which further comprise cellulose molecules arranged in crystalline and amorphous regions. Cellulose microfibrils range in diameter from about 5 to about 100 nanometers for different species of plant, and are most typically in the range of from about 25 to about 35 nanometers in diameter. The microfibrils are present in bundles which run in parallel within a matrix of amorphous hemicelluloses (specifically xyloglucans), pectinic polysaccharides, lignins, and

hydroxyproline rich glycoproteins (includes extensin). Microfibrils are spaced approximately 3-4 nm apart with the space occupied by the matrix compounds listed above. The specific arrangement and location of the matrix materials and how they interact with the cellulose microfibrils is not yet fully known.

5 For purposes of the present invention polysaccharide microfibrils refer to small diameter, high length-to-diameter ratio substructures which are comparable in dimensions to those of cellulose microfibrils occurring in nature. By way of non-limiting example, polysaccharide microfibrils may have diameters in the range of about 20 to about 100 nanometers, combined with lengths providing high aspect ratios, such
10 as in excess of 100, in excess of 500, or in excess of 1,000. While the present specification and claims refer to microfibrils and microfibrillation, the scope of the present invention also includes nanofibrils (cellulosic or otherwise), and the rheology modification, stabilization, and other properties that may be obtained with microfibrils by practicing the present invention may also be obtained using nanofibrils, either alone
15 or in combination with microfibrils.

In nature many polysaccharides are not present in microfibril arrangements, however, by using fiber spinning techniques it is possible to manufacture fibers from these polysaccharides. In one embodiment of this invention it is contemplated that fibers spun from polysaccharides can be derivatized and microfibrillated into fibrous
20 structures having dimensions on the order of those found naturally in cellulose. Further background on the structure, functions, and biogenesis of native cellulose may be found in Haigler, C.H., Cellular Chemistry and Its Applications, Nevell, pp. 30-83 (1985), the entirety of which is hereby incorporated by reference.

The derivatized microfibrillar polysaccharide of the present invention is
25 characterized by being in microfibrillar form, and by the presence of substituents that provide steric and/or electrostatic functionality. The amount of substituent present may be quantified by the degree of substitution, or DS, in the case of some anionic and cationic substituents, and by the molar substitution, or MS, in the case of steric substituents. The degree of substitution, which will vary with the molecular weight of
30 the polysaccharide, is the average number of substituted hydroxyl groups per anhydrosaccharide unit, while the molar substitution is the average number of substituent groups added per anhydrosaccharide unit. The DS and MS determine the

solubility of the derivatized polysaccharide, and may be readily adjusted to obtain a derivatized polysaccharide that is substantially insoluble in the environment of use, whether aqueous or non-aqueous. While the environment of use will frequently be aqueous, the derivatized microfibrillar polysaccharides of the present invention have 5 utility in applications having other solvents or liquid carriers, such as paints, coating, lacquers, oil-rich foods, inks (including but not limited to ink-jet inks), personal care products, cosmetics, and water-in-oil emulsions.

Any suitable method may be used to obtain the derivatized microfibrillar polysaccharide. In particular, the steps of microfibrillation and derivatization to impart 10 steric and/or electrostatic functionality to the polysaccharide may be carried out separately or combined to arrive at the end result. Therefore, a non-microfibrillar polysaccharide starting material may either be derivatized with anionic groups, with both anionic and cationic groups, or with a blend or mixture of anionic groups and cationic groups, and then microfibrillated, or may first be microfibrillated and then 15 derivatized. Alternatively, if the starting material is microfibrillar polysaccharide, only the derivatizing step would be necessary, whereas if the starting material is a polysaccharide that has already been properly derivatized with anionic or both anionic and cationic groups, only the microfibrillation step is required.

The degree of substitution (for electrostatic derivatization), and/or of molar 20 substitution (for steric derivatization), of the polysaccharide should be sufficiently low so that the derivatized microfibrillar polysaccharide will be substantially insoluble in the solvent or carrier that is present in the intended environment of use. In many applications the solvent or carrier will be water, and in such applications the degree of substitution and/or the molar substitution should be such that the derivatized 25 microfibrillar polysaccharide is substantially insoluble in water. However, in other applications a polar solvent or carrier (such as an alcohol) may be used having different solubility characteristics, or a non-polar solvent or carrier (such as an oil) may be used, and in such cases the degree of substitution and/or the molar substitution should be adjusted to obtain a derivatized microfibrillar polysaccharide that is substantially 30 insoluble in the solvent or carrier used in the application of interest, which, for purposes of convenience, will hereafter be referred to as the "solvent of use". Functionally, the

derivatized microfibrillar polysaccharide should be sufficiently insoluble in the environment of use to provide the desired properties in the intended application.

The presence of substantially insoluble material may be confirmed by observation of a 1-5% suspension of the material in question in the solvent or carrier of use under a light microscope at sufficient magnification to see insoluble material. A size determination may be made by preparing a suspension of the material under consideration at approximately 0.1-0.01% in a liquid non-solvent which is effective in dispersing microfibrils. This suspension is then dried on a transmission electron microscope (TEM) grid, the sample is coated to protect it from electron beam damage, and examined at sufficient magnification and focus to observe structure in the 1-1000 nanometer range. If microfibrillar elements are present they can be detected under these conditions, and the combination of insolubility under the light microscope and microfibrillar structure under the TEM will indicate the presence of substantially insoluble microfibrillar material. See Figure 9 for an example transmission electron micrograph of a microfibrillar carboxymethylcellulose prepared as in example 3 below, having a DS of about 0.17

For purposes of simplicity, unless specifically indicated otherwise the term "substituents" shall be used herein to mean chemical species that provide steric stabilization to the polysaccharide; chemical species that provide electrostatic functionality to the polysaccharide through anionic charge; chemical species that provide electrostatic functionality to the polysaccharide through a combination of both anionic and cationic charge; and combinations of the foregoing. In addition, "electrostatic" means either anionic charge, or a combination of both anionic and cationic charge, whether as groups both present on a single substituent, or as groups provided separately on two or more substituents. "Derivatization" refers not only to chemical reactions resulting in covalent bonds, but to any process whereby the substituents become sufficiently associated with the polysaccharide to provide the rheological and other benefits of the present invention, and may include, for example, adsorption. Finally, references to the combination of both anionic and cationic charge on the polysaccharide include the use of substituents that contain both types of charge (i.e., amphoteric and/or zwitterionic substituents); the combined use of substituents which individually contain only anionic or only cationic charge, resulting in derivatized

polysaccharide with a distribution of substituents that includes both anionic groups and cationic groups; and, blending of two or more derivatized polysaccharides where at least one derivatized polysaccharide includes at least anionic substituents and at least one other derivatized polysaccharide includes at least cationic substituents, resulting in a
5 blend that contains both anionically derivatized polysaccharide and cationically derivatized polysaccharide. However, "derivatized" does not include the naturally- occurring, de minimis presence of groups that would only provide the steric and/or electrostatic functionality required by the present invention at concentrations higher than those found in nature. For example, naturally-occurring cellulose may contain very low
10 levels of anionic charge, which may still be present after microfibrillation. However, such microfibrillated cellulose is not "derivatized" as that term is used in the present application, both because its degree of substitution has not been changed from its natural state, and because the amount of charge present in such microfibrillated cellulose would not provide the benefits of the present invention.

15 The sequence of steps used to arrive at the derivatized microfibrillar polysaccharide of the present invention is not critical. Therefore, the starting material used to make the derivatized microfibrillar polysaccharide may be in microfibrillar or non-microfibrillar form. Similarly, the starting material may already be derivatized with steric and/or electrostatic substituents, or not. If the starting material is non-
20 microfibrillar polysaccharide, substituents may be placed on the polysaccharide followed by microfibrillation, or the microfibrillation may be carried out first, followed by the placement of the substituents onto the resulting microfibrils. It is also acceptable to process polysaccharide into fibrils, place the substituents on the fibrils, and then further process the fibrils into microfibrils. Similarly, any non-microfibrillar form of
25 polysaccharide which already contains such substituents may be processed into microfibrillar form. Moreover, derivatization and microfibrillation may be carried out simultaneously.

It will be understood that most, if not all, polysaccharides will contain some quantity of both microfibrillar and non-microfibrillar structure both before and after
30 processing, and that the ratio between the two structures may range from polysaccharide that is substantially completely microfibrillar, to polysaccharide that is substantially completely non-microfibrillar. As used herein, the terms "microfibrillar",

"microfibrillated", and the like include polysaccharides that are substantially completely microfibrillated, and those which may be substantially microfibrillated while containing minor but significant amounts of non-microfibrillar structure, provided the polysaccharide is sufficiently microfibrillated to confer the benefits afforded by the 5 present invention.

Processes which minimize the energy needed to produce microfibrils from non-microfibrillar starting material, and/or which reduce the amount of water extracted during the process or at its end, are preferred. In this regard, it should be noted that while the derivatized microfibrillar polysaccharide of the present invention can be made 10 by derivatizing a microfibrillated polysaccharide, the microfibrillation process generally requires less energy, and/or is more efficient, if the polysaccharide has already been derivatized. Without being bound by theory, this may be because the presence of the steric and/or electrostatic functionalities on the polysaccharide 'loosens' the structure of fibril bundles.

15 The ability to use less energy not only offers cost savings, but results in less breakage of the polysaccharide microfibrils. Therefore, microfibrillating a polysaccharide that has already been derivatized may result in a derivatized microfibrillar polysaccharide with relatively longer microfibrils as compared to effecting derivatization after microfibrillation. This is particularly significant because 20 the energy required for microfibrillation can be significantly reduced by amounts of derivatization which are below the level that would render the resulting derivatized microfibrillar polysaccharide freely soluble in water. For example, derivatization of cellulose resulting in a DS on the order of 0.1 or 0.2 will 'loosen' the fibril bundles in cellulose enough to permit microfibrillation using conventional shearing devices such as 25 a homogenizer, impingement mixer, or ultrasonicator. These low DS cellulose microfibrils have diameters on the order of 50 nanometers combined with lengths of up to 500 microns, resulting in aspect ratios in excess of 1,000. While the low DS allows microfibrillation, it is too low to allow the resulting material to be fully soluble in the solvent or carrier of use at the concentrations of interest. Without being bound by 30 theory, the presence of insoluble regions in the fibers may explain the data showing maximum gel formation at low DS's. These gels may be strengthened by weak association of the more hydrophobic unsubstituted regions.

The stabilization or derivatization is accomplished by the generation or placement of substituents onto the fibril and/or microfibril. It appears that the substituents become associated predominantly with the surface regions of the fibrils or microfibrils.

Regardless of the precise mechanism, in functional terms microfibril-microfibril contact
5 is inhibited by steric and/or electrostatic mechanisms or forces. The presence of the substituents also causes the microfibrils to occupy more volume than when they are not derivatized, possibly due to inhibition of contact along at least part of the length of the microfibrils. Rheological performance of the resulting derivatized microfibrillar polysaccharide is enhanced at low concentration since volume is better occupied and the materials are distributed more homogeneously.
10

With regard to use of steric force, steric functionality or stabilization is provided by the formation of a protective barrier or sheath around a particle (such as a cellulose fibril or microfibril) to prevent flocculation. For example, it may be achieved by a material, such as a polymer, being physically adsorbed on the surface of the particle,
15 thereby preventing two particles from coming closer than a distance that is twice the sum of the radius of the particle and the thickness of the adsorbed layer. As two particles approach and the distance between them approaches the distance noted above, the adsorbed layers on two particles interact. This interaction, which as noted may be a polymer-polymer interaction, results in forces, such as osmotic and/or entropic forces,
20 that repel the particles. This prevents flocculation of the two particles, providing stabilization. Because steric forces are generally provided by the size and/or configuration of the substituent, a substituent used to provide the polysaccharide with steric functionality or stabilization may be neutral, anionic, cationic, amphiphilic, amphoteric, and/or zwitterionic.

Without being bound by theory, the surfaces of the derivatized microfibrils appear
25 to have some areas free of the substituents such that some limited interaction between microfibrils still takes place. Limited interaction may even be necessary to facilitate network formation, and may be a cause of the rheological attributes of interest such as yield stress, shear reversible gelation, and insensitivity of the modulus to temperature. It
30 also appears that the length/diameter ratio, or aspect ratio, of the fibrils and microfibrils also contributes to the performance of the materials of the present invention.

Any suitable process may be used to generate or place the substituents on the polysaccharide. For convenience, the possible processes will generally be referred to collectively as "derivatization" herein; however, within the context of this invention, derivatization is used to mean any process which results in a polysaccharide (including 5 fibrillar and microfibrillar polysaccharide) having the substituents sufficiently associated with the polysaccharide to provide the desired benefit(s), and includes not only chemical reactions resulting in covalent bonding, but also physical adsorption. In addition, the present application will refer both to "derivatization" and to "stabilization". Chemically, both terms refer to the same type of process, namely, the placement or 10 generation of substituents on the cellulosic substrate. Functionally, "derivatization" is generally the broader term, as "stabilization" implies a functionality which is usually observed primarily or exclusively when the polysaccharide is in microfibrillar form.

Possible derivatization processes include any synthetic method(s) which may be used to associate the substituents with the polysaccharide. More generally, the 15 stabilization or derivatization step may use any process or combination of processes which promote or cause the placement or generation of the substituents. For example, the conditions for treating non-microfibrillar polysaccharide should generally include both alkalinity and swelling of the polysaccharide, in order to make the surface of the fibrils more accessible to the placement or generation of the substituents. Alkalinity and 20 swelling may be provided by separate agents, or the same agent may both provide alkalinity and cause swelling of the polysaccharide. In particular, alkaline agents often serve multiple purposes, in that they may catalyze the reaction between the polysaccharide and the substituent, optionally de-protonate the derivative, and swell 25 open the polysaccharide structure to allow access of the reagents to carry out the derivatization.

Specific chemical methods which may be used to achieve the present invention include but are not limited to generation of anionic groups (such as carboxyl, sulfate, sulfonate, phosphonate, and/or phosphate); generation of both anionic and cationic groups (such as quaternary amine and/or amine); and generation of steric groups, on or 30 near the surface of the particulate polysaccharide. Alkaline conditions are preferably obtained by using sodium hydroxide. Any material that functions as a solvent for the polysaccharide of choice may be used, and alternative alkaline agents include alkali

metal or alkaline earth metal oxides or hydroxides; alkali silicates; alkali aluminates; alkali carbonates; amines, including aliphatic hydrocarbon amines, especially tertiary amines; ammonium hydroxide; tetramethyl ammonium hydroxide; lithium chloride; N-methyl morpholine N-oxide; and the like. In addition to catalytic amounts of alkaline agent, swelling agents may be added to increase access for derivatization. Interfibrillar and intercrystalline swelling agents are preferred, particularly swelling agents used at levels which give interfibrillar swelling, such as sodium hydroxide at an appropriately low concentration.

These derivatization reactions, if carried out on the original fibrous polysaccharide structure, may require specific conditions to maximize the efficiency of location of the derivatization onto the surface of the polysaccharide. For example, in the case of cellulose from wood pulp the concentration of the swelling agent used appears to have an effect on the performance of the final cellulose. In particular, in using sodium hydroxide it has been determined that the level of the sodium hydroxide can have a significant effect on the rheological performance.

It is preferred that derivatization of these fibrous polysaccharides be performed in a manner which limits the formation of microfibrils which are soluble in the intended end use composition, as these may not contribute significantly to the desired rheological performance. This typically limits the degree of derivatization which can be made where derivatization at higher levels would make the polysaccharide soluble in the end use composition. Specific limits may be readily determined based on the application in question, but as a matter of general guidance it is preferred that the degree of substitution (DS) be below about 0.5, or below about 0.35, or below about 0.2, or below about 0.18, or below about 0.1.

The derivatization may be carried out in any suitable manner, including but not limited to suspension in water; in organic solvent, either alone or in mixtures with water; in solution; and in high solids, either with water alone or with water and a minor amount of organic solvent. (For purposes of the present disclosure, "high solids" refers to a polysaccharide content of greater than about 25%).

Optional derivatizations or functionalities which may also be placed on the polysaccharide include but are not limited to short chain aliphatic and other hydrophobic-type substitutions; oligomeric and polymeric substitutions; uncharged

substitutions, as for example short chain ethylene and propylene glycols; other associative-type functionality; surfactant-like functionality; methyl; ethyl; propyl; and combinations of these. These substitutions are optional in that they may not be intended for stabilization of the polysaccharide, and will instead provide additional functionality
5 such as surface activity, emulsification power, adsorption characteristics, and the like.

The method for processing a non-microfibrillar form of polysaccharide into the microfibrillar form may be carried out either before or after the derivatization reaction. The preferred method involves the use of a homogenizer on a dilute suspension of the non-microfibrillar polysaccharide in an aqueous medium. The aqueous medium
10 optionally may have additives such as swelling agents, in particular interfibrillar and/or intercrystalline swelling agents, for example sodium hydroxide, to aid in improving the ease of microfibril generation. A more preferred method of microfibrillation involves the use of mechanical energy on an aqueous suspension of derivatized polysaccharide which has not been dried. Other microfibrillation processes include, by way of non-limiting example, use of an impingement mixer; heat; steam explosion; pressurization-depressurization cycle; freeze-thaw cycle; impact; grinding (such as a disc grinder); pumping; mixing; ultrasound; microwave explosion; and milling. Combinations of
15 these may also be used, such as milling followed by homogenization. Essentially any method of reducing particle size may be used, but methods for reducing particle size while preserving a high aspect ratio in the polysaccharide are preferred. As described previously, the degree of substitution of the polysaccharide also affects the ease of
20 processing the polysaccharide to microfibrillar form.

The process to generate the particulate may either be run by the consumer in the final application such that the particulate is generated in situ, or be run as described
25 above in aqueous media, the material dehydrated, and the resulting particulate dried. The dried particulate of this invention, hereafter referred to as the ready-to-gel or RTG form, can be rehydrated readily in polar solvents to obtain the desired rheological attributes. Dehydration can be accomplished by displacing water with less polar
30 solvents and drying, and can be accelerated by protonation or shielding of charged groups if they are present.

In terms of general properties, applications where the derivatized microfibrillar polysaccharide of the present invention have particular utility include those where the

desired rheological attributes include at least one of yield stress, shear reversible gelation, and a modulus which is insensitive to temperature. The ability to provide the rheological attributes described herein also makes it possible to provide stabilization of mixtures of liquids and solids having different densities; gel-like properties, including mouth feel; pumpable gels; stabilization at elevated temperatures; and, control of hydration and diffusion.

In terms of more specific applications or fields of use, the utility of the present derivatized microfibrillar polysaccharides includes, without limitation, foods, personal care products, household products, pharmaceuticals, neutraceuticals, paper manufacture and treatment, coating compositions, water treatment, drilling fluids, agriculture, construction, and spill control and/or recovery.

In food applications, the derivatized microfibrillar polysaccharides of the present invention may be useful as rheology modifiers; as stabilizers, such as by inhibiting creaming or settling in suspensions; and as non-digestable dietary fiber. They may also be used to control ice crystal growth during, for example, ice cream manufacture and storage.

In personal care products, the derivatized microfibrillar polysaccharides may be used to stabilize emulsions, dispersions, suspensions, and foams, and may find use in creams, lotions, gels, and pastes, including those intended for epidermal application.

Representative but not exhaustive examples include sunscreens; moisturizing or anti-aging creams and lotions; cleaning soaps or gels; antiperspirants and deodorants, including those in stick, pump spray, aerosol, and roll-on form; fragrance releasing gels; lipsticks, lip glosses, and liquid makeup products; oral care products, including toothpastes, tooth polishing and whitening agents, and denture care products such as cleaners and adhesives, and further including use in sorbitol, sorbitol-water mixtures, and glycerol-water mixtures; products where controlled, sustained, or delayed release of an ingredient would be desirable; wound care products, such as ointments (including anesthetic, antiseptic, and antibiotic ointments), dressings, and products such as ostomy rings where good liquid retention is desirable; and absorbent products, such as diapers.

The present invention may have particular utility, not only in personal care products but in other applications, with products dispersed by a pumping action. The shear-reversible gelation exhibited by the derivatized microfibrillar polysaccharide is well

suited for pump dispensing, and may be advantageously combined with its ability to stabilize emulsions, dispersions, and foams to improve the uniform delivery of product.

In the area of household products, the rheological properties of the present derivatized microfibrillar polysaccharides, and their ability to stabilize emulsions, 5 dispersions, and foams, provide utility in areas such as detergents, shampoos, cleaners, and air fresheners. Specific examples include, without limitation, laundry products (including detergents, pre-spotting cleaners, and fabric treatment compositions, such as softeners); rug and upholstery shampoos; toilet bowl cleaners (particularly those dispensed in liquid or gel form); air fresheners; and general purpose cleaning agents, 10 including liquids, gels, pastes, and foams used in cleaning and/or disinfecting household surfaces.

In pharmaceutical applications, the derivatized microfibrillar polysaccharides may have utility in controlled, sustained, or delayed release formulations; as disintegrants; as dietary fiber; in wound care, particularly in applications (such as ostomy rings) where 15 liquid-holding ability is important; and as rheology modifiers.

In the area of paper manufacture and treatment, the derivatized microfibrillar polysaccharides of the present invention have utility in emulsion modification and/or stabilization; sizing; retention; clarification; absorbence; drainage; formation (such as by functioning as flocculation aids); deposit or scale control (by inhibiting the formation 20 and/or growth of inorganic deposits); water treatment; dewatering; film and membrane formation; polyelectrolyte cross-linking; removal of detrimental organic and/or inorganic materials; in paper coatings; and in improving properties such as stiffness, wet strength, absorbancy, softness, toughness, tear resistance, and fold resistance.

In the context of paper manufacture, scale control refers to the prevention of 25 calcium carbonate and calcium oxalate deposits forming during the pulping process. Scale control can be achieved by dispersion of salt crystals in the medium to prevent growth and deposition, inhibition of nucleation, or modification of the crystal growth mechanism to prevent the formation of crystal forms that will lead to deposits. The use of derivatized microfibrillar cellulose having micron and smaller particle size, stabilized 30 with appropriate functional groups, would serve to control scale deposit because such microcarriers inhibit the crystal growth which leads to deposition. Moreover, cellulosic materials would be easier to recover from the pulping process due to their organic

nature. Preferred functional groups would include phosphate/phosphonate groups, carboxylate groups, and sulfate/sulfonate groups. Alternative functional groups and appropriate use levels may be readily determined by those of ordinary skill in the art, based on the particular environment of use.

5 The derivatized microfibrillar cellulose may also be used in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture; to retain organic and/or inorganic dispersed particles (such as pulp fines, fillers, sizing agents, pigments, and/or clays); to retain detrimental organic and inorganic particulate materials; to improve the uniformity of formation of a
10 sheet of paper; and to improve the strength of a sheet of paper. With particular regard to drainage, drainage aids are additives that increase the rate at which water is removed from a paper slurry on a paper machine. These additives increase machine capacity, and hence profitability, by allowing faster sheet formation.
15 Anionically charged microfibrillar cellulosic derivatives are capable of greatly increasing drainage, either alone or in combination with other charged polymers.

The derivatized microfibrillar cellulose of the present invention may also be used in coated papers, where cellulose derivatives may be used to control the rheology of the color coating and to provide water retention, thereby controlling the amount of liquid that permeates into the base sheet.

20 In coating compositions, such as paints and inks, the derivatized microfibrillar polysaccharides can provide rheology modification, improving properties such as spatter, leveling, sag resistance, flooding, and floating, and may have particular utility in gel paints. They may also improve pigment dispersion and/or stabilization, and function as charge control or flow control agents, including in inks, such as ink jet inks.

25 In the area of water treatment, the derivatized microfibrillar polysaccharides of the present invention can provide scale control, that is, inhibiting the formation and/or growth of inorganic deposits in aqueous systems; clarification; flocculation; sedimentation; coagulation; charge delivery; and softening.

30 In drilling fluids, the present derivatized microfibrillar polysaccharides can provide rheology modification, reduce or prevent fluid loss, and improve secondary oil recovery.

In agricultural applications, the derivatized microfibrillar polysaccharides of the present invention can be used in soil treatment, and may provide moisture retention, erosion resistance, frost resistance, and controlled, sustained, or delayed release of agricultural materials such as fertilizers, pesticides, fungicides, and herbicides. They 5 may also be used for crop protection, such as to minimize or prevent frost damage.

In construction, the derivatized microfibrillar polysaccharides can be used in dry wall muds, caulk, water-soluble adhesives, and board manufacture.

In other areas, the derivatized microfibrillar polysaccharides can be used for control and cleanup of liquid spills, as absorbents for oil; in general, as stabilizers for 10 emulsions, dispersions, and foams (including but not limited to oil-in-water and water-in-oil emulsions); and for emulsification. Stability of commercial emulsions, such as paper size emulsions, is a recurring issue in industry. Current commercial emulsions include those which generally consist of an oil, waxy, or rosin phase dispersed in water. These dispersions are generally stabilized by the addition of charged materials such as 15 cationic starches, sodium lignin sulfonate, and aluminum sulfate. Such materials are generally added in amounts equal to about 10-20% by weight of the size component. The resulting dispersions are typically 0.2 to 2 micron particles, thought to be stabilized by charge repulsion, for example, with the positively charged starches on particle surfaces repelling each other.

20 One cause of emulsion failure is density-driven separation. This can be limited by increasing viscosity, or internal structure within the fluid. For example, an emulsion which maintains a viscosity of less than about 20 centipoise throughout a standard aging test might have its viscosity increased initially by as much as 100 centipoise through addition of a viscosifier to the formulation, and still be within acceptable commercial 25 viscosity, provided that the viscosity did not then increase over time to exceed acceptable limits.

One method to accomplish this result would be to use a viscosifying agent that does not cause a substantial increase in viscosity when first added to an emulsion 30 formulation, but which does provide an increase in viscosity during normal processing of the emulsion formulation to produce the emulsion. This can be accomplished by including, as an additive to the emulsion formulation, polysaccharide that has been derivatized as described herein but not yet microfibrillated. When the emulsion

formulation is then subjected to energy, typically high shear, during the processing used to turn the emulsion formulation into an emulsion, the shear will also microfibrillize the derivatized polysaccharide, resulting in the derivatized microfibrillar polysaccharide of the present invention, which will be present as part of the emulsion. The gel produced by the derivatized microfibrillar polysaccharide will then thin under shear stress but reform when shear stops. Moreover, the insolubility of such low DS/MS polysaccharide may cause it to concentrate at the oil/water interface of oil-and-water emulsions, rather than the aqueous bulk phase, which may be desirable.

Effectively the same result may be achieved by adding the derivatized microfibrillar polysaccharide of the present invention to an emulsion formulation, or to the final emulsion, or at any point during production of the emulsion. Further variations would include introducing derivatized polysaccharide that is only partially microfibrillated into the emulsion-making process at a point where subsequent processing would provide sufficient energy to complete the microfibrillation. It may also be possible to accomplish some or all of the derivatization as part of the emulsion production process; for example, the emulsion formulation may include a charged species that will adsorb onto the polysaccharide microfibrils, or such a species may be added during processing of the emulsion formulation, separately or in combination with the polysaccharide. Therefore, the derivatized microfibrillar polysaccharides of the present invention may serve as stabilizing additives to emulsions, with several process routes being available to accomplish this end result.

While the choice of method may cause some variation in the properties of the resulting emulsion, the basic benefit of improved emulsion stability should be achieved by any procedure which has, as its final result, the presence of the derivatized microfibrillar polysaccharide of the present invention in the final emulsion.

Commercially, it may be desirable to supply customers with derivatized, non-microfibrillated polysaccharide as a powder which, when added to a formulation and subjected to high shear or other appropriate forms of energy, will microfibrillate and yield the derivatized microfibrillar polysaccharide of the present invention.

This improved emulsion stability may enable use of emulsion formulations which would not perform satisfactorily in the absence of the derivatized microfibrillar polysaccharide. Other benefits may include improved retention in paper, improved

drainage of water from paper systems due to association of pulp and filler fines with the retained microfibrils, and resistance to emulsion breakage in the presence of high salt concentrations.

The subject electrostatically derivatized materials of this invention have also been discovered to provide rheology to aqueous systems over a wide pH range (namely from about 2.5 to 10 or higher) and ionic strength. This insensitivity to pH and ionic strength facilitates use in areas where low pH and high salt conditions exist, such as in personal care creams and lotions, food products, and the like.

In addition to the above, the derivatized microfibrillar polysaccharides of the present invention represent a vehicle for providing charge, whether anionic, cationic, or both, to a given environment. This may, as a representative example, have utility in water treatment, where charged particles are used to flocculate particulates and other contaminates.

The following examples indicate various possible methods for making and using the derivatized microfibrillar cellulose of present invention. These examples are merely illustrative, and are not to be construed as limiting the present invention to particular compounds, processes, conditions, or applications. Throughout this description, "gelling" is defined to occur when $G' > G''$, where G' is the dynamic storage modulus and G'' is the dynamic loss modulus. This is the functional definition used in EP '011; for general background, see Ferry, J.D., Viscoelastic Properties of Polymers, John E. Wiley & Sons, NY, 1980.

Example 1 (Comparative): Microfibrillated, Non-Derivatized Cellulose.

The following three components were weighed into a one gallon jar at the following wt% levels:

| | | <u>Weight</u> | <u>Weight%</u> | <u>Dry Wt. Basis</u> |
|----|--|---------------|----------------|----------------------|
| | Bleached sulfate wood pulp (5.2% moisture) (Weyerhaeuser Company) | 74.82g | 2.11 | 2.00 |
| 30 | Germaben® II biocide (Sutton Laboratories, New Jersey) | 17.50g | 0.49 | 0.49 |
| | Deionized (DI) water | 3445.58g | 97.39 | 97.50 |

The cellulose quickly settled to the bottom of the jar when there was no agitation of the slurry. The jar was shaken to disperse the solids. The slurry was then processed in a dual stage Gaulin Model 15MR homogenizer. The secondary stage was set at about 1000psi and the primary stage was adjusted so that the total pressure was about 8000psi. The 5 slurry was processed for a total of 3.5 hours. The resulting slurry had a much thicker consistency and the cellulose remained suspended. When this suspension was diluted to 1.0% solids in DI water, the resulting suspension was a viscous slurry which did not exhibit gel properties. Over time the 1% suspension settled, leaving free water on the surface.

10 **Example 2: Preparation and Microfibrillation of Carboxymethylcellulose I (CMC I).**

Isopropanol (IPA) and DI water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. 15 Sulfate wood pulp (approximately 400 µm length) was added to the reactor and the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15° C. The reactor was inerted. Aqueous 50% NaOH was slowly added to the reactor while maintaining the mixture slurry's temperature at about 15° C. The slurry was agitated for 1 hour after 20 completion of caustic addition. Aqueous monochloroacetic acid (80% MCA) was slowly added to the reactor by funnel while maintaining reaction slurry temperature at about 15°C. After MCA addition, the reaction slurry was heated to 70° C and held for 1.5 hours. The reaction slurry was cooled below 30° C and glacial acetic acid was added to the reactor. The reaction mixture was then aspirator vacuum filtered with a 25 sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80% methanol for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three washes was slurried in 1000g of pure methanol using an air driven stirrer and a grounded 30 stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in a Lab-Line fluidized bed dryer (model number 23852) for 35 minutes (air-dry for 5 minutes, heat-

dry at 50° C for 10 minutes, and heat-dry at 70° C for an additional 20 minutes) The carboxymethylcellulose (CMC) product was ground using a Retsch Grinding Mill (model 2M1) with a 1mm screen. (Although the examples herein show washing of the product, the need for, or amount of, washing will depend on the intended application.)

5

Table 1: CMC I Recipes

(all weights in grams)

| Sample # | Cellulose Length | Wt. Cellulose (dry wt. Basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. 80% MCA (aq) | Wt. Glacial Acetic Acid | DS |
|----------|------------------|-------------------------------|---------|----------------------|-------------------|------------------|-------------------------|------|
| 1 | ~400 µm | 61.36 | 729 | 73.6 | 60 | 11.8 | 32.2 | 0.16 |
| 2 | ~400 µm | 61.36 | 729 | 73.6 | 60 | 11.8 | 32.2 | 0.18 |

Preparation of CMC slurry: An 800 g 1% CMC slurry was made from each Sample in Table 1 using the following materials:

10

| | <u>Weight</u> | <u>Weight%</u> |
|------------------------|---------------------|---------------------|
| CMC | 8.00 grams | 1.0 ± 0.06% |
| Germaben ® II biocide | 4.00 grams | 0.5% |
| <u>Deionized water</u> | <u>788.00 grams</u> | <u>98.5 ± 0.06%</u> |
| Total | 800.00 grams | |

15 The container was closed and shaken to wet and disperse the CMC solids. The solids will settle if left standing, so the container was shaken just prior to pouring the slurry into the homogenizer.

20 **Homogenization of CMC slurries:** The suspension was processed in the homogenizer equipped with an agitated feed pot as follows: the homogenizer was turned on before the slurry was loaded. An 800 gram slurry was processed for about 20 minutes at about 3000 psi by recycling the discharged stream from the homogenizer to the feed pot. Pressure was monitored and appropriate adjustments made to the primary stage handwheel to keep the total pressure at about 3000 psi. After the processing was completed, the discharge tube was redirected so that the sample was collected and stored 25 in a capped jar.

Rheological testing of microfibrillated CMC I: Each microfibrillated CMC sample prepared in Example 2 was then tested for rheological properties. Data was collected on a Bohlin CS Rheometer (Bohlin Instruments, Cranbury, New Jersey).

Dynamic mechanical properties were measured including the dynamic storage modulus, the dynamic loss modulus, complex viscosity, and yield stress.

Rheometer Test Conditions

Temperature Sweep: Measuring System: PP 40; 25° C - 65° C; Shear Stress: automatic;

5 Frequency: 1 Hz; Temperature Ramp Rate: 5° C/60 seconds; Measurement Interval: 20 seconds; Gap: 1 mm.

Yield Stress Test: Measuring System: CP 4/40; Stress: 6.0E-02 - 1.0E+02; Sweep Time: 60.0 seconds; Number of Steps: 30; Temperature: Manual (25° C); No of measurements: 1; Measurement Interval: 5 seconds.

10 Stress Sweep Test: Measuring System: PP 40; Temperature: Manual (25 °C); Number of Measurements: 1; Gap: 1 mm; Measurement Interval: 5 seconds; Frequency: 1 Hz.

Table 2: Rheology of Microfibrillated CMC I

| Sample # | Cellulose Length | DS of CMC I | Yield Stress (Pa) | G' @ 5.75 Pa (Pa) |
|----------|------------------|-------------|-------------------|-------------------|
| 1 | ~400 µm | 0.16 | 8.08 | 256 |
| 2 | ~400 µm | 0.18 | Not Tested | 192 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 15 1 is given in Figure 1.

Example 3: Preparation and Microfibrillation of Carboxymethylcellulose II (CMC II).

Isopropanol (IPA) and DI water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing 20 addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple.

Sulfate wood pulp (approximately 400 µm length) was added to the reactor, the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15° C. The reactor was inerted. Aqueous 50% NaOH was slowly added to the reactor maintaining the mixture slurry's 25 temperature at about 15° C. The slurry was agitated for 1 hour after completion of caustic addition. Aqueous monochloroacetic acid (80% MCA) was slowly added to the reactor by funnel while maintaining reaction slurry temperature at about 15°C. After MCA addition, the reaction slurry was heated to about 70° C and held for 1.5 hours. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered

with a sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80% methanol for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three washes
 5 was slurried in 1000g of pure methanol using an air driven stirrer and a grounded stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in a Lab-Line fluidized bed dryer (model number 23852) for 35 minutes (air-dry for 5 minutes, heat-dry at 50° C for 10 minutes, and heat-dry at 70° C for an additional 20 minutes). The
 10 carboxymethylcellulose (CMC) product was ground using a Retsch Grinding Mill (model 2M1) with a 1mm screen.

Table 3: CMC II Recipes(all weights in grams)

| Sample # | Cellulose Length | Wt Cellulose (dry wt. basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. 80% MCA (aq) | DS |
|----------|------------------|------------------------------|---------|----------------------|-------------------|------------------|------|
| 1 | ~400 µm | 77.11 | 937.5 | 141.64 | 12.50 | 8.63 | 0.04 |
| 2 | ~400 µm | 61.69 | 750 | 113.32 | 10.00 | 6.90 | 0.06 |
| 3 | ~400 µm | 77.11 | 937.5 | 141.64 | 25.00 | 17.25 | 0.13 |
| 4 | ~400 µm | 61.91 | 750 | 113.09 | 20.00 | 13.95 | 0.15 |
| 5 | ~400 µm | 61.30 | 750 | 113.71 | 20.00 | 13.86 | 0.16 |
| 6 | ~400 µm | 61.91 | 750 | 113.09 | 20.00 | 13.79 | 0.17 |
| 7 | ~400 µm | 61.43 | 750 | 113.58 | 23.60 | 16.27 | 0.19 |
| 8 | ~400 µm | 61.62 | 750 | 109.38 | 28.00 | 19.32 | 0.23 |
| 9 | ~400 µm | 61.88 | 750 | 108.12 | 30.00 | 20.70 | 0.28 |
| 10 | ~400 µm | 61.43 | 750 | 106.08 | 35.00 | 24.15 | 0.31 |
| 11 | ~400 µm | 61.43 | 750 | 108.58 | 30.00 | 20.70 | 0.34 |
| 12 | ~200 µm | 62.60 | 750 | 116.41 | 12.00 | 8.28 | 0.10 |
| 13 | ~200 µm | 62.60 | 750 | 112.91 | 19.00 | 13.11 | 0.17 |

Slurry preparation and homogenizer processing were performed as in example 2.

15 Rheological testing was performed as described in example 2.

Table 4: Rheology of Microfibrillated CMC II

| Sample # | Cellulose Length | DS of CMC I | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) | G' @25 °C/50 °C(Pa) |
|----------|------------------|-------------|------------------|------------------|---------------------|
| 1 | ~400 µm | 0.04 | Not Tested | 125 | 145/168 |
| 2 | ~400 µm | 0.06 | Not Tested | 139 | 161/160 |
| 3 | ~400 µm | 0.13 | 18.0 | 467 | 508/493 |
| 4 | ~400 µm | 0.15 | Not Tested | 467 | 441/429 |
| 5 | ~400 µm | 0.16 | 18.1 | 474 | 436/450 |
| 6 | ~400 µm | 0.17 | 34.7 | 436 | 452/462 |
| 7 | ~400 µm | 0.19 | 28.1 | 306 | 331/352 |
| 8 | ~400 µm | 0.23 | 21.4 | 148 | 137/145 |
| 9 | ~400 µm | 0.28 | 18.0 | 114 | Not Tested |
| 10 | ~400 µm | 0.31 | 14.7 | 12.9 | 12.3/12.6 |
| 11 | ~400 µm | 0.34 | 11.4 | 19 | 23.4/24.9 |
| 12 | ~200 µm | 0.10 | 8.08 | 339 | Not Tested |
| 13 | ~200 µm | 0.17 | 16.1 | 354 | Not Tested |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 3 is given in Figure 2.

5 **Example 4: Preparation and Microfibrillation of Carboxymethylcellulose III (CMC III).**

Isopropanol and DI water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. 10 Sulfate wood pulp (approximately 400 µm length) was added to the reactor, the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to about 15° C. The reactor was inerted. Aqueous NaOH (50% NaOH) was slowly added to the reactor maintaining the mixture slurry's temperature at about 15 ° C. The slurry was agitated for 1 hour after completion 15 of caustic addition. Aqueous sodium monochloroacetate was prepared by mixing 80% MCA, 50% aqueous NaOH and DI water. This solution was slowly added to the reactor by addition funnel while maintaining reaction slurry temperature at about 15° C. After MCA addition, the reaction slurry was heated to about 70° C and held for 1.5 hours. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered 20 with a sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80%

methanol for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three washes was slurried in 1000g of pure methanol using an air driven stirrer and a grounded

5 stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was broken into small particles using a rubber spatula and then dried in the fluidized bed dryer for 35 minutes. (Air-dry for 5 minutes, heat-dry at 50 ° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes) The product was ground using the Retsch mill with a 1mm

10 screen.

Table 5: CMC III Recipes

(all weights in grams)

| Sample # | Cellulose Length | Wt Cellulose (dry wt. basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | NaMCA Solution | | | DS |
|----------|------------------|------------------------------|---------|----------------------|-------------------|----------------|----------|------------------|------|
| | | | | | | 80% MCA | 50% NaOH | H ₂ O | |
| 1 | ~400 µm | 61.88 | 750 | 117.12 | 6.39 | 8.28 | 5.61 | 3.0 | 0.06 |
| 2 | ~400 µm | 61.88 | 750 | 114.32 | 9.38 | 12.14 | 8.22 | 5.0 | 0.12 |
| 3 | ~400 µm | 61.62 | 750 | 113.38 | 12.58 | 16.27 | 11.02 | 10.0 | 0.16 |
| 4 | ~400 µm | 61.62 | 750 | 108.38 | 15.98 | 20.70 | 14.02 | 10.0 | 0.24 |
| 5 | ~400 µm | 61.62 | 750 | 105.88 | 18.64 | 24.15 | 16.36 | 10.0 | 0.29 |
| 6 | ~400 µm | 61.88 | 750 | 102.47 | 21.31 | 27.60 | 18.69 | 10.0 | 0.31 |
| 7 | ~200 µm | 62.60 | 750 | 116.41 | 6.39 | 8.28 | 5.61 | 10.0 | 0.08 |
| 8 | ~200 µm | 62.60 | 750 | 112.91 | 10.12 | 13.11 | 8.88 | 10.0 | 0.16 |
| 9 | ~200 µm | 62.60 | 750 | 110.61 | 12.57 | 16.28 | 11.03 | 10.0 | 0.21 |
| 10 | ~200 µm | 62.60 | 750 | 117.12 | 15.67 | 20.30 | 13.75 | 10.0 | 0.26 |

Slurry preparation and homogenizer processing were performed as in example 2 except

15 for Sample #7, which was processed for 30 minutes. Rheological testing was performed as described in example 2.

Table 6: Rheology of Microfibrillated CMC III

| Sample # | Cellulose Length | DS of CMC III | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) | G' @ 25°C/50°C(Pa) |
|----------|------------------|---------------|------------------|------------------|--------------------|
| 1 | ~400 µm | 0.06 | 14.7 | 281 | 316/310 |
| 2 | ~400 µm | 0.12 | 51.4 | 568 | 520/586 |
| 3 | ~400 µm | 0.16 | 28.1 | 564 | 607/649 |
| 4 | ~400 µm | 0.24 | 18.1 | 457 | 414/474 |
| 5 | ~400 µm | 0.29 | 21.4 | 298 | 292/303 |
| 6 | ~400 µm | 0.31 | 44.7 | 288 | Not Tested |
| 7 | ~200 µm | 0.08 | 4.70 | 238 | Not Tested |
| 8 | ~200 µm | 0.16 | 29.5 | 483 | Not Tested |
| 9 | ~200 µm | 0.21 | 18.1 | 339 | Not Tested |
| 10 | ~200 µm | 0.26 | 21.4 | 288 | Not Tested |

¹ 30 minute homogenizer processing time.

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 3 is given in Figure 3.

5 **Example 5: CMC Preparation with Water Washing of Wetcake.**

Isopropanol and DI water were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. Sulfate wood pulp (approximately 400 µm length) was added to the reactor, the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15° C. The reactor was inerted. Aqueous NaOH (50% NaOH) was slowly added to the reactor maintaining the mixture slurry's temperature at about 15° C. The slurry was agitated for 1 hour after completion of caustic addition. Aqueous sodium monochloroacetate was prepared by mixing 80% MCA, 50% aqueous NaOH and DI water. This solution was slowly added to the reactor by addition funnel while maintaining reaction slurry temperature at about 15° C. After MCA addition, the reaction slurry was heated to about 70° C and held for 1.5 hours. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 650g of DI water for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated one additional time. The wetcake obtained from the previous two washes was slurried in 1000g DI water using an air driven stirrer and a grounded stainless steel

beaker for 15 minutes and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in the fluidized bed dryer for 35 minutes (air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes). The product was ground using the Retsch mill with a 1mm screen.

Table 7: Water Washed CMC Recipes

(all weights in grams)

| Sample # | Wt Cellulose (dry wt. Basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | NaMCA Solution | | | DS |
|----------|------------------------------|---------|----------------------|-------------------|----------------|----------|------------------|------|
| | | | | | 80% MCA | 50% NaOH | H ₂ O | |
| 1 | 61.88 | 750 | 110.5 | 10.12 | 13.11 | 8.88 | 10.0 | 0.10 |
| 2 | 60.06 | 750 | 110.5 | 10.12 | 13.11 | 8.88 | 10.0 | 0.13 |

Slurry preparation, homogenizer processing, and rheological testing were performed as described in example 2.

Table 8 Rheology of Water Washed CMC Samples

| Sample | DS of CMC | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) |
|--------|-----------|------------------|------------------|
| 1 | 0.10 | 37.4 | 724 |
| 2 | 0.13 | 34.7 | 855 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 2 is given in Figure 4.

15 Example 6: High Solids Reactions.

Sulfate wood pulp (about 200 µm length) was charged to an Abbey Ribbon Blender (model 0 RM, Paul O. Abbe, Inc., Little Falls, New Jersey) equipped with a spray nozzle. The reactor was sealed and the system was inerted with nitrogen under slow agitation. Agitation was increased to approximately 125 rpm and a solution of 20 50% aqueous NaOH and DI water was sprayed into the reactor. The mixture was mixed for one hour at ambient temperature. An aqueous solution of sodium monochloroacetate (NaMCA) was sprayed into the reactor and the reactor temperature was increased to 75° C and held for 2 hours. Glacial acetic acid was sprayed into the reactor and the reactor was cooled to approximately 30° C. The product was slurried in 3 liters of water for 15 25 minutes and filtered using a rubber dam. This slurry/filtration process was repeated

three additional times. The final filter cake was dried in the fluidized bed dryer and ground in the Retsch mill using a 1 mm screen.

Table 9: High Solids Recipes

(all weights in grams)

| Sample | Wt. Cellulose (dry wt. Basis) | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. NaMCA (NaMCA/H ₂ O) | Acetic Acid | DS |
|--------|-------------------------------------|----------------------|----------------------|---------------------------------------|----------------|------|
| 1 | 500 | 93 | 62.8 | 105/128.3 | 0 | 0.10 |
| 2 | 180 | 64.8 | 43.2 | 45.3/55.4 | 8.6 | 0.17 |

5 Slurry preparation: As in Example 2, except that Sample #2 (DS = 0.17) was worked up as a 10% solids slurry in water. This slurry was then mixed with more water and Germaben® II to make the new slurry which was processed in the homogenizer.

| | | <u>Weight</u> | <u>Weight%</u> |
|----|------------------------|---------------------|----------------|
| 10 | 10% CMC slurry | 80.07 grams | 10.00% |
| | Germaben® II biocide | 4.01 grams | 0.50% |
| | <u>Deionized water</u> | <u>716.88 grams</u> | <u>89.50%</u> |
| | Total | 800.96 grams | |

Since the final slurry is 10% by weight of a 10% CMC slurry, the actual CMC level is 15 the normal 1% by weight. Homogenization was performed as in Example 2 except that Sample #1 was processed for 25 minutes, and rheological testing was performed as in example 2.

Table 10: Rheology of High Solids Samples

| Sample | DS of CMC | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) |
|--------|--------------|---------------------|---------------------|
| 1 | 0.10 | 18.1 | 248 |
| 2 | 0.17 | 31.4 | 427 |

20 A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 2 is given in Figure 5.

Example 7: Preparation of Ready-to-Gel Microfibrillated CMC.

Gels were made as described in the slurry preparation and homogenization processing steps in Example 2 using CMC II as made in example 3 (DS about 0.16).

25 The gels were then processed as follows (the following description pertains to Sample #1 in Table 11, and a similar procedure was used for all of the other samples):

Approximately 2800 ml of isopropyl alcohol was added to a grounded 12 quart stainless steel (SS) beaker. The IPA was stirred at the top speed of an overhead stirrer driven by house air. A SS cowls blade on a SS shaft was used to stir the IPA. about 1400 grams of 1% CMC II gel was slowly added to the stirring IPA. The material ratio 5 was 2 ml IPA/1 gram gel. It took about 5 minutes to add the gel to the IPA. The beaker was covered with plastic film and the slurry was stirred for ten minutes.

When ten minutes had passed, the slurry was filtered through a synthetic straining cloth. The slurry was filtered using gravity. The slurry was covered with plastic film during the filtration to reduce IPA evaporation. Occasionally the gel on the cloth was 10 stirred with a plastic spatula to help speed filtration. When it appeared that the filtration had gone about as far as it could, the wet cake was transferred back to the 12 quart SS beaker.

Approximately 2800 ml of fresh IPA was added to the beaker and the slurry was again stirred for ten more minutes with the cowls blade/air stirrer. The slurry was then 15 filtered on a 20 cm Büchner funnel with #415 VWR filter paper. The wet cake was transferred to a glass crystallization dish. The dish and wet cake were placed into an 80° C oven under vacuum overnight for drying. The sample was dried to constant weight. The solids were ground in a Waring Blender.

The dehydrated gels were examined by rehydration as follows: a premix of DI 20 water and Germaben® II was prepared.

| | <u>Weight</u> | <u>Weight%</u> |
|----------------------|---------------|----------------|
| Deionized water | 788.00 grams | 99.49% |
| Germaben® II biocide | 4.00 grams | 0.51% |

The water/Germaben® II solution was then weighed into a small Waring blender cup along with the Ready-to-gel dry CMC according to the recipes in Table 11. The blender 25 cup was covered and the sample was mixed until it appeared to be homogeneous. The resulting gel was transferred to a glass jar. It was then shaken on a vortex mixer.

Rheological testing was performed as described in example 2.

Table 11: Rheology of RTG CMC

| Sample | Wt. % water/Germaben® II | Wt% RTG CMC | Yield Stress(Pa) | G' @ 5.75 Pa(Pa) |
|--------|--------------------------|-------------|------------------|------------------|
| 1 | 99.75 | 0.25 | 2.4 | 5.61 |
| 2 | 99.5 | 0.50 | 10.7 | 68.6 |
| 3 | 99.0 | 1.00 | 25.7 | 328 |
| 4 | 98.5 | 1.50 | 51.0 | 731 |
| 5 | 98.0 | 2.00 | 95.3 | 1400 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Sample 1 through 5 are given in Figures 6 through 10, respectively.

5 **Example 8A: Acid Process for Preparation of Ready-to-Gel Microfibrillar CMC.**

A gel as prepared in example 3 was acidified using HCl to adjust the pH to about 2.7. The gel was centrifuged to remove about 60% of the water. The concentrated gel was then converted to RTG form by mixing with IPA equivalent to 2 times the weight of the gel, followed by filtration on a Büchner funnel and a second mix with another 2 times weight of IPA. The wet cake was dried in a vacuum oven.

10 The dried solids were rehydrated at 1% in water/Germaben® II biocide. A small amount of baking soda was added and the sample was mixed on the blender. Viscosity rose gradually with stirring and the sample became gel-like. The pH was about 6.9.

Rheological testing was performed as described in example 2. G' @ 5.75 Pa: 15 226 Pa, Yield Stress: 17.4 Pa. A copy of the dynamic mechanical spectra (obtained by the stress sweep test) is given in Figure 11.

Example 8B: Acid Process for Preparation of Ready-to-Gel Microfibrillar CMC.

A second batch of gel as made in example 3 had its pH adjusted to about 2.7 with concentrated HCl. The sample was centrifuged and about 62% of the water was removed. About 97g of concentrated gel was slurried with 150 ml IPA. The pH was adjusted to 7.0 during the stirring of the slurry by addition of a small amount of baking soda. The slurry was filtered on a Büchner funnel, and half of the wet cake (Sample A) was weighed into a crystallization dish for drying. For Sample B, the other half of the wet cake was reslurried in about 75 ml IPA. This wet cake was filtered on a Büchner funnel and was pressed with rubber dam to remove as much IPA as possible. Both wet

cakes were dried to constant weight under vacuum, and the solids were ground up in a Waring blender.

Sample A was mixed with water for a total solids level of 1%, and gelled quickly. The pH was about 5.8. Sample B gelled quickly when stirred in water at a solids level of 5 1%.

Rheological testing was performed as described in example 2.

Sample A: G' @ 5.75 Pa: 471 Pa, Yield Stress: 34.0 Pa. A copy of the dynamic mechanical spectra (obtained by the stress sweep test) is given in Figure 12.

Sample B: G' @ 5.75 Pa: 403 Pa, Yield Stress: 35.7 Pa. A copy of the dynamic 10 mechanical spectra (obtained by the stress sweep test) is given in Figure 13.

Example 9: Derivatization of Microfibrillar Cellulose.

Isopropanol (602.8g) and DI water (86.4g) were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and 15 thermocouple. Microfibrillated cellulose of Example 1 was vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 565g of 80% isopropanol (IPA) for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three 20 washes was slurried in 1000g of pure IPA using an air driven stirrer and a grounded stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The resulting wet cake, comprised of 36g microfibrillated cellulose, 228g IPA, and 36g DI water was added to the reactor, the mixture slurry was agitated for 10 minutes, after which the mixture was nitrogen sparged for 1 hour while cooling the slurry temperature to 15° C. The reactor was 25 inerted. Aqueous 50% NaOH (10.52g) was slowly added to the reactor maintaining the mixture slurry's temperature at about 15° C. The slurry was agitated for 1 hour after completion of caustic addition. Aqueous monochloroacetic acid (7.26g of 80% aq MCA) was slowly added to the reactor by funnel while maintaining reaction slurry 30 temperature at about 15° C. After MCA addition, the reaction slurry was heated to about 70° C and held for 1.5 hours. The reaction slurry was cooled down to below 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The

wetcake was slurried in 565g of 80% methanol for 15 minutes using an air driven stirrer and a ground stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two more times. The wetcake obtained from the previous three washes was slurried in 1000g of pure methanol using an air driven stirrer and a ground stainless steel beaker for 15 minutes to dehydrate and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in the fluidized bed dryer for 35 minutes (air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes). The product was ground using the Retsch mill with a 1mm screen. DS of the resulting material was 0.14.

A 1% aqueous suspension of the product was mixed in a Waring blender for 15 minutes. This produced a viscous suspension which did not settle with time.

Slurry preparation: Same as in example 2. Homogenization was performed as in example 2, except where otherwise stated, and rheological testing was performed as in example 2.

Yield Stress: 5.75 Pa, G' @ 5.75 Pa: 363 Pa. A copy of the dynamic mechanical spectra (obtained by the stress sweep test) is given in Figure 14.

Example 10: Alternative Cellulose.

CMC was produced as in example 3 using the cellulose source and recipe in Table 12.

20

Table 12: Alternative Cellulose Recipe

(all weights in grams)

| Sample | Cellulose Source | Wt Cellulose (dry wt. basis) | Wt. IPA | Wt. H ₂ O | Wt. 50% NaOH (aq) | Wt. 80% MCA (aq) | DS |
|--------|------------------------|------------------------------|---------|----------------------|-------------------|------------------|------|
| 1 | Avicel® pH-101NF (-90) | 62.01 | 750 | 113.49 | 19.00 | 13.11 | 0.16 |
| 2 | Solka® Floc (1) | 61.23 | 750 | 114.27 | 19.00 | 13.11 | 0.19 |
| 3 | CTMP (2) | 54.5 | 750 | 121 | 19.00 | 13.11 | 0.22 |

(1) Solka Floc (grade 300 FCC) obtained from Fiber Sales & Development Corp.,

Urbana, Ohio.

25 (2) Bleached CTMP (Chemical Thermomechanical Pulp) Fluff obtained from SCA Graphic Sundsvall AB, Timra, Sweden

Slurry preparation of the Solka Floc sample (Sample 2) was prepared as in Example 2. Homogenizer processing was performed as in Example 2, and rheological testing was performed as in Example 2.

Table 13: Rheology

| Sample | Cellulose Source | DS of CMC | Yield Stress ¹ (Pa) | G' @ 5.75 Pa(Pa) |
|--------|------------------|-----------|--------------------------------|------------------|
| 2 | Solka Floc | 0.19 | 22.4 | 141 |

5 ¹ From yield stress test/ from stress sweep test.

A copy of the dynamic mechanical spectra of sample 2 is given in Figure 15.

Example 11: Microfibrillation of CMC with Impingement Mixer.

The samples used were 0.5%, 1.0% and 1.5% suspensions of low DS CMC prepared as in Example 3. Each slurry weighed a total of 100 grams. No Germaben® II biocide was used in the samples processed in the impingement mixer. The slurries were prepared by weighing the components into four ounce glass jars. The jars were capped and shaken to wet and disperse the CMC solids.

| | <u>Sample #1 (0.5%)</u> | <u>Sample #2 (1.0%)</u> | <u>Sample #3 (1.5%)</u> |
|----------|-------------------------|-------------------------|-------------------------|
| CMC | 0.50 grams | 1.0 grams | 1.5 grams |
| DI water | 99.5 grams | 99.0 grams | 98.5 grams |

A Microfluidics Corporation Model M110 Series impingement mixer was flushed with DI water prior to use. The pressure was adjusted to the desired setting as the water was pumped. The impingement mixer was run such that the DI water was pumped until it was just at the bottom of the charge funnel. A heating bath used to control the temperature of the impingement mixer piping was set at 50° C.

The sample jar was shaken again just before charging the sample funnel. The sample was charged into the funnel. An electric overhead stirrer was in the sample funnel. This was turned on to help keep the CMC homogeneously suspended. After the first pass, the stirrer is not needed. The sample was pumped through the microfluidizer and out into a collection jar. The material initially collected which contains the initial DI residue was discarded. Processing was then continued until the entire sample had been processed for 1 pass through the equipment.

The 0.5% solids gel was processed at 6000 psi for 4 passes. The 1.0% solids gel was processed under the same conditions. The 1.5% solids gel was processed at 6000 psi for just 3 passes.

Table 14: Rheology of Impingement Mixer Microfibrillated CMC

| Sample | Cellulose Length | DS of CMC | Yield Stress(Pa) | G' @ 5.75 Pa (Pa) | G' @ 25°C/50°C (Pa) |
|--------|---------------------------|-----------|------------------|-------------------|---------------------|
| 1 | ~400 µm(0.5% solids gel) | 0.17 | 4.82 | 79.3 | 97/109 |
| 2 | ~400 µm(1.0% solids gel) | 0.17 | Not Tested | 270 | 222/242 |
| 3 | ~400 µm (1.5% solids gel) | 0.17 | Not Tested | 522 | 363/434 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Samples 1 through 3 are given in Figures 16 through 18.

5 **Example 12: Microfibrillated Hydrophobically Modified Carboxymethyl Cellulose (HMCMC)**

Tert-butyl alcohol (TBA, 750 g) and Hercules CMC 7H (DS of about 0.7, 100 g) were charged to a nitrogen sparged, jacketed resin kettle equipped with an air driven stirrer, stainless steel agitator, two pressure equalizing addition funnels, a reflux condenser, nitrogen inlet, vacuum line and thermocouple. The mixture was nitrogen sparged for 1 hour at 25 ° C. Aqueous NaOH (54 g of 7.5% NaOH) was slowly added to the reactor maintaining the mixture slurry's temperature at about 25° C. The slurry cooled to about 15° C and was agitated for 1 hour at about 15° C. A 50% solution of cetyl glycidal ether (40 g of solution) was slowly added to the reactor by addition funnel while maintaining reaction slurry temperature at about 15° C. The reaction slurry was heated to about 80° C and held for 3.25 hours. The reaction slurry was cooled down to about 50° C and 9 g of 70% nitric acid was added. The mixture was cooled to about 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 1000 g of 85% acetone for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two additional times. The wetcake obtained from the previous three washes was slurried in 1000g of 100% acetone using an air driven stirrer and a grounded stainless steel beaker for 15 minutes and then aspirator vacuum filtered with a sintered glass funnel and rubber dam. The final wetcake was dried in the fluidized bed dryer for 35 minutes. (Air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes)

The product was ground using the Retsch mill with a 1mm screen. The cetyl content of the resulting product was \leq 0.03 wt.%.

Slurry preparation, homogenizer processing, and rheological testing were performed as described in example 2. G' @ 5.75 Pa: 319 Pa, Yield Stress: 14 Pa. A copy of the dynamic mechanical spectra (obtained by the stress sweep test) is given in Figure 19.

While the use of hydrophobically modified derivatized microfibrillar cellulose has been demonstrated herein by a particular example, for purposes of the present invention a derivatized microfibrillar cellulose may be hydrophobically modified by carbon groups having from about 4 to about 30 carbons.

10 **Example 13: Microfibrillated Hydroxyethylcellulose (HEC).**

Sulfate wood pulp, tert-butyl alcohol (TBA), acetone, isopropanol (IPA) and DI water were charged to a nitrogen sparged, agitated Chemco reactor (3 pint reactor, Chemco, Tulsa, OK). The reactor was inerted with nitrogen and the reaction slurry temperature was adjusted to 20° C. Aqueous NaOH (50% NaOH) was added to the reactor and the mixture was agitated for 45 minutes at 20 ° C. Ethylene oxide (EO) was charged to the reactor over a period of about 5 minutes, maintaining the reaction slurry at 20° C. After EO addition, the reaction slurry was heated to 50° C and maintained at 50° C with agitation for about 45 minutes. The reaction slurry was then heated to about 90° C and maintained at 90° C with agitation for 30 minutes. The reaction slurry was cooled to about 50° C and 70% nitric acid was added. The reaction slurry was cooled to below 30° C and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. The wetcake was slurried in 600g of 80% acetone for 15 minutes using an air driven stirrer and a grounded stainless steel beaker and then aspirator vacuum filtered with a sintered glass funnel and a rubber dam. This was repeated two additional times.

15 The wetcake obtained from the previous three washes was slurried in 600g of 100% acetone water using an air driven stirrer and a grounded stainless steel beaker for 15 minutes and then aspirator vacuum filtered with a sintered glass funnel and rubber dam.

20 The final wetcake was dried in the fluidized bed dryer for 35 minutes (air-dry for 5 minutes, heat-dry at 50° C for 10 minutes and heat-dry at 70° C for an additional 20 minutes). The product was ground using the Retsch mill with a 1mm screen.

Table 15:HEC Recipes

(all weights in grams)

| Sample # | Cellulose | TBA | IPA | Acetone | H ₂ O | 50% NaOH | EO | 70% Nitric Acid | MS |
|----------|-----------|-------|-----|---------|------------------|----------|------|-----------------|-----|
| 1 | 46.0 | 517.8 | 8.6 | 7.9 | 63.5 | 13.0 | 16.1 | 14.6 | 0.7 |
| 2 | 49.77 | 517.8 | 8.6 | 7.9 | 59.73 | 12.7 | 10.6 | 14.6 | 0.8 |
| 3 | 49.77 | 517.8 | 8.6 | 7.9 | 59.73 | 13.0 | 19.5 | 14.6 | 1.3 |

Slurry preparation and homogenizer processing were performed as in example 2, except that fewer passes were required to process to a gel.

5

Table 16: Rheology of Microfibrillated HEC

| Sample | MS of HEC | Yield Stress (Pa) | G' @ 5.75 Pa (Pa) |
|--------|-----------|-------------------|-------------------|
| 1 | 0.7 | 1.66 | 43.6 |
| 2 | 0.8 | 3.65 | 10.3 |
| 3 | 1.3 | 2.98 | 2.96 |

A copy of the dynamic mechanical spectra (obtained by the stress sweep test) of Samples 1 though 3 are given in Figures 20 through 22.

10 **Drainage Aids in Paper Manufacture:** the following examples demonstrate the effectiveness of derivatized microfibrillar polysaccharide as a drainage-improvement aid.

15 Drainage measurements were performed on a Canadian Standard Freeness (CSF) tester, using a bleached kraft pulp consisting of 70% hardwood and 30% softwood. All freeness testing was performed in hard water having a pH of 7.95-8.05, alkalinity of 50 ppm (as calcium carbonate), and hardness of 100 ppm (as calcium carbonate) using TAPPI method T 227 om-92. A pulp consistency of 0.3% was used. Higher CSF values indicate better (faster) drainage.

20 The following results were obtained using RTG microfibrillated CMC prepared in example 7, which has a degree of substitution of about 0.17 charge group per anhydroglucosamine unit. All loadings are calculated as percent of additive (dry basis) relative to pulp.

Example 14: RTG CMC Sample Material Alone.

| | % RTG CMC Material <u>(based on pulp)</u> | % RTG | |
|---|---|--------------|------------|
| | | CMC Material | |
| | | | <u>CSF</u> |
| 5 | 0 | | 210 |
| | 0.025 | | 274 |
| | 0.050 | | 285 |
| | 0.100 | | 315 |
| | 0.200 | | 317 |

10 **Example 15: RTG CMC Sample Material and Hercules Reten® 1232 (R-1232).**

| | % RTG Material <u>(based on pulp)</u> | CSF VALUES | |
|----|--|---------------|---------------|
| | | 0.1% | 0.2% |
| | | <u>R-1232</u> | <u>R-1232</u> |
| 15 | 0 | 380 | 462 |
| | 0.1 | 485 | 591 |
| | 0.2 | 526 | 608 |
| | 0.4 | 587 | 637 |
| | 0.6 | 572 | 671 |

16 **Example 16: RTG CMC Sample Material and Hercules Kymene® 557H resin (K-557H).**

A constant 2:1 ratio of K-557H to material was employed. (Kymene is a registered trademark of Hercules Incorporated.) Two different starting pulps were used, one with a relatively high freeness, and one relatively low.

| | % RTG Material <u>(based on pulp)</u> | % | Pulp 1 | Pulp 2 |
|----|--|--------|------------|------------|
| | | K-557H | <u>CSF</u> | <u>CSF</u> |
| | | | | |
| 25 | 0 | 0 | 184 | 413 |
| | 0.1 | 0.2 | 281 | 531 |
| | 0.2 | 0.4 | 321 | 565 |
| | 0.4 | 0.8 | 382 | 574 |

30 **Example 17: RTG CMC Material and Hercules Kymene 450 resin (K-450).**

A constant 2:1 ratio of K-450 to sample material was employed. Two different starting pulps were used, one with a relatively high freeness, and one relatively low.

| | % RTG Material <u>(based on pulp)</u> | % <u>K-450</u> | Pulp 1 <u>CSF</u> | Pulp 2 <u>CSF</u> |
|---|--|-------------------|----------------------|----------------------|
| 5 | 0 | 0 | 184 | 413 |
| | 0.1 | 0.2 | 285 | 536 |
| | 0.2 | 0.4 | 335 | 546 |
| | 0.4 | 0.8 | 357 | 562 |

As with ordinary CMC, the sample material extends the wet and dry strength activity of additives such as Hercules Kymene 557H or Kymene 450 resin. Thus an advantage of the use of the sample material is the provision of a combined wet strength/dry strength/drainage/retention aid.

10 **Use in paper sizing compositions:** the following examples relate to use CMC II as made in example 3 having a DS of about 0.15 in connection with compositions used in paper sizing.

15 **Example 18.** A 600 ml beaker was used to combine 66.0 grams of Precis® 787 ketene dimer (available from Hercules Incorporated, Wilmington, Delaware; Precis is a registered trademark of Hercules Incorporated), 1.5g of CMC II (as made in example 3, DS about 0.15), and 232.5 grams of DI water. The pre-mix was dispersed by stirring for two minutes using a Tekmar Ultra-turax SD45 rotor-stator high shear mixer (Tekmar Company, Cincinnati, Ohio) at a power setting of 50. This pre-mix was then quickly poured into the feed chamber of the impingement mixer. With mechanical stirring at about 250 RPM, premix was passed through the impingement mixer with its pressure set at 5000 psi. The emulsion was collected and a second pass was made. The second pass product was collected in a clean jar, a stir bar was added, the jar was capped, and then cooled in a 5 to 15°C water bath.

20 **Example 19.** Same as Example 18, using 66.0 g Precis ketene dimer, 1.5g of the sample material, 66.0g of 50% aluminum sulfate ($18\text{H}_2\text{O}$) solution in water, and 166.5 g DI water.

Example 20.

Same as Example 18, using 66.0 g Precis ketene dimer; 1.5g of the sample material; 132.0g of a solution containing 25% (wt) aluminum sulfate ($18\text{H}_2\text{O}$), deionized water, and sufficient alkalinity to raise the pH to 4.0; and 100.5 g DI water.

5 **Example 21.**

Same as Example 18, using 66.0 g Precis ketene dimer; 75.0g of a 2% solution of CMC 7M (DS of 0.7) (Hercules Incorporated, Wilmington DE) in deionized water; and 132.0g of a solution containing 25% (wt) aluminum sulfate ($18\text{H}_2\text{O}$), deionized water, and sufficient alkalinity to raise the pH to 4.0; and 27.0 g DI water.

10 **Example 22.**

3.0g of CMC II (as made in example 3, DS about 0.15) were dispersed in 465g DI water for 5 minutes using the high shear mixer at a power setting of 50, then given three passes through the impingement mixer at 5000 psi. As in Example 18, 66.0 g Precis ketene dimer were combined with 234.0 g of the sample material in DI water gel, 15 stirred using the high shear mixer at a power setting of 50, then given two passes through the impingement mixer at 5000 psi and cooled.

Example 23.

4.0g of CMC II (as made in example 3, DS about 0.15) was dispersed in 400g DI water for 5 minutes using the high shear mixer at a power setting of 50, then given 20 three passes through the Microfluidizer at 5000 psi to give a gel.

In an 8 ounce wide mouth jar, 176.0 grams of Precis 787 ketene dimer and 224.0 grams of DI water were combined. The pre-mix was sheared in the high shear mixer for 5 minutes at a power setting of 50, then quickly poured into the feed chamber of the impingement mixer. With mechanical stirring at about 250 RPM, the premix was 25 passed twice through the impingement mixer set at 5000 psi

150.0 g of the gel made above was combined with 150.0 g Precis ketene dimer 44% emulsion, and stirred 5 minutes using the high shear mixer at a power setting of 50.

Example 24.

In an 8 ounce wide mouth jar, 66.0 grams of Precis 787 ketene dimer, 1.5g of 30 pre-sheared, solvent exchange dried material as made in Example 7 (DS of about 0.16), and 232.5 grams of DI water were combined. The pre-mix was sheared in the high shear mixer for 5 minutes at a power setting of 50, then quickly poured into the feed

chamber of the impingement mixer. With mechanical stirring at about 250 RPM, the premix was passed through the impingement mixer at 5000 psi. The emulsion was collected and a second pass was made. The second pass product was collected in a clean jar, a stir bar was added, and the jar was capped and cooled in a 5 to 15°C water

5 bath.

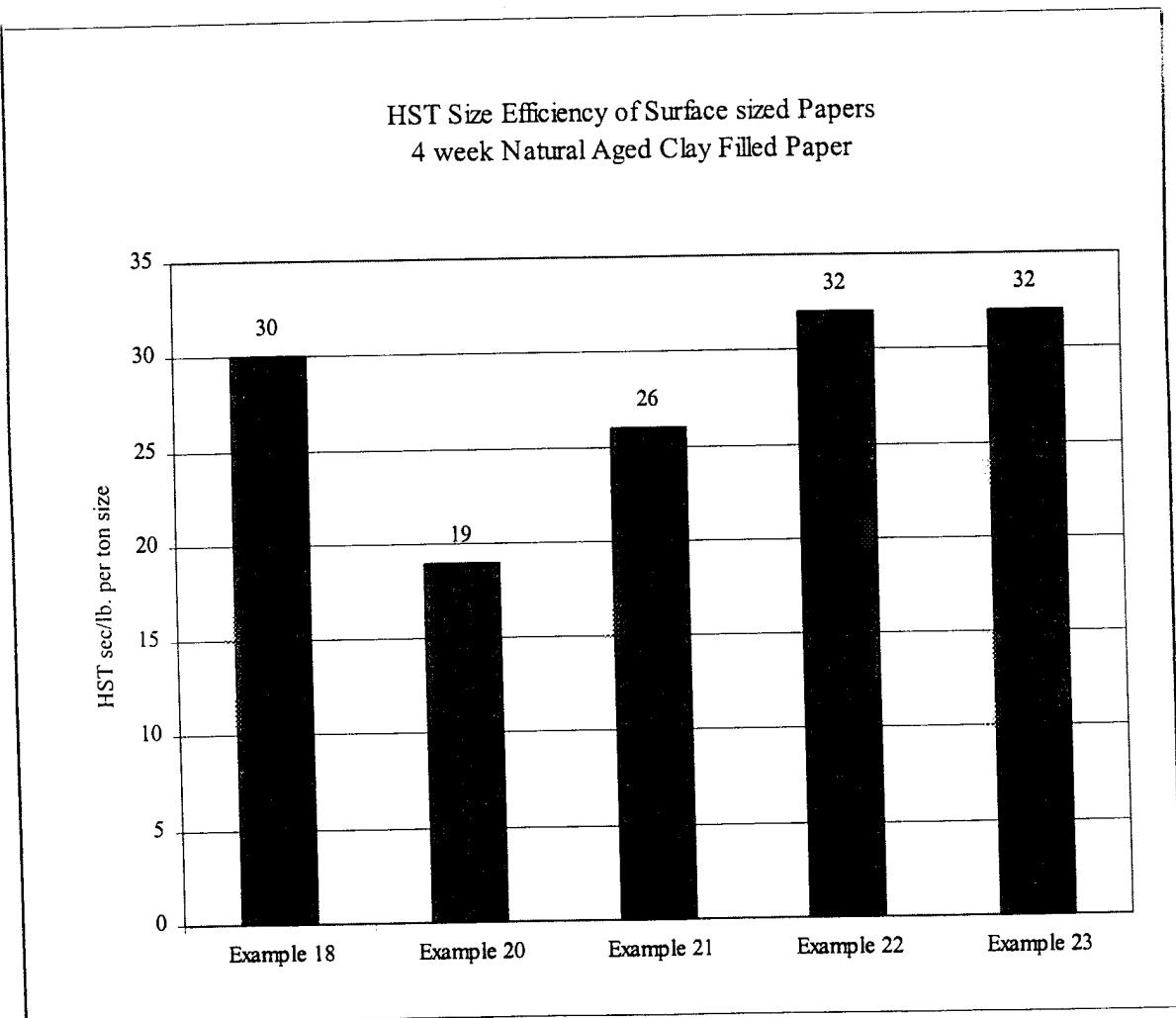
The following pages provide testing results for the sample emulsions using TAPPI Standard Method T560:

Table 17: Surface Sizing of Example 18 through Example 24 Size Emulsions
 (formulation weight in grams)

¹Examples 19 and 23 gave emulsions which broke overnight and were not suitable for surface sizing the next day. The failure of Example 19 is
most likely due to low pH resulting from the presence of the 50% alum, and can be corrected by raising the pH of the alum. Without being
5 bound by any particular theory, it is known that aluminum can appear in a polymeric form, and so may form a co-acervate, at higher pH. In
general, the pH of the alum, poly-aluminum chloride, or other aluminum salts should preferably be as near as possible to the pKa of the
derivatized microfibrillar cellulose. Thus, in Example 18 the addition of low pH 50% alum solution gave an emulsion with poor stability, while
similar recipes in Examples 18 and 20, made without alum or with alum whose pH had been raised to pH 4.0, gave good emulsions. In Example
23, adding the microfibrillated gel without a second impingement mixer shearing as in Example 22 gave an emulsion which was not stable
10 overnight, and thus could not be size tested the next day.

The emulsions from Examples 18, 20, 21, 23, and 24 were then tested in sizing compositions, and the results are shown in Chart 1. The procedure used to obtain this data was as follows: all samples were made with 5% (wt.) D-150 starch (Grain Processing Corp., Muscatine, IA). Five pieces of paper and a wet pick-up sheet for each run were size pressed using a wet nip size press. Each sheet was dry pressed with a drum dryer at 220 °F ± 5 °F for 20 seconds. The weight of wet the pick-up sheet was determined before and after the size press to give wet pick-up percent. Hercules Size Testing (HST) was performed on each paper sheet (5 per run) utilizing TAPPI procedure T560.

Chart 1



10

Examples 25 - 27.

A series of emulsions was made using Aquapel® 364 sizing agent rather than Precis ketene dimer as the size, with the formulations shown in Table 18. In each case the

sample was sonicated on a Branson 350 Ultrasonicator at a power setting of 6. Samples of fine paper were made on a continuous Fourdrinier-type machine, using the emulsions and sizing tested after 100 hours natural aging using a standard HST ink resistance test (TAPPI Method T-530) using a 1% formic acid ink. Chart 2 shows the HST sizing results, which show the samples to be at least as good as or better than three commercial controls using Hercon® paper sizing agent.

Table 18

| | Example 25 | Example 26 | Example 27 |
|---|------------|------------|------------|
| Aquapel 364 (1) | 10 | 10 | 10 |
| Carrageenan 2% (2) | 50 | | |
| CMC II (prepared in Example 3, DS about 0.15) | | 1 | |
| Ambergum® CMC 2% (3) | | | 50 |
| pH 4 Alum | 20 | 20 | 20 |
| Reten® 203 20% (4) | 5 | 5 | 5 |
| Biocide AMA 415 | 0.02 | 0.02 | 0.02 |
| Water | 14.98 | 63.98 | 14.98 |

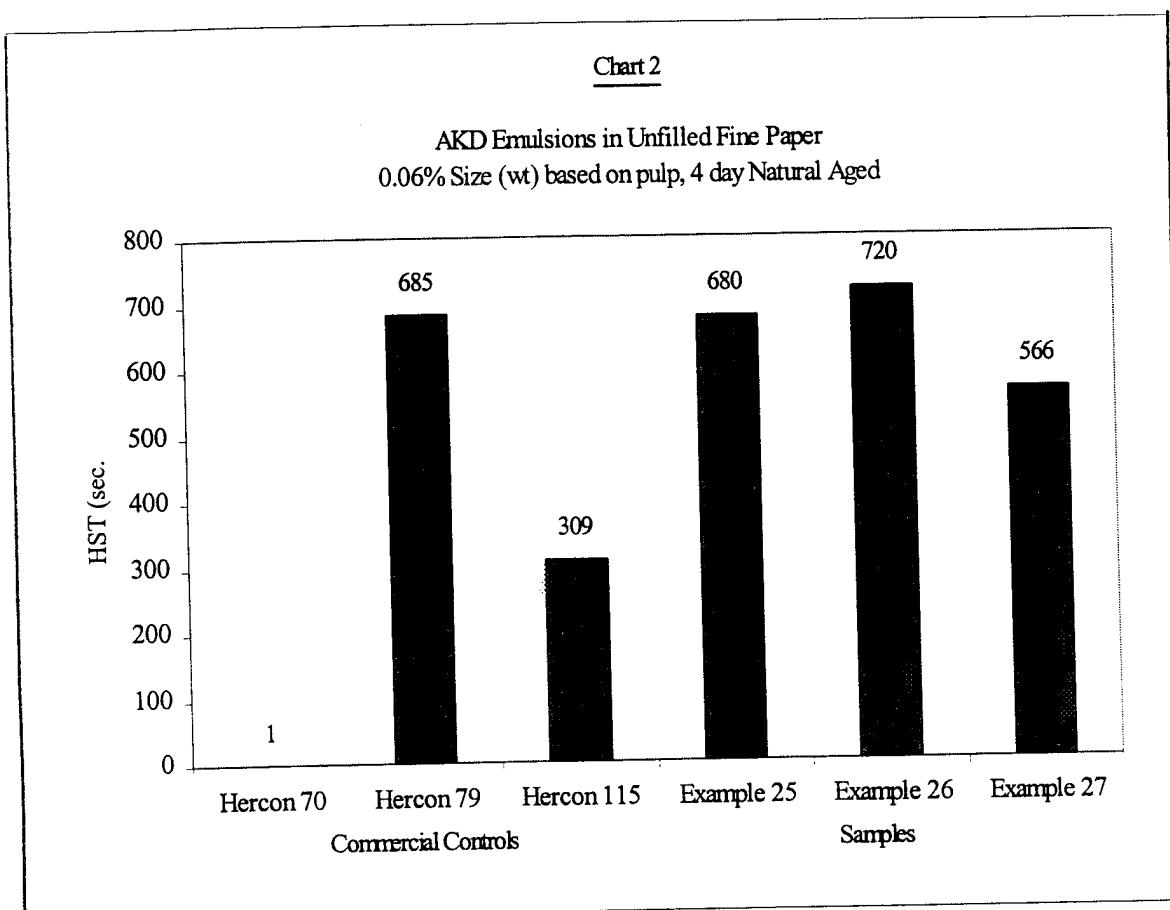
(1) Aquapel 364 Ketene Dimer sizing agent - Hercules Incorporated

(2) Carrageenan - GenuGel® Carrageenan Type LC-5, Hercules Incorporated

10 (3) Ambergum - Type 99-3021, Hercules Incorporated

(4) Reten 203 - Cationic resin, Hercules Incorporated

(Ambergum, Aquapel, Hercon, Genugel, and Reten are registered trademarks of Hercules Incorporated)



Papermaking

The paper used in the sizing examples was made at pH 7 from a 75:25 blend of hardwood and softwood pulps beaten to a Canadian standard freeness of 525 and formed into sheets having a basis weight of 65.1 g/m². Hercon 70, Hercon 79, and Hercon 115 sizing agents were all added at 0.06%, based on the pulp (corresponding to 1.2 pounds per ton). Laboratory water was used, having a hardness of 50 ppm, an alkalinity of 25 ppm, and a pH of 8.1 - 8.4.

Use in food and personal care compositions: the following examples relate to the use or derivatized microfibrillar polysaccharides in food and personal care products.

Example 28: use as fat replacer, viscosifier in food applications.

Fat Free Mayonnaise Model System

| Ingredients (wt. %) | 1 | 2 | 3 |
|--------------------------|------|------|------|
| RTG Microfibrillated CMC | 0.8 | | |
| Microfibrillated CMC | | 0.8 | |
| water | 76.2 | 76.2 | 77.0 |
| starch (Pureflo)* | 4.0 | 4.0 | 4.0 |
| maltodextrin | 10.0 | 10.0 | 10.0 |

Fat Free Mayonnaise Model System (con't)

| <u>Ingredients (wt. %)</u> | 1 | 2 | 3 |
|----------------------------|-------|-------|------|
| salt | 2.0 | 2.0 | 2.0 |
| vinegar (12% acetic acid) | 4.0 | 4.0 | 4.0 |
| 5 egg yolk | 3.0 | 3.0 | 3.0 |
| viscosity (cps) | 42000 | 45000 | 6000 |

*marketed by National Starch and Chemical Co.

Procedure 1: RTG Microfibrillated CMC prepared in example 7 above (DS about 0.16) was dispersed in water with agitation. Starch and maltodextrin were added with agitation. The mixture was heated to 80° - 90° C followed by cooling to 15° - 20° C. Egg yolk then vinegar were added. The product was then mixed by means of a colloid mill. This mixing consists of one pass through a Greerco colloid mill model W250V-B (Greerco Corp., Hudson, NH) with an emulsion rotor and stator at a 0.001 inch gap setting. The texture of this product is then evaluated after 24 hours.

Procedure 2: to a 1% microfibrillated CMC gel as made in example 3 above (DS about 0.16) the balance of the water was added. Starch and maltodextrin were then added with agitation. The mixture was heated to 80° - 90° C followed by cooling to 15° - 20° C. Egg yolk then vinegar were added. The product was then mixed by means of a colloid mill. The texture of this product is then evaluated after 24 hours.

Procedure 3: starch and maltodextrin were added to water with agitation. The mixture was heated to 80° - 90° C followed by cooling to 15° - 20° C. Egg yolk then vinegar were added. The product is then mixed by means of a colloid mill. The texture of this product is then evaluated after 24 hours.

Evaluation: viscosity was measured with a Brookfield (Model DV-II+), 20° C, helipath, 5 rpm spindle C, program S93.

The appearance of the product containing either RTG Microfibrillated CMC or Microfibrillated CMC is that of a gel that holds its shape for a period of time when cut and does not synerese. When a portion of the product is lifted with a spoon or spatula, it does not appear to have stringiness or excessive tackiness; the texture is described as short. These are subjective textural features similar to that of reduced fat spoonable dressings and mayonnaises.

Example 29: use in personal care products.Moisturizing Lotion

| Phase | Ingredient | Wt % |
|-------|--|-------|
| A | DI water | 81.85 |
| | Hydrophobe Modified Hydroxyethyl Cellulose (Natrosol® Plus 330, Hercules Incorporated) | 0.24 |
| | Glycerin | 2.00 |
| | Disodium ethylene diamine tetraacetic acid | 0.05 |
| B | Petrolatum | 5.00 |
| | Mineral Oil | 3.00 |
| | Glycol Stearate | 2.00 |
| | Isostearyl Benzoate | 2.00 |
| | Parraffin | 2.00 |
| | Dimethicone | 0.50 |
| | RTG microfibrillar CMC as in example 7 (DS about 0.16) | 0.36 |
| C | Germaben® II (preservative) | 1.00 |

Procedure: the Part A ingredients were combined, mixed until the water-soluble

- 5 polymer dissolved, and heated to 60-65 °C. All Part B ingredients were combined except the microfibrillar CMC, and heated to 60-65 °C until homogeneous. The RTG microfibrillar CMC was then dispersed into part B, and part B was added to part A with vigorous agitation, which was continued until the mixture was smooth and homogeneous. It was then cooled to 30 °C, and part C was added.

10

Properties

pH.....5.7

Viscosity* (cP) at 25 °C.....16,600

Appearance.....Milky-white emulsion

Stability.....> 5 weeks at 50 °C

- 15 *Complex viscosity in the linear viscoelastic regime was measured with a Bohlin controlled stress rheometer.

This example demonstrates the ability of the RTG CMC material to stabilize an oil in water emulsion, performing a role typically performed by surfactant/cosurfactant network forming systems.

Night Cream

| Phase | Ingredient | Wt % |
|-------|---|------|
| A | DI water | 78.3 |
| | Glycerin | 2.00 |
| | Germaben® II (preservative) | 0.50 |
| | Hydrophobically Modified Hydroxyethyl Cellulose (Natrosol® Plus 330, Hercules Incorporated) | 0.72 |
| B | Avocado Oil | 4.00 |
| | Isostearyl Isostearate | 4.00 |
| | Octyl Stearate | 3.00 |
| | Isopropyl Myristate | 3.00 |
| | Propylene Glycol Isostearate | 4.00 |
| | RTG Microfibrillar CMC as in example 7 (DS about 0.16) | 0.48 |

5

Procedure: the ingredients for part A were combined and mixed until the water-soluble polymer dissolved. The ingredients for part B were then combined, and part B was added to part A with vigorous agitation, which was continued until the mixture was smooth and homogeneous.

10

Properties

pH.....6.0

Viscosity* (cP) at 25 °C.....30,200

Appearance.....Creamy white emulsion

Stability.....> 5 weeks at 50 °C

15 *Complex viscosity in the linear viscoelastic regime was measured with the Bohlin rheometer.

This example demonstrates the ability of the RTG CMC material to stabilize an oil in water emulsion, performing a role typically performed by surfactant/cosurfactant network-

forming systems. The RTG CMC also is processed at room temperature, while typical surfactant/cosurfactant systems require heat.

Alpha-Hydroxy Acid Anti-Age Cream

| Phase | Ingredient | Wt % |
|-------|---|------|
| A | DI water | 71.9 |
| | Glycerin | 5.4 |
| B | Cetyl Alcohol | 3.2 |
| | Glyceryl Stearate and PEG-100 Stearate (Arlacel 165, ICI) | 4.8 |
| | Stearic Acid | 1.6 |
| | Isopropyl Palmitate | 4.8 |
| | Mineral Oil and Lanolin Alcohol (Amerchol L-101, Amerchol) | 4.8 |
| | Dimethicone | 1.6 |
| | RTG Microfibrillar CMC as made in example 7 (DS about 0.16) | 0.6 |
| C | Lactic Acid (88%) | 0.3 |
| | Germaben® II (preservative) | 1.0 |

(As used herein, "anti-age" refers to that category of epidermal lotions and creams intended

- 5 to contribute to a more youthful appearance by the user, such as by the reduction or removal of wrinkles.) Procedure: The ingredients for part A were combined and heated to 75 °C. The part B ingredients, except RTG microfibrillar CMC, were then combined and heated to 75 °C until homogeneous. The RTG microfibrillar CMC was then dispersed into part B. Part B was next added to part A until the mixture became smooth and
10 homogeneous. The mixture was then cooled to 40 °C, and part C was added. This composition was formulated at pH 3.5-4.0, and stabilized with microfibrillar CMC rather than with typical xanthan, clay mixtures.

Properties

pH.....3.7

15 Viscosity* (cP) at 25 °C.....932,000

Appearance.....Glossy white, stiff cream

Stability.....> 5 weeks at 50 °C

*Complex viscosity in the linear viscoelastic regime was measured with the Bohlin rheometer.

This example demonstrates the ability of the RTG CMC material to stabilize an oil in water emulsion at low pH.

5

High SPF Organic Sunscreen Cream

| Phase | Ingredient | Wt % |
|-------|---|------|
| A | DI water | 63.9 |
| B | Cetearyl Alcohol and Cetearyl Phosphate (Crodafos CES, Croda) | 6.6 |
| C | Benzophenone-3 | 5.0 |
| | Octyl methoxycinnamate | 7.5 |
| C | Octyl Salicylate | 5.0 |
| | Menthyl Anthranilate | 5.0 |
| D | Octyl Stearate | 5.0 |
| | RTG Microfibrillar CMC as in example 7 (DS about 0.16) | 0.3 |
| E | NaOH, 18% | 0.6 |
| F | Butylated hydroxytoluene | 0.1 |
| | Germaben® II (preservative) | 1.0 |

10

Procedure: The ingredients for part A and part B were combined and heated to 70 °C. Part C was then added separately, mixing after addition of each part C ingredient. Part D was then added with vigorous agitation, which was continued until the mixture became smooth and homogeneous. Part E was then added, the mixture was cooled to 45 °C, and part F was added.

Properties

pH.....5.9

Viscosity* (cP) at 25 °C.....613,000

Appearance.....Light, off-white cream

Stability.....> 5 weeks at 50 °C

15

*Complex viscosity in the linear viscoelastic regime was measured with the Bohlin rheometer.

This example demonstrates use of microfibrillated CMC with organic sunscreen.

Formulation of a TiO₂ Based Sunscreen Lotion

| Phase | Ingredient | Wt % |
|-------|--|------|
| A | DI water | 67.2 |
| | Disodium ethylene diamine tetraacetic acid | 0.1 |
| | Propylene Glycol | 5.0 |
| B | C ₁₂₋₁₅ Alkyl Benzoate | 3.0 |
| B | Butyl Stearate | 3.0 |
| | Myristyl Myristate | 4.0 |
| | Sorbitan Oleate | 0.1 |
| | RTG Microfibrillar CMC as in example 7 (DS about 0.16) | 0.6 |
| C | Germaben® II (preservative) | 1.0 |
| D | Titanium Dioxide | 6.0 |
| | Octyl Palmitate | 9.0 |
| | Polyglyceryl-10 decanoate | 1.0 |

Procedure: the ingredients for part A were combined and heated to 50 °C. All of the part B ingredients, except microfibrillar CMC, were combined and heated to 60-65 °C until homogeneous. The microfibrillar CMC was then dispersed into part B, which was then added to part A with vigorous agitation, and agitation was continued until the mixture was smooth and homogeneous. The ingredients for part D were combined and mixed well. Part C was added to the AB emulsion; then, with moderate agitation, part D was slowly added to the emulsion and cooled to 30 °C.

Properties

10 pH.....7.1

Viscosity* (cP) at 25 °C.....33,900

Appearance.....Glossy, white emulsion gel

Stability.....> 5 weeks at 50 °C

*Complex viscosity in the linear viscoelastic regime was measured with the Bohlin 15 rheometer.

This example demonstrates use of microfibrillated CMC with inorganic sunscreen. The present invention has of necessity been discussed herein by reference to certain specific methods and materials. The enumeration of these methods and materials was

merely illustrative, and in no way constitutes any limitation on the scope of the present invention. It is to be expected that those skilled in the art may discern and practice variations of or alternatives to the specific teachings provided herein, without departing from the scope of the present invention.

5 The present invention has of necessity been discussed herein by reference to certain specific methods and materials. The enumeration of these methods and materials was merely illustrative, and in no way constitutes any limitation on the scope of the present invention. It is to be expected that those skilled in the art may discern and practice variations of or alternatives to the specific teachings provided herein, without departing
10 from the scope of the present invention.

WHAT I/WE CLAIM IS:

1. A derivatized microfibrillar polysaccharide, derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality comprises anionic charge.

5 2. The derivatized microfibrillar polysaccharide of claim 1, wherein the polysaccharide in said derivatized microfibrillar polysaccharide comprises at least one of cellulose, hemicellulose, chitin, chitosan, guar gum, pectin, alginate, agar, xanthan, starch, amylose, amylopectin, alternan, gellan, mutan, dextran, pullulan, fructan, locust bean gum, 10 carrageenan, glycogen, glycosaminoglycans, murein, bacterial capsular polysaccharides, and derivatives thereof.

3. The derivatized microfibrillar polysaccharide of claim 2, wherein said polysaccharide is at least one of cellulose, chitin, chitosan, pectin, agar, starch, 15 carrageenan, and derivatives thereof.

4. The derivatized microfibrillar polysaccharide of claim 3, comprising derivatized microfibrillar cellulose.

5. The derivatized microfibrillar polysaccharide of claim 4, wherein said cellulose is obtained from at least one of chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal 20 hemp, bagasse, corn, wheat, bamboo, velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.

6. The derivatized microfibrillar polysaccharide of claim 5, wherein said cellulose is obtained from at least one of purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton 25 linters; fruits; and vegetables.

7. The derivatized microfibrillar cellulose of claim 4, comprising at least one of hydroxyethyl cellulose, ethylhydroxyethyl cellulose, carboxymethylcellulose, carboxymethylhydroxyethyl cellulose, hydroxypropylhydroxyethyl cellulose, methyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose, 30 carboxymethylmethyl cellulose, hydrophobically modified carboxymethylcellulose, hydrophobically modified hydroxyethyl cellulose, hydrophobically modified hydroxypropyl cellulose, hydrophobically modified ethylhydroxyethyl cellulose,

hydrophobically modified carboxymethylhydroxyethyl cellulose, hydrophobically modified hydroxypropylhydroxyethyl cellulose, hydrophobically modified methyl cellulose, hydrophobically modified methylhydroxypropyl cellulose, hydrophobically modified methylhydroxyethyl cellulose, hydrophobically modified carboxymethylmethyl cellulose, nitrocellulose, cellulose acetate, cellulose sulfate, cellulose vinyl sulfate, cellulose phosphate, and cellulose phosphonate.

5 8. The derivatized microfibrillar cellulose of claim 4, wherein said derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 100% in water.

10 9. The derivatized microfibrillar cellulose of claim 8, wherein said derivatized microfibrillar cellulose forms a gel throughout the concentration range of between about 0.01 % and about 50 % in water.

15 10. The derivatized microfibrillar cellulose of claim 4, wherein said derivatized microfibrillar cellulose forms a gel at at least one point in the concentration range of from about 0.05 % up to about 0.99% in water.

11. The derivatized microfibrillar polysaccharide of claim 1, further comprising a solvent, wherein said derivatized microfibrillar polysaccharide is substantially insoluble in said solvent.

20 12. The derivatized microfibrillar polysaccharide of claim 11, wherein said solvent is water, alcohol, or oil.

13. The derivatized microfibrillar polysaccharide of claim 12, wherein said solvent is water.

25 14. The derivatized microfibrillar polysaccharide of claim 13, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic functionality.

15. The derivatized microfibrillar polysaccharide of claim 1, wherein said derivatized microfibrillar polysaccharide is derivatized microfibrillar cellulose having a degree of substitution of less than about 0.5.

30 16. The derivatized microfibrillar polysaccharide of claim 15, wherein said degree of substitution is less than about 0.35.

17. The derivatized microfibrillar polysaccharide of claim 16, wherein said degree of substitution is less than about 0.2.

18. The derivatized microfibrillar polysaccharide of claim 17, wherein said degree of substitution is less than about 0.18.

19. The derivatized microfibrillar polysaccharide of claim 18, wherein said degree of substitution is less than about 0.1.

5 20. The derivatized microfibrillar polysaccharide of claim 15, wherein said degree of substitution is between about 0.02 and about 0.5.

21. The derivatized microfibrillar polysaccharide of claim 20, wherein said degree of substitution is between about 0.05 and about 0.2.

10 22. The derivatized microfibrillar polysaccharide of claim 1, derivatized to comprise substituents that provide electrostatic functionality in the form of anionic charge, wherein the degree of substitution representing substituents that provide electrostatic functionality in the form of anionic charge is at least about 0.02.

15 23. The derivatized microfibrillar polysaccharide of claim 1, wherein said anionic charge is provided by carboxyl, sulfate, sulfonate, phosphonate, or phosphate groups, or combinations thereof.

24. The derivatized microfibrillar polysaccharide of claim 14, wherein said electrostatic functionality is provided by both anionic and cationic charge.

20 25. The derivatized microfibrillar cellulose of claim 24, wherein said electrostatic functionality is provided by substituents that contain both anionic and cationic charge in the same substituent.

26. The derivatized microfibrillar cellulose of claim 24, wherein said electrostatic functionality is provided both by substituents having anionic charge and by substituents having cationic charge.

27. The derivatized microfibrillar polysaccharide of claim 13, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide steric functionality.

28. The derivatized microfibrillar polysaccharide of claim 27, having a molar substitution of less than about 3.0.

29. The derivatized microfibrillar polysaccharide of claim 28, wherein said molar substitution is less than about 1.5.

30 30. The derivatized microfibrillar polysaccharide of claim 29, wherein said molar substitution is less than about 1.0.

31. The derivatized microfibrillar polysaccharide of claim 30, wherein said molar substitution is less than about 0.5.

32. The derivatized microfibrillar polysaccharide of claim 28, wherein said molar substitution is between about 0.5 and 3.0.

5 33. The derivatized microfibrillar polysaccharide of claim 27, wherein said substituents comprise at least one of hydroxyethyl groups; hydroxypropyl groups; methyl groups; ethyl groups; straight- or branched-chain alkyl, alkenyl, or alkynyl groups having from about 4 to about 30 carbons; aryl, arylalkyl, arylalkenyl, cyclic, and heterocyclic hydrocarbons having from about 4 to about 30 carbons; or combinations thereof.

10 34. The derivatized microfibrillar polysaccharide of claim 33, further wherein said derivatized microfibrillar polysaccharide is a derivatized microfibrillar cellulose.

35. The derivatized microfibrillar cellulose of claim 4, comprising carboxymethylcellulose.

15 36. The derivatized microfibrillar cellulose of claim 34, having a degree of substitution of less than about 0.35.

37. The derivatized microfibrillar cellulose of claim 36, wherein said degree of substitution is less than about 2.0.

38. The derivatized microfibrillar cellulose of claim 37, wherein said degree of substitution is between about 0.02 and about 0.2.

20 39. The derivatized microfibrillar cellulose of claim 38, wherein said degree of substitution is between about 0.10 and about 0.2.

40. The derivatized microfibrillar polysaccharide of claim 4, wherein said derivatized microfibrillar cellulose forms a gel at a concentration of less than about 1% in water.

25 41. Microfibrillar carboxymethylcellulose having a degree of substitution of between about 0.10 and about 0.20.

42. A comestible composition of matter comprising derivatized microfibrillar polysaccharide derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality is provided by anionic charge.

30 43. The comestible composition of matter of claim 42, in the form of a low fat, reduced fat, or fat-free mayonnaise.

44. The comestible composition of matter of claim 42, in the form of a salad dressing.

45. The comestible composition of matter of claim 42, further comprising a pharmaceutically active ingredient.

5 46. The comestible composition of claim 45, wherein said derivatized microfibrillar polysaccharide at least partially provides controlled, sustained, or delayed release of said pharmaceutically active ingredient.

10 47. A non-comestible composition of matter comprising derivatized microfibrillar polysaccharide derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality is provided by anionic charge.

48. The non-comestible composition of matter of claim 47, in the form of a wound care product.

15 49. The non-comestible composition of matter of claim 48, wherein said wound care product is a wound dressing.

50. The non-comestible composition of matter of claim 48, wherein said wound care product is an ostomy ring.

51. The non-comestible composition of matter of claim 47, in the form of a skin care lotion or cream.

20 52. The non-comestible composition of matter of claim 47, in the form of a sunscreen lotion or cream.

53. The non-comestible composition of matter of claim 47, in the form of an oral care composition.

25 54. The non-comestible composition of matter of claim 53, wherein said oral care product is a toothpaste.

55. The non-comestible composition of matter of claim 47, further comprising a fertilizer, herbicide, fungicide, or pesticide.

30 56. The non-comestible composition of matter of claim 55, wherein said derivatized microfibrillar polysaccharide at least partially provides controlled, sustained, or delayed release of said fertilizer, herbicide, or pesticide.

57. The non-comestible composition of matter of claim 47, in the form of a drilling fluid.

58. A paper composition comprising derivatized microfibrillar cellulose derivatized to comprise groups that provide electrostatic and/or steric functionality, further wherein said electrostatic functionality comprises the presence of anionic charge.

59. The paper composition of claim 58, wherein said derivatized microfibrillar cellulose is microfibrillar carboxymethylcellulose.

60. A method for producing derivatized microfibrillar polysaccharide, said method comprising at least one of the following:

a) a derivatizing step of treating a microfibrillar polysaccharide to obtain a derivatized microfibrillar polysaccharide;

10 b) a microfibrillizing step of treating a derivatized non-microfibrillar polysaccharide to produce a derivatized microfibrillar polysaccharide; or,

c) microfibrillizing and derivatizing a non-microfibrillar polysaccharide substantially simultaneously,

15 wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic and/or steric functionality, further wherein said electrostatic functionality is provided by anionic charge.

61. The method of claim 60, wherein the polysaccharide is at least one of cellulose, hemicellulose, chitin, chitosan, guar gum, pectin, alginate, agar, xanthan, starch, amylose, amylopectin, alternan, gellan, mutan, dextran, pullulan, fructan, locust bean gum, 20 carrageenan, glycogen, glycosaminoglycans, murein, bacterial capsular polysaccharides, and derivatives thereof.

62. The method of claim 61, wherein said polysaccharide is at least one of cellulose, chitin, chitosan, pectin, agar, starch, carrageenan, and derivatives thereof.

63. The method of claim 62, wherein the polysaccharide is cellulose and said 25 derivatized microfibrillar polysaccharide is derivatized microfibrillar cellulose.

64. The method of claim 63, wherein said cellulose is obtained from at least one of chemical pulps, mechanical pulps, thermal mechanical pulps, chemical-thermal mechanical pulps, recycled fibers, newsprint, cotton, soybean hulls, pea hulls, corn hulls, flax, hemp, jute, ramie, kenaf, manila hemp, sisal hemp, bagasse, corn, wheat, bamboo, 30 velonia, bacteria, algae, fungi, microcrystalline cellulose, vegetables, and fruits.

65. The method of claim 64, wherein said cellulose is obtained from at least one of purified, optionally bleached wood pulps produced from sulfite, kraft, or prehydrolyzed kraft pulping processes; purified cotton linters; fruits; and vegetables.

66. The method of claim 60, comprising the steps of:

5 a) derivatizing cellulose with monochloroacetic acid or a salt thereof under alkaline conditions to produce carboxymethylcellulose;

b) suspending the carboxymethylcellulose in water to form a suspension; and

c) homogenizing said suspension to produce microfibrillated carboxymethylcellulose.

10 67. The method of claim 60, wherein said derivatizing step comprises contacting a non-microfibrillar polysaccharide with a swelling agent.

68. The method of claim 67, further wherein said contacting takes place under alkaline conditions.

69. The method of claim 68, wherein said swelling agent is an anionic reagent.

15 70. The method of claim 69, wherein the polysaccharide is cellulose.

71. The method of claim 70, further wherein said alkaline conditions comprise contacting the cellulose with said anionic reagent in the presence of an alkaline reagent which is at least one of sodium hydroxide, an oxide or hydroxide of an alkali metal or alkaline earth metal, an alkali silicate, an alkali aluminate, an alkali carbonate, an amine, 20 ammonium hydroxide, tetramethyl ammonium hydroxide, or combinations thereof.

72. The method of claim 60, wherein said derivatizing step takes place at high solids.

73. The method of claim 60, wherein said anionic charge comprises the presence of carboxyl, sulfate, sulfonate, phosphonate, or phosphate groups, or 25 combinations thereof.

74. The method of claim 73, wherein said derivatizing step comprises carboxymethylation of the cellulose.

75. The method of claim 63, wherein said derivatized microfibrillar cellulose comprises at least one of hydroxyethyl cellulose, ethylhydroxyethyl cellulose, 30 carboxymethylcellulose, carboxymethylhydroxyethyl cellulose, hydroxypropylhydroxyethyl cellulose, methyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose, carboxymethylmethyl cellulose, hydrophobically modified

carboxymethylcellulose, hydrophobically modified hydroxyethyl cellulose, hydrophobically modified hydroxypropyl cellulose, hydrophobically modified ethylhydroxyethyl cellulose, hydrophobically modified carboxymethylhydroxyethyl cellulose, hydrophobically modified hydroxypropylhydroxyethyl cellulose, 5 hydrophobically modified methyl cellulose, hydrophobically modified methylhydroxypropyl cellulose, hydrophobically modified methylhydroxyethyl cellulose, hydrophobically modified carboxymethylmethyl cellulose, nitrocellulose, cellulose acetate, cellulose sulfate, cellulose vinyl sulfate, cellulose phosphate, and cellulose phosphonate.

76. The method of claim 60, wherein said microfibrillizing step comprises 10 applying energy to said polysaccharide under conditions sufficient to produce microfibrillar polysaccharide.

77. The method of claim 76, further comprising enzyme-treating said non-microfibrillar polysaccharide prior to said microfibrillizing step

78. The method of claim 76, comprising applying at least one of 15 homogenization, pumping, mixing, heat, steam explosion, pressurization-depressurization cycle, impact, grinding, ultrasound, microwave explosion, and milling to said non-microfibrillar polysaccharide.

79. The method of claim 78, comprising passing said non-microfibrillar 20 polysaccharide through a homogenizer under conditions sufficient to produce microfibrillar polysaccharide.

80. The method of claim 79, wherein said conditions comprise passing said non-microfibrillar polysaccharide through a pressure differential of at least about 3,000 psi.

81. The method of claim 80, further comprising passing said non-microfibrillar polysaccharide through said homogenizer at least three times.

82. The method of claim 60, wherein said derivatized microfibrillar 25 polysaccharide forms a gel throughout a concentration range of from about 0.01 % to about 100% in water.

83. The method of claim 82, wherein said derivatized microfibrillar 30 polysaccharide forms a gel throughout a concentration range of between about 0.01 % and about 50 % in water.

84. The method of claim 60, wherein said derivatized microfibrillar polysaccharide forms a gel at at least one point in the concentration range of from about 0.05 % to about 0.99% in water.

5 85. The method of claim 84, wherein said derivatized microfibrillar polysaccharide forms a gel at a concentration of about 0.9% in water.

86. The method of claim 60, wherein said derivatized microfibrillar polysaccharide is substantially insoluble in the solvent of use.

87. The method of claim 86, wherein the solvent of use is water.

10 88. The method of claim 87, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic functionality.

89. The method of claim 88, wherein said derivatized microfibrillar polysaccharide is derivatized microfibrillar cellulose having a degree of substitution of less than about 0.5.

15 90. The method of claim 89, wherein said degree of substitution is less than about 0.35.

91. The method of claim 90, wherein said degree of substitution is less than about 0.2.

20 92. The method of claim 91, wherein said degree of substitution is less than about 0.18.

93. The method of claim 92, wherein said degree of substitution is less than about 0.1.

94. The method of claim 89, wherein said derivatized microfibrillar cellulose has a degree of substitution of between about 0.02 and about 0.5.

25 95. The method of claim 94, wherein said degree of substitution is between about 0.05 and about 0.2.

96. The method of claim 86, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise a steric substituent.

30 97. The method of claim 96, further wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic functionality.

98. The method of claim 96, wherein said derivatized microfibrillar polysaccharide has a molar substitution of less than about 3.0.

99. The method of claim 98, wherein said molar substitution is less than about 1.5.

5 100. The method of claim 99, wherein said molar substitution is less than about 1.0.

101. The method of claim 100, wherein said molar substitution is less than about 0.5.

102. The method of claim 98, wherein said molar substitution is between about 10 0.5 and 3.0.

103. The method of claim 63, wherein said derivatized microfibrillar cellulose is a carboxymethylcellulose.

104. The method of claim 103, wherein said carboxymethylcellulose has a degree of substitution of less than about 0.35.

15 105. The method of claim 104, wherein said degree of substitution is less than about 2.0.

106. The method of claim 105, wherein said degree of substitution is between about 0.02 and about 2.0.

20 107. The method of claim 106, wherein said degree of substitution is between about 0.1 and about 0.2.

108. Derivatized microfibrillar polysaccharide produced by the method of claim 60.

109. Derivatized microfibrillar cellulose produced by the method of claim 63.

25 110. The derivatized microfibrillar cellulose of claim 63, derivatized to comprise substituents that provide steric functionality.

111. The derivatized microfibrillar cellulose of claim 110, wherein said substituents comprise at least one of hydroxyethyl groups; hydroxypropyl groups; methyl groups; ethyl groups; straight- or branched-chain aliphatic groups having from about 4 to about 30 carbons; or combinations thereof.

30 112. The derivatized microfibrillar cellulose of claim 109, derivatized to comprise substituents that provide electrostatic functionality by anionic charge.

113. The derivatized microfibrillar cellulose of claim 112, wherein said anionic charge comprises the presence of carboxyl, sulfate, sulfonate, phosphonate, or phosphate groups, or combinations thereof.

114. The derivatized microfibrillar cellulose of claim 113, wherein said anionic charge comprises the presence of carboxyl groups.

115. The derivatized microfibrillar cellulose of claim 112, wherein said electrostatic functionality is provided by both anionic and cationic charge.

116. The derivatized microfibrillar cellulose of claim 115, wherein said electrostatic functionality is provided by substituents that contain both anionic and cationic charge in the same substituent.

117. The derivatized microfibrillar cellulose of claim 115, wherein said electrostatic functionality is provided both by substituents having anionic charge and by substituents having cationic charge.

118. A method of modifying the rheological properties of a composition of matter, said method comprising the step of incorporating, into said composition of matter, derivatized microfibrillar polysaccharide that is derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality is provided by anionic charge.

119. The method of claim 118, wherein said composition comprises a liquid.

120. The method of claim 119, wherein said liquid is water.

121. The method of claim 120, comprising using said derivatized microfibrillar polysaccharide in an amount effective to provide scale control and/or corrosion control.

122. The method of claim 118, wherein said derivatized microfibrillar polysaccharide is derivatized microfibrillar cellulose.

123. The method of claim 119, wherein said rheological properties are at least one of viscosity, suspension stability, gel insensitivity to temperature, shear reversible gelation, yield stress, and liquid retention.

124. The method of claim 118, wherein said composition of matter is a food, pharmaceutical, neutraceutical, personal care, fiber, paper, paint, coating, or construction composition.

125. The method of claim 124, wherein said composition of matter is an oral care product.

126. The method of claim 124, wherein said composition of matter is a cream or lotion for epidermal application.

127. The method of claim 124, wherein said composition of matter is moisturizing, night, anti-age, or sunscreen cream or lotion.

5 128. The method of claim 124, wherein said composition of matter is a food spread.

129. The method of claim 128, wherein said food spread is a reduced fat, low fat, or fat free food spread.

10 130. The method of claim 129, wherein said food spread is a reduced fat, low fat, or fat free mayonnaise.

131. The method of claim 124, wherein said composition of matter is a drilling fluid.

15 132. A method of improving the physical and/or mechanical properties of a coating composition by incorporating, into said coating composition, an effective amount of a derivatized microfibrillar polysaccharide derivatized to comprise substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality is provided by anionic charge.

20 133. The method of claim 132, wherein said physical and/or mechanical properties include at least one of film forming, leveling, sag resistance, strength, durability, dispersion, flooding, floating, and spatter.

25 134. A method of improving at least one of sizing, strength, scale control, drainage, dewatering, retention, clarification, formation, adsorbency, film formation, membrane formation, and polyelectrolyte complexation during paper manufacture, said method comprising the step of using a derivatized microfibrillar cellulose during said manufacture, wherein said derivatized microfibrillar cellulose is derivatized by electrostatic and/or steric substituents, further wherein said electrostatic substituents comprise the presence of either anionic charge or both anionic and cationic charge.

135. The method of claim 134, wherein said derivatized microfibrillar cellulose is used as a drainage aid and/or as a sizing agent.

30 136. The method of claim 134, wherein said derivatized microfibrillar cellulose is microfibrillated carboxymethylcellulose.

137. The method of claim136, comprising using said microfibrillated carboxymethylcellulose in a papermaking machine to increase the rate of drainage and/or dewatering during paper manufacture.

138. The method of claim137, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; and combinations thereof.

139. The method of claim137, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

140. The method of claim137, further wherein said microfibrillated carboxymethylcellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

141. The method of claim136, comprising using said microfibrillated carboxymethylcellulose in a papermaking machine for retention of organic and/or inorganic dispersed particles in a sheet of paper during its manufacture

142. The method of claim141, wherein said dispersed particles comprise at least one of pulp fines, fillers, sizing agents, pigments, clays, detrimental organic particulate materials, detrimental inorganic particulate materials, and combinations thereof.

143. The method of claim141, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; and combinations thereof.

144. The method of claim141, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

5 145. The method of claim141, further wherein said microfibrillated carboxymethylcellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

10 146. The method of claim136, comprising using said microfibrillated carboxymethylcellulose in a papermaking machine to improve the uniformity of formation of a sheet of paper during its manufacture.

147. The method of claim146, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose 15 containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; and combinations thereof.

148. The method of claim146, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

149. The method of claim146, further wherein said microfibrillated carboxymethylcellulose is used in the presence of: at least one polymer of ethylene oxide, 25 ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

150. The method of claim136, comprising using said microfibrillated carboxymethylcellulose in a papermaking machine to improve the strength of a sheet of paper produced on a papermachine.

30 151. The method of claim150, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: cationic polyacrylamides; polydiallyldimethyl-ammonium chloride; cationic starch; derivatives of cellulose

containing ammonium or mono-, di-, or trialkyl ammonium substituents; derivatives of guar gum containing ammonium or mono-, di-, or trialkyl ammonium substituents; resins formed by the reaction of amines and/or polyamines with epichlorohydrin; and combinations thereof.

5 152. The method of claim 150, further wherein said microfibrillated carboxymethylcellulose is used in the presence of at least one of: aluminum salts; hydrolyzed or partially hydrolyzed aluminum salts; complexes of hydrolyzed or partially hydrolyzed aluminum salts with organic or inorganic species; and combinations thereof.

10 153. The method of claim 150, further wherein said microfibrillated carboxymethylcellulose is used in the presence of: at least one polymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; at least one copolymer or terpolymer of ethylene oxide, ethyleneimine, allylamine, or vinylamine; and combinations thereof.

15 154. A method for improving the stability of an emulsion, dispersion, or foam system, said method comprising the step of including, in the system, a derivatized microfibrillar polysaccharide derivatized by electrostatic and/or steric substituents, further wherein said electrostatic substituents comprise the presence of anionic charge.

155. The method of claim 154, wherein said derivatized microfibrillar polysaccharide is added to the system.

156. The method of claim 155, wherein said system comprises an emulsion, further wherein said emulsion is produced by processing of an emulsion formulation.

157. The method of claim 156, further wherein said derivatized microfibrillar polysaccharide is added prior to completion of processing of said emulsion formulation.

158. The method of claim 156, wherein a non-microfibrillated polysaccharide is added prior to completion of processing of said emulsion formulation, and said emulsion formulation is processed under conditions sufficient to microfibrillate said non-microfibrillated polysaccharide.

159. The method of claim 158, further wherein said non-microfibrillated or only partially microfibrillated polysaccharide is non-derivatized or only partially derivatized, and said emulsion formulation is further processed under conditions sufficient to derivatized said non-derivatized polysaccharide, or to complete derivatization of said only partially derivatized polysaccharide, respectively.

160. The method of claim 156, wherein a non-derivatized or only partially derivatized polysaccharide is added prior to completion of processing of said emulsion formulation, and the emulsion formulation is processed under conditions sufficient to derivatize said non-derivatized polysaccharide, or to complete derivatization of said only partially derivatized polysaccharide, respectively.

161. The method of claim 160, further wherein said non-derivatized or only partially derivatized polysaccharide is non-microfibrillated or only partially microfibrillated, and said emulsion formulation is further processed under conditions sufficient to microfibrillate said non-derivatized polysaccharide, or to complete microfibrillation of said only partially derivatized polysaccharide, respectively.

162. The method of claim 155, wherein said system is a water-in-oil or oil-in-water emulsion.

163. The system produced by the method of claim 154.

164. A system comprising an emulsion, dispersion, or foam containing a derivatized microfibrillar polysaccharide, wherein said derivatized microfibrillar polysaccharide is derivatized to comprise substituents that provide electrostatic and/or steric functionality, further wherein said electrostatic functionality is provided by anionic charge.

165. A polyelectrolyte complex comprising a derivatized microfibrillar polysaccharide comprising substituents that provide electrostatic and/or steric functionality, wherein said electrostatic functionality comprises anionic charge.

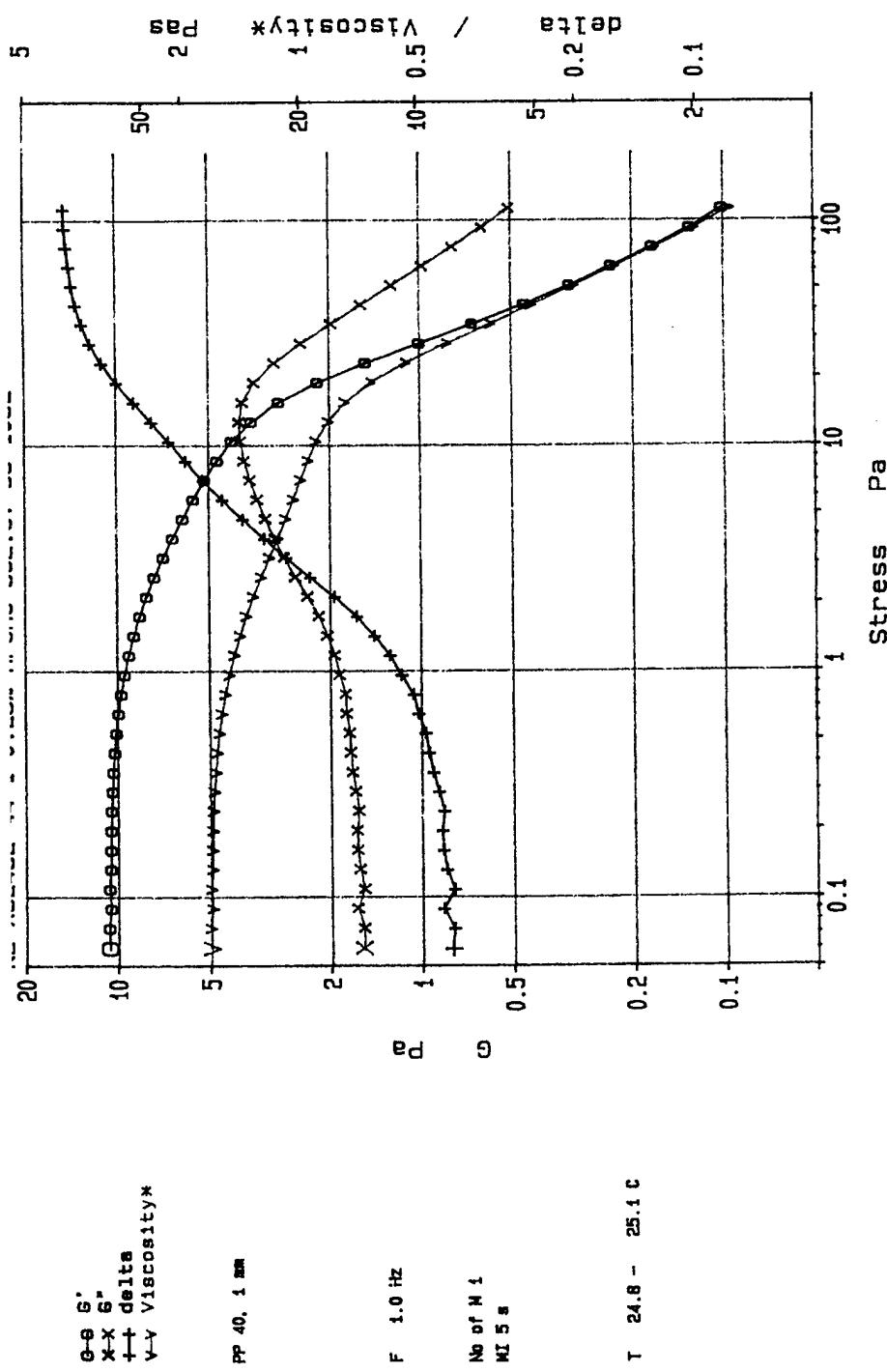
Figure 1

Figure 2

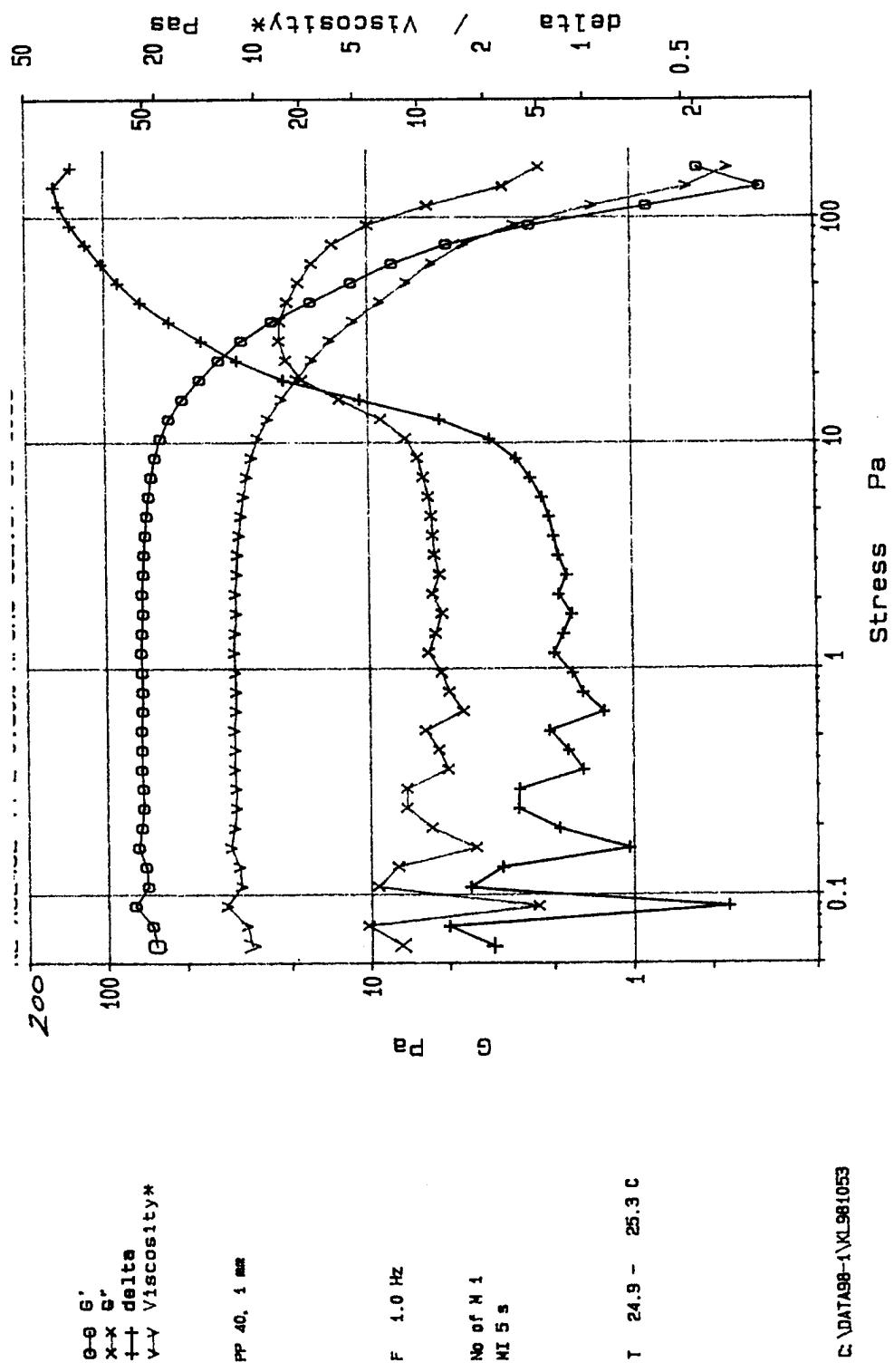


Figure 3

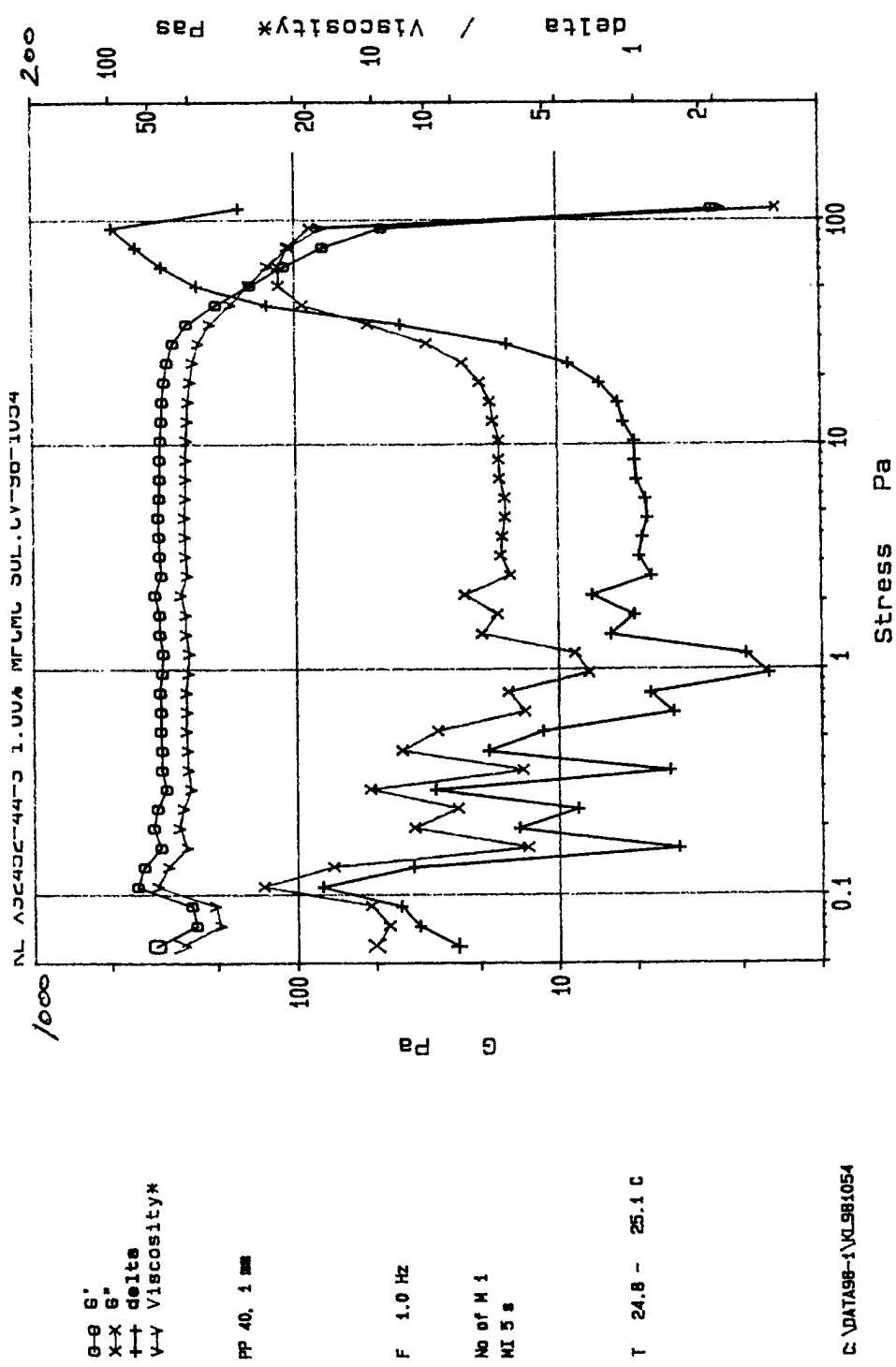


Figure 4

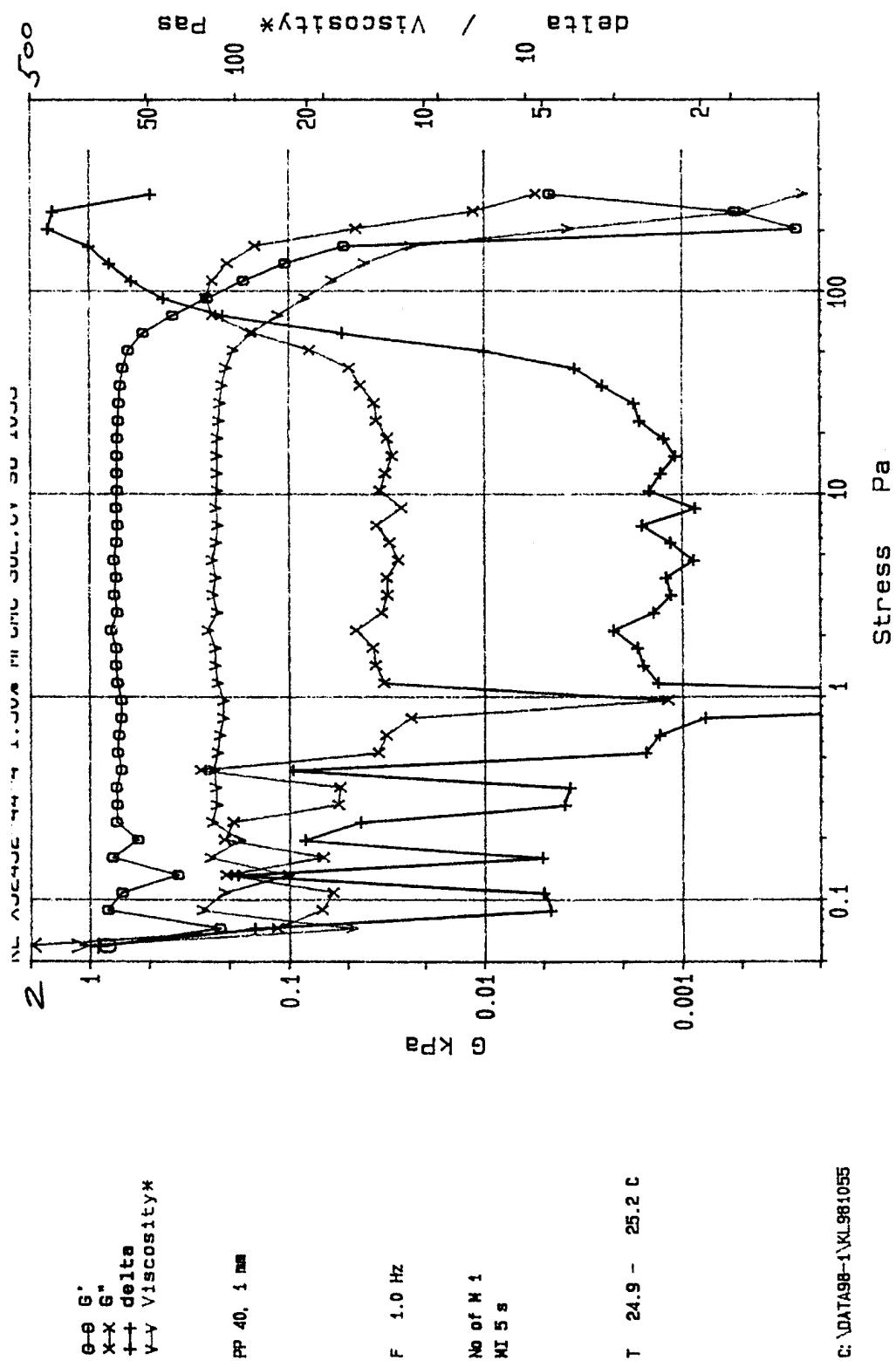


Figure 5

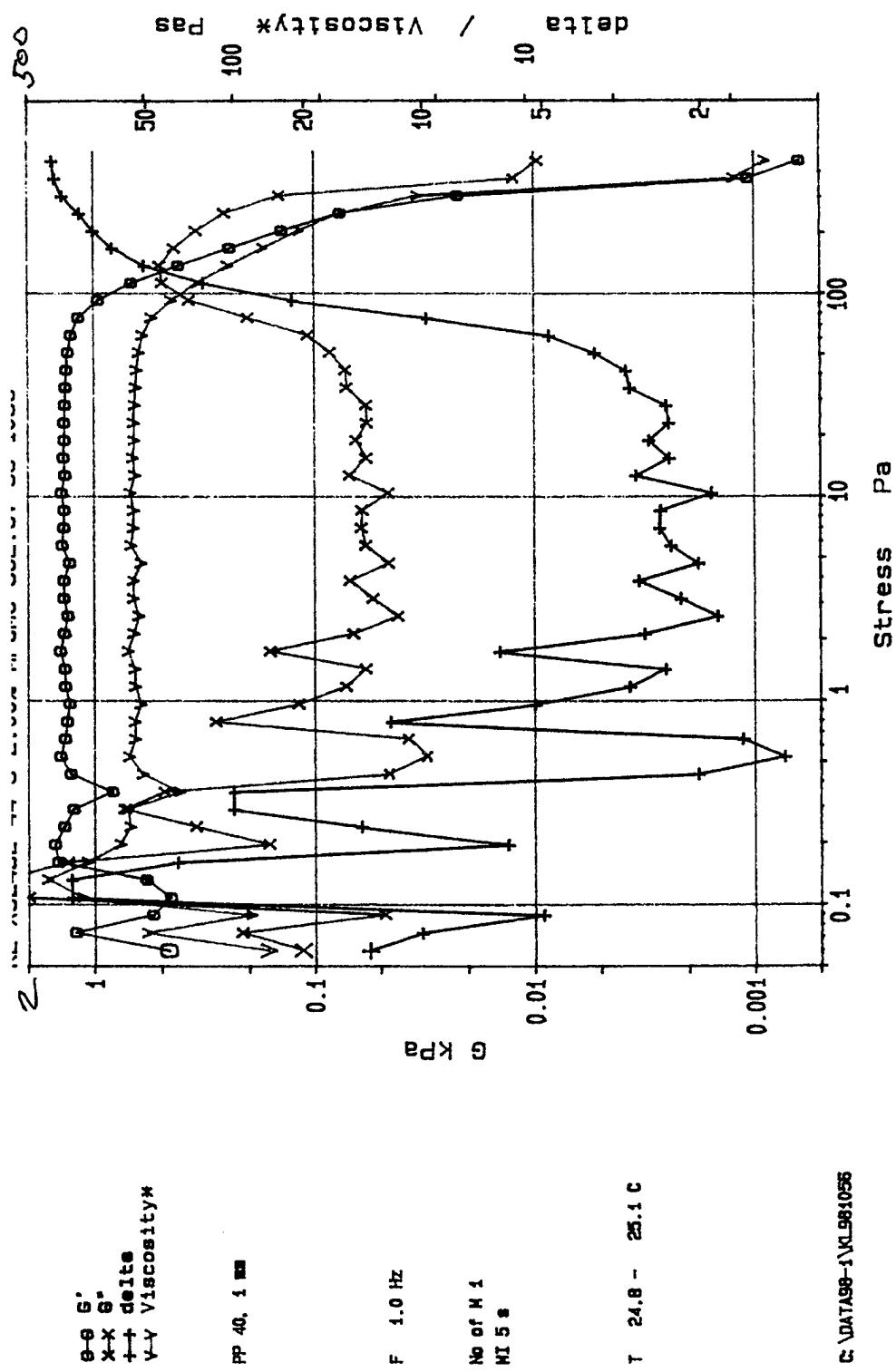


Figure 6

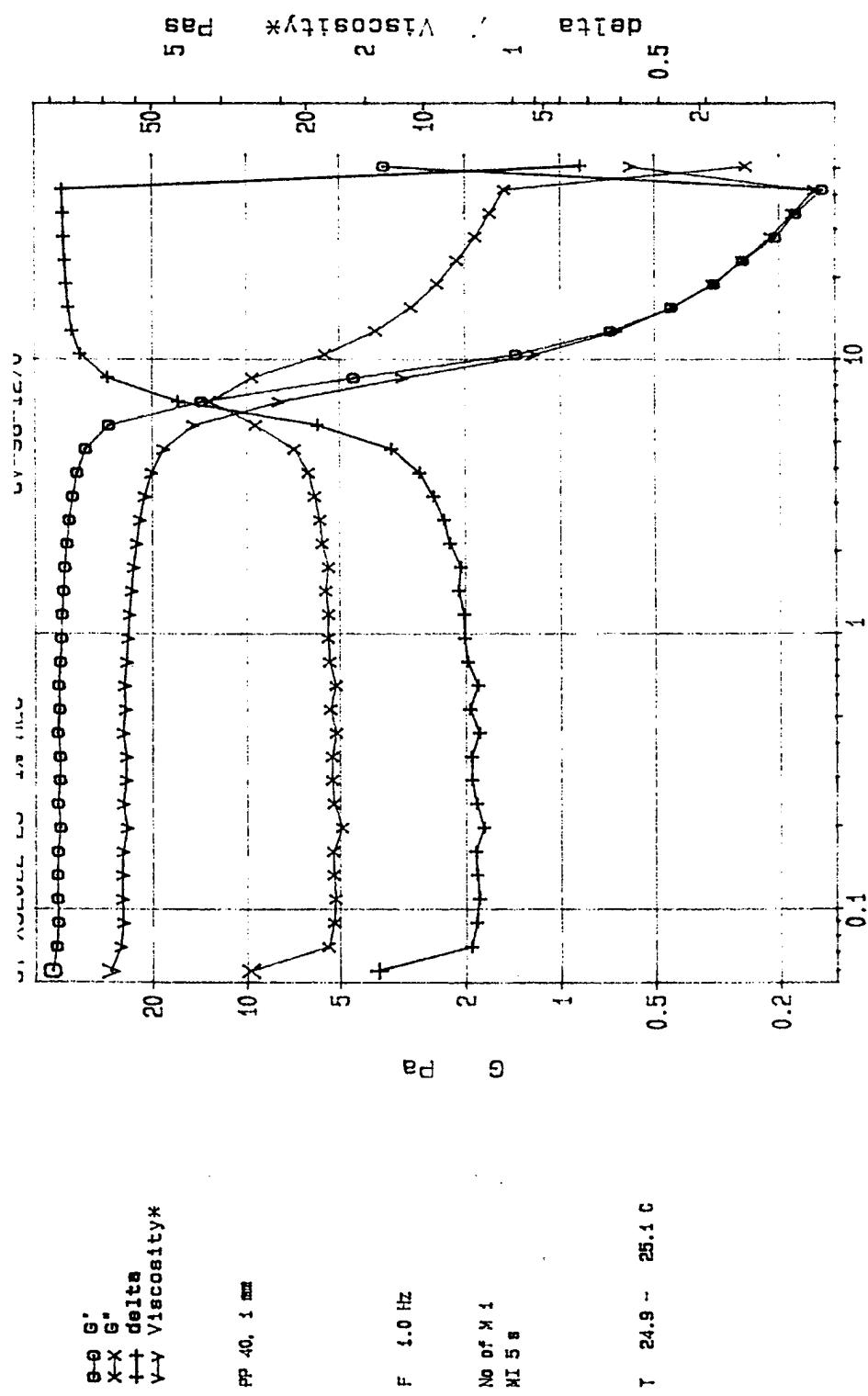


Figure 7

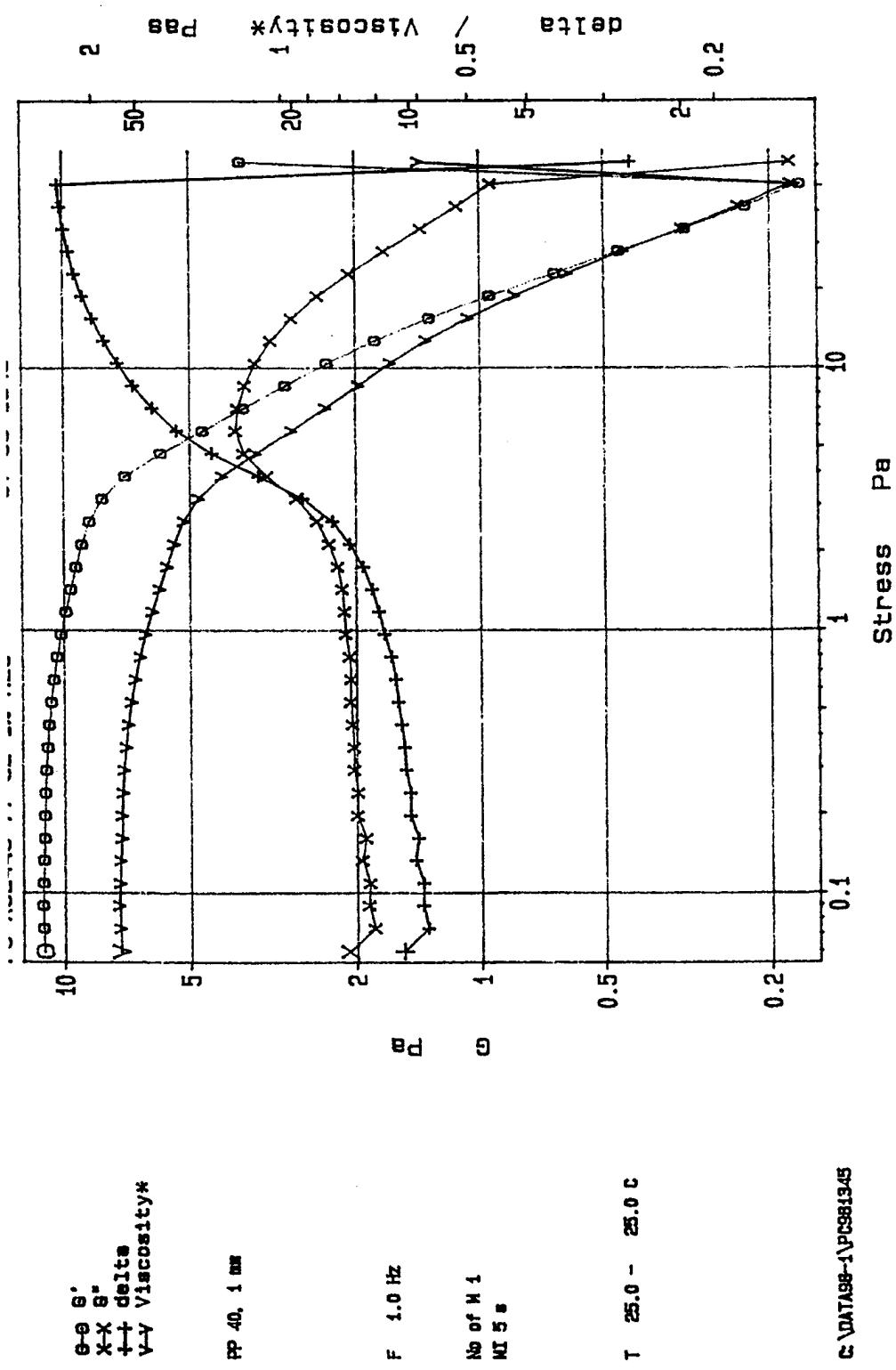


Figure 8

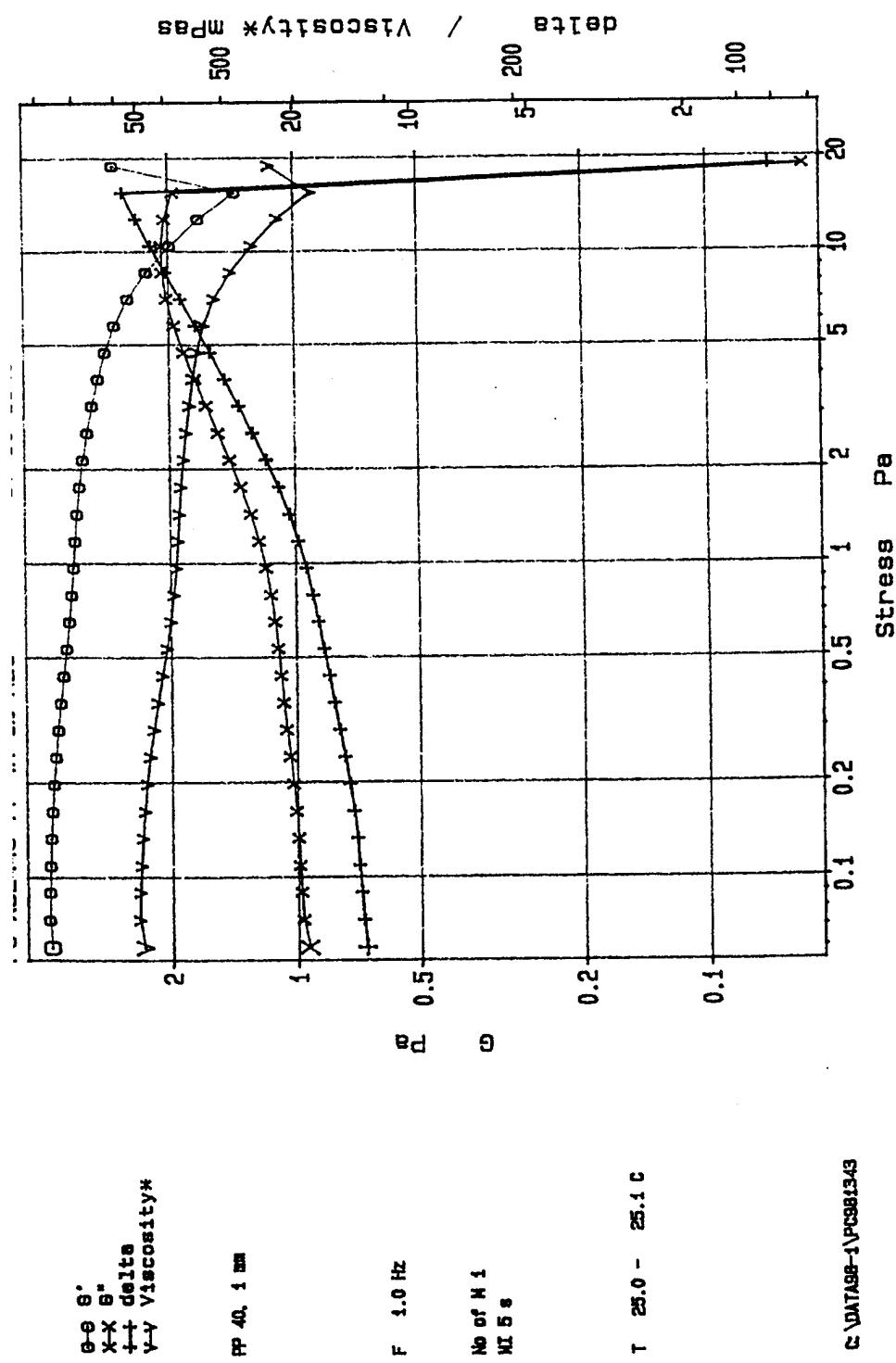
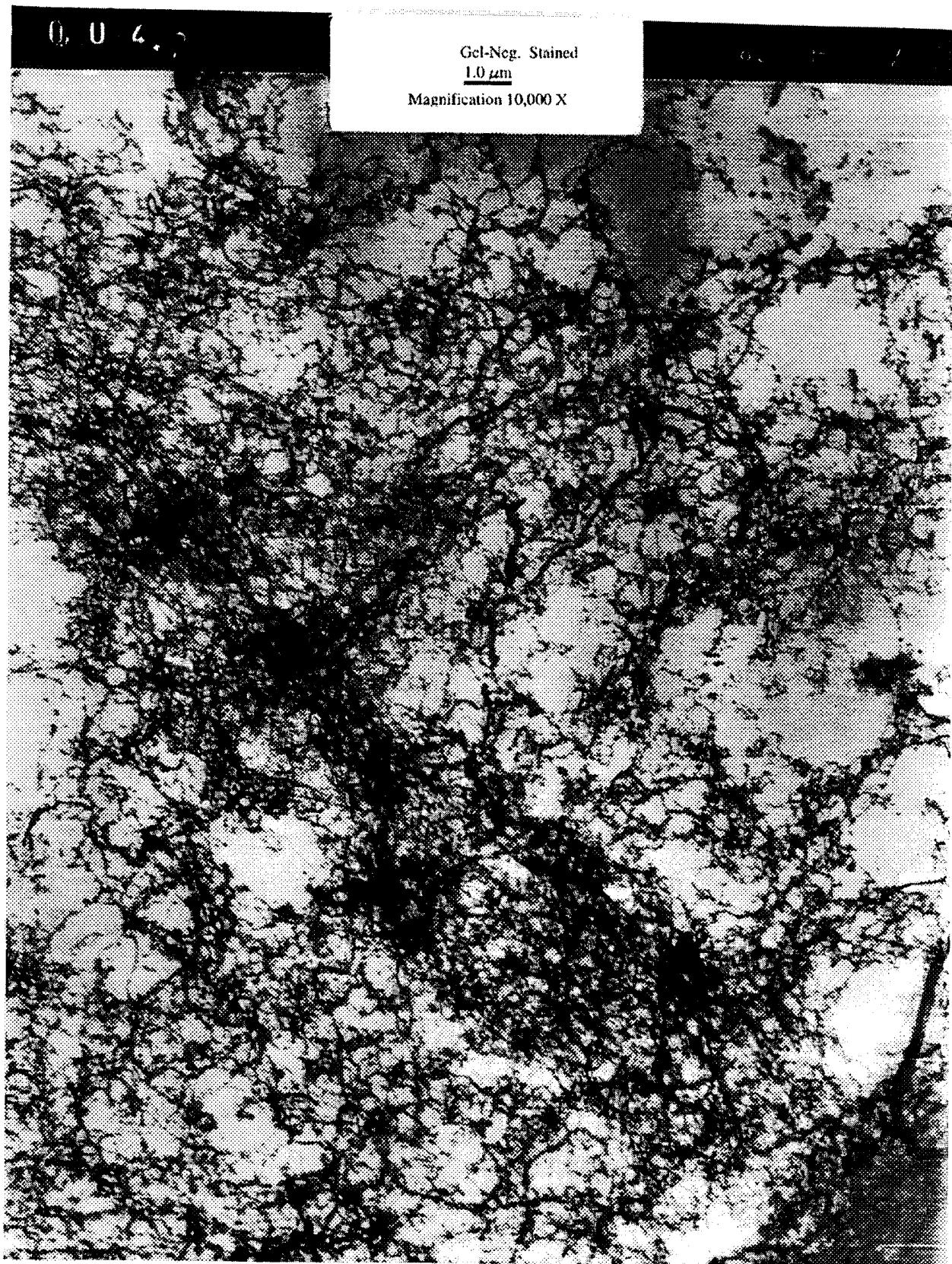
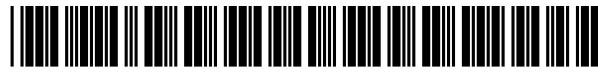


Figure 9



US007967904B2

(12) **United States Patent**
Bowden et al.

(10) **Patent No.:** US 7,967,904 B2
(45) **Date of Patent:** *Jun. 28, 2011

(54) **BIODEGRADABLE OR COMPOSTABLE CONTAINERS**

(75) Inventors: **Joe A. Bowden**, Durango, CO (US);
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(73) Assignee: **New Ice Limited**, Isle of Man

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **12/367,628**

(22) Filed: **Feb. 9, 2009**

(65) **Prior Publication Data**

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Related U.S. Application Data

(60) Continuation of application No. 11/486,722, filed on Jul. 14, 2006, now abandoned, which is a continuation of application No. 10/977,082, filed on Oct. 29, 2004, now Pat. No. 7,083,673, which is a division of application No. 10/341,288, filed on Jan. 13, 2003, now Pat. No. 6,878,199.

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(51) **Int. Cl.**

B32B 21/02 (2006.01)
C08L 3/02 (2006.01)

(52) **U.S. Cl.** **106/162.51**; 264/109; 264/112;
428/535

(58) **Field of Classification Search** None
See application file for complete search history.

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(57) **ABSTRACT**

The present invention provides an improved method and materials for forming biodegradable containers that can hold food products in dry, damp or wet conditions and provides the biodegradable containers prepared according to the disclosed process. The containers are produced through the use of a pre-gelled starch suspension that is unique in its ability to form hydrated gels and to maintain this gel structure in the presence of many other types of materials and at low temperatures.

30 Claims, No Drawings

BIODEGRADABLE OR COMPOSTABLE CONTAINERS

This application is a continuation of U.S. patent application Ser. No. 11/486,722, filed Jul. 14, 2006, now abandoned, which is a continuation of U.S. patent application Ser. No. 10/977,082, filed Oct. 29, 2004, now U.S. Pat. No. 7,083,673, which is a divisional of U.S. patent application Ser. No. 10/341,288, filed Jan. 13, 2003, now U.S. Pat. No. 6,878,199, which claims the benefit of U.S. Provisional Application No. 60/348,003, filed Jan. 11, 2002.

FIELD OF THE INVENTION

This application is in the field of biodegradable and in particular compostable containers that can hold items in a dry, damp or wet condition. The products are based on novel starch compositions that can form and maintain a hydrated gel at low temperatures.

BACKGROUND OF THE INVENTION

Materials such as paper, paperboard, plastic, polystyrene, and even metals are presently used in enormous quantity in the manufacture of articles such as containers, separators, dividers, lids, tops, cans, and other packaging materials. Modern processing and packaging technology allows a wide range of liquid and solid goods to be stored, packaged, and shipped in packaging materials while being protected from harmful elements, such as gases, moisture, light, microorganisms, vermin, physical shock, crushing forces, vibration, leaking, or spilling. Many of these materials are characterized as being disposable, but actually have little, if any, functional biodegradability. For many of these products, the time for degradation in the environment can span decades or even centuries.

Each year, over 100 billion aluminum cans, billions of glass bottles, and thousands of tons of paper and plastic are used in storing and dispensing soft drinks, juices, processed foods, grains, beer and other products. In the United States alone, approximately 5.5 million tons of paper are consumed each year in packaging materials, which represents only about 15% of the total annual domestic paper production.

Packaging materials (e.g., paper, paperboard, plastic, polystyrene, glass, or metal) are all, to varying extents, damaging to the environment. For example, the manufacture of polystyrene products involves the use of a variety of hazardous chemicals and starting materials, such as benzene (a known mutagen and a probable carcinogen). Chlorofluorocarbons (or "CFCs") have also been used in the manufacture of "blown" or "expanded" polystyrene products. CFCs have been linked to the destruction of the ozone layer.

Due to widespread environmental concerns, there has been significant pressure on companies to discontinue the use of polystyrene products in favor of more environmentally safe materials. Some groups have favored the use of products such as paper or other products made from wood pulp. However, there remain drawbacks to the sole use of paper due to the tremendous amount of energy that is required to produce it. A strong need to find new, easily degradable materials that meet necessary performance standards remains.

Degradability is a relative term. Some products which appear to be degraded merely break apart into very small pieces. These pieces are hard to see, but can still take decades or centuries to actually break down. Other products are made from materials which undergo a more rapid breakdown than non-biodegradable products. If the speed of this degradation

is such that the product will degrade within a period of less than approximately 24 days under normal environmental conditions, the product is said to be compostable. Achievement of products made of compostable materials which also meet a variety of needs, such as containers for products in a damp or wet condition, has posed a significant challenge.

One solution has been to make packaging materials out of baked, edible sheets, e.g., waffles or pancakes made from a mixture of water, flour and a rising agent. Although edible sheets can be made into trays, cones, and cups which are easily decomposed, they pose a number of limitations. For example, since fats or oils are added to the mixture to permit removal of the sheet from the baking mold, oxidation of these fats cause the edible sheets to go rancid. In general, edible sheets are very brittle and far too fragile to replace most articles made from conventional materials. They are also overly sensitive to moisture and can easily mold or decompose prior to or during their intended use.

Starch is a plentiful, inexpensive and renewable material that is found in a large variety of plant sources, such as grains, tubers, and fruits. In many cases, starch is discarded as an unwanted byproduct of food processing. Starch is readily biodegradable and does not persist in the environment for a significant period after disposal. Starch is also a nutrient, which facilitates its breakdown and elimination from the environment.

Due to the biodegradable nature of starch, there have been many attempts to incorporate it into a variety of materials. Starch has been incorporated into multi-component compositions in various forms, including as filler and binder, as has been used as a constituent within thermoplastic polymer blends.

Starch can be used as a binder or glue to adhere solid constituents together to form a heterogeneous mixture of different components. At some point before or during the molding phase, the starch is typically dissolved or gelatinized in an appropriate solvent, such as water, so that the starch becomes a flowable material into which the other components can be dispersed. Since native starch has a melting point that approaches its decomposition temperature, it is necessary to add polar liquids or solvents to allow the starch to become molten, solvated or otherwise liquified into a plastic state at a temperature that is safely below its decomposition temperature. Upon resolidification of the gelatinized starch, typically by removing enough of the water by evaporation so that the starch recrystallizes or otherwise dries out, the starch forms a solid or semi-solid binding matrix that can bind the remaining components together. Although many have attempted for years to perfect a starch blend that would yield an environmentally sound material while, at the same time, being economical to make, such a combination has not yet been achieved.

There remains a need in the art to provide a fully compostable product that is strong, not prone to mold or pests, and can be readily and inexpensively made. Furthermore, there is a need to develop a robust method to develop compostable products that can be used to hold dry, wet or damp material at a range of temperatures.

PCT Publication No. WO 99/02598, filed by Business Promotions, Inc., describes a method for making a biodegradable product for use as a container for foodstuffs, including hot and cold liquids. The product is manufactured under pressure and heat in a mold, based on a basic material made of amylose-comprising flour derived from an edible crop plant, wood flour, natural wax and water. The basic material consists substantially of a moist granulate comprising 50-250 parts by

weight flour, 10-85 parts by weight wood flour, 2-30 parts by weight natural wax and 50-250 parts by weight water.

European Patent 0773721B1 to Coöperatieve Verkoop discloses compounds made of a starch suspension and a wax coating, which is baked into a base mold. The coating is made of a wax composition comprising at least 50% wax and having a melting temperature of at least 40° C. The starch composition is preferably made by a process that includes 5-75% of a starch derivative which has a reduced swelling capacity at increased temperatures when compared to native starch.

PCT Publication No. WO 01/60898, filed by Novamont describes products such as sheets of different thicknesses and profile based on destructured or complexed starch, which are biodegradable. In particular, the patent claims partly-finished products, for example a foam sheet material, comprising destructured or complexed starch foamed as a continuous phase, having a density between 20 and 150 kg/m³, cell dimensions in a range between 25 and 700 µm with a cell distribution such that 80% of them have a dimension between 20 and 400 µm.

U.S. Pat. No. 6,451,170 to Cargill, Inc. describes improved starch compositions of cross-linked cationic starch, used in the papermaking process. The '170 patent claims the following papermaking process: 1) providing a cationized cross-linked starch component having a hot paste viscosity in the range of from about 200 cps to about 3000 cps as measured in a Brookfield viscometer at about 95° C. using a No. 21 spindle; 2) cooking a first portion of the starch component to generate a cooked starch component at an average cooking temperature below 330° F. for a period of time; 3) dewatering a paper furnish (the paper furnish including: (i) cellulosic fibers in an aqueous slurry, (ii) inorganic particles comprising at least 50 percent by weight particles having an average particle size of no greater than 1 micron, and (iii) the cooked starch component); and 4) adjusting the dewatering rate by cooking a second portion of the starch component at an average temperature at least 10° F. different than the first cooking temperature. The fourth step in the papermaking process can also include adjusting the first pass retention during dewatering by cooking a second portion of the starch composition at an average temperature at least 10° F. different than the first cooking temperature.

U.S. Pat. No. 5,122,231 to Cargill, Inc. describes a new cationic cross-linked starch for use in papermaking in the wet end system of a paper machine using a neutral or alkaline finish. The '231 patent claims methods to increase starch loading capacity in a papermaking process in which the papermaking process has a pH of about 6 or greater. One method is directed to adding the cationized cross-linked starch to a paper furnish of the process prior to the conversion of the furnish to a dry web wherein the starch is cationized to a degree of substitution on the hydroxyl groups of the starch between about 0.005 and about 0.050 and wherein after the cationization the starch is cross-linked to a hot paste viscosity in the range of from about 500 cps to about 3000 cps as measured on a Brookfield viscometer at about 95° C. using a No. 21 spindle. Another method is directed to adding cationized cross-linked starch to a paper furnish of the process in an amount effective for making Zeta potential of the furnish about zero and wherein the starch is cationized with monovalent cations and has a degree of substitution of monovalent cations on the hydroxyl groups of the starch between about 0.005 and about 0.050 and wherein after cationization the starch is cross-linked to a hot paste viscosity in the range of from about 500 cps to about 3000 cps as measured on a Brookfield viscometer at about 95° C. using a No. 21 spindle.

U.S. Pat. Nos. 5,569,692 and 5,462,982, both assigned to Novanont, disclose a composition for a biodegradable material which can be used at high temperatures comprising destructured starch, a thermoplastic polymer, and a plasticizer having a boiling point higher than 150° C. in an amount from 20 to 100% based on the weight of starch, said destructured-starch being obtained by destructuring starch as it is, without the addition of water. The inventors found that if a starch is destructured as it is, with the addition of a high-boiling plasticizer (such as glycerine) and a destructuring agent (such as urea), in an extruder heated to a temperature below the boiling point of the plasticizer (but between 120 and 170° C.), destructured starch compositions are obtained which can be mixed with polymers having relatively high melting points and are suitable for extrusion at temperatures higher than 120° C. at low pressure. The compositions thus obtained are particularly suitable for subsequent operations such as thermoforming and blowing.

U.S. Pat. No. 5,252,271 to Bio-Products International discloses a material that is based on a dry starch composition, having no greater than 30% water content; which is mixed with a mild acid in dry, powdered form (preferably malic acid, tartaric acid, citric acid, maleic acid and succinic acid) at a percentage of 0.2 to 7% of the total starch composition. Adding a dry, powdered carbonate composition capable of reacting with acid to generate CO₂ gas at a composition percentage of 0.1 to 2% of the total starch composition and mixing and advancing the product with water within an extrusion barrel of the extrusion means to generate elevated heat and pressure for converting the material to a gelatinous state that can be dried and remain pliable.

U.S. Pat. No. 4,863,655 to National Starch and Chemical Corp. discloses a biodegradable packaging material comprising an expanded, high amylose starch product having at least 45% (by weight of the final material) amylose content and a low density, closed cell structure with good resilience and compressibility. Another embodiment provides a method of preparing the packaging material with a total moisture content of 21% or less by weight, at a temperature of from 150 to 250° C.

U.S. Pat. No. 5,428,150 to Cerestar Holdings discloses a method for making a starch-containing composition to produce a material suitable for the production of molded articles in which the composition contains in addition to the starch a starch degradation product selected from starch hydrolysis products having dextrose equivalent's of 1 to 40, particularly a maltodextrin, oxidized starches and pyrodext.

U.S. Pat. Nos. 5,660,900, 5,868,824, and PCT Publication No. WO 96/05254 filed by Khashoggi disclose compositions for manufacturing biodegradable articles from highly inorganically filled materials having a starch-based binder. These documents describe articles of manufacture that have high levels of the inorganic filler in a polymer matrix without adverse affects on the properties of the binding system. The articles contain a matrix of starch and at least one inorganic aggregate, present as at least about 20% by weight (or 5% by volume) of the final mixture. The matrix is prepared from about 10% to 80% of a starch-based binder that has been substantially gelatinized by water and then hardened through the removal of a substantial quantity of the water by evaporation with an inorganic aggregate dispersed throughout the starch-bound cellular matrix. The mixture is designed with the primary considerations of maximizing the inorganic components, minimizing the starch component and solvent, and selectively modifying the viscosity to produce articles that have the desired properties for their intended use.

U.S. Pat. Nos. 5,736,209 and 5,810,961, and PC Publication No. WO 97/37842, also assigned to Khashoggi Industries, disclose methods to develop biodegradable paper and products which include a binding matrix of starch and cellulosic ether, and fibers substantially homogeneously dispersed throughout the matrix. The '209 patent discloses a concentration range for the starch of about 5% to about 90% by weight of solids in the sheet, for the cellulosic ether a range from about 0.5% to about 10% by weight of solids, and for fibers a concentration range from about 3% to about 40%. Optionally, an inorganic mineral filler can be added. Sheets produced using this biodegradable material having a thickness less than about 1 cm and a density greater than about 0.5 g/cm³ are described.

PCT Publication No. WO 01/51557, also filed by Khashoggi, is directed to compositions and methods for manufacturing thermoplastic starch compositions having a particulate filler (present in an amount greater than about 15% by weight of the thermoplastic starch) and, optionally, fiber reinforcement. Native starch granules are made thermoplastic by mixing and heating in the presence of an appropriate plasticizer (including somewhat polar solvents such as water or glycerin) to form a starch melt. The starch melt is then blended with one or more non-starch materials in order to improve the properties and reduce the cost of the resulting thermoplastic starch composition. A particulate filler component is thereafter blended with the starch melt, preferably an inexpensive, naturally occurring mineral particulate filler ("inorganic filler"), included in an amount greater than about 15% by weight of the thermoplastic starch composition. In addition, this reference discloses a composition comprising a thermoplastic starch melt having a water content of less than about 5% by weight while in a melted state, wherein at least one plasticizer has a vapor pressure of less than about 1 bar when in a melted state and in which a solid particulate filler phase is dispersed and included in an amount from about 5% to about 95% by weight. An additional embodiment discloses dispersion of a solid particulate filler phase in an amount from about 5% to about 95% by weight of the thermoplastic starch composition and a fibrous phase in a concentration of from about 3% to about 70% by weight.

U.S. Pat. No. 6,168,857 to Khashoggi Industries discloses a starch-bound sheet having a thickness less than about 1 cm and a density greater than about 0.5 g/cm³ comprising: (a) a binding matrix including starch and an auxiliary water-dispersible organic polymer, wherein the starch has a concentration greater than about 5% by weight of total solids in the sheet; and (b) fibers substantially homogeneously dispersed throughout the starch-bound sheet; and optionally an inorganic mineral filler.

U.S. Pat. Nos. 5,618,341, 5,683,772, 5,709,827, and 5,679,145 and PCT publication No. WO 97/2333, assigned to Khashoggi Industries, disclose starch-based compositions that can be used in making containers. U.S. Pat. Nos. '341 and '145 teach methods for dispersing fibers within a fibrous composition comprising the steps of: (a) combining together water, fibers, and a thickening agent such that the thickening agent (such as a pregelatinized starch) and water interact together to form a fluid fraction that is characterized by a yield stress and viscosity that enables the fibers to be substantially uniformly dispersed throughout the fibrous composition as the fibers and fluid fraction are mixed together, the fibers having an average length greater than about 2 mm and an average aspect ratio greater than about 25:1; and (b) mixing together the combined thickening agent, water, and fibers in order to substantially uniformly disperse the fibers throughout the fibrous composition. The thickening agent is included

in an amount in a range from about 5% to about 40% by weight of the fluid fraction. The inventive method involves a fluid system that is able to impart shear from a mechanical mixing apparatus down to the fiber level in order to obtain a starch-based composition having substantially uniformly dispersed fibers. U.S. Pat. No. '772 additionally discloses an inorganic filler to enhance the strength and flexibility of the articles. '827 additionally discloses methods to make the article of manufacture that is developed from mixtures including fibers having an average aspect ratio greater than about 25:1. The '341, '772, '827, and '145 patents and WO 97/2333 application, disclose high aspect ratios (i.e., about 25:1 or greater) and long-length (i.e., at least about 2 mm) fibers to reinforce the structure. PCT publication No. WO 97/2333 discloses articles that contain high starch contents (from about 50% to about 88% by weight ungelatinized and about 12% to about 50% by weight of gelatinized starch).

U.S. Pat. No. 6,303,000 to Omnova Solutions discloses a method to improve the strength of paper by adding an aqueous cationic starch dispersion modified with a blocked glyoxal resin to a paper pulp slurry. The starch dispersion is prepared by gelatinizing an aqueous suspension of starch granules (including potato, corn, waxy corn, red and white milo, wheat and tapioca, thin-boiling starches, and starches that have been additionally chemically modified) and reacting the starch with a blocked glyoxal resin at temperatures of at least 70° C., preferably 85 to 95° C. Suitable blocked glyoxal resins which can be used with the invention include cyclic urea/glyoxal/polyol condensates, polyol/glyoxal condensates, urea or cyclic urea/glyoxal condensates and glycol/glyoxal condensates in an amount from about 3% to about 30%, preferably 9 to 20%, of the total dry weight of starch. The resulting gelatinized starch composition can be cooled and stored, or directly added to a dilute paper pulp slurry to increase the tensile strength and elasticity of the resulting paper product.

PCT Publication No. WO 01/05892 filed by Kim & Kim describes methods for manufacturing plastic-substitute goods by using natural materials by preparing a glue made by mixing 20% by weight of a starch and 80% by weight of water together, heating this mixture; washing and drying rice husks to a drying extent of 98%; mixing the glue and the rice husks together so as to form a mixture of the glue and the rice husks, drying them to a drying extent of 98%, and crushing them to a size range of 0.1-0.1 mm. Then, mixing 80% by final weight of the mixture of the glue and the rice husks, 5% by final weight water, and 15% by final weight of rosin to form a final mixture; and molding the final mixture using a molding machine at a temperature of 100-350° C. under a pressure of 5 kg/cm at a production frequency of 30-80 seconds per product.

PCT Publication No. WO 02/083386 also filed by Kim & Kim describes methods for manufacturing plastic-substitute goods by using natural materials using a starch-based glue and melamine-resin. Melamine or urea resin is a thermosetting resin which is formed by reaction of melamine or urea acting upon formaldehyde. The products are manufactured by first preparing a mixture of 20% by weight of a starch and 80% by weight of water, heating this mixture; washing and drying rice husks to a drying extent of 98%; mixing the glue and the rice husks together so as to form a mixture of the glue and the rice husks, drying them to a drying extent of 98%, and crushing them to a size range of 0.01-0.1 mm. Melamine resin is obtained by a process of first, mixing 30% by weight of formaldehyde solution and 70% by weight of water, 30% by weight of melamine or urea and heating the mixture at a temperature of 350° C. A mixture is then made of 70% by final

weight of the mixture of the glue and the rice husks, 15% by weight of water, and 15% by weight of melamine resin to form a final mixture. The final mixture is molded by a molding machine at a temperature of 100-350° C. under a pressure of 5 kg/cm at a product ion frequency of 30-80 seconds per product.

U.S. Publication No. US 2002/0108532 and PCT Publication No. WO 00/39213 filed by Apack AG disclose methods to produce a shaped body made of biodegradable material that shows good expansion behavior during thermoforming from 7.6 to 8.5% by weight of cellulosic fibers, from 16.1 to 17.6% by weight of native starch, from 5.4 to 6% by weight of pregelatinized starch and from 68.0 to 70.6% by weight of water. First, the pregelatinized starch is produced by mixing between 5.4-6% starch and 94-94.6% water, heating the mixture to 68-70° C., holding the mixture constant at 68-70° C. for 10 minutes, and cooling the pregelatinized starch to 50° C. Then, adding the 16.1 to 17.6% by weight of native starch, 7.6 to 8.5% by weight of cellulosic fibers, and 68.0 to 70.6% by weight of water to the pregelatinized solution at a temperature of 50° C.; mixing for 5 minutes to achieve a homogeneous mixture at 40° C., not allowing the mixture to substantially cool, and placing the mixture in a baking mold, and baking the mixture at 100-200° C. for 10-100 seconds to form the shaped body.

German patent DE 19,706,642 to Apack Verpackungen GmbH discloses the production of a biodegradable article from 25-75% fibers, 13-38% starch and 13-38% water. First, the 25-75% fibers, 13-38% starch are mixed in a dry state in a continuous process; then water is admixed continuously. The mixture is then subjected to a baking process to obtain the finished molded article, and then the molded article is coated with a biologically degradable film that is impermeable to humidity.

Although numerous attempts have been made to provide suitable biodegradable and compostable materials for packaging, the resulting substances are not ideal. The currently available materials either cannot successfully be used to package materials, particularly those that are wet, or do not effectively degrade under normal environmental conditions. A need exists to develop materials that will reduce the build up of disposed, slowly degrading materials, and to limit the environmental damage caused by toxic chemicals used in the production of packaging materials.

It is therefore an object of the present invention to provide a robust process and materials for the production of an efficiently biodegradable container.

It is a further object of the present invention to provide a materials and a process for producing a biodegradable container that can hold products in dry, wet or damp conditions.

It is another object of the present invention to provide material and a process to produce biodegradable containers through the use of a pregelatinized starch solution that is stable at a wide range of temperatures.

It is a further object of the present invention to provide a process and material to produce biodegradable containers through the use of a pregelatinized paper starch solution that is stable at a wide range of temperatures.

It is another object of the present invention to provide a process and material to produce biodegradable containers from a wide range of materials.

It is yet another object of the present invention to provide a process and material to produce biodegradable containers under a wide range of environmental conditions.

It is still another object of the present invention to provide biodegradable and compostable products.

SUMMARY OF THE INVENTION

The present invention provides an improved method and materials, for forming biodegradable containers that can hold food products in dry, damp or wet conditions. The containers are produced through the use of a pre-gelled starch suspension that is unique in its ability to form hydrated gels and to maintain this gel structure in the presence of many other types of materials and at low temperatures. In addition, this pre-gelled starch has the ability to melt into plastic like materials at relatively low temperatures in the presence of a wide range of materials under varying environmental conditions. Further, this pre-gelled material allows for the development of containers with high binding strengths and open cell structures to provide insulation and cross-linking of components.

One aspect of the present invention is a process for forming a biodegradable container by:

(a) forming a pre-gelled starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) adding to the pre-gelled starch suspension a dry or damp, homogeneous mixture containing at least wood fibers having an aspect ratio between approximately 1:2 and 1:8 (width:length) to form a homogenous moldable composition; and

(c) molding the homogenous moldable composition with heat to form a biodegradable container.

In another embodiment, the present invention is a process for forming a biodegradable container by:

(a) forming a first pre-gelled starch suspension that is maintained at a low temperature, for example, preferably 0-60° C., most preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), a second pre-gelled starch suspension, and/or a native starch to form a homogenous mixture;

(c) adding to the pre-gelled starch suspension the dry or damp, homogeneous mixture to form a homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

In a specific embodiment, the present invention is a process for forming a biodegradable container by:

(a) forming a pre-gelled starch suspension (the pre-gel) produced from approximately 3-10% potato starch by weight of the pre-gel and approximately 90-97% water by weight of the pre-gel such that the pre-gelled suspension is maintained at low temperatures, for example, preferably 0-60° C., most preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), a pre-gelled starch suspension produced from approximately 15% corn starch (by weight of the pre-gel) and approximately 85% water by weight of the pre-gel, and a native starch (for example approximately 50-70%, or, more specifically, 57-65.8%, corn starch (by weight of the homogenous moldable composition) or approximately 2-15% or, more specifically, 3-5% potato starch (by weight of the homogenous moldable composition)) to form a homogeneous mixture;

(c) adding to the pre-gelled potato starch suspension the homogeneous mixture to form a final homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

Another aspect of the present invention is a process for forming a biodegradable container by:

(a) forming a pre-gelled paper starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) adding to the pre-gelled paper starch suspension a dry or damp, homogeneous mixture containing at least wood fibers having an aspect ratio between approximately 1:2 and 1:8 (width:length) to form a homogeneous moldable composition; and

(c) molding the homogeneous moldable composition with heat to form a biodegradable container.

In other embodiments, the present invention is directed to a process for forming a biodegradable container by:

(a) forming a first pre-gelled paper starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), and a native starch(s) to form a homogeneous mixture;

(c) adding to the first pre-gelled starch suspension the homogenous mixture to form a homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

In a specific embodiment, the present invention is directed to a process for forming a biodegradable container by:

(a) forming a pre-gelled starch suspension produced from approximately 2-15% potato starch (by weight of the pre-gel), preferably about 2.5, 5, 10, or 15%; approximately 5-10% paper pulp (by weight of the pre-gel), preferably about 5.9-8%; and approximately 75-95% water (by weight of the pre-gel) such that the pre-gelled suspension is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8, preferably between 1:2 and 1:4), native corn starch and native potato starch to form a homogeneous mixture;

(c) adding to the pre-gelled potato starch suspension the homogeneous mixture to form a homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

In other embodiments, the following materials can be added to the wood fibers to form a homogeneous mixture:

(i) waxes, fatty alcohols, phospholipids or other high molecular weight biochemicals, such as glycerol, for example between approximately 1-5% or, more specifically, 2.6-3.7% glycerol (by weight of the homogenous moldable composition);

(ii) approximately 0.5-20% water (by weight of the homogenous moldable composition), preferably about 0.5-10%, 0.5-11% 0.5-12%, 10 or 20%;

(iii) baking powder, for example between approximately 0.1-15% by weight of the homogenous moldable composition, preferably about 0.42, 1 or 12%; and/or

(iv) additional materials, such as up to approximately 5% by weight of the homogenous moldable composition of natural earth fillers, for example, clays such as bentonite, amorphous raw products such as gypsum and calcium sulfate, minerals such as limestone, or man made materials such as fly-ash.

In still other embodiments, the process comprises the steps of:

(a) forming a pre-gelled starch suspension or paper starch suspension that is maintained at a low temperature, for example, preferably from about 0-60° C., most preferably from about 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8) and (i) dry or damp starch, such as corn starch; (ii) pre-gelled starch, such as a

10 pre-gelled corn starch produced from approximately 15% corn starch (by weight of the pre-gel) and 85% water; (iii)

waxes, fatty alcohols, phospholipids and other high molecular weight biochemicals, such as glycerol, for example between approximately 1-5% glycerol (by weight of the

15 homogenous moldable composition); (iv) approximately 0.5-20% water, preferably about 0.5-10%, 0.5-11% 0.5-12%, 10 or 20% (by weight of the homogenous moldable composition); (v) baking powder, for example between approximately

15 0.1-15% (by weight of the homogenous moldable composition), preferably 0.42, 1 or 12%; and/or (vi) additional mate-

rials, such as up to approximately 5%, 0-4%, 0-13%, 2-13%, or 0-15% by weight of the homogenous moldable composi-

20 tion of natural earth fillers, for example, clays such as bentonite, amorphous raw products such as gypsum and calcium sulfate, minerals such as limestone, and man made materials such as fly-ash to form a homogeneous mixture;

(c) adding to the pre-gelled starch suspension the dry or damp, homogeneous mixture to form a homogenous moldable composition; and

25 (d) molding the homogenous moldable composition with heat to form a biodegradable container.

In one embodiment, the pre-gelled starch suspension is produced from approximately 2.5-15% starch (by weight of the pre-gel), such as potato or corn starch, and from approxi-

30 mately 85-97.5% of water by weight of the homogenous moldable composition. In another embodiment, the pre-

35 gelled starch suspension is produced from approximately 2.5-5.5% starch and from approximately 94.5-97.5% water (by weight of the pre-gel). In preferred embodiments, the

40 pre-gelled starch suspension is produced from approximately 2.5-10% potato starch, more preferably 3%, 5%, 7.5% or 10%

potato starch, and 90, 92.5, 95 or 97% water (by weight of the pre-gel). In another preferred embodiment, the pre-gelled

45 starch suspension is produced from approximately 15% corn starch (by weight of the pre-gel).

In another embodiment, the pregelled paper starch solution is produced from approximately 5-10% paper pulp (by

50 weight of the pre-gel), preferably 5.9-8%, more preferably, 7.3-7.5, 6.5-6.7, or 5.9-6.1%; approximately 5-15%, prefer-

ably 10% potato or other natural starch (such as corn starch), and approximately 75-90% water (by weight of the pre-gel).

In one embodiment, the native starch can be corn starch or

55 potato starch. In another embodiment potato starch and corn starch can be used together. In a further embodiment, the corn

starch can comprise approximately 4-18%, preferably from 4.45-17.9%, or from about 5-35%, preferably 5.9-34.4% by

weight of the homogenous moldable composition, preferably, 4, 5, 6, 13, 15, 16, 17, 18, 20, 21, 22, 26, 28, 29, 30, 31 or 34%.

In a still further embodiment, the wood fibers or flour can

60 comprise approximately 11-24%, preferably 11, 12, 13, 14, 16, 17, 18, 19, 20, 21, 22, 23, or 23.3% by weight of the

homogenous moldable composition that contains the pregelled starch solution. In an alternate embodiment, the

65 wood fibers or flour can comprise approximately 7-11%, preferably 7, 8, 9, 10 or 11%, by weight of the homogenous moldable composition that contains the pregelled paper starch solution. The wood fibers or flour can have an aspect

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ratio, width to length of between approximately 1:2 and 1:10, 1:2 and 1:9, 1:2 and 1:8, 1:2 and 1:7, 1:2 and 1:6, 1:2 and 1:5, 1:2 and 1:4, 1:2 and 1:3, or a fraction thereof, for example a ratio of between 1:2 and 1:9.9.

In another embodiment, the containers which are formed using the method of the invention are efficiently biodegradable, preferably disintegrating to component parts in less than one year. In another embodiment, the containers are compostable, disintegrating to component molecules in less than six months, preferably in less than approximately 24 days.

In further embodiments, pressure can also be used in combination or alternation with heat to mold the biodegradable container. Any amount of pressure can be used that achieves the desired product, for example, pressure between approximately 2-3 psi may be appropriate. Likewise, any amount of heat may be used that achieves the desired result. For example, in one embodiment, the heat used to mold the biodegradable containers is between approximately 150-250° C.; preferably 195-225° C., most preferably 215° C.

In another embodiment, the container can be coated with any suitable liquid-resistant coating. Examples include, but are not limited to, coatings such as PROTECOAT® (from New Coat, Inc.), ZEIN® (a biodegradable material isolated from corn); polylactic acid (PLA, a polymer of lactic acid from fermentation feed stock); poly hydroxyalkanoates (PHA, from microbial fermentation); bacterial cellulose; chitosan based polymers (for example from shell fish wastes); or waxes and oil based coatings. These materials can be applied either as a thin film or can be sprayed/dipped onto the product. Bonding processes for application of thin films of water-resistant material are known in the art.

In one embodiment, a method is provided for creating a waterproof container by:

(a) forming a first pre-gelled starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), and wax, fatty alcohol, phospholipids or other high molecular weight biochemicals, such as glycerol;

(c) adding to the first pre-gelled starch suspension the homogeneous mixture containing the wood fiber and other material;

(d) molding the homogeneous composition with heat to form a biodegradable container; and

(e) coating the container with a liquid-resistant coating, such as PROTECOAT® (from, New Coat, Inc.), ZEIN® (a biodegradable material isolated from corn); poly lactic acid (PLA, a polymer of lactic acid from fermentation feed stock); poly hydroxyalkanoates (PHA, from microbial fermentation); bacterial cellulose; chitosan based polymers (for example from shell fish wastes); or waxes and oil based coatings.

In another embodiment, it is recognized that to facilitate the coating of the molded article, as well as for other specific indications, such as decreasing the residual odor of wood in the final product, the amount of paper pulp can be increased to 50%, or 30-50%, by weight of the final mixture, and the amount of wood flour or fiber can be decreased to 0%.

In a further embodiment, a vacuum can be used to form a film around the molded article. When using a vacuum to form a film around the molded article, it is recognized that increasing the levels of wood flour/fiber and/or paper pulp can facilitate the vacuuming process. In one embodiment, the wood flour/fiber and/or paper pulp levels can be increased to 30, 40 or 50% by weight of the final mixture.

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Thus, in an alternate aspect of the present invention, a process is provided for forming a biodegradable container by:

(a) forming a paper starch suspension, wherein the paper pulp that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.; and

(b) molding the homogeneous moldable composition with heat to form a biodegradable container.

In one embodiment, a process is provided for forming a biodegradable container by:

(a) forming a paper starch suspension, wherein the pregelled paper starch solution is produced from up to approximately 50, 60, 75, 85 or 90% paper pulp (by weight of the pre-gel) and approximately 5-15%, preferably 10% potato or other natural starch (such as corn starch), and approximately 5.90% water (by weight of the pre-gel), and wherein the paper pulp that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.; and

(b) molding the homogeneous moldable composition with heat to form a biodegradable container.

Another embodiment of the present invention provides a process for forming a biodegradable container by:

(a) forming a pre-gelled paper starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together (i) 0-24% wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8) by weight of the homogenous moldable composition; (ii) dry or damp starch, such as corn starch; (iii) pre-gelled starch, such as a pre-gelled corn starch produced from approximately 15% corn starch (by weight of the pre-gel) and 85% water; (iv) waxes, fatty alcohols, phospholipids and other high molecular weight biochemicals, such as glycerol, for example between approximately 1-5% glycerol (by weight of the homogenous moldable composition); (v) approximately 0.5-20% water, preferably about 0.5-10%, 0.5-11%, 0.5-12%, 10 or 20% (by weight of the homogenous moldable composition); (vi) baking powder, for example between approximately 0.1-15% (by weight of the homogenous moldable composition), preferably 0.42, 1 or 12%; and/or (vii) additional materials, such as up to approximately 5%, 0-4%, 0-13%, 2-13%, or 0-15% by weight of the homogenous moldable composition of natural earth fillers, for example, clays such as bentonite, amorphous raw products such as gypsum and calcium sulfate, minerals such as limestone, and man made materials such as fly-ash to form a homogeneous mixture;

(c) adding to the pre-gelled starch suspension the dry or damp, homogeneous mixture to form a homogenous moldable composition; and

(d) molding the homogenous moldable composition with heat to form a biodegradable container.

In a further embodiment, a process is provided for forming a biodegradable container by:

(a) forming a pre-gelled paper starch suspension that is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together (i) 0-24% wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8) by weight of the homogenous moldable composition; (ii) dry or damp starch, such as corn starch; (iii) pre-gelled starch, such as a pre-gelled corn starch produced from approximately 15% corn starch (by weight of the pre-gel) and 85% water; (iv) waxes, fatty alcohols, phospholipids and other high molecular weight biochemicals, such as glycerol, for example between approximately 1-5% glycerol (by weight of the homogenous moldable composition); (v) approximately 0.5-

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20% water, preferably about 0.5-10%, 0.5-11% 0.5-12%, 10 or 20% (by weight of the homogenous moldable composition); (vi) baking powder, for example between approximately 0.1-15% (by weight of the homogenous moldable composition), preferably 0.42, 1 or 12%; and/or (vii) additional materials, such as up to approximately 5%, 0-4%, 0-13%, 2-13%, or 0-15% by weight of the homogenous moldable composition of natural earth fillers, for example, clays such as bentonite, amorphous raw products such as gypsum and calcium sulfate, minerals such as limestone, and man made materials such as fly-ash to form a homogeneous mixture;

(c) adding to the pre-gelled starch suspension the dry or damp, homogeneous mixture to form a homogenous moldable composition;

(d) molding the homogenous moldable composition with heat to form a biodegradable container; and

(e) coating the container with a liquid-resistant coating, such as PROTECOAT® (from New Coat, Inc.), ZEIN® (a biodegradable material isolated from corn); poly lactic acid (PLA, a polymer of lactic acid from fermentation feed stock); poly hydroxyalkanoates (PHA, from microbial fermentation); bacterial cellulose; chitosan based polymers (for example from shell fish wastes); or waxes and oil based coatings.

It is recognized that in any embodiment of the present invention, paper pulp can be substituted for wood fibers/flour.

In another embodiment, a process is provided for creating an open cell foam container by:

(a) forming a first pre-gelled starch suspension that is maintained at a low temperature, for example, preferably from 0-60° C., most preferably from 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), a second pre-gelled starch suspension to form a homogeneous composition, and a source of gas, such as a source of carbon dioxide gas;

(c) adding to the first pre-gelled starch suspension a dry or damp, homogeneous mixture containing the wood fibers and second pre-gelled starch; and

(d) molding the homogeneous composition with heat to form a biodegradable container.

In a specific embodiment, the present invention is directed to a process for forming an open cell foam container by:

(a) forming a pre-gelled starch suspension produced from approximately 3-5% potato starch (by weight of the pre-gel) and approximately 95-97% water (by weight of the pre-gel) such that the pre-gelled suspension is maintained at low temperatures, for example, between 0-60° C., preferably between 0-40° C.;

(b) mixing together wood fibers or flour (having an aspect ratio between approximately 1:2 and 1:8), a second pre-gelled starch suspension (the second pre-gel) produced from approximately 15% corn starch (by weight of the second pre-gel) and approximately 85% water (by weight of the second pre-gel), and baking powder, for example between 0.42-12% baking powder (by weight of the homogeneous moldable composition) to form a homogeneous mixture;

(c) adding to the pre-gelled potato starch suspension a homogeneous mixture containing the wood fibers and pre-gelled corn starch to form a homogeneous moldable composition; and

(d) molding the homogeneous moldable composition with heat to form a biodegradable container.

The processes described herein will produce biodegradable containers that are formed from different combinations of materials by weight. For example, containers can be formed from approximately 16-61% pre-gelled potato starch

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suspension (by weight of the homogenous moldable composition) and approximately 11-37% (or 11-15%) wood fibers or flour (by weight of the homogenous moldable composition). In addition, various combinations of other materials can be added to the wood fibers or flour to produce a homogenous mixture before mixing it with the pre-gelled starch suspension, including, but not limited to:

(i) approximately 57-66% pre-gelled corn starch suspension (by weight of the homogenous moldable composition) (suspension formed from approximately 5-15% corn starch (by weight of the pre-gel) and approximately 85-95% water by weight of the pre-gel);

(ii) approximately 4-35% native starch (by weight of the homogenous moldable composition), for example 3-5% (preferably 3.7% or 4.2%) native potato starch, and/or 15.4-34.4% native corn starch;

(iii) approximately 1-5% glycerol (by weight of the homogenous moldable composition);

(iv) up to approximately 10 or 20% water (by weight of the homogenous moldable composition);

(v) approximately 0.1-15% baking powder (by weight of the homogenous moldable composition);

(vi) less than approximately 5% natural materials (by weight of the homogenous moldable composition), such as bentonite clay.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

The term "sheet" as used herein refers to any substantially flat, corrugated, curved, bent, or textured sheet made using the methods described herein. The sheets can also include organic coatings, printing, other sheets laminated thereto. The sheets within the scope of the present invention can have greatly varying thicknesses depending on the particular applications for which the sheets are intended. The sheets can be as thin as about 0.001 mm or as thick as 1 cm or greater where strength, durability, and/or bulk are important considerations.

The term "film" is not inherently different from the term "sheet" except that "film" normally denotes a very thin sheet. Films are often formed by processes that are different from how sheets are normally formed, such as by film blowing rather than sheet calendering. In general, films will be defined as sheet-like articles having thicknesses as low as about 1 micron and up to about 1 mm.

The term "molded article" shall refer to articles that are shaped directly or indirectly from starch compositions using any molding method known in the art.

The term "container" as used in this specification and the appended claims is intended to include any article, receptacle, or vessel utilized for storing, dispensing packaging portioning, or shipping various types of products or objects (including, but not limited to, food and beverage products). Specific examples of such containers include, among others, boxes, cups, "clam shells," jars, bottles, plates, bowls, trays, cartons, cases, crates, cereal boxes, frozen food boxes, milk cartons, bags, sacks, carriers for beverage containers, dishes, egg cartons, lids, straws, envelopes, or other types of holders. In addition to integrally formed containers, containment products used in conjunction with containers are also intended to be included within the definition "container". Such articles include, for example, lids, liners, straws, partitions, wrappers, cushioning materials, utensils, and any other product used in packaging, storing, shipping, portioning, serving, or dispensing an object within a container.

As used herein, the term "dry or damp" refers to a solid composition that can be dry, or can be moist or wetted, gen-

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erally with water, although other solvents may be used. The amount of liquid in the composition is not sufficient to act as a carrier between particles in the composition.

As used herein, the term "homogeneous mixture" refers to mixtures of solid particulates or of solids in a liquid carrier which are substantially uniform in composition on a macroscopic scale. It will be appreciated that mixtures of different types of solid particles or of solids in a liquid carrier are not homogeneous when viewed on a microscopic scale, i.e., as the particle size level.

Pre-Gelled Starch Suspensions

The starch component can include any known starch material, including one or more unmodified starches, modified starches, and starch derivatives. Preferred starches can include most any unmodified starch that is initially in a native state as a granular solid and which will form a thermoplastic melt by mixing and heating. Starch is typically considered a natural carbohydrate chain comprising polymerized glucose molecules in an alpha-(1,4) linkage and is found in nature in the form of granules. Such granules are easily liberated from the plant materials by known processes. Starches used in forming the pre-gelled starch suspension used in the method of the invention desirably possess the following properties: the ability to form hydrated gels and to maintain this gel structure in the presence of many types of other materials; and the ability to melt into plastic-like materials at low temperatures, for example, between 0-75° C., preferably between 0-65° C., and in the presence of a wide range of materials and in moist environments and to exhibit high binding strengths and produce an open cell structure for both insulation and cross linking of components. The preferred sources of starch for pregels are cereal grains (e.g., corn, waxy corn, wheat, sorghum, rice, and waxy rice, which can also be used in the flour and cracked state), tubers (potato), roots (tapioca (i.e., cassava and maniac), sweet potato, and arrowroot), modified corn starch, and the pith of the sago palm.

While not intending to be bound to any specific mechanistic explanation for the desirable properties observed when the method of the invention is employed, it is believed that the gel property holds other components in suspension until the product can be molded and to hold the moisture levels constant within the mixture until and during molding. The second property is evident in the transition in the mold of the gel structure into a drier and dried form that will then melt into the binding plastic-like product within the confines of the mold. This complex three dimensional cross linked structure is the backbone for the product, exhibiting both strength and insulation properties. The pre-gelled starch is prepared by mixing the starch with water (for example at levels of approximately 2% to 15% by weight of the pre-gel, preferably at least 2.5%, 3%, 5%, 10%, or 15%) at about ambient temperature (approximately 25° C.). The gel is formed by slowly heating the water-starch mixture with constant agitation until a gel forms. Continued heating will slowly degrade the gel, so the process should be stopped as soon as an appropriate level of gelation is achieved. Gels can be used cold. The gel is stable for a few days if refrigerated. For storage a biocide can be added, preferably at a concentration of about 10 to about 500 ppm.

Preferred starch-based binders are those that gelate and produce a high viscosity at a relatively low temperature. For example, potato starch quickly gelates and reaches a maximum viscosity at about 65° C. The viscosity then decreases, reaching a minimum at about 95° C. Wheat starch acts in a similar fashion and can also be used. Such starch-based binders are valuable in producing thin-walled articles having a smooth surface and a skin with sufficient thickness and density to impart the desired mechanical properties.

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In general, starch granules are insoluble in cold water; however, if the outer membrane has been broken by, e.g., by grinding, the granules can swell in cold water to form a gel. When the intact granules are treated with warm water, the granules swell and a portion of the soluble starch diffuses through the granule wall to form a paste. In hot water, the granules swell to such an extent that they burst, resulting in gelation of the mixture. The exact temperature at which a starch swells and gelates depends on the type of starch. Gelation is a result of the linear amylose polymers, which are initially compressed within the granules, stretching out and cross-linking with each other and with the amylopectin. After the water is removed, the resulting mesh of inter-connected polymer chains forms a solid material that can have a tensile strength up to about 40-50 MPa. The amylose polymers can also be used to bind individual aggregate particles and fibers within the moldable mixture.

It is possible to reduce the amount of water in starch melts by replacing the water inherently found in starch with an appropriate low volatile plasticizer capable of causing starch to melt below its decomposition temperature, such as glycerin, polyalkylene oxides, mono- and diacetates of glycerin, sorbitol, other sugar alcohols, and citrates. This can allow for improved processability, greater mechanical strength, better dimensional stability over time, and greater ease in blending the starch melt with other polymers.

Water can be removed before processing by using starch that has been pre-dried so as to remove at least a portion of the natural water content. Alternatively, water can be removed during processing by degassing or venting the molten mixture, such as by means of an extruder equipped with venting or degassing means. Native starch can also initially be blended with a small quantity of water and glycerin in order to form starch melts that are subjected to a degassing procedure prior to cooling and solidification in order to remove substantially all of the water therefrom.

In one aspect of the present invention, the pre-gelled starch suspension is produced from approximately 3-10%, preferably, 3, 5, 7.5 or 10%, starch by weight of the pre-gel, preferably, potato starch, and 90-97% water by weight of the pre-gel such that the pre-gelled suspension is maintained at low temperatures. In one embodiment, the pregeled starch solution can be maintained at all temperatures above freezing, 0° C. In another embodiment, the pregelled starch solution can be maintained for greater than 24 hours, up to a few days, if stored refrigerated, for example, between 3-15° C.

In another aspect of the present invention, a pre-gelled paper starch suspension is produced from approximately 5-15%, preferably 10%, starch (by weight of the pre-gel), preferably potato starch; 5-10% paper pulp (by weight of the pre-gel), preferably 5.9-8%, more preferably, 7.3-7.5, 6.5-6.7, or 5.9-6.1%; and 75-92.5% water (by weight of the pre-gel), such that the pre-gelled suspension is maintained at low temperatures. In one embodiment, the pregelled paper starch solution can be maintained at all temperatures above freezing, 0° C. In another embodiment, the pregelled paper starch solution can be maintained for greater than 24 hours, up to a few days, if stored refrigerated, for example, between 3-15° C.

Paper Pulp

In one aspect of this invention, prepulped paper is mixed with the pregel. The preferred amount of paper pulp added is in the range of 5-10% by weight of the pre-gel, preferably 5.9-8%, more preferably, 7.3-7.5, 6.5-6.7, or 5.9-6.1%. The prepulped paper can be mixed with 5-15%, preferably 10% potato or other natural starch (such as corn starch), and 75-90% water, for example, 580 gm water, 57.5 gm dry potato

starch, and 42.31 gm paper pulp. The mixture is stirred at slow rpm while increasing the temperature to 60-70° C., after which premixed dry ingredients (wood flour (preferably 5-10% (w/w) with an aspect ratio of 1:8; 1:9.9; 1:9 or 1:5), native potato starch (preferably 10-15% (by weight)) and/or native corn starch (preferably 10-20% (by weight)) can be added.

Paper pulp for this invention can be produced by any method known in the art. Paper pulp is a fibrous material produced by mechanically or chemically reducing woody plants into their component parts from which, pulp, paper and paperboard sheets are formed after proper slushing and treatment, or used for dissolving purposes (Lavigne, J R "Pulp & Paper Dictionary" 1993: Miller Freeman Books, San Francisco). Cellulose pulp production is a process that utilizes mainly arboreal species from specialized cultivations. To produce the paper pulp, wood, typically reduced to dimensions of about 30-40 mm and a thickness of about 5-7 mm, is treated at high temperature and pressure with suitable mixes of chemical reagents that selectively attack lignin and hemicellulose macromolecules, rendering them soluble. Pulps coming from this first treatment, commonly called "cooking", are called "raw pulps"; they still contain partly modified lignin and are more or less Havana-brown colored. Raw pulps can be submitted to further chemical-physical treatments suitable to eliminate almost entire lignin molecules and colored molecules in general; this second operation is commonly referred to as "bleaching". For this process, rapid growth ligneous plants are mainly used, which, with the help of chemical substances (alkali or acids), in condition of high pressure and temperature, are selectively delignified to obtain pulps containing cellulose and other components of lignocellulose. These pulps are then submitted to mechanical and chemical-physical treatments, in order to complete the removal of lignin and hemicellulose residual components, and utilized thereafter for paper production. Any form of paper pulp can be used in the packaging materials described herein.

Dry or Damp Starch

After formation of a pregel, dry or damp materials can be added (such as fibers, flour, pulp, or dry starches) to produce the final moldable mixture. The dry or damp materials can be pre-mixed before addition to the pregel, to increase the homogeneity of the final product and increase the structural integrity of the final molded product. Preferably, the amount of pregel added to the final mixture is in the range of about 7-60% by weight of the homogenous moldable composition. Preferably, the pregel is about at least 7%, 8%, 9%, 10%, 11%, 12%, 16.3%, 25%, 33%, 42%, 47%, 54%, 50%, 52%, 55%, 56%, 60% or 60.4% by weight of the homogenous moldable composition.

One component in the dry/damp material that can be added to the pre-gelled starch is a dry or damp starch binder component. This starch can be corn or other dry starch (for example potato, rice or wheat starch). Pre-gelatinized starch-based binders can also be added to the moldable mixture. Pregelatinized starch-based binders are starches that have previously been gelated, dried, and ground back into a powder. Since pre-gelatinized starch-based binders gelate in cold water, such starch-based binders can be added to the moldable mixture to increase the mixture viscosity prior to being heated. The increased viscosity prevents settling and helps produce thicker cell walls. This starch component can be pre-gelled in a manner similar to that described above. For example, the second starch component can be pregelled in a mixture of between about 1 and 15% starch (for example 15% corn starch) and 85-99% water. In these cases additional dry starch can be added as necessary to the homogeneous mixture

to adsorb excess water. If the pregelled second starch is still damp, the preferred amount to be added is in the range of 55-65% by weight of the homogenous moldable composition, most preferably about 57% or about 65%.

The concentration of the native starch binder within the moldable mixtures of the present invention are preferably in a range from about 5% to about 60% by weight of the homogenous moldable composition, more preferably in a range from about 15% to about 30%, and most preferably about at least 6%, 20%, 21%, 25%, 26%, 27%, 28%, 29%, 30%, 31%, or 34% by weight of the homogenous moldable composition. Furthermore, combinations of different starches can be employed to more carefully control the viscosity of the mixture throughout a range of temperatures, as well as to affect the structural properties of the final hardened article. For example, the mixture can consist of a mixture of dry or damp corn and potato starch (16-44% of corn and potato starch by weight of the homogenous moldable composition), such that the corn starch comprises between about 13-30%, preferably between about 13-18% or 28-30%, and the potato starch comprises between about 3-14%, preferably approximately 1-14% or 3-5% of the final homogenous moldable composition.

Starch is produced in many plants, and many starches can be suitable, however, as with the starch used in the pre-gel, preferred sources of starches are seeds of cereal grains (e.g., corn, waxy corn, wheat, sorghum, rice, and waxy rice), which can be used in the flour and cracked state. Other sources of starch include tubers (potato), roots (tapioca (i.e., cassava and maniac), sweet potato, and arrowroot), and the pith of the sago palm. The starch can be selected from natural starch, chemically and/or physically modified starch, biotechnologically produced and/or genetically modified starch and mixtures thereof.

Suitable starches can also be selected from the following: ahipa, aipo (arracacha), arrowhead (arrowroot, Chinese potato, jicama), baddo, bitter casava, Brazilian arrowroot, casava (yucca), Chinese artichoke (crosne), Japanese artichoke (chorogi), Chinese water chestnut, coco, cocoyam, dasheen, eddo, elephant's ear, girasole, goo, Japanese potato, Jerusalem artichoke (sunroot, girasole), lily root, ling gaw, malanga (tanier), plantain, sweet potato, mandioca, manioc, Mexican potato, Mexican yam bean, old cocoyam, saa got, sato-imo, seegoo, sunchoke, sunroot, sweet casava, tanier, tannia, tannier, tapioca root, taro, topinambour, water chestnut, water lily root, yam bean, yam, yautia, barley, corn, sorghum, rice, wheat, oats, buckwheat, rye, kamut brand wheat, triticale, spelt, amaranth, black quinoa, hie, millet, plantago seed husks, psyllium seed husks, quinoa flakes, quinoa, teff.

Starches that can be used for the present invention include unmodified starches (amylose and amylopectin) and modified starches. By modified, it is meant that the starch can be derivatized or modified by typical processes known in the art such as, e.g. esterification, etherification, oxidation, acid hydrolysis, cross-linking, and enzyme conversion. Typical modified starches include esters, such as the acetate and, the half-esters of dicarboxylic acids/anhydrides, particularly the alkenylsuccinic acids/anhydrides; ethers, such as the hydroxyethyl and hydroxypropyl starches; oxidized starches, such as those oxidized with hypochlorite; starches reacted with cross-linking agents, such as phosphorus oxychloride, epichlorohydrin, hydrophobic cationic epoxides, and phosphate derivatives prepared by reaction with sodium or potassium orthophosphate or tripolyphosphate, and combinations thereof. Modified starches also include seagel, long-chain alkylstarches, dextrins, amine starches, and dialdehyde

starches. Unmodified starch-based binders are generally preferred over modified starch-based binders because they are significantly less expensive and produce comparable articles.

The dry ingredients, such as corn starch and wood flour are preferably pre-mixed into a homogeneous mixture before being added to the pregel. The dry/damp starch and the wood flour or fibers can be mixed to form a homogeneous mixture using any suitable means, such as, for example, a Kitchen Aid® Commercial Mixer.

Wood Flour or Fibers

In the present invention, additional fibers can be employed as part of the dry/damp material added to the pre-gelled starch. The fibers used are preferably organic, and most preferably cellulose-based materials, which are chemically similar to starches in that they comprise polymerized glucose molecules. "Cellulosic fibers" refers to fibers of any type which contain cellulose or consist of cellulose. Plant fibers preferred here are those of differing lengths typically in the range from 600 micron to 3000 micron, principally from hemp, cotton, plant leaves, sisal, abaca, bagasse, wood (both hard wood or soft wood, examples of which include southern hardwood and southern pine, respectively), or stems, or inorganic fibers made from glass, graphite, silica, ceramic, or metal materials. The cellulosic fibers include wood fibers and wood flour. In one embodiment, 11-24% by weight of wood fibers or flour are added to the final mixture. In the preferred embodiments, wood fibers or flour comprise about at least 11%, 12%, 13%, 14%, 16%, 17%, and 23.3% by weight of the homogenous moldable composition.

Wood flour and fibers are very much like rough tooth picks that have small barb like structures coming out from the main fiber to participate in the cross linkage process with the cooling starch melt. This property adds both strength and water resistance to the surface produced within the mold. The rapid grinding process to produce flour or short fibers by-passes the expensive and polluting processes that are used to manufacture pulp and paper. The wood flour can be a resinous wood flour. Preferably, the wood flour is softwood flour, which contains relatively large amounts of resin. Moreover, softwood is used industrially on a large scale, such as in the building trade, with the consequence that an abundance of wood flour from, for instance, saw mills, is available at a low price. Wood flours can be graded based on the mesh size the flour. In general, wood flour having a mesh size of 20-100 is suitable, and an aspect ratio or 1:8 or 1:9, or 1:10 or less.

Larger particles are considered to be fibers. The expression "fibers" refers to fine, thin objects restricted in their length, the length being greater than the width. They can be present as individual fibers or as fiber bundles. Such fibers can be produced in a manner known to those skilled in the art. Preferred fibers have a low length to diameter ratio and produce materials of excellent strength and light weight. In general, the fibers used in the invention will have an aspect ration of about between 1:2 and 1:10; 1:2 and 1:9; 1:2 and 1:8; 1:2 and 1:7; 1:2 and 1:6; 1:2 and 1:5; 1:2 and 1:4; 1:2 and 1:3; 1:2 and 1:2; or 1:2 and 1:9.9.

It should also be understood that some fibers, such as southern pine and abaca, have high tear and burst strengths, while others, such as cotton, have lower strength but greater flexibility. In the case where better placement, higher flexibility, and higher tear and burst strength are desired, a combination of fibers having varying aspect ratios and strength properties can be added to the mixture.

In a additional aspect of the present invention, it is recognized that to decrease the residual odor of the wood in the final product, the amount of paper pulp can be increased to 50%, or

30-50%, by weight of the final mixture, and the amount of wood flour or fiber can be decreased to 0%.

Additional Materials

In addition to the dry/damp starch and the wood flour, the homogenous mixture can also include one or more additional materials depending on desired characteristics of the final product. Natural earth fillers can be included for a stronger product. Suitable fillers include but are not limited to clays such as bentonite, amorphous raw products such as gypsum (calcium sulfate dehydrate) and calcium sulfate, minerals such as limestone and man made materials such as fly ash. These natural earth fillers are able to take part in the cross linking and binding that occurs during the molding process. Other examples of useful fillers include perlite, vermiculite, sand, gravel, rock, limestone, sandstone, glass beads, aerogel, xerogels, seagel, mica, clay, synthetic clay, alumina, silica, fused silica, tabular alumina, kaolin, microspheres, hollow glass spheres, porous ceramic spheres, calcium carbonate, calcium aluminate, lightweight polymers, xonotlite (a crystalline calcium silicate gel), lightweight expanded clays, hydrated or unhydrated hydraulic cement particles, pumice, exfoliated rock, and other geologic materials. Partially hydrated and hydrated cement, as well as silica fume, have a high surface area and give excellent benefits such as high initial cohesiveness of the freshly formed article. Even discarded inorganically filled materials, such as discarded containers or other articles of the present invention can be employed as aggregate fillers and strengtheners. It will also be appreciated that the containers and other articles of the present invention can be easily and effectively recycled by simply adding them to fresh moldable mixtures as an aggregate filler. Hydraulic cement can also be added in either its hydrated or unhydrated form. Both clay and gypsum can be important aggregate materials because they are readily available, relatively inexpensive, workable, form easily, and can also provide a degree of binding and strength if added in high enough amounts (for example in the case of gypsum hemihydrate). Because gypsum hemihydrate can react with the water within the moldable mixture, it can be employed as a means for holding water internally within the molded article. Preferably, the inorganic materials are added in an amount from up to approximately 5%, 0-4%, 0-13%, 2-13% or 0-15% by weight of the weight of the final composition.

Because of the wide variety of agents that can be used as fillers, preferred concentration ranges are difficult to calculate. For bentonite clay a preferred range is from about 2.5-4% of the weight of the final mixture. The additional agents can be predissolved or can be added dry. A preferred clay slurry is 20% bentonite clay in water.

In addition, further cellulose-based thickening agents can be added, which can include a wide variety of cellulosic ethers, such as methylhydroxyethylcellulose, hydroxyethylethylethylcellulose, carboxymethylcellulose, methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxyethylpropylcellulose, hydroxypropylmethylcellulose, and the like. Other natural polysaccharide-based thickening agents include, for example, alginic acid; phycocolloids, agar, gum arabic, guar gum, locust bean gum, gum karaya, xanthan gum, and gum tragacanth. Suitable protein-based thickening agents include, for example, ZEIN® (a prolamine derived from corn), collagen (derivatives extracted from animal connective tissue such as gelatin and glue), and casein (derived from cow's milk). Suitable synthetic organic thickening agents include, for example, polyvinyl pyrrolidone, polyethylene glycol, polyvinyl alcohol, polyvinylmethyl ether, polyacrylic acids, polyacrylic acid salts, polyvinyl acrylic acids, polyvinyl acrylic acid salts, polyacrylamides, ethylene oxide polymers,

polylactic acid, and latex. Latex is a broad category that includes a variety of polymerizable substances formed in a water emulsion. An example is styrene-butadiene copolymer. Additional copolymers include: vinyl acetate, acrylate copolymers, butadiene copolymers with styrene and acetonitrile, methylacrylates, vinyl chloride, acrylamide, fluorinated ethylenes. Hydrophilic monomers can be selected from the following group: N-(2-hydroxypropyl)methacrylamide, N-isopropyl acrylamide, N,N-diethylacryl-amide, N-ethylmethacrylamide, 2-hydroxyethyl methacrylate, acrylic acid 10 2-(2-hydroxyethoxy)ethyl methacrylate, methacrylic acid, and others, and can be used for the preparation of hydrolytically degradable polymeric gels. Suitable hydrophobic monomers can be selected from the 2-acetoxyethyl methacrylate group of monomers comprising dimethylaminoethyl methacrylate, n-butyl methacrylate, tert-butylacrylamide, n-butyl acrylate, methyl methacrylate, and hexyl acrylate. The polymerization can be carried out in solvents, e.g. in dimethylsulfoxide, dimethylformamide, water, alcohols as methanol and ethanol, using common initiators of the radical polymerization. The hydrophilic gels are stable in an acidic environment at pH 1-5. Under neutral or weak alkaline conditions at pH above 6.5, the gels degrade. The gels mentioned above are nontoxic as well as the products of their biodegradation.

Other copolymers include: aliphatic polyester, polycaprolactone, poly-3-hydroxybutyric acid, poly-3-hydroxyvaleric acid, polyglycolic acid, copolymers of glycolic acid and lactic acid, and polylactide, PVS, SAN, ABS, phenoxy, polycarbonate, nitrocellulose, polyvinylidene chloride, a styrene/alyl alcohol copolymer, polyethylene, polypropylene, natural rubber, a styrene/butadiene elastomer and block copolymer, polyvinylacetate, polybutadiene, ethylene/propylene rubber, starch, and thermoplastic segmented polyurethane, homopolymers on copolymers of polyesters, polyorthoesters, polylactides, polyglycolides, polycaprolactones, polyhydroxybutyrate, polyhydroxyvalerate, poro acids, pseudopolyamino acids, polyamides and polyanhydrides, homopolymers and copolymers of polylactic acid, polyglycolic acid, polycaprolactone (PCL), polyanhydrides, polyorthoesters, polyaminoacids, pseudopolyaminoacids, polyhydroxybutyrate, polyhydroxyvalerate, polyphosphazenes, and polyalkylecyanoacrylates.

Additional polymers that can be added include: citrates, diethyl citrate (DEC), triethyl citrate (TEC), acetyl triethyl citrate (ATEC), tributyl citrate (TBC), acetyl tributyl citrate (ATBC), phthalates such as dimethyl phthalate (DMP), diethyl phthalate (DEP), triethyl phthalate (TEP), dibutyl phthalate (DBP), dioctyl phthalate, glycol ethers such as ethylene glycol diethyl ether, propylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether (Transcutol™), propylene glycol monotertiary butyl ether, dipropylene glycol monomethyl ether, n-methylpyrrolidone, 2 pyrrolidone (2-Pyrrol™), propylene glycol, glycerol, glyceryl dioleate, ethyl oleate, benzylbenzoate, glycofuran sorbitol sucrose acetate isobutyrate, butyryltri-n-hexyl-citrate, acetyltri-n-hexyl citrate, sebacates such as dibutyl sebacate, tributyl sebacate, dipropylene glycol methyl ether acetate (DPM acetate), propylene carbonate, propylene glycol laurate, propylene glycol caprylate/caprate, caprylic/capric triglyceride, gamma butyrolactone, polyethylene glycols (PEG), glycerol and PEG esters of acids and fatty acids (Gelucires™, Labrafils™ and Labrasol™) such as PEG-6 glycerol mono oleate, PEG-6 glycerol linoleate, PEG-8 glycerol linoleate, PEG-4 glyceryl caprylate/caprate, PEG-8 glyceryl caprylate/caprate, polyglyceryl-3-oleate, polyglyceryl-6-dioleate, polyglyceryl-3-isostearate, PEG-32

glyceryl laurate (Gelucire 44/1™), PEG-32 glyceryl palmitostearate (Gelucire 50/13™), PEG-32 glyceryl stearate (Gelucire 53/10™), glyceryl behenate, cetyl palmitate, glyceryl di and tri stearate, glyceryl palmitostearate, and glyceryl triacetate (Triacetin™), vegetable oils obtained from seeds, flowers, fruits, leaves, stem or any part of a plant or tree including cotton seed oil, soy bean oil almond oil, sunflower oil, peanut oil, sesame oil. The use of two or more plasticizers in a combination or blend of varying ratios and hydrophilicity or hydrophobicity is also encompassed by the present invention. Plasticizers also include: phthalates, glycol ethers, n-methylpyrrolidone, 2 pyrrolidone, propylene glycol, glycerol, glyceryl dioleate, ethyl oleate, benzylbenzoate, glycofuran sorbitol, sucrose acetate isobutyrate, butyryltri-n-hexylcitrate, acetyltri-n-hexyl citrate, sebacates, dipropylene glycol methyl ether acetate (DPM acetate), propylene, carbonate, propylene glycol laurate, propylene glycol caprylate/caprate, caprylic/capric triglyceride, gamma butyrolactone, polyethylene glycols (PECs), vegetable oils obtained from seeds, flowers, fruits leaves, stem or any part of a plant or tree including cotton seed oil, soy bean oil, almond oil, sunflower oil, peanut oil, sesame oil, glycerol and PEG esters of acids and fatty acids, polyglyceryl-3-oleate, polyglyceryl-6-dioleate, polyglyceryl-3-isostearate, PEG-32 glyceryl laurate, PEG-32 glyceryl palmitostearate, PEG-32 glyceryl stearate, glyceryl behenate, cetyl palmitate, glyceryl di and tri stearate, glyceryl palmitostearate, and glyceryl triacetate. These materials can also be added in combination with other polymers to improve flexibility.

The addition of these items will increase the efficiency of production of the product on an item basis. Baking powder and other materials, such as leavening agents, which release gases, (e.g., sodium or calcium bicarbonates or carbonates) 35 can be included in the compositions of the invention to elevate the number of open cells in the final structure by introducing a source of carbon dioxide gas which is released in the mold.

Glycerol, microcrystalline wax, fatty alcohols and other similar organic molecules can be added as a mold release agent, and to produce a smoother surface on the finished product Examples of agents that can be added, either as plasticizers or as mold releasing agents are ethylene glycol, propylene glycol, glycerin, 1,3-propanediol, 1,2-butandiol, 1,3-butandiol, 1,4-butanediol, 1,5-pentandiol, 1,5-bexandiol, 45 1,6-hexandiol, 1,2,6-hexantriol, 1,3,5-hexantriol, neopenetylglycol, sorbitol acetate, sorbitol diacetate, sorbitol monoethoxylate, sorbitol diethoxylate, sorbitol hexaethoxylate, sorbitol dipropoxylate, arrunosorbitol, trihydroxymethylaminomethane, glucose/PEG, the reaction product of ethylene oxide with glucose, trimethylolpropane monoethoxylate, mannitol monoacetate, mannitol monoethoxylate, butyl glucoside, glucose monoethoxylate, a-methyl glucoside, the sodium salt of carboxymethylsorbitol, polyglycerol monoethoxylate, erythritol, pentaerythritol, arabitol, adonitol, xylitol, mannitol, iditol, galactitol, aitol, sorbitol, polyhydric alcohols generally, esters of glycerin, formamide, N-methylformamide, DMSO, mono- and diglycerides, alkylarrides, polyols, trimethylolpropane, polyvinylalcohol with from 3 to 20 repeating units, polyglycerols with from 2 to 10 repeating units, and derivatives of the foregoing. Examples of derivatives include ethers, thiethers, inorganic and organic esters, acetals, oxidation products, amides, and amines. These agents can be added from 0-10%, preferably 3-4% (w/w). A consideration of the inventive mixture should be that the composition preferably contains at least 75%, more preferably at least 95% of natural or organic-derived materials by weight of the homogenous moldable composition,

Preparation of Molded Articles

The starch-wood flour mixture, with any included additives, is added to the pre-gelled starch and mixed (for example with a Kitchen Aid Commercial Mixer) until a homogeneous mixture is generated. The mixture can be as thick as peanut butter or as thin as a pancake batter. Varying amounts of additional water can be added to facilitate different types of molding, since the form of the pre-molded [green] product is dependent on the mold, heating rate and drying/melt time. If the product is to be molded by classic injection methods the material is thinner, if the material is molded on the equipment described below the mixture is thicker. The material can also be rolled into green sheets and molded, extruded and made into dry pellets for other processes. The means of production for the product could be created from any of several possible process approaches. One specific methodology is described below, but this description is intended only to describe one possible means of production, and shall not be construed in any way to represent a limitation to the outlined approach. While the compression molding process detailed herein is useful, other types of compression molding, injection molding, extrusion, casting, pneumatic shaping, vacuum molding, etc can be used. One embodiment involves a means of production incorporating moving upper and lower continuous track assemblies each with an upper and lower substantially elongated horizontal section, and with a curved portion of track joining the upper and lower horizontal section for each of the upper and lower tracks. Riding in each of the track assemblies is a linked belt made from any material or combination of materials that allows the belt or belt assembly to be in constant or intermittent motion about the tracks. The track assemblies are located vertically such that the upper portion of the lower track and the lower portion of the upper track are in close proximity such that the belts of each track move at a synchronized speed and in a common direction, in this embodiment, the male mold portion is mounted to the belt following the upper track, and the female portion of the mold is mounted to the belt following the lower track, with the tracks synchronized in a fashion that causes the mold halves to join and close as they merge between the upper and lower tracks. In this embodiment, the material to be processed is deposited into the female mold half prior to the mold halves closing, or is injected into the mold after it has been closed. The track and belt assemblies hold the mold halves together during drying by any of a number of, or combination of, methods including without limitation spring force, pneumatic force, or mechanical compression. Other forcing methods are possible. One possible arrangement of the curved end of the tracks aligns them such that the lower tracks' upper horizontal section are located to start before the upper tracks' lower horizontal section to allow the female mold half on the upper section of the lower track to assume a substantially horizontal orientation prior to the male mold half attached to upper track, thereby allowing the female mold half to receive deposited material before it engages the corresponding male mold half merging from the upper track and belt assembly. Other aspects that can be incorporated in this embodiment include, removable cavity inserts and/or multiple cavities in the molds: heating of the molds or product to speed drying by electric, microwave, hot gas, friction, ultrasonic, or any other means; on the fly cleaning of the molds, on the fly coating of product with any of a number of coating agents.

In another embodiment, once the moldable mixture has been prepared, it is positioned within a heated mold cavity. The heated mold cavity can comprise many different embodiments, including molds typically used in conventional injection molding processes and die-press molds brought together

after placing the inorganically filled mixture into the female mold. In one preferred embodiment, for example, the moldable mixture is placed inside a heated female mold. Thereafter, a heated male mold is complementarily mated with the heated female mold, thereby positioning the mixture between the molds. As the mixture is heated, the starch-based binder gelates, increasing the viscosity of the mixture. Simultaneously, the mixture increases in volume within the heated molds cavity as a result of the formation of gas bubbles from the evaporating solvent, which are initially trapped within the viscous matrix. By selectively controlling the thermodynamic parameters applied to the mixture (e.g., pressure, temperature, and time), as well as the viscosity and solvent content, the mixture can be formed into a form-stable article having a selectively designed cellular structural matrix.

In a non-limiting embodiment, a temperature between 195-225° C., preferably 200° C. is used for baking for a time period of 60-90 seconds, preferably 75 seconds. Temperatures can vary based on the article being manufactured, for example, 200° C. is preferred for the rapid production of thin-walled articles, such as cups. Thicker articles require a longer time to remove the solvent and are preferably heated at lower temperatures to reduce the propensity of burning the starch-based binder and fiber. Leaving the articles within the locked molds too long can also result in cracking or deformation of the articles.

The temperature of the mold can also effect the surface texture of the molds. Once the outside skin is formed, the solvent remaining within the interior section of the mixture escapes by passing through minute openings in the outside skin and then traveling between the skin and the mold surface to the vent holes. If one mold is hotter than the other, the laws of thermodynamics would predict, and it has been empirically found, that the steam will tend to travel to the cooler mold. As a result, the surface of the article against the hotter mold will have a smoother and more uniform surface than the surface against the cooler mold.

A variety of articles can be produced from the processes and compositions of the present invention. The terms "article" and "article of manufacture" as used herein are intended to include all goods that can be formed using the disclosed process.

Coating of Molded Article

Before, during, or after any of the molding processes, coatings can be applied to the surface of a substantially dried article for any desired purpose, such as to make the article more waterproof, grease and food product proof, more flexible, or to give it a glossier surface. Coatings can be used to alter the surface characteristics including sealing and protecting the article made therefrom. Coatings can provide protection against moisture, base, acid, grease, and organic solvents. They can provide a smoother, glossier, or scuff-resistant surface, they can help reinforce the article and coatings can also provide reflective, electrically conductive or insulative properties.

Water resistance can be achieved through the use of a water resistant layer applied on one or both sides of the product. There are many currently available coatings that can be used to coat this product. Some of these are: PROTECOAT® 6616B by New Coat, Inc.; ZEIN® a biodegradable material isolated from corn; poly lactic acid [PLA]—a polymer of lactic acid from fermentation feed stock; polyhydroxyl-kanoates [PHA] from microbial fermentation; bacterial cellulose; chitosan based polymers—from shell fish wastes; natural waxes and oil based coatings.

Appropriate organic coatings include edible oils, melamine, polyvinyl chloride, polyvinyl alcohol, polyvinyl

acetate, polyacrylates, polyamides, hydroxypropylmethylcellulose, polyethylene glycol, acrylics, polyurethane, polyethylene, polylactic acid, Biopol™ (a polyhydroxybutyrate-hydroxyvalerate copolymer), starches, soybean protein, polyethylene, and synthetic polymers including biodegradable polymers, waxes (such as beeswax or petroleum based wax), elastomers, edible oils, fatty alcohols, phospholipids and other high molecular weight biochemicals, and mixtures or derivatives thereof. Biopol® is manufactured by ICI in the United Kingdom. Elastomer, plastic, or paper coatings can aid in preserving the integrity of the article. Appropriate inorganic coatings include sodium silicate, calcium carbonate, aluminum oxide, silicon oxide, kaolin, clay, ceramic and mixtures thereof. The inorganic coatings can also be mixed with one or more of the organic coatings set forth above. Coatings based upon materials such as soybean oil or Methocel® (available from Dow Chemical), either alone or in combination with polyethylene glycol, can be applied to the surface in order to permanently soften the article or a hinge area within the article.

The coating can be applied either during the forming process or after the article is formed. The coating can be formed during the forming process by adding a coating material that has approximately the same melting temperature as the peak temperature of the mixture. As the mixture is heated, the coating material melts and moves with the vaporized solvent to the surface of the article where it coats the surface.

The coatings can be applied to the shaped articles using any coating means known in the art of manufacturing paper, paperboard plastic, polystyrene, sheet metal, or other packaging materials, including blade, puddle, air-knife, printing, Dahlgren, gravure, and powder coating. Coatings can also be applied by spraying the article with any of the coating materials listed below or by dipping the article into a vat containing an appropriate coating material. These materials can be applied either as a thin film or can be sprayed/dipped onto the product. The apparatus used for coating will depend on the shape of the article. For example, cups will usually be coated differently than flat plates. Bonding processes for application of thin films of water-resistant material are known in the art. Each of these coatings are biodegradable and should not significantly impact the compostability of the product. The second method of improving the water resistance of the product is to add one or more biodegradable materials to the material either before molding or as part of the molding process. In each of these cases the basic composition of the product will remain fairly constant.

A waterproof coating is desirable for articles intended to be in contact with water. As the articles having a starch-based binder have a high affinity for water, the preferred coatings are non-aqueous and have a low polarity. Appropriate coatings include paraffin (synthetic wax); shellac; xylene-formaldehyde resins condensed with 4,4'-isopropylidenediphenolepichlorohydrin epoxy resins; drying oils; reconstituted oils from triglycerides or fatty acids from the drying oils to form esters with various glycols (butylene glycol, ethylene glycol), sorbitol, and trimethylol ethane or propane; synthetic drying oils including polybutadiene resin; natural fossil resins including copal (tropical tree resins, fossil and modern), damar, elemi, gilsonite (a black, shiny asphaltite, soluble in turpentine), glycol ester of damar, copal, elemi, and sandarac (a brittle, faintly aromatic translucent resin derived from the sandarac pine of Africa), shellac, Utah coal resin; rosins and rosin derivatives including rosin (gum rosin, tall oil rosin, and wood rosin), rosin esters formed by reaction with specific glycols or alcohols, rosin esters formed by reaction formaldehydes, and rosin salts (calcium resinate and zinc resinate);

phenolic resins formed by reaction of phenols with formaldehyde; polyester resins; epoxy resins, catalysts, and adjuncts; coumarone-indene resin; petroleum hydrocarbon resin (cyclopentadiene type); terpene resins; urea-formaldehyde resins and their curing catalyst; triazine-formaldehyde resins and their curing catalyst; modifiers (for oils and alkyls, including polyesters); vinyl resinous substances (polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, etc.); cellulosic materials (carboxymethylcellulose, cellulose acetate, ethylhydroxyethylcellulose, etc.); styrene polymers; polyethylene and its copolymers; acrylics and their copolymers; methyl methacrylate; ethyl methacrylate; waxes (paraffin type I, paraffin type II, polyethylene, sperm oil, bees, and spermaceti); melamine; polyamides; polylactic acid; Biopol® (a polyhydroxybutyrate-hydroxyvalerate copolymer); soybean protein; other synthetic polymers including biodegradable polymers; and elastomers and mixtures thereof. Biopol® is manufactured by ICI in the United Kingdom. Appropriate inorganic coatings include sodium silicate, calcium carbonate, aluminum oxide, silicon oxide, kaolin, clay, ceramic and mixtures thereof. The inorganic coatings can also be mixed with one or more of the organic coatings set forth above.

If the articles are used as containers or for other products intended to come into contact with foodstuffs, the coating material will preferably include an FDA-approved coating. An example of a particularly useful coating is sodium silicate, which is acid resistant. Resistance to acidity is important, for example, where the article is a container exposed to foods or drinks having a high acid content, such as soft drinks or juices. It is generally unnecessary to protect the article from basic substances, but increased resistance to basic substances can be provided by an appropriate polymer or wax coating, such as those used to coat paper containers.

Polymeric coatings, such as polyethylene, are useful in forming generally thin layers having low density. Low density polyethylene is especially useful in creating containers which are liquid-tight and even pressure-tight to a certain extent. Polymeric coatings can also be utilized as an adhesive when heat sealed.

Aluminum oxide and silicon oxide are useful coatings, particularly as a barrier to oxygen and moisture. The coatings can be applied to the article by any means known in the art, including the use of a high energy electron beam evaporation process, chemical plasma deposition and sputtering. Another method of forming an aluminum oxide or silicon oxide coating involves treating article with an aqueous solution having an appropriate pH level to cause the formation of aluminum oxide or silicon oxide on the article due to the composition of the article.

Waxes and wax blends, particularly petroleum and synthetic waxes, provide a barrier to moisture, oxygen, and some organic liquids, such as grease or oils. They also allow an article such as a container to be heat sealed. Petroleum waxes are a particularly useful group of waxes in food and beverage packaging and include paraffin waxes and microcrystalline waxes.

In some cases, it can be preferable for the coating to be elastomeric or deformable. Some coatings can also be used to strengthen places where the articles are severely bent. In such cases, a pliable, possibly elastomeric, coating can be preferred.

Of course, it should be understood that the starch compositions of the present invention can themselves be used as coating materials in order to form a synergistic composite with, or otherwise improve the properties of, any number of other materials. Such disparate materials such as paper,

paperboard, molded starch-bound articles such as starch-based foams, metals, plastics, concrete, plaster, ceramics, and the like can be coated with starch composition.

It can be desirable to apply print or other indicia, such as trademarks, product information, container specifications, or logos, on the surface of the article. This can be accomplished using any conventional printing means or processes known in the art of printing paper or cardboard products, including planographic, relief, intaglio, porous, and impactless printing. Conventional printers include offset, Van Dam, laser, direct transfer contact, and therrographic printers. However, essentially any manual or mechanical means can be used.

In a further aspect of the present invention, it is recognized that to facilitate the coating of the molded article, as well as for other specific indications, the amount of paper pulp can be increased to 50%, or 30-50%, by weight of the final mixture, and the amount of wood flour or fiber can be decreased to 0%.

When using a vacuum to form a film around the molded article, increasing the levels of wood flour/fiber and/or paper pulp can facilitate the vacuuming process. For example, wood flour/fiber and/or paper pulp levels can be increased to 30, 40 or 50% by weight of the final mixture.

Types of Articles Produced

Materials capable of holding dry, damp and wet products have diverse uses. Containers suitable for holding dry materials can be used to hold dried fruit, or raw nuts such as almonds. Containers suitable for holding damp materials can be used to hold fresh mushrooms or tomatoes (for example in groups of 4 or 6) and should be able to perform this function for a period of at least about two to three weeks since normal packing to use time is about 14 days. Damp food packing can also be used with a hot fast food item such as french fries or hamburger, in which case the container needs to last for only a short time, for example about one hour after addition of the damp food. Damp food packing could also be used, in combination with an adsorbent pad, to package raw meat. In this case, the container needs to withstand exposure to the meat for a period of seven days or longer and desirably can stand at least one cycle of freeze and thaw. If possible this package should be able to withstand a microwave signal. When formulated for holding wet foods, the containers of the invention will suitably have the ability to hold a hot liquid, such as a bowl of soup, a cup of coffee or other food item for a period of time sufficient to allow consumption before cooling, for example within one hour of purchase. Such containers can also be used to hold a dry product that will be re-hydrated with hot water such as the soup-in-a-cup products.

Articles made from the present invention can be manufactured into a wide variety of finished articles that can presently be made plastics, paper, paperboard, polystyrene, metals, ceramics, and other materials. Merely by way of example, it is possible to manufacture the following exemplary articles: films, bags, containers, including disposable and nondisposable food or beverage containers, cereal boxes, sandwich containers, "clam shell" containers (including, but not limited to, hinged containers used with fast-food sandwiches such as hamburgers), drinking straws, baggies, golf tees, buttons, pens, pencils, rulers, business cards, toys, tools, Halloween masks, building products, frozen food boxes, milk cartons, fruit juice containers, yoghurt containers, beverage carriers (including, but not limited to, wraparound basket-style carriers, and "six pack" ring-style carriers), ice cream cartons, cups, french fry containers, fast food carryout boxes, packaging materials such as wrapping paper, spacing material, flexible packaging such as bags for snack foods, bags with an open end such as grocery bags, bags within cartons such as a dry cereal box, multiwell bags, sacks, wraparound casing,

support cards for products which are displayed with a cover (particularly plastic covers disposed over food products such as lunch meats, office products, cosmetics, hardware items, and toys), computer chip boards, support trays for supporting products (such as cookies and candybars), cans, tape, and wraps (including, but not limited to, freezer wraps, tire wraps, butcher wraps, meat wraps, and sausage wraps); a variety of cartons and boxes such as corrugated boxes, cigar boxes, confectionery boxes, and boxes for cosmetics, convoluted or spiral would containers for various products (such as frozen juice concentrate, oatmeal, potato chips, ice cream, salt, detergent, and motor oil), mailing tubes, sheet tubes for rolling materials (such as wrapping paper, cloth materials, paper towels and toilet paper), and sleeves; printed materials and office supplies such as books, magazines, brochures, envelopes, gummed tape, postcards, three-ring binders, book covers, folders, and pencils-, various eating utensils and storage containers such as dishes, lids, straws, cutlery, knives, forks, spoons, bottles, jars, cases, crates, trays, baking trays, bowls, microwavable dinner trays, "TV" dinner trays, egg cartons, meat packaging platters, disposable plates, vending plates, pie plates, and breakfast plates, emergency emesis receptacles (i.e., "barf bags"), substantially spherical objects, toys, medicine vials, ampules, animal cages, firework shells, model rocket engine shells, model rockets, coatings, laminates, and an endless variety of other objects.

The container should be capable of holding its contents, whether stationary or in movement or handling, while maintaining its structural integrity and that of the materials contained therein or thereon. This does not mean that the container is required to withstand strong or even minimal external forces. In fact, it can be desirable in some cases for a particular container to be extremely fragile or perishable. The container should, however, be capable of performing the function for which it was intended. The necessary properties can always be designed into the material and structure of the container beforehand.

The container should also be capable of containing its goods and maintaining its integrity for a sufficient period of time to satisfy its intended use. It will be appreciated that, under certain circumstances, the container can seal the contents from the external environments, and in other circumstances can merely hold or retain the contents.

The terms "container" or "containers" as used herein, are intended to include any receptacle or vessel utilized for, e.g., packaging, storing, shipping, serving, portioning, or dispensing various types of products or objects (including both solids and liquids), whether such use is intended to be for a short-term or a long-term duration of time.

Containment products used in conjunction with the containers are also intended to be included within the term "containers." Such products include, for example, lids, straws, interior packaging, such as partitions, liners, anchor pads, corner braces, corner protectors, clearance pads, hinged sheets, trays, funnels, cushioning materials, and other object used in packaging, storing, shipping, portioning, serving, or dispensing an object within a container.

The containers within the purview of the present invention can or can not be classified as being disposable. In some cases, where a stronger, more durable construction is required, the container might be capable of repeated use. On the other hand, the container might be manufactured in such a way so as to be economical for it to be used only once and then discarded. The present containers have a composition such that they can be readily discarded or thrown away in conventional waste landfill areas as an environmentally neutral material.

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The articles within the scope of the present invention can have greatly varying thicknesses depending on the particular application for which the article is intended. They can be as thin as about 1 mm for uses such as in a cup. In contrast, they can be as thick as needed where strength, durability, and/or bulk are important considerations. For example, the article can be up to about 10 cm thick or more to act as a specialized packing container or cooler. The preferred thickness for most articles is in a range from about 1.5 mm to about 1 cm, with about 2 mm to about 6 mm preferred.

Using a microstructural engineering approach, the present invention can produce a variety of articles, including plates, cups, cartons, and other types of containers and articles having mechanical properties substantially similar or even superior to their counterparts made from conventional materials, such as paper, polystyrene foam, plastic, metal and glass. The inventive articles can also be made at a fraction of the cost of their conventional counterparts. The minimal cost is a result of the relatively inexpensive aggregate which typically comprises a large percentage of the mixture and the minimum processing energy required.

The method of the present invention provides basic methodologies which can be utilized with little modification and a basic material from which product items can be produced by tailoring of the additives and additional processing steps employed. The composition preferably contains at least 75%, at least 85% or at least 95% or more of natural or organic-derived materials by weight of the homogenous moldable composition.

EXAMPLES

The following examples are presented in order to more specifically teach compositions and process conditions for forming the thermoplastic starch compositions according to the present invention, as well as articles therefrom. The examples include various mix designs, as well as various processes for manufacturing thermoplastic starch compositions, including sheets, films, pellets, containers, and other articles of manufacture.

Examples of Articles Formed from Pregelled Starch Suspensions

Example Mixture A

31.5 gm of 5% potato starch gel
18 gm of dry corn starch
6 gm of dry wood flour [60 mesh soft wood]

Test characteristics—the thick stiff mixture was flat molded in a 4"x4" flat mold at a low pressure (between 2 and 3 psi) to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 9 (on a scale of 10, with 1=breaks with little resistance and 10=breaks with significant resistance. A styrofoam tray for meat=8 on this scale and a styrofoam burger clamshell box=5). This mixture was to test a thick mixture and was determined that for a complete molded test item the mixture had to be pre shaped into a flat rolled sheet about 2" square.

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Example Mixture B

5 gm 5% potato starch gel
19.5 gm of 15% corn starch gel
0.125 gm of 80 mesh softwood flour
0.125 gm baking powder—[added to elevate the number of open cells in the final structure by introducing a source of carbon dioxide released by heat and water.]

10 The flat test [2-3 psi and 250° C. mold] item was dry and had a large number of air cells in the cross linked test pad. The strength test was 2 indicating that items molded from this mixture would be used for low breakage packaging, such as shock spacers.

Example Mixture C

15 16.3% 3% potato starch gel
5.9% dry corn starch
14% 80 mesh softwood flour
1% dry baking powder
1% glycerol-[added to produce a product that would release from the mold and to produce a smoother surface on the finished product.]

20 25 The flat test [2-3 psi and 250 deg C. mold] item has a stronger strength index of 4, greater than mixture C with the same open cell structure. This mixture will allow for a stronger product, while still retaining the open cell structure for items such as spacers in packing boxes, e.g., dimpled trays to separate layers of apples in a packing box. This item would, as mixture C, provide good shock protection [crush strength].

Example Mixture D

35 25% of a 3% potato starch gel
57% of a 15% corn starch gel
17% 80 mesh softwood flour
1% baking powder
40 To this mixture was added various amounts of natural material fillers in an effort to reduce the cost per item. In this test group powdered calcium carbonate or bentonite clay was added to the potato starch gel before mixing with the corn starch/wood flour mix. At low levels [up to 5% there is no effect on the strength or amount of entrapped air pockets, suggesting that low levels of these two fillers are appropriate]. At higher levels the basic formulation had to be changed to accommodate the chemical and physical changes that the fillers produced.

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Example Mixture E

10 gms of a gel mix of 5% potato starch & 20% bentonite clay
55 6 gms of dry corn starch
7 gms of 80 mesh softwood flour
1 gm glycerol
6 grams of water

60 Test characteristics—the thick stiff mixture was flat molded in a 4"x4" flat mold at a low pressure [between 2 and 3 psi] to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 7 with a high level of entrained air pockets. This type of product is hard and has a high degree of strength for use as a primary package. The inclusion of the clay produces a product with higher strength, in addition to reducing the unit cost.

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Example F

16.3 gms of a 5% potato starch gel
5.9 gms of dry corn starch
3.8 gms of 80 mesh softwood flour
1 gm of glycerol

Test characteristics—the thick mixture was flat molded in a 4"×4" flat mold at a low pressure [between 2 and 3 psi] to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 8 with a very high level of entrained air pockets.

Example G

15.1 gms of a 5% potato starch gel
9.1 gms of dry corn starch
4.3 gms of 80 mesh softwood flour
1 gm of glycerol

Test characteristics—the somewhat thick mixture was flat molded in a 4"×4" flat mold at a low pressure (between 2 and 3 psi) to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 9 with a high level of entrained air pockets. This mixture is the strongest of the basic formula tests using a mixture that was thick. The next test was to use the same basic formula but with additional water to allow the mixture to be injected as a thinner mix.

Example H

15.1 gms of a 5% potato starch gel
9.1 gms of dry corn starch
4.3 gms of 80 mesh softwood flour
1 gm glycerol
4 gms of water

Test characteristics—the thinner mixture was flat molded in a 4"×4" flat mold at a low pressure (between 2 and 3 psi) to a thickness of 3 mm. The mold temperature was 250° C. 25 grams of the mixture was molded. The test item was both dry and strong after molding. The strength test was 9 with a high level of entrained air pockets. The addition of more water allowed the product to fill the mold more quickly thereby producing a product with strength similar to styrofoam (2 mm thickness standard production). Three millimeter thick trays were made by molding for various times between 3 and 5 minutes at temperatures between 300 and 375° F. using the following formulations. Satisfactory products were obtained.

Example I

10.8 gm wood flour [6020 grade]
23.2 gm corn starch
41.8 gm 5% pre-gelled potato starch in water
12 gm 20% bentonite clay slurry in water

Example J

10.8 gm of wood flour [6020 grade]
23.2 gm corn starch
41.8 gm of 7.5% pre-gelled potato starch in water
2 mm thick tray were molded at various times between 45 seconds and 2 minutes at temperatures between 350 and 450° F. using the following formulations. Satisfactory products were obtained.

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Example K

10.8 gm wood flour [4025 grade]
23.2 gm corn starch
3.3 gm potato starch
41.8 gm 10% pre-gelled potato starch in water

Example L

10.8 gm wood flour [4025 grade]
23.2 gm corn starch
3.1 gm potato starch
3.3 gm bentonite clay
41.8 gm of 10% pre-gelled potato starch in water

These trays (in the above examples) have also been coated with a thin film of food grade polymer and/or food grade paraffin wax A specific aspect of this product is the observation that the addition of components is very important. When the dry ingredients, such as corn starch and wood flour are added to the potato starch gel, without premixing into a homogenous mixture, the product suffers a dramatic reduction in strength and will not spread evenly in the mold, producing open voids and unfilled corners. The observation of specific addition was seen in a dozen or more trial mixtures that used a different order of mixing of components. In addition the surface of the molded product can be rough vs the smooth surface of sequentially mixed products. More recently the product was tested in a three dimensional mold, using classic compression molding techniques, i.e., heated mold with a constant pressure applied during the process. In these test the requirement for a specific order of mixing was also observed and when this order was not observed the finished product suffered significant problems, including incomplete product spread during the molding process, reduction in smoothness of the molded product and a reduction in strength, as measured by classic penetrometer methods.

Example M

1. Form pregelled paper potato starch suspension:

57.5 g potato starch: 8.5%
43.2 g recycled paper pulp: 6.3%
575 g water: 85%

Add components, heat to 60-70° C. (ideal) 65° C. with mixing on high speed with a wire whisk to form gel. Once gelled, it is a stable gel that can be cooled, refrigerated, etc, but not frozen.

2. Premix the following materials:

92.3 g wood flour (aspect ratio 1:4)
132.7 g potato starch
159 g corn starch

to from homogeneous mixture

3. Add homogenous mixture of wood and starches with the pregelled paper potato starch, mix with a dough hook mixer on low speed

This mixture is stable and can be cooled, refrigerated, etc, but not frozen.

4. Place mixture into mold (50-55 g) and bake at 195-225.degree. C. (ideal 215.degree. C.) for 60-90 seconds (ideal 75)

5. Coating: Especially like PROTECOAT® 6616B by New Coat, Inc, commercial, biodegradable, acrylic based, FDA approved for food.

Examples of Articles Formed from Pregelled Paper
Starch Suspensions

Example N

10 1. Form pregelled paper potato starch suspension:

57.5 g dry potato starch: 8.5%

42.31 g recycled paper pulp: 6.2%

580 g water: 85.3%

Add components in a mixer, heat to 60-70° C. (ideal temp 65° C.) with mixing on low RPM with a wire whisk to form gel. When the paper pulp is dispersed, and as the temperature begins to rise (above 30° C.), the RPM of the mixer is increased until the maximum RPM is reached.

The heating continues until the temp reaches 65.degree. C. At this time, the mixture is a homogeneous gel suspension. The heat is turned off and beater heads changed to classic dough hook and speed is lowered to 10% of maximum KITCHENAID®. Alternatively, for smaller batches, see for example, step #2 below, the mixing is done by hand. Once gelled, it is a stable gel that can be cooled, refrigerated, etc, but not frozen.

2. Premix the following materials:

4.8 g wood flour (aspect ratio 1:4 or less)

6.9 g potato starch

8.3 g corn starch

to form homogeneous mixture

3. Add homogenous mixture of wood and starches to 29.9 g of the pregelled paper potato starch, mix with a dough hook mixer on low speed. This mixture is stable and can be cooled or refrigerated, but not frozen.

4. Place mixture into mold (50-55 g) and bake at 195-225° C. (ideal 215° C.) for 60-90 seconds (ideal 75° C.)

5. Coating: Especially like PROTECOAT® 6616B by New Coat, Inc, commercial, biodegradable, acrylic based, FDA approved for food.

The following examples and formulas work with both the compression molding process and injection molding processes to produce strong products as measured by pentrometers. In addition, these examples and formulas produce products with thicknesses between 1.5 and 3.0 mm, for example, thicknesses of 1.5 mm, 1.75 mm, 2.0 mm or 3.0 mm.

| List of | Weight in grams mixed by Formula ID # | | | |
|-----------------------|---------------------------------------|------|------|------|
| Ingredients | O | P | Q | R |
| 4025 wood flour | 4.8 | 4.8 | 4.5 | 5.0 |
| Potato starch | 6.9 | 5.9 | 6.5 | 7.2 |
| Corn starch | 8.3 | 9.3 | 7.8 | 8.6 |
| paper pulp | 2.2 | 2.2 | 2.1 | 2.3 |
| 10% Potato starch gel | 29.9 | 29.9 | 31 | 28.9 |
| Total wt. Molded | 52.1 | 52.1 | 51.9 | 52.0 |

Each modification listed in the above table is based on what works best for a specific flexibility and/or method of molding. For example, as you change the concentration of potato starch, the flexibility will change.

| List of | Weight in grams mixed by Formula ID # | |
|-----------------------|---------------------------------------|------|
| Ingredients | S | T |
| 4025 wood flour | 6.7 | 4.8 |
| Potato starch | 9.6 | 6.9 |
| Corn starch | 11.6 | 8.3 |
| paper pulp | 3.1 | 2.2 |
| 10% Potato starch gel | 41.8 | 29.9 |

| | | |
|---------------------|---------------------------------|-------|
| 10 Total wt. Molded | 72.8 | 52.0 |
| Thickness of Mold | 3 mm. (deeper sides than #T) | 2 mm. |

| List of | Weight in grams mixed by Formula ID # | | |
|-----------------------|---------------------------------------|------|------|
| Ingredients | U-1 | U-2 | U-3 |
| 4025 wood flour | 3.3 | 5.6 | 3.5 |
| Potato starch | 6.2 | 10.5 | 6.6 |
| Corn starch | 6.1 | 10.3 | 6.5 |
| paper pulp | 1.8 | 3.0 | 1.9 |
| 10% Potato starch gel | 27.6 | 46.6 | 29.4 |

| | | | |
|---------------------|-------|-------|-------|
| 20 Total wt. Molded | 45 | 76.0 | 48 |
| Thickness of Mold | 2 mm. | 3 mm. | 2 mm. |

| List of | Weight in grams mixed by Formula ID # | | |
|-----------------------|---------------------------------------|------|------|
| Ingredients | V-1 | V-2 | V-3 |
| 4025 wood flour | 4.8 | 8.2 | 5.4 |
| Potato starch | 6.9 | 11.8 | 7.8 |
| Corn starch | | | |
| paper pulp | 1.8 | 3.1 | 2.0 |
| 10% Potato starch gel | 29.9 | 51.0 | 33.8 |

| | | | |
|---------------------|-------|-------|-------|
| 25 Total wt. Molded | 43.4 | 74.0 | 49 |
| Thickness of Mold | 2 mm. | 3 mm. | 2 mm. |

| List of | Weight in grams mixed by Formula ID # | |
|-----------------------|---------------------------------------|------|
| Ingredients | W-1 | W-2 |
| 4025 wood flour | 3.8 | 6.3 |
| Potato starch | 6.9 | 11.5 |
| Corn starch | 2 | 3.3 |
| paper pulp | 1.8 | 3.0 |
| 10% Potato starch gel | 29.8 | 49.8 |

| | | |
|---------------------|-------|-------|
| 45 Total wt. Molded | 44.4 | 74.0 |
| Thickness of Mold | 2 mm. | 3 mm. |

The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications will be obvious to those skilled in the art from the foregoing detailed description of the invention and may be made while remaining within the spirit and scope of the invention.

We claim:

1. A process for forming a biodegradable material by:
 - forming a pre-gelled starch suspension that is maintained between approximately 0 and 60° C.;
 - adding to the pre-gelled starch suspension a dry or damp, homogeneous mixture containing at least wood fibers having an aspect ratio between approximately 1:2 and 1:8 width:length to form a homogenous moldable composition; and
 - molding the homogenous moldable composition with heat to form a biodegradable material.
2. The process of claim 1, wherein the homogenous mixture further comprises a second pre-gelled starch suspension, and/or a native starch.

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3. The process of claim 1 wherein the pre-gelled starch suspension is a pre-gelled paper starch suspension.

4. The process of claim 3, wherein the pre-gelled starch suspension comprises approximately 2-15% potato starch by weight of the pre-gel; approximately 5-10% paper pulp by weight of the pre-gel; and approximately 75-95% water by weight of the pre-gel such that the pre-gelled suspension is maintained at low temperatures; and wherein the homogenous mixture comprises wood fibers or flour having an aspect ratio between approximately 1:2 and 1:8, native corn starch and native potato starch.

5. The process of claim 1 further comprising adding a material selected from the following list to the wood fibers to form a homogeneous mixture: (i) waxes, fatty alcohols, phospholipids or other high molecular weight biochemicals; (ii) approximately 0.5-20% water by weight of the homogenous moldable composition; (iii) baking powder; and/or (iv) natural earth fillers, clays, bentonite, amorphous raw products, gypsum or calcium sulfate, minerals or man made inert fillers.

6. The process of claim 1, wherein the pregelled starch suspension is produced from approximately 2.5-15% starch by weight of the pre-gel, and from approximately 85-97.5% of water by weight of the homogenous moldable composition.

7. The process of claim 1, wherein the pre-gelled starch suspension is produced from approximately 2.5-5.5% starch and from approximately 94.5-97.5% water.

8. The process of claim 1, wherein the pre-gelled starch suspension is produced from approximately 2.5-10% potato starch, and 90 to 97.5% water by weight of the pre-gel.

9. The process of claim 1, wherein the pre-gelled starch suspension is produced from approximately 15% corn starch by weight of the pre-gel.

10. The process of claim 1, wherein the pregelled paper starch solution is produced from approximately 5-10% paper pulp by weight of the pre-gel, approximately 5-15%, natural starch, and approximately 75-90% water by weight of the pre-gel.

11. The process of claim 1, wherein the starch is corn starch or potato starch.

12. The process of claim 1, wherein the starch is a mixture of potato starch and corn starch.

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13. The process of claim 1, wherein corn starch comprises approximately 4-18%, by weight of the homogenous moldable composition.

14. The process of claim 1, wherein wood fibers or flour comprise approximately 11-24% of the homogenous moldable composition that contains the pregelled starch solution.

15. The process of claim 1, wherein the wood fibers or flour comprise approximately 7-11% by weight of the homogenous moldable composition that contains the pregelled paper starch solution.

16. A biodegradable, compostable material made according to a process of claim 1.

17. The process of claim 1 further comprising using pressure in combination or alternation with heat to mold the biodegradable material.

18. The process of claim 17, wherein the heat used to mold the biodegradable materials is between approximately 150-250° C. and the pressure is between 2-3 psi.

19. The material of claim 16 coated with a suitable liquid-resistant coating.

20. The material of claim 16, wherein the material is in the form of a cup, a tray, a bowl, a plate, or a utensil.

21. The process of claim 4, wherein the potato starch is about 2.5% by weight of the pre-gel.

22. The process of claim 4, wherein the potato starch is about 5% by weight of the pre-gel.

23. The process of claim 4, wherein the potato starch is about 10% by weight of the pre-gel.

24. The process of claim 4, wherein the potato starch is about 15% by weight of the pre-gel.

25. The process of claim 4, wherein the paper pulp is about 5.9% by weight of the pre-gel.

26. The process of claim 4, wherein the paper pulp is about 7.3% by weight of the pre-gel.

27. The process of claim 4, wherein the paper pulp is about 8% by weight of the pre-gel.

28. The process of claim 4, wherein wood fibers or flour have an aspect ratio between about 1:2 and 1:4.

29. The process of claim 5, wherein the high molecular weight biochemical is glycerol.

30. The process of claim 5, wherein the mineral is limestone.

* * * * *



US006303000B1

(12) **United States Patent**
Floyd et al.(10) **Patent No.:** US 6,303,000 B1
(45) **Date of Patent:** Oct. 16, 2001(54) **PAPER MAKING PROCESS UTILIZING A REACTIVE CATIONIC STARCH COMPOSITION**(75) Inventors: **William C. Floyd**, Chester; **Nolan Thompson**; **Louis R. Dragner**, both of Rock Hill, all of SC (US)(73) Assignee: **Omnova Solutions Inc.**, Fairlawn, OH (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/143,556**(22) Filed: **Aug. 31, 1998**(51) Int. Cl.⁷ **D21H 21/18**(52) U.S. Cl. **162/175**; 106/206.1

(58) Field of Search 162/175, 158; 106/162.51, 206.1

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(57) **ABSTRACT**

A method for manufacturing paper with improved strength by introducing into the paper pulp in the wet end of a paper making process an aqueous starch dispersion of a gelatinized cationic starch and a blocked glyoxal resin.

12 Claims, No Drawings

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**PAPER MAKING PROCESS UTILIZING A
REACTIVE CATIONIC STARCH
COMPOSITION**

BACKGROUND OF THE INVENTION

The present invention relates to a process for manufacturing paper and more particularly to adding to a dilute paper pulp slurry prior to sheet formation a modified starch dispersion of a cationic starch which has been gelatinized and reacted with a blocked glyoxal resin.

Industrial starch may be utilized in a wide variety of applications including as coatings for paper or paper board and as a bonding wet end additive in papermaking. Starch compositions may desirably be prepared in the form of aqueous dispersions capable of being added to the pulp slurry.

For many commercial applications starch is gelatinized by the end user prior to being used. Gelatinization occurs after starch granules are dispersed as a slurry in water with the resultant aqueous slurry being heated to over 50° C. and usually over about 65° C. Under such conditions starch grains tend to absorb water, swell, and eventually rupture to allow starch fragments and molecules to disperse in water. This rupturing and dispersion is generally referred to as "gelatinization" and is an irreversible reaction resulting in a relatively thick starch dispersion.

The cross-linking of starches with multi functional reagents which are reactive with starch hydroxyl groups is well known. Glyoxals and polyaldehyde compounds and resins have been previously utilized as cross-inkers. The simple mixing of glyoxal with a starch dispersion will provide a gel. U.S. Pat. No. 4,455,416 describes a paper coating containing starch binder and a cyclic urea/glyoxal/polyol condensate as an insolubilizer for the binder. As an insolubilizer the glyoxal condensate is inactive until the coating is applied and cured upon drying whereupon the glyoxal crosslinks the starch to impart water resistance. U.S. Pat. No. 4,021,260 describes ethoxylated fatty alcohols as starch viscosity control agents. U.S. Pat. No. 3,324,057 discloses the use of dialdehyde starch in the preparation of paper coatings. U.S. Pat. No. 3,740,391 describes the production of aqueous dispersions of a starch first reacted with an acrylamide and, subsequently, with glyoxal. U.S. Pat. No. 4,013,629 discloses a glyoxal binder system. U.S. Pat. No. 4,425,452 discloses coating paper material via an enzymatically converted starch. British Patent No. 2017124 discloses polysaccharides cross-linked with glyoxal.

A stable fluid aqueous modified starch dispersion is prepared in U.S. Pat. No. 5,032,683, the disclosure of this patent being incorporated herein by reference. This starch dispersion is prepared by gelatinizing an aqueous slurry of a starch and reacting with a glyoxal compound. The present invention has found that a cationic starch dispersion modified with blocked glyoxal resin when added in the wet end of a papermaking process provides significant improvements in strength to the resultant paper.

BRIEF DESCRIPTION OF THE INVENTION

It is an object of this invention to provide a process of manufacturing paper having improved strength.

This and other objects are achieved by introducing into the paper pulp in the wet end of a papermaking process an aqueous starch dispersion of a gelatinized cationic starch and a blocked glyoxal resin.

**DETAILED DESCRIPTION OF THE
INVENTION**

An aqueous cationic starch dispersion modified with a blocked glyoxal resin is prepared which is readily flowable

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and wherein gelation and viscosity increases over time are inhibited. The starch dispersion is prepared by gelatinizing an aqueous suspension or slurry of starch granules and adding, preferably reacting the starch with a blocked glyoxal resin at temperatures of at least 70° C., preferably 85 to 95° C. Preferably gelatinization and the reaction with the blocked glyoxal resin are carried out simultaneously, although the starch can be pre-gelatinized and then reacted with the glyoxal compound with heating.

It is theorized that by reacting gelatinized starch at the higher temperatures with the blocked glyoxal resin the amylose is derivatized with the glyoxal so that retrogradation of the amylose and the formation of amylose fatty acid complexes upon cooling is inhibited, resulting in aqueous dispersions having a flowable viscosity and in which gelation and viscosity increases over time are inhibited. Without intending to be bound by theory it is believed that the glyoxals react with amylose to make highly labile hemiacetals which disrupt the crystallinity of amylose, thus significantly inhibiting retrogradation. Further, it is believed that glyoxal added after gelatinization and cool-down does not form hemi-acetals with the same efficiency as those added during heating because after gelatinization and cool-down crystallization occurs which limits the sites of reaction with glyoxal. Further, the use of a blocked glyoxal resins provides improved starch rheology reducing the tendency for gelling and is less prone to retrogradation and precipitation.

The starch dispersion prepared according to this invention will generally have a viscosity of less than 1000 cps, preferably less than 350 cps. Except where otherwise indicated, viscosity readings set forth herein are taken in aqueous solution at 35% solids content (by weight), are Brookfield viscosities (RV, #3 spindle at 100 rpm), and viscosity readings are taken at room temperature.

Suitable blocked glyoxal resins which may be used in accordance with the invention are described in U.S. Pat. No. 4,695,606 and include but are not limited to cyclic urea/glyoxal/polyol condensates, polyol/glyoxal condensates, urea or cyclic urea/glyoxal condensates and glycol/glyoxal condensates. The amount of glyoxal compound may be adjusted within broad limits, but is generally from about 3% to about 30%, preferably 9 to 20%, of the total dry weight of starch (and/or derivatives thereof) present.

In accordance with the invention, an aqueous slurry of cationic starch is prepared. Preferably the starch is an amylose containing starch. The starch may be obtained from any conventional source, including potato, corn, waxy corn, red milo, white milo, wheat and tapioca and may be pearl or lightly thinned and may have been oxidized, hydroxyalkylated, acid modified, enzyme converted or various combinations thereof. Also, suitable to this invention are thin-boiling starches that have been additionally chemically modified to reduce the setback or retrogradation tendencies of the starch. The prior art describes methods for making a wide variety of starch derivatives that display reduced setback. Higher molecular weight starches are preferred because of greater strength than low molecular weight starches. In certain preferred embodiments a blend of hydroxyethylated starch and an acid and/or enzyme-converted starch may be utilized with cationic starch. For example, cationic corn or potato starch may be utilized together with an acid modified or an oxidized hydroxyethylated starch such as a hydroxyethylated potato starch.

It is important for the starch to contain cationic functionality to enhance retention on the anionic paper fibers. Such

functionality is commonly introduced via tertiary or quaternary amino groups appended to the starch.

Preferably, the blocked glyoxal resin is added to the aqueous starch slurry and the slurry is heated to about 90° C. for at least about 30 minutes to gelatinize the starch. The starch slurry and blocked glyoxal resin may be heated briefly to higher temperatures such as those obtained with a steam injection cooker. The heat beneficially drives the reaction of the blocked glyoxal resin and starch simultaneously with starch gelatinization. The resulting gelatinized starch composition is then preferably treated with a biocide if it will be stored, preferably after it has been allowed to cool to about 40° C. Biocide is preferably added at a concentration by weight, of about 10 ppm to about 500 ppm. Suitable biocides include Kathon® LX from Rohm & Haas which is a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one and Proxel® GXL from ICI which is 1,2 benzothiazolin-3-one. Gelatinization in the presence of the glyoxal resin preferably takes place in an aqueous slurry at a solids content between about 15% and about 50% by weight, preferably between about 25% and about 35%. In alternative methods, dry starch and dry glyoxal resin may be intermixed prior to introduction into an aqueous slurry for the gelatinization and/or reaction steps.

Typically, an aqueous slurry of the granular cationic starch is prepared, and the blocked glyoxal resin is added to the agitated slurry. The starch is then gelatinized, or cooked out, either in a batch process or by a jet cooker. The cationic starch glyoxal resin condensate dispersion is then added to the dilute pulp slurry prior to sheet formation and thoroughly fixed. Generally the starch dispersion is added to the pulp slurry at a level of 2 to 50 lbs. dry starch, preferably 5 to 20 lbs. dry starch, per ton of dry pulp. The resin is attached to the cationic starch, which is attracted to the anionic pulp fibers thereby introducing the resin to the fiber. The sheet of paper is then formed, containing both the cationic starch and the resin. Upon drying the sheet, the resin reacts further with the cationic starch and/or cellulosic fiber, resulting in improved sheet properties such as wet tensile.

Polyacrylamide and acrylamide copolymers can also be added to improve tensile strength of the starch films drawn down from these compositions. These polymers also react with glyoxal to form a polymer-reinforced starch film upon drying. Generally the acrylamide polymer or acrylamide copolymer is added at a level of up to 50% by weight of the blocked glyoxal resin. The acrylamide is preferably a copolymer of acrylamide and is water soluble.

The invention is further illustrated by the following examples which are set forth only as illustrations of the invention and not as limitations thereof.

EXAMPLE I

An acid-modified corn starch (Keofilm® 90, available from Hubinger Corporation) was selected for film studies. As a control, a 20% solution of Keofilm® 90 was prepared, heated to 90° C. for 30 minutes, then cooled. A film, Sample A, was drawn down on Mylar, then dried and cured for 2 minutes at 250° F.

A second batch of Keofilm® 90, identical to the first, was prepared. Upon cooling, 10% by dry weight of a blocked glyoxal resin (Sequex®R) was added and thoroughly mixed. A film, Sample B was drawn down on Mylar, then dried and cured for 2 minutes at 250° F.

A third batch of Keofilm® 90 was prepared, identical to the first, except that the 10% of blocked glyoxal resin (Sequex®R) was added before the starch was heated. After cooking at 90° C. for 30 minutes, the starch dispersion was cooled, and a film drawn down on Mylar. This film, Sample C, was then dried and cured for 2 minutes at 250° F. All 3 films were tested for tensile and elongation on an Instron Model 1110 Tensile Tester (films where 2 inches^{7/16} inches and 12–13 mil. thick) with the results as shown in Table 1.

TABLE 1

| Sample | Dry Tensile (Kg) | Dry Elongation (%) | Wet Tensile (Kg) | Wet Elongation (%) |
|--------|------------------|--------------------|------------------|--------------------|
| A | 7.19 | 5.6 | 0.11 | 3.72 |
| B | 8.82 | 5.6 | 1.81 | 8.26 |
| C | 9.42 | 6.1 | 1.98 | 8.94 |

Table 1 shows the benefits of this invention in that Sample C showed greater wet and dry tensile strength and elongation. The improved strength performance obtained by this invention for the starch films has also been observed in waxy starches which do not contain amylose.

EXAMPLE II

The presence of the blocked glyoxal resin in the paper sheet may be determined by the improved sheet properties or calorimetrically. A dilute solution of N-methyl benzo thiazolinone hydrazone hydrochloride (MBTH) when spotted on the paper and warmed will evolve a yellow coloration if glyoxal or glyoxal based resins are present. If the glyoxal compound and cationic starch are merely mixed together, or added separately to the pulp slurry, inferior results are obtained.

The following examples are provided to illustrate this invention. Hand sheets were made using a 50/50 hardwood/softwood fiber blend. The freeness was held at approximately 370–350 at 1.5% consistency and adjusted to pH 4.5 with sulfuric acid. The hand sheet were made using 250 g of cellulose paper pulp to produce a 3.5 g hand sheet. Test samples were selected based on sample weight.

An aqueous slurry of Sta-lok® 400 (a cationic potato starch from A. E. Staley Mfg. Co.) was prepared at 4% solids. To this was added 9% (dry on dry) Sequex®R (a cyclic urea/glyoxal condensate, 45% solids, from Sequa Chemicals, Inc.). This was agitated and heated to 90° C. for 30 minutes to afford a clear amber solution which thickened upon cooling. Sufficient quantities of this were added to pulp slurries so as to achieve the equivalent of 40, 60 and 80 pounds of cationic starch per ton of pulp. Sheets of each dosage were prepared in triplicate. For controls, handsheets were prepared with no additives, and with cationic starch only at the equivalent of 40, 60 and 80 pounds of cationic starch per ton of pulp.

The results show that this invention provides an improvement in dry tensile, a substantial improvement in wet tensile and superior Mullen burst strength compared to the controls. Testing was done on 1×4 inch strips of paper on an Instrum Model 1100 Tensile Tester.

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| Additive Dosage | Cationic Starch | | | | Cationic Starch/Resin | | |
|-------------------------|-----------------|------|------|------|-----------------------|------|------|
| | None | 40 | 60 | 80 | 40 | 60 | 80 |
| Sheet wt, g | 3.2 | 3.6 | 3.6 | 3.6 | 3.3 | 3.7 | 3.7 |
| Tensile, Dry, kg | 15.4 | 17.8 | 17.5 | 17.4 | 13.9 | 18.5 | 22.4 |
| % stretch | 4.9 | 4.7 | 5.0 | 5.4 | 4.9 | 5.3 | 5.6 |
| Wet, kg | 0.36 | 0.54 | 0.76 | 0.90 | 0.8 | 1.1 | 1.4 |
| % stretch | 2.3 | 2.7 | 3.4 | 3.7 | 3.6 | 3.7 | 4.4 |
| Tabor Stiffness | 3.7 | 4.4 | 8.2 | 2.8 | 2.8 | 3.7 | 4.1 |
| Mullen Burst | 60.4 | 82.6 | 72.4 | 66.6 | 65.4 | 82.8 | 80.2 |
| Hercules Size Test, sec | 1.0 | 0.8 | 0.7 | 0.8 | 0.2 | 0.4 | 0.3 |

EXAMPLE III

A series similar to that described in Example II was prepared consisting of a base sheet with no additives, (A) a set with cationic starch applied at a rate equivalent to 40, 60 and 80 pounds per ton, (B) a set with 9% blocked glyoxal resin (Sequez®R, dry resin on starch) reacted with the cationic starch and applied at a rate of 40, 60 and 80 pounds of cationic starch per ton of pulp, (C) a set similar to B except that the amount of blocked glyoxal reacted with the cationic starch was 12% (dry on dry), and (D) a set similar to B except that the amount of blocked glyoxal resin reacted with the cationic starch was 20% (dry on dry). The appropriate amount of starch was added to the pulp slurry and mixed, then handsheets were formed and dried on a rotary drier. Three handsheets for each formulation were tested and average results are reported on attached sheets.

These results show that higher levels of resin may not be beneficial and that the system may be overdosed. The 9% level of resin gives the best overall performance, particularly at the 60 and 80 pound per ton levels. It should be noted that as the level of cationic starch increased in A, wet tensile increases while Mullen Burst strength decreases, and dry tensile is level. With the B set of samples, as the level cationic starch increases, dry tensile increases, wet tensile increases and Mullen Burst Strength rises and stays high.

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EXAMPLE IV

This example sought to examine the effect of different modes of combining the blocked glyoxal resin with the cationic starch and their introduction to the pulp slurry. A set of control base sheets was made having no additives followed by (A) a series in which cationic starch was added to the pulp slurry at the equivalent dosages of 40, 60 and 80 pounds per ton. A similar series (B) followed in which 9% of the blocked glyoxal resin was cooked out with the starch at 90° C. for 30 minutes. This was followed by a series, (C) in which the starch was cooked out then cooled to 50° C., whereupon the blocked glyoxal resin was stirred in. A final series (D) was prepared in which the cationic starch was cooked out then added to the pulp slurry. The blocked glyoxal resin was then added to the pulp slurry. Handsheets were formed from these slurries and dried on a rotary drier. Sheets were tested as before with results shown as follows.

These results show that reacting the resin with the cationic starch during the gelatinization is the preferred process. Some reaction apparently does take place when the starch is first cooked out and cooled prior to introducing the resin. This procedure is less efficient in that it requires a dosage of 80 pounds per ton to achieve performance equivalent to 60 pounds per ton prepared by the preferred procedure. The 80 pound per ton samples of set B are lower than expected, which may indicate poor mixing. Set D gives inferior results similar to set A with cationic starch only. This indicates that very little resin was retained on the fiber.

| Addition | A | | | | B | | | |
|----------|------------|------|-------|-------|------|-------|-------|------|
| | Conditions | Base | 40 | 60 | 80 | 40 | 60 | 80 |
| Dry | | 12.3 | 13.75 | 14.84 | 14.3 | 16.64 | 18.01 | 16.1 |
| Tensile | | 4.05 | 4.2 | 4.1 | 4.1 | 4.8 | 7.84 | 4.8 |
| % Dry | | | | | | | | |
| Stain | | | | | | | | |
| West | | .244 | .57 | .21 | .234 | .79 | .965 | .792 |
| Tensile | | | | | | | | |
| % Wet | | | | | | | | |
| Strain | | | | | | | | |
| Mullens | | 38.4 | 53.4 | 54 | 56 | 58.8 | 62 | 58.2 |
| Burst | | | | | | | | |

| Addition | C | | | | D | | |
|----------|---|--|--|--|---|--|--|
| | | | | | | | |

| | A | | | | B | | | | C | | | | D | | | |
|---------|------|------|-------|-------|------|------|-------|------|------|------|-------|-------|------|----|----|----|
| | Base | 40 | 60 | 80 | 40 | 60 | 80 | 40 | 60 | 80 | 40 | 60 | 80 | 40 | 60 | 80 |
| Dry | 15.4 | 17.6 | 17.48 | 17.41 | 13.9 | 18.5 | 22.36 | 15.7 | 17.0 | 16.6 | 18.58 | 16.74 | 19.7 | | | |
| Tensile | | | | | | | | | | | | | | | | |
| % Dry | 4.89 | 4.7 | 4.98 | 5.4 | 4.9 | 5.26 | 5.65 | 4.3 | 4.53 | 5.06 | 4.98 | 4.36 | 4.47 | | | |
| Strain | | | | | | | | | | | | | | | | |
| Wet | .36 | .543 | .76 | .905 | .82 | 1.1 | 1.39 | .95 | .93 | 1.01 | .757 | 1.14 | 1.4 | | | |
| Tensile | | | | | | | | | | | | | | | | |
| % Wet | 2.3 | 2.68 | 3.42 | 3.67 | 3.6 | 3.67 | 4.4 | 4.04 | 4.1 | 4.3 | 3.72 | 4.6 | 3.9 | | | |
| Strain | | | | | | | | | | | | | | | | |
| Mullen | 60.4 | 82.6 | 72.4 | 66.6 | 65.4 | 82.8 | 80.2 | 6.7 | 78.4 | 70.6 | 78.6 | 66.8 | 73.2 | | | |
| Burst | | | | | | | | | | | | | | | | |

Base Sheet-No Additives

A. STA-LOK 400 only

B. STA-LOK 400 plus 9% Sequez®R (Converted 210° F.)

C. STA-LOK 400 plus 12% Sequez®R (Converted 210° F.)

D. STA-LOK 400 plus 20% Sequez®R (Converted 210° F.)

| -continued | | | | | | | | |
|---------------------------|------|-------|-------|-------|-------|-------|-------|--|
| Conditions | Base | 40 | 60 | 80 | 40 | 60 | 80 | |
| Dry Tensile % Dry | 12.3 | 13.75 | 14.94 | 18.21 | 15.05 | 13.63 | 13.10 | |
| Stain | 4.05 | 4.7 | 4.6 | 4.7 | 4.77 | 4.88 | 4.45 | |
| West Tensile % Wet Strain | .244 | .669 | .49 | .977 | .662 | .687 | .525 | |
| Mullens Burst | 3.04 | 3.5 | 3.74 | 4.11 | 3.43 | 3.58 | 3.51 | |
| | 38.4 | 51.6 | 63.4 | * | 51.4 | 46.6 | 47.1 | |

The terms and descriptions used herein are preferred embodiments set forth by way of illustration only, and are not intended as limitations on the many variations which those of skill in the art will recognize to be possible in practicing the present invention as defined by the following claims.

What is claimed is:

1. A method for manufacturing paper sheet comprising: adding to a paper pulp slurry in the wet end of a paper making machine an aqueous reaction product of a cationic starch and a blocked glyoxal compound, wherein said reaction occurs during the gelatinization of said starch and prior to said addition; forming the paper sheet; and drying the paper sheet.
2. Method of claim 1 wherein the cationic starch is selected from the group consisting of potato starch, corn-starch and wheat starch.
3. Method of claim 1 wherein the amount of glyoxal resin is within the range of 3 to 30% of the dry weight of the starch.

4. Method of claim 3 wherein the amount of glyoxal resin is within the range of 9 to 20% of the dry weight of the starch.
5. Method of claim 1 wherein the glyoxal resin is selected from the group consisting of polyol/glyoxal condensate and cyclic urea/glyoxal condensate.
6. Method of claim 1 wherein the said reaction product is added to the paper slurry at a level of 2 to 50 pounds dry starch per ton of dry pulp.
7. A method for manufacturing paper comprising: adding an aqueous reaction product of a cationic starch and a blocked glyoxal compound to a paper pulp slurry in a wet end of a paper making machine, wherein said reaction occurs during gelatinization of said starch and prior to said addition; forming paper; and drying the paper.
8. A method according to claim 7, wherein the cationic starch is selected from the group consisting of potato starch, cornstarch and wheat starch.
9. A method according to claim 7, wherein the amount of glyoxal resin is within the range of 3 to 30% of the dry weight of the starch.
10. A method according to claim 9, wherein the amount of glyoxal resin is within the range of 9 to 20% of the dry weight of the starch.
11. A method according to claim 10, wherein the glyoxal resin is selected from the group consisting of polyol/glyoxal condensate and cyclic urea/glyoxal condensate.
12. A method according to claim 11, wherein the said reaction product is added to the paper slurry at a level of 2 to 50 pounds dry starch per ton on dry pulp.

* * * * *

United States Patent [19]

Floyd et al.

[11] Patent Number: 4,695,606

[45] Date of Patent: Sep. 22, 1987

[54] COATING BINDER ADDITIVE

[75] Inventors: William C. Floyd, Chester; Sai H. Hui, Rock Hill, both of S.C.

[73] Assignee: Sun Chemical Corporation, New York, N.Y.

[21] Appl. No.: 909,621

[22] Filed: Sep. 22, 1986

[51] Int. Cl.⁴ C08F 8/28; C08L 61/00

[52] U.S. Cl. 525/160; 525/154; 525/157; 525/161; 525/162; 525/163; 525/383

[58] Field of Search 525/154, 383, 326.9, 525/515, 162, 160, 161, 163; 528/245; 162/168.3

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| Re. 30,259 | 4/1980 | Moriya et al. | 162/167 |
| 2,886,557 | 5/1959 | Talet | 525/154 |
| 3,549,568 | 12/1970 | Coscia et al. | 260/17.3 |
| 3,869,296 | 3/1975 | Kelly, Jr. et al. | 106/214 |
| 4,100,137 | 7/1978 | Lemieux et al. | 525/154 |
| 4,343,655 | 8/1982 | Dodd et al. | 106/214 |
| 4,544,609 | 10/1985 | Hui | 428/507 |

Primary Examiner—Theodore E. Pertilla

Attorney, Agent, or Firm—Mitchell D. Bittman

[57]

ABSTRACT

A coating binder additive is prepared comprising a blocked glyoxal resin mixed with a vinyl or acrylic water soluble polymer which is reactive with free glyoxal.

11 Claims, No Drawings

COATING BINDER ADDITIVE

This invention relates to paper coating compositions. More particularly it relates to an additive which insolubilizes the binders in coatings for paper.

BACKGROUND OF THE INVENTION

Paper coating compositions are generally a fluid suspension of pigment, such as clay with or without titanium dioxide, calcium carbonate, or the like, in an aqueous medium which includes a binder such as starch, modified starch, styrene-butadiene copolymer, acrylic polymer, or protein to adhere the pigment to paper.

The hydrophilic nature of the binder requires the presence of an insolubilizing material which crosslinks the binder making it hydrophobic and thus improving the off-set characteristics of the surface of the coated paper. The most widely-used crosslinking materials are glyoxal resins and formaldehyde-donor agents such as melamine-formaldehyde, urea-melamine-formaldehyde, and partially or wholly methylated derivatives thereof.

Glyoxal is a highly reactive monomer which cures quickly and has excellent insolubilizing properties. As a result of this rapid crosslinking of glyoxal and binder, however, the viscosity of the coating composition increases so rapidly and is so great that the composition cannot be used. Frequently glyoxal-insolubilized coatings gel completely, particularly in high solids formulations. Gelling can also occur in moderate or low solids formulations if they are not used promptly. Thus in situations where it is required that the viscosity remain stable for many hours, for example when high-solids coatings are to be applied by blade coating techniques, a glyoxal system is unsuitable.

Melamine-formaldehyde resins do not build viscosity in the coating compositions, but they have the disadvantage of having an unpleasant odor and of releasing free formaldehyde. Curing with such resins involves the crosslinking of the binder molecule with the methylol or methylated methylol group of the melamine resin, usually in an acid or neutral coating, and full insolubilization of the binder takes place slowly over a period of several days. Free formaldehyde can be released either directly from the coating mixture or when the coating is cured on the drying machine. The presence of even less than one percent of free formaldehyde, based on the total weight of the product, is undesirable, not only because of its objectionable odor, but because it is an allergen and an irritant, causing severe reactions in the operators who manufacture the coatings and who treat and handle the coated paper.

Various compositions have been disclosed in the art as useful as insolubilizers. The use of the reaction product of urea and glyoxal as an insolubilizer is disclosed in U.S. Pat. No. 3,869,296. Treating agents formed by the reaction of ethylene urea with glyoxal are disclosed in Japanese publication No. 5 3044-567, but they too do not have satisfactory properties. The use of an acrylamide/glyoxal adduct was disclosed in U.S. Pat. No. 3,549,568 to improve the wet rub of paper coating compositions. U.S. Pat. No. 4,343,655 teaches the use of the alkylated products of the reaction of glyoxal and cyclic ureas as crosslinking resins for binders for paper coating compositions. U.S. Pat. No. Re. 30,259 disclosed paper strengthening resins in which water soluble thermosetting polyvinylamide resins are reacted with glyoxal.

In particular, U.S. Pat. No. 4544609 discloses an insolubilizer which is useful as a binder for a paper coating composition comprising the reaction product of polyacrylamide, glyoxal and cyclic urea. While this insolubilizer has been effective, due to its high viscosity gelling can occur in concentrates of the insolubilizer containing greater than 20-25% solids.

SUMMARY OF THE INVENTION

10 Briefly, the coating binder additive comprises a blocked glyoxal resin mixed with a vinyl or acrylic water soluble polymer which is reactive with free glyoxal. This additive is an excellent crosslinking resin for binders for paper coating compositions. It does not build viscosity as does free glyoxal; it does not contain or evolve free formaldehyde; it has insolubilizing effects similar to those of the previously known agents; and imparts strength to the binder and enhances various printing properties of the coated substrate.

20 DETAILED DESCRIPTION OF THE INVENTION

25 In accordance with the present invention a binder additive is prepared which is useful for insolubilizing and strengthening starch, protein and polyvinyl alcohol binders for paper coating compositions. The binder additive is prepared as follows: (1) an acrylic or vinyl polymer which is water soluble and which reacts with free (unblocked) glyoxal or glyoxal resin is prepared; and 30 (2) the polymer is mixed with a blocked glyoxal resin, preferably the reaction product of glyoxal and a urea or a cyclic urea, to give the product of this invention.

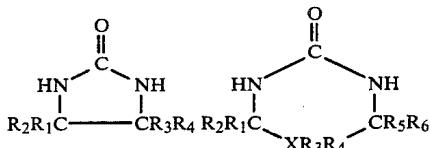
35 The glyoxal resin component of this mixture is blocked to inhibit it from reacting with the other components of the paper coating composition prior to curing. Inhibiting the reactivity of the glyoxal resin allows a product to be formulated at higher solids and/or lower viscosity than otherwise possible with unblocked glyoxal resin. Further, by blocking the glyoxal resin, the reaction is delayed until the paper is cured. The 40 curing process unblocks the glyoxal and resin allowing them to react with the binder and polymer resulting in a cross-linked binder with superior strength and improved printing properties. Using this invention, it is possible to prepare a paper coating with a high level of natural binder that performs as well as a coating with a high level of synthetic (latex) binder. With free (unblocked) glyoxal, the coating additive can be unstable 45 resulting in thickening or gelling of the additive, or the coating may show unacceptably high viscosity or gelling over time.

50 Glyoxal readily reacts with binders such as starch, protein and polyvinyl alcohol and with polyacrylamide and other polymeric agents in a crosslinking reaction. Crosslinking causes the mixture of glyoxal resin and the binders and/or polymeric agents to thicken or gel. By suitably blocking the glyoxal resin, it may be mixed with these binders and polymeric agents without reacting to 55 any great degree. The reactivity can be controlled so that it occurs in a paper coating as it is being dried and cured. Furthermore, judicious choice of polymeric agent allows coating properties to be enhanced as the glyoxal resin reacts with binder and the polymer. Mixing a suitable polymeric agent with free (unblocked) glyoxal, or adding free glyoxal to a coating containing a suitable polymeric agent generally causes thickening or 60 gelling due to premature reaction.

The glyoxal may be blocked by reaction with a blocking component becoming a blocked glyoxal resin. Suitable blocking components include urea, substituted ureas (such as dimethyl urea), various cyclic ureas such as ethylene urea, substituted ethylene ureas (such as 4,5-dihydroxyethylene urea), propylene urea, substituted propylene ureas (such as 4-hydroxy-5-methylpropylene urea), carbamates (such as isopropyl or methyl carbamate), glycols (such as ethylene glycol to make 2,3-dihydrodioxane, or dipropylene glycol to make an oligomeric condensation product), polyols (i.e. containing at least three hydroxy groups such as glycerin, to make 2,3-dihydroxy-5-hydroxymethyl dioxane) as well as unalkylated or partially alkylated polymeric glyoxal derived glycols such as poly (N-1',2-dihydroxyethyl-ethylene urea). Preferably, the blocking component is a urea or cyclic urea because the blocked glyoxal resins formed are very stable providing long shelf life.

The reaction of the glyoxal and the blocking component, preferably a urea or cyclic urea, generally takes place within the temperature range of about 25° to 100° C., and preferably about 40° to 80° C. In general the pH of the reactants and resultant binder additive is about 2.5 to 8.0 and preferably is about 4 to 6.5

The urea reactant may be urea, monourein or the like. If a cyclic urea is selected it may have one of the following general formulas:



wherein R₁, R₂, R₃, R₄, R₅ and R₆ may be the same or different and each may be H, OH, COOH, R, OR, or COOR wherein R is an alkyl or a substituted alkyl group having 1 to 4 carbon atoms and X may be C, O, or N; when X is O, R₃ and R₄ are each zero; when X is N, R₃ or R₄ is zero.

Typical examples of such urea reactant compounds include, but are not limited to ethylene urea, propylene urea, uron, tetrahydro-5(2 hydroxyethyl)-1,3,5-triazin-2-one, 4,5-dihydroxy-2-imidazolidinone, 4,5-dimethoxy-2-imidazolidinone, 4-methyl ethylene urea, 4-ethyl ethylene urea, 4-hydroxyethyl ethylene urea, 4,5-dimethyl ethylene urea, 4-hydroxy-5-methyl propylene urea, 4-methoxy-5-methyl propylene urea, 4-hydroxy-5,5-dimethyl propylene urea, 4-methoxy-5,5-dimethyl propylene urea, tetrahydro-5-(ethyl)-1,3,5-triazin-2-one, tetrahydro-5-(propyl)-1,3,5-triazin-2-one, tetrahydro-5-(butyl)-1,3,5-triazin-2-one, 4-hydroxy-5,5-dimethyl pyrimid-2-one, and the like, and mixtures thereof.

A polymer is chosen which is water soluble and which will react with free (unblocked) glyoxal and glyoxal resin. Since the polymer is mixed with a blocked glyoxal resin in the binder additive, the polymer will react under curing conditions with the released glyoxal and resin resulting in crosslinking between the polymer, glyoxal, resin and binder (e.g. starch) which will strengthen the binder considerably. Since the polymer does not react with the crosslinker until curing of the coating composition, the binder additive and coating composition can maintain a low viscosity without gelling over time (i.e. storage stable). In addition, since the polymer has not been reacted with the glyoxal resin, the reactivity of the glyoxal resin can be maintained for

subsequent curing with the binder. Further, the hydrophilic nature of the polymer results in a coating which can hold moisture and can benefit subsequent printing of the coated substrate.

Preferably a low molecular weight polymer is prepared with the molecular weight being controlled by, for example, using an alcohol such as isopropanol as a chain terminator, using a low concentration of acrylamide monomer, or using a low monomer concentration per unit time (using monomer feed instead of bulk). The preferred molecular weight is less than 100,000 daltons, optimally less than 30,000 daltons, which helps provide a binder additive and coating composition with a low viscosity and which does not gel.

Suitable polymers include polymers of monomers such as acrylamide, 2-hydroxyethyl acrylate, methacrylamide, N-(hydroxymethyl) acrylamide, N-substituted acrylamides and N-substituted methacrylamides, as well as co- or ter polymers of the above with monomers such as acrylic acid, acrylonitrile, crotonic acid, fumaric acid, itaconic acid, maleic acid, methacrylic acid, monoethyl maleate, vinyl pyrrolidone, or vinyl sulfonic acid. The monomers may also be with small amounts of vinyl acetate or C-1 to C-4 alkyl esters of acrylic or methacrylic acid. One preferred embodiment is a copolymer of acrylamide and methacrylic acid. Another preferred embodiment is a polymer containing acrylamide reacted with either formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde or isobutyraldehyde. The polymer may also be partially hydrolyzed polyvinyl acetate.

In the binder additive the ingredients are generally present in a ratio of 25:1 to 1:2, preferably 10:1 to 1:1, parts by dry weight of the blocked glyoxal resin to polymer. The blocked glyoxal resin generally comprises a mole ratio of about 4:1 to 1:2, preferably 2:1 to 1:1, of glyoxal to blocking component.

The binder additive of this invention has reactive sites capable of reacting with the cellulosic hydroxyl group, thus binding the starch or protein molecules in the coating composition. Because of its polymeric nature, the additive is capable of reacting with several binder molecules, leading to greater insolubilizing efficiency and so requiring less of the additive of this invention than of glyoxal or of a melamine-formaldehyde resin to accomplish the same degree of insolubilization. The additive is not excessively reactive, as is glyoxal, so no viscosity build-up takes place in the coating composition. Since there is no formaldehyde in the system, the problems found with free formaldehyde are avoided.

The binder additive of this invention is useful as an insolubilizer for natural binders. The binders used in the paper coating compositions of this invention include, but are not limited to, unmodified starch; oxidized starch; enzyme-converted starch; starches having functional groups such as hydroxyl, carboxyl, amido, and amino groups; proteins, such as casein; polyvinyl alcohol; and the like, and their mixtures. Through use of the binder additive, the coating composition containing natural binders are able to impart properties, such as gloss, strength, etc. which are closer to those imparted by latex binders, but at a fraction of the cost of latex binders.

The coating composition will generally contain pigments which may be clay with or without titanium dioxide and/or calcium carbonate, and the like, and mixtures thereof. In addition to the binder, the pigment

material, and the additive described above, the paper coating composition may also include materials such as dispersants (e.g. sodium hexametaphosphate), lubricants (e.g. calcium stearate), defoamers (e.g. oil based emulsions or ethyl alcohol), preservatives, colored pigments, viscosity modifiers (e.g. carboxymethylcellulose), and the like, in conventional amounts, as well as a latex (e.g. a polymer such as a styrene-butadiene copolymer or acrylic polymer) which may be used as a binder in addition to the natural binders.

In the paper coating compositions described herein the amount of binder is based upon the amount of pigment with the ratio varying with the amount of bonding desired and with the adhesive characteristics of the particular binder employed. In general, the amount of binder is about 5 to 25 percent and preferably about 12 to 18 percent, based on the weight of the pigment. The amount of additive varies with the amount and properties of the binder and the amount of insolubilization desired. In general, the additive is added at about 1 to 10 percent, and preferably about 3 to 7 percent, based on the weight of the binder (solids or dry basis). The total solids content of the paper coating composition generally is within the range of about 40 to 70 percent, depending upon the method of application and the product requirements.

The coating composition of this invention can be applied to paper or paper-like substrates by any known and convenient means.

EXAMPLE I

A blocked glyoxal resin, identified herein as Resin A, was prepared by reacting glyoxal with cyclic urea (4-hydroxy-5-methylpyrimidone) as follows. A two-liter flask was equipped with a mechanical stirrer, thermometer and condenser. To the flask was charged propionaldehyde (95.5 g, 1.64 moles) and 50% aqueous formaldehyde (98.7 g, 1.64 moles). As this mixture was stirred, a solution of 98.7 g (1.64 moles) of urea in 86.6 g of water was added. The reaction exothermed to 55° C. and was held there for 3 hours, becoming milky white. Sulfuric acid (40%, 19.5 g) was added causing the reaction to exotherm to 85° C., passing through a thickened state before thinning out again. After 2 hours, the reaction was clear amber. The temperature was held at 85° C. for another two hours. The reaction was cooled to 45° C. and 456 g (3.1 moles) of 40% glyoxal was added. This was heated to 65°-70° C. for 1 hour and vacuum stripped to 50% solids. The pH was adjusted to 5.0 with caustic soda and solids adjusted to 45%. A clear, amber solution was obtained.

EXAMPLE II

A blocked glyoxal resin, identified herein as Resin B, was obtained by reacting glyoxal with ethylene urea as follows. A one-liter flask was fitted with a mechanical stirrer, thermometer and condenser. To this was charged 290 g (2.0 moles) of 40% glyoxal and 90 g (1.05 moles) of ethylene urea. This was stirred as the pH was adjusted to 4.0 to 5.0 with sodium bicarbonate. The reaction was heated to 50°-60° C. for 2 hours. The pH was then adjusted to 2.5 with 40% sulfuric acid and held at 50°-60° C. for 3 more hours. After cooling to 35° C., the pH was adjusted to 5.0 with 25% caustic soda. Solids were adjusted to 45% with 110 g of water. This was filtered to afford a clear, light yellow solution.

EXAMPLE III

A polymer, identified herein as Polymer A, was prepared by copolymerizing acrylamide and methacrylic acid as follows. A two-liter resin kettle was equipped with a mechanical stirrer, N₂ sparge, condenser, thermometer and two addition funnels. To the kettle was charged 280 g of water and 114 g of isopropanol. This mixture was heated to 70° C. and sparged with nitrogen. As the mixture was heating, 261 g of 50% acrylamide (1.84 moles), 10 g (0.11 moles) of methacrylic acid, and 279 g of deionized water were mixed together and charged to one funnel. To the other funnel was charged a mixture of 54 g of deionized water and 1.34 g of ammonium persulfate. The contents of the two funnels were added simultaneously over a 1.5 hour period. During this addition and for two hours thereafter the temperature was held as 70° C. The reaction mixture was then cooled to 30° C. and the pH adjusted from 4.2 to 5.5 with caustic soda. The polymer had a Brookfield viscosity of 60 cps with a #2 spindle at 50 rpm and 200 cps with #2 spindle at 100 rpm and had a solids level of 17.6% by weight.

EXAMPLE IV

A N-hydroxy propyl acrylamide polymer, identified herein as Polymer B, was prepared by reacting propionaldehyde with polyacrylamide as follows. A one-liter flask was fitted with a nitrogen sparge, mechanical stirrer, condenser and 2 addition funnels. To the flask was charged 599 g of deionized water and 12 g of isopropanol. This was sparged with nitrogen and heated to 70° C. To one addition funnel was charged 160 g of 50% acrylamide. To the other was charged a solution of 0.8 g of ammonium persulfate in 32 g of deionized water. The contents of the two funnels were added simultaneously over 1 hour. The reaction was held at 70° C. for another two hours, then cooled. The finished product had a Brookfield viscosity of 70 cps with a #2 spindle at 50 rpm and a solids level of 12% by weight.

A portion of this product (185.1 g) was placed in a 250 ml flask with a magnetic stirrer, pH probe and thermometer, then cooled to 15° C. The pH was adjusted to 10.0 with caustic soda solution. To this was added 3 g (approx. 20 mole % with respect to acrylamide) of propionaldehyde over a 10 minute period. The pH was maintained at 10.0 and held there for 1 hour. The pH was then adjusted to 6.0 with acetic acid.

EXAMPLE V

A mixture was made of 3 parts by weight of Resin A and 1 part by weight of Polymer A. Liquid chromatography showed that the product was a mixture and that the components had not reacted. A similar mixture was made of Resin B and Polymer A, and was also found to be a mixture.

EXAMPLE VI

Binder additives were prepared containing as a blocked glyoxal resin either Resin A or Resin B, mixed with one of the following polymers: a 1:1 copolymer of acrylamide and N-methylol acrylamide; and poly(N-methylol acrylamide). These binder additives when added to a coating composition all gave coatings that were superior (better wet rub, higher pick strength, better smoothness, more porosity, better gloss and brightness) to a control coating composition containing

a conventional insolubilizer which comprised a cyclic urea-glyoxal reaction product.

EXAMPLE VII

One part Polymer B was blended with 3 parts Resin B to give a binder additive with superior coating properties. Dry pick results were particularly impressive.

EXAMPLE VIII

Paper coatings compositions were prepared either as a high latex coating containing 4 parts starch (Penford Gum 280, hydroxyethylated corn starch) and 8 parts latex (Dow 620, styrene-butadiene copolymer) or as a high starch coating containing 9 parts starch (Penford Gum 280) and 3 parts latex (Dow 620). Each coating composition also contained 50 parts No. 1 clay, 50 parts No. 2 clay and 0.15% Dispex N-40 (sodium polyacrylate dispersant). A binder additive was added where indicated at a level of 4% by weight of the starch. For comparison, certain coating samples used a commercial starch insolubilizer (Sunrez 700C, a cyclic urea-glyoxal reaction product blended with glyoxal and propylene glycol) as the additive. Paper was coated with a blade coater and tested as indicated below. The object was to produce a high starch coating that had properties similar to the high latex coating. The following coating samples 1-8 were high starch or high latex coatings containing the identified additive.

| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|------------------|----|----|----|----|----|----|----|----|
| Gloss | 64 | 63 | 56 | 58 | 57 | 54 | 68 | 55 |
| Smoothness | 26 | 22 | 31 | 23 | 24 | 20 | 18 | 30 |
| IGT Dry Pick | 84 | 84 | 62 | 66 | 72 | 68 | 77 | 65 |
| Wet rub, spec 20 | 85 | 90 | 51 | 55 | 68 | 76 | 83 | 55 |
| Brightness | 82 | 81 | 81 | 81 | 82 | 82 | 82 | 82 |
| Porosity | 15 | 20 | 35 | 33 | 38 | 25 | 23 | 38 |
| Crock (Rank) | 3 | 2 | 4 | 5 | 1 | 7 | 6 | 8 |
| Printed Gloss | 87 | 86 | 80 | 77 | 80 | 82 | 86 | 80 |

1 high latex, no additive;
2 high latex, with Sunrez 700C;
3 high starch, no additive;
4 high starch, with Sunrez 700C;
5 high starch, with Resin A;
6 high starch, with Resin B;
7 high starch, with Polymer A/Resin B mixture (1:6.75 by dry weight ratio); and
8 high starch, with Polymer A

These results show that the binder additive of this invention containing a mixture of blocked glyoxal resin and polymer (Sample 7) gave a high starch paper coating with performance that closely matches that of the more expensive high latex coatings of Samples 1 and 2. It further shows that the addition to a high starch coating of the blocked glyoxal resin alone (Samples 4, 5 and 6) or polymer alone (Sample 8) does not give the performance of either a high starch coating containing the binder additive of this invention (Sample 7) or a high latex coating (Samples 1 and 2). The enhanced synergistic performance of the binder additive of this invention is an unexpected benefit. A coating product formulated with a binder additive containing a mixture of Resin A and Polymer A showed similar results to the binder additive containing the mixture of Polymer A and Resin B above.

EXAMPLE IX

A reaction product of polyacrylamide, glyoxal and urea was prepared as follows. To a 400 ml beaker was charged 121.5 g (0.84 moles) of 40% glyoxal and 18.0 g (0.21 moles) of ethylene urea. The pH was adjusted to 6.0 and allowed to stir one hour. The pH was then adjusted to 7.9, and 150 g of polyacrylamide (11% solids, RV viscosity, #1 spindle at 50 rpm is 66 cps) was

added. This stirred one hour with pH dropping to 6.1. Propylene glycol (15.9 g) was added with 98g of water, reducing the solids to 32%. This reaction product compared with the Resin A/Polymer A blend of Example V (32% solids). The reaction product performed reasonably well when tested shortly after preparation; however, it gelled in less than one month. In contrast, the Resin A/Polymer A blend was still fluid after 6 weeks. The short shelf life of the reaction product is probably due to insufficiently blocked glyoxal.

EXAMPLE X

A reaction product, similar to those produced in U.S. Pat. No. 4,544,609, of polyacrylamide, glyoxal and urea was produced as follows. Polyacrylamide (150 g, 14% solids, 0.29 moles, RV viscosity #2 spindle at 50 rpm is 40 cps) and 17.7 g urea (0.29 moles) were mixed together and heated to 60° C. The pH was 4.7. Over a one hour period, 128 g (0.88 moles) of 40% glyoxal was added, maintaining 60° C. After the glyoxal was added, the pH was adjusted to 4.0 and held at 60° C. for 3 hours. Solids were 30.6%. This reaction product also gelled in about 1 month.

What is claimed is:

- 25 1. An additive for binders for paper coating compositions which comprises:
a blocked glyoxal resin, which is the reaction product of a glyoxal and a blocking component, mixed with a vinyl or acrylic water soluble polymer which is reactive with free glyoxal, the amounts being within the ratio of 25:1 to 1:2 parts by dry weight of the blocked glyoxal resin to the polymer.
2. Additive of claim 1 wherein the blocking component is selected from the group consisting of urea, cyclic urea, carbamate, glycol, polyol containing at least three hydroxy groups and unalkylated or partially alkylated polymeric glyoxal derived glycol.
3. Additive of claim 2 wherein the blocking component is a urea or cyclic urea.
- 40 4. Additive of claim 3 wherein the polymer has a molecular weight of less than 100,000 daltons.
5. Additive of claim 1 wherein the polymer is made from a monomer selected from the group consisting of acrylamide, 2-hydroxyethyl acrylate, methacrylamide, 45 N-substituted acrylamide and N-substituted methacrylamide and co- and ter- polymers thereof.
6. Additive of claim 5 wherein the polymer is a copolymer of the monomer of claim 5 with a monomer selected from the group consisting of acrylic acid, acrylonitrile, crotonic acid, fumaric acid, itaconic acid, maleic acid, methacrylic acid, monoethyl maleate, vinyl pyrrolidone, vinyl sulfonic acid, vinyl acetate, and C-1 to C-4 alkyl esters of acrylic or methacrylic acid.
7. Additive of claim 4 wherein the polymer is a copolymer of acrylamide and methacrylic acid.
- 55 8. Additive of claim 4 wherein the polymer contains acrylamide reacted with an aldehyde selected from the group consisting of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and isobutyraldehyde.
- 60 9. Additive of claim 5 wherein the ratio of blocked glyoxal resin to polymer is within the range of 10:1 to 1:1 parts by dry weight.
10. Additive of claim 1 wherein mole ratio of glyoxal to blocking component is within the range of 4:1 to 1:2.
- 65 11. Additive of claim 3 wherein the mole ratio of glyoxal to blocking component is within the range of 2:1 to 1:1.

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ФЕДЕРАЛЬНАЯ СЛУЖБА
ПО ИНТЕЛЛЕКТУАЛЬНОЙ СОБСТВЕННОСТИ

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(54) СПОСОБ ВОССТАНОВЛЕНИЯ НЕДОСТАЮЩИХ ЧАСТЕЙ ЛИСТОВ БУМАГИ

(57) Реферат:

Изобретение относится к бумажной промышленности. Для реставрации листов проводят их подготовку, подготовку волокнистой массы со связующим, отлив волокнистой массы со связующим на недостающие части листа и сушку листа. При этом в качестве связующего используют бактериальную целлюлозу, культивированную штаммом Acetobacter xylinum BKM B-880 в

количестве 2-6% от массы абсолютно сухой сульфатной хвойной беленой целлюлозы. После отлива листы подвергают сушке при температуре 80°C. Способ позволяет повысить прочность шва между восполняющей частью и реставрируемым документом. Прочность шва сохраняется на высоком уровне после 12 суток искусственного тепло-влажного старения при температуре 80°C и влажности 65%. 2 з.п. ф-лы, 2 табл., 8 пр.

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(54) METHOD TO RESTORE MISSING PARTS OF PAPER SHEETS

(57) Abstract:

FIELD: textiles, paper.

SUBSTANCE: for restoration paper sheets they are prepared, pulp with a binder is prepared, pouring of the pulp with the binder on the missing parts of the sheet, and drying the sheet. At that, as a binder, bacterial cellulose is used cultured by strain Acetobacter xylinum B-880 of All-Russian collection of microorganisms, in the amount of 2-6%

by weight of oven-dry softwood sulfate bleached pulp. After pouring the sheets are dried at a temperature of 80°C. Seam strength remains at high level after 12 days of artificial thermo-humid at a temperature of 80°C and humidity 65%.

EFFECT: method enables to improve the seam strength between the compensative part and the restored document.

3 cl, 2 tbl, 8 ex

R U 2 4 7 2 8 9 1 C 1

Изобретение относится к способам восстановления недостающих частей листов бумаги при механизированной реставрации книг, карт, гравюр, газет, рукописных и архивных материалов методом восполнения утраченных частей листа и предназначено для использования в практике работы крупных книгохранилищ, архивов и в целлюлозно-бумажной промышленности.

В настоящее время большинство крупных реставрационных подразделений в мире располагают аппаратурой для механизированной реставрации методом долива утраченных частей листов документов. Одним из недостатков метода является невысокая прочность шва между старой и восполняемой частью листа. Для упрочнения шва в бумажную массу можно вводить различные связующие.

В патенте СА №1.279.450 описан способ использования бактериальной целлюлозы в качестве связующего для получения нетканых и бумагоподобных материалов из различных волокон, в том числе из волокон растительного происхождения.

15 Определено оптимальное количество вводимой в массу бактериальной целлюлозы - 20%. Также заявлен способ культивирования бактериальной целлюлозы в динамических условиях. Однако в данном патенте не исследовалось влияние добавок бактериальной целлюлозы на прочность шва между старой и восполняемой частью

20 листа при механизированной реставрации документов и влияние на прочность шва ускоренного тепло-влажного старения.

В настоящей заявке бактериальную целлюлозу, предлагаемую к использованию в качестве связующего в бумажную массу для механизированной реставрации документов, получают путем поверхностного культивирования

25 штамма *Gluconacetobacter xylinus* ВКМ В 880. Наногель-пленка бактериальной целлюлозы (НГПЦ GX) получена на питательных средах, содержащих в качестве источника углерода отходы или полуотходы производств, имеющих моносахара, например гидролизат древесины или щелока целлюлозно-бумажного производства

30 (патент RU №2189394, опубл. 20.09.2002). Способ реализован на модельной установке для производства НГПЦ GX.

Наиболее близким по технической сущности и техническому результату является способ восстановления недостающих частей листов бумаги (А.С. №1151635, Опубл. 23.04.85, Бюл. №15), включающий подготовку реставрируемых листов, отлив

35 волокнистой массы со связующим на недостающие части листа, прессование и сушку с одновременным растворением связующего, при этом в качестве связующего используют поливинилспиртовые волокна. Известная добавка обеспечивает повышение производительности реставрационных работ при сохранении

40 качественных показателей листов. Однако известный способ требует особого режима прессования и сушки бумаги для набухания и растворения поливинилспиртовых волокон. Кроме того, поливинилспиртовые волокна как связующее хорошо зарекомендовали себя при введении в бумажную массу только из хлопковой целлюлозы в количестве не более 10% к массе целлюлозного волокна (Бланк М.Г.

45 Поливинилспиртовые волокна как связующее при механизированной реставрации бумаги // Теория и практика сохранения книг в библиотеке, вып.6, Л, ГПБ, 1974, с 87-105.)

Технической задачей и положительным результатом данного способа являются

50 повышение механической прочности шва между документом и восполняющей частью при использовании бумажной массы из сульфатной беленой хвойной целлюлозы, стабильность прочности шва в процессе искусственного тепло-влажного старения, а также исключение процесса прессования и упрощение процесса сушки бумаги.

Указанная задача и положительный результат достигаются за счет того, что способ восстановления недостающих частей листов бумаги включает подготовку реставрируемых листов, подготовку волокнистой массы со связующим, отлив волокнистой массы со связующим на недостающие части листа и сушку листа, отличающийся тем, что для повышения прочности шва между восполняющей частью и реставрируемым листом документа в качестве связующего используют бактериальную целлюлозу, культивированную штаммом *Gluconacetobacter xylinus* ВКМ

В 880 в количестве 2-6% от массы абсолютно сухой сульфатной хвойной беленой целлюлозы. Способ характеризуется тем, что НГПЦ ГХ предварительно подвергают распуску в течение 100-120 мин с последующим размолом: рафинирующий размол 20-30 мин, рубка 1-3 мин при концентрации 0,2%.

Реализация предлагаемого способа восстановления недостающих частей листов бумаги, иллюстрируется следующими примерами его осуществления.

Пример 1-8. Подготовку бумажной массы проводят следующим способом: сульфатную беленую хвойную целлюлозу распускают и размалывают до 35 и 45° ШР, затем в размолотую массу добавляют подготовленную ЦГХ в количестве 2-6% к массе абсолютно сухого волокна, перемешивают в течение 10-15 минут и используют для долива недостающих частей на реставрационной машине РОМ-4. ЦГХ подвергают распуску в течение 100-120 минут с последующим размолом (рафинирующий размол в течение 20-30 минут и рубка в течение 1-3 минут). Распуск и размол проводят при концентрации 0,2%. В качестве модельных образцов документов для реставрации использовали листы книги начала XX в. из сульфитной целлюлозы и листы документа первой половины XIX в. из тряпичной полумассы. Предварительно обработанные реставрируемые листы укладывают на сетку, подают массу с волокнистым связующим и производят отлив под вакуумом. При этом, в результате фильтрации воды сквозь сетку волокна заполняют незанятые листами участки сетки. Затем отлитый лист подвергают сушке при температуре 80°C (щадящий режим для документов).

Результаты определения прочности шва между реставрируемым документом и восполняющей частью представлены в таблице 1.

Таблица 1

| Прочность шва между реставрируемым документом и восполняющей частью | | | | | | | | |
|---|--|------|------|------|------|------|--|------|
| Показатели | Примеры | | | | | | | |
| | №1 | №2 | №3 | №4 | №5 | №6 | №7 | №8 |
| Основа композиции | Сульфатная беленая хвойная целлюлоза (35°ШР) | | | | | | Сульфатная беленая хвойная целлюлоза (45°ШР) | |
| Вид добавки | ЦГХ | | | | | | ЦГХ | |
| Количество добавки | 0 | 2 | 4 | 6 | 0 | 2 | 4 | 6 |
| Разрушающее усилие шва с листами документа начала ХХ в., Н | 1,5 | 3,7 | 4,0 | 4,0 | 3,5 | 6,0 | 6,2 | 6,2 |
| Разрушающее усилие шва с листами документа начала первой половины XIX в., Н | 9,5 | 15,5 | 16,0 | 16,0 | 11,0 | 18,7 | 19,5 | 20,5 |

Анализ экспериментальных результатов, представленных в таблице 1, показывает, что введение ЦГХ в композицию бумажной массы для механизированной реставрации документов (примеры 1-8) способствует повышению прочности шва между восполняемой и восполняющей частями листа документа. Так, при содержания ЦГХ в количестве 2-4% в композиции бумажной массы прочность шва при реставрации документа начала ХХ в. увеличивается в 2,5-2,7 раза (примеры 2, 3) и в 1,7-1,8 раза

(примеры 6, 7), при реставрации документа начала первой половины XIX в. - в 1,6-1,8 раза (примеры 2, 3, 6, 7).

Для исследования стабильности прочности шва в процессе хранения образцы подвергали искусственному тепло-влажному старению в камере «ТАВАИ». Режим старения соответствовал стандарту ISO 56-30: 1986 «Бумага. Картон. Ускоренное старение (4.3). Обработка влажным теплом при температуре 80°C и относительной влажности 65%». Искусственное старение проводили в течение 12 суток. Результаты испытаний представлены в таблице 2.

Из таблицы 2 видно, что прочность шва между восполняющей частью, содержащей добавки, ЦГХ и документом после 12 суток тепло-влажного старения остается выше (примеры 2-4, 6-8), чем с восполняющей частью, не содержащей добавки ЦГХ (примеры 1, 5).

| Таблица 2 Прочность шва между реставрируемым документом и восполняющей частью после 12 суток искусственного тепло-влажного старения | | | | | | | | |
|--|--|------|------|------|--|------|------|------|
| Показатели | Примеры | | | | | | | |
| | №1 | №2 | №3 | №4 | №5 | №6 | №7 | №8 |
| Основа композиции | Сульфатная беленая хвойная целлюлоза (35°ШР) | | | | Сульфатная беленая хвойная целлюлоза (45°ШР) | | | |
| Вид добавки | ЦГХ | | | | ЦГХ | | | |
| Количество добавки | 0 | 2 | 4 | 6 | 0 | 2 | 4 | 6 |
| Разрушающее усилие шва с листами документа начала ХХ в., Н | 1,0 | 2,0 | 2,0 | 2,2 | 2,5 | 3,5 | 3,5 | 3,5 |
| Разрушающее усилие шва с листами документа начала первой половины XIX в., Н | 7,5 | 11,0 | 12,5 | 12,5 | 8,5 | 15,0 | 15,0 | 16,0 |

Формула изобретения

1. Способ восстановления недостающих частей листов бумаги, включающий подготовку реставрируемых листов, подготовку волокнистой массы со связующим, отлив волокнистой массы со связующим на недостающие части листа и сушку, отличающийся тем, что для повышения прочности шва между восполняющей частью и реставрируемым листом документа в качестве связующего используют бактериальную целлюлозу, культивированную штаммом *Gluconacetobacter xylinus* ВКМ В-880 в количестве 2-6% от массы абсолютно сухой сульфатной беленой хвойной целлюлозы.

2. Способ по п.1, отличающийся тем, что бактериальную целлюлозу предварительно подвергают роспуску в течение 100-120 мин с последующим размолом: рафинирующий размол 20-30 мин, рубка 1-3 мин при концентрации массы 0,2%.

3. Способ по п.1, отличающийся тем, что комплекс: реставрируемый лист плюс восполняющая часть подвергают искусственному тепло-влажному старению при температуре 80°C и влажности 65% в течение 12 суток, после этого проверяют прочность шва.



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DESCRIPTION RU2472891

METHOD FOR RESTORING MISSING PARTS OF PAPER SHEETS

The invention relates to methods for recovering the missing parts of paper sheets during the mechanized restoration of books, maps, prints, newspapers, manuscripts and archival materials by the method of replenishing the lost parts of the sheet and is intended for use in the practice of large book depositories, archives and in the pulp and paper industry.

Currently, most major restoration divisions in the world have equipment for mechanized restoration by adding to the lost parts of sheets of documents. One of the disadvantages of the method is the low strength of the seam between the old and the replenished part of the sheet. To strengthen the seam in the paper pulp, you can enter various binders.

CA patent No. 1,279,450 describes a method for using bacterial cellulose as a binder for the production of non-woven and paper-like materials from various fibers, including from fibers of plant origin. The optimal amount of bacterial cellulose introduced into the mass was determined - 20%. A method for cultivating bacterial cellulose under dynamic conditions is also claimed. However, this patent did not investigate the effect of bacterial cellulose additives on the strength of the joint between the old and the replenished part of the sheet during mechanized restoration of documents and the effect on the strength of the joint of accelerated warm-wet aging.

In this application, bacterial cellulose, proposed for use as a binder in a paper pulp for mechanized restoration of documents, is obtained by surface cultivation of a strain of *Gluconacetobacter xylinus* BKM B 880. Nanogel-film of bacterial cellulose (НГПЦ GX) was obtained on nutrient media containing waste or semi-waste from monosugar production as a carbon source, for example, wood hydrolyzate or pulp and paper liquor production (patent RU No. 2189394, publ. 20.09.2002). The method is implemented on a model plant for the production of NGPTs GX.

The closest in technical essence and technical result is a method of restoring the missing parts of sheets of paper (A.S. No. 1151635, Publ. 23.04.85, Bull. No. 15), including the preparation of restored sheets, the casting of the pulp with a binder onto the missing parts of the sheet, pressing and drying with the simultaneous dissolution of the binder, while polyvinyl alcohol fibers are used as the binder. Known additive provides increased productivity of restoration work while maintaining the quality indicators of the sheets. However, the known method requires a special mode of pressing and drying paper for swelling and dissolving polyvinyl alcohol fibers. In addition, polyvinyl alcohol fibers as a binder have proven themselves when introduced into paper pulp only from cotton pulp in an amount of not more than 10% by weight of cellulose fiber (Blank M.G. Polyvinyl alcohol fibers as a binder in mechanized paper restoration // Theory and Practice of Book Preservation in the library, issue 6, L, GPB, 1974, pp. 87-105.

)

The technical task and the positive result of this method is to increase the mechanical strength of the seam between the document and the replenishing part when using pulp of sulphate bleached softwood pulp, stability of the strength of the seam during artificial heat-wet aging, as well as the elimination of the pressing process and simplification of the drying process of paper.

This task and a positive result are achieved due to the fact that the method of restoring the missing parts of the paper sheets includes preparing the restored sheets, preparing the pulp with a binder, casting the pulp with a binder to the missing parts of the sheet and drying the sheet, characterized in that to increase the strength of the seam between the bacterial cellulose cultured with the *Gluconacetobacter xylinus* BKM B 880 strain in an amount of 2-6% by weight of abs understood softwood kraft dry bleached pulp. The method is characterized in that NGPC GX is preliminarily dissolved for 100-120 minutes, followed by grinding: refining grinding 20-30 minutes, chopping 1-3 minutes at a concentration of 0.2%.

The implementation of the proposed method for recovering the missing parts of sheets of paper is illustrated by the following examples of its implementation.

Example 1-8. The paper pulp is prepared in the following way: sulfate bleached softwood pulp is dissolved and milled to 35 and 45 ° C, then the prepared CGX is added to the ground pulp in an amount of 2-6% by weight of absolutely dry fiber, mixed for 10-15 minutes and used for topping up the missing parts on the ROM-4 restoration machine. CGX is subjected to dissolution for 100-120 minutes, followed by grinding (refining grinding for 20-30 minutes and chopping for 1-3 minutes). Dissolution and grinding is carried out at a concentration of 0.2%. As model samples of documents for restoration, sheets of a book from the beginning of the 20th century were used. from sulphite pulp and sheets of the document of the first half of the XIX century. from rag half mass. The pre-treated restoration sheets are laid on a grid, the mass is fed with a fibrous binder, and vacuum casting is performed. At the same time, as a result of filtering water through the grid, the fibers fill unoccupied sheets of the grid. Then the cast sheet is dried at a temperature of 80 ° C (sparing mode for documents).

The results of determining the strength of the seam between the restored document and the replenishing part are presented in table 1.

Table 1 Strength of the seam between the restored document and the replenishing part Indicators Examples No. 1 No. 2 No. 3 No. 4 No. 5 < SEP> No. 6 No. 7 No. 8 Basis of composition Sulfated bleached softwood pulp (35 ° SR) Sulfated bleached softwood pulp (45 ° SR) Type of additive <SEP> TSGX TSGX Additive amount 0 2 4 6 0 2 4 6 Destructive seam force with sheets of a document from the beginning of the 20th century, N 1,5 3,7 4,0 4,0 3,5 6,0 6,2 6,2 Destructive force of a seam with sheets of a document from the beginning of the first half of the 19th century, H 9.5 15.5 16.0 16.0 11.0 18.7 19.5 20,5

Analysis of the experimental results presented in table 1 shows that the introduction of UGX in the composition of the paper pulp for mechanized restoration of documents (examples 1-8) helps to increase the strength of the seam between the filled and filling parts of the sheet of the document. So, when the content of CGX in the amount of 2-4% in the composition of the paper pulp, the strength of the seam during restoration of the document of the beginning of XX century. increases by 2.5-2.7 times (examples 2, 3) and 1.7-1.8 times (examples 6, 7), with the restoration of the document beginning of the first half of the XIX century. - 1.6-1.8 times (examples 2, 3, 6, 7).

To study the stability of the weld strength during storage, the samples were subjected to artificial warm-wet aging in a TABAI chamber. The aging regime was in accordance with ISO 56-30: 1986 "Paper. Cardboard. Accelerated Aging (4.3)." "Wet heat treatment at a temperature of 80 ° C and a relative humidity of 65%." Artificial aging was carried out for 12 days. The test results are presented in table 2.

From table 2 it is seen that the strength of the seam between the replenishing part containing additives, CGX and the document after 12 days of warm-wet aging remains higher (examples 2-4, 6-8) than with the replenishing part, not containing additives CGX (examples 1 , 5).

Table 2 Strength of the seam between the restored document and the replenishing part after 12 days of artificial warm-wet aging Indicators Examples No. 1 No. 2 No. 3 No. 4 No. 5 No. 6 No. 7 No. 8 Basis of composition Sulfated bleached softwood pulp (35 ° SR) Sulfated bleached softwood pulp (45 ° SR) Type of additive ЦГХ ЦГХ Amount of additive 0 2 4 6 0 2 4 6 Destructive force of a seam with sheets of a document from the beginning of the 20th century, H 1,0 2,0 2,0 2,2 2,5 < SEP> 3,5 3,5 3,5 Destructive force of a seam with sheets of a document of the beginning of the first half of the 19th century, N 7.5 11.0 12.5 12.5 8.5 15.0 15.0 <SEP> 16,0



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CLAIMS RU2472891

1.

A method of recovering missing parts of paper sheets, including preparing restored sheets, preparing pulp with a binder, casting the pulp with a binder into the missing parts of the sheet and drying, characterized in that bacterial cellulose is used as a binder to increase the strength of the seam between the filling part and the restored sheet of the document cellulose cultivated with a strain of *Gluconacetobacter xylinus* VKM B-880 in an amount of 2-6% by weight of absolutely dry sulphate bleached softwood pulp.

2.

The method according to claim 1, characterized in that the bacterial cellulose is first subjected to dissolution for 100-120 minutes, followed by grinding: refining grinding 20-30 minutes, chopping 1-3 minutes at a mass concentration of 0.2%.

3.

The method according to claim 1, characterized in that the complex: the restored sheet plus the replenishing part is subjected to artificial warm-wet aging at a temperature of 80 ° C and a humidity of 65% for 12 days, after which the strength of the seam is checked.



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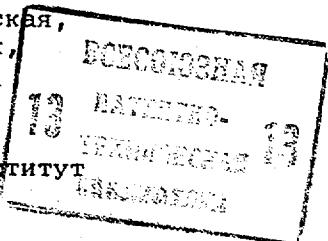
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(54) ВОЛОКНИСТАЯ МАССА ДЛЯ ИЗГОТОВЛЕНИЯ РЕСТАВРАЦИОННОЙ БУМАГИ

1

Изобретение относится к получению волокнистой массы для изготовления реставрационной бумаги, которая предназначена для восстановления недостающих частей листа книг, рукописей, произведений искусства, выполненных на бумажной основе.

В настоящее время для реставрации документов используют бумаги из различных полуфабрикатов, например из сульфатной беленой целлюлозы, хлопковой беленой целлюлозы [1].

Известные бумаги имеют высокую степень белизны, однако при использовании для реставрации документов их необходимо оттенять под цвет реставрируемого материала, например, обрабатывать с поверхности синтетическими красителями или экстрактами растительного происхождения, содержащими окрашенные вещества, например водными экстрактами чая или кофе. Таким образом, удается получить бумагу от светло-желтого до интенсивно коричневого цвета.

Наиболее близкой к изобретению по технической сущности и достигаемому положительному эффекту является волокнистая масса для изготовления реставрационной бумаги, содержащая

сульфатную хвойную беленую целлюлозу и облагороженную низкозольную хвойную целлюлозу [2].

В качестве облагороженной низкозольной целлюлозы волокнистая масса содержит сульфитную беленую облагороженную целлюлозу с зольностью 0,5-1,5% при следующем соотношении компонентов, мас.%: сульфатная беленая целлюлоза 75; сульфитная беленая облагороженная целлюлоза 25.

Недостатком известной волокнистой массы является то, что полученная из нее бумага требует дополнительной обработки красителями. Готовую бумагу необходимо выдерживать в течение 30 с в ванне с красителем, затем сушить таким образом, чтобы предотвратить коробление. Кроме того, указанная бумага сравнительно легко поддается старению.

Целью изобретения является повышение долговечности бумаги.

Поставленная цель достигается тем, что согласно изобретению волокнистая масса для изготовления реставрационной бумаги, содержащая сульфатную хвойную беленую целлюлозу и облагороженную низкозольную хвойную целлюлозу, согласно изобретению в качестве

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облагороженной низкозольной хвойной целлюлозы содержит сульфатную небеленую хвойную целлюлозу с зольностью 0,05-0,8% при следующем соотношении компонентов, мас.%: сульфатная беленая хвойная целлюлоза 50-95 и сульфатная небеленая хвойная целлюлоза с зольностью 0,05-0,8% 5-50.

Границные значения содержания введенной в композицию бумаги сульфатной небеленой целлюлозы определены пределами колористических свойств бумаги, подверженной естественному старению. Введение в композицию бумажной массы менее 5% сульфатной небеленой целлюлозы практически не меняет белизны и желтизны бумаги, а содержание в композиции бумажной массы более 50% указанной целлюлозы снижает белизну бумаги до 45%, что практически не характерно для старинных бумаг.

В качестве облагороженной низкозольной целлюлозы предлагаемая бумажная масса содержит целлюлозу, подвергнутую кислотному облагораживанию. Содержание минеральных примесей в целлюлозе в пределах 0,05-0,8% обусловлено невозможностью получения в производственных условиях зольности менее 0,05%, а зольность более 0,8% отрицательно влияет на долговечность бумаги. pH водной вытяжки хвойной сульфатной целлюлозы должна находиться в пределах 7,2-8,5. Указанные границы являются оптимальными с точки зрения достижения минимальной скорости старения.

Для придания бумаге необходимых физико-механических свойств в композицию бумажной массы вводят химические добавки: различного рода наполнители, проклеивающие вещества и коагулирующие вещества. Обязательным условием изготовления реставрационных видов бумаги является проведение процесса отлива в нейтральной или слабо-щелочной среде.

Пример 1. В волокнистую массу, содержащую, мас.%: сульфатная небеленая целлюлоза ГОСТ 5186-74 (марки ЭК-2) 20 с зольностью 0,45% и pH водной вытяжки 8,1 и сульфатная беленая целлюлоза ГОСТ 3914-60 (марки АС-1) 80, размолотые раздельно до 46°ШР, вводят минеральный наполнитель - мел в количестве 10% от массы волокна, канифольный клей в количестве 1% от массы волокна. Величину pH до 7,2 регулируют введением алюмината натрия и сульфата алюминия. На экспериментальной машине отливают бумагу массой 80 г/м². Бумагу в исходном состоянии и после ускоренного термического старения (72 ч при 105°C) подвергают испытаниям на оптические и физико-механические свойства.

Пример 2. В волокнистую массу, содержащую, мас.%: сульфатная небеленая целлюлоза с зольностью 0,05-5 (pH водной вытяжки 7,2) и сульфатная беленая целлюлоза 95, размолотые раздельно до 43°ШР, вводят минеральный наполнитель - каолин в количестве 20% от массы волокна и канифольный клей в количестве 2% от массы волокна. В качестве коагулянта используют уксуснокислую соль продукта конденсации дициандиамида и формальдегида в количестве 1% от массы волокна. Величину pH регулируют введением сульфата алюминия. Из подготовленной бумажной массы получают бумагу массой 60 г/м² и испытывают ее, как в примере 1.

Пример 3. В волокнистую массу, содержащую, мас.%: сульфатная небеленая целлюлоза с содержанием золы 0,8% 50 (pH водной вытяжки 8,5); сульфатная беленая целлюлоза 50, размолотые отдельно до 50°ШР, вводят мел в количестве 5% от массы волокна и канифольный клей в количестве 2% от массы волокна. Величину pH регулируют до 8,0. В качестве коагулянта используют алюминат натрия. Из приготовленной бумажной массы получают бумагу массой 60 г/м² и испытывают, как в примере 1.

Пример 4 (контрольный). В волокнистую массу, содержащую, мас.%: сульфатная небеленая целлюлоза (марки НС-1) с содержанием золы 1,5% 30 (pH водной вытяжки 7,0) и сульфатная беленая целлюлоза (марки АС-1) 70, размолотые раздельно до 48°ШР, вводят минеральный наполнитель - каолин в количестве 10% от массы волокна и канифольный клей в количестве 1%. Величину pH регулируют при помощи сернокислого алюминия до значения 7,0. В качестве коагулянта используют алюминат натрия. Из приготовленной бумажной массы получают бумагу массой 80 г/м² и испытывают, как в примере 1.

Пример 5 (прототип). Составляют композицию, содержащую, мас.%: сульфатная беленая целлюлоза 75 и сульфитная беленая облагороженная целлюлоза 25. На бумагоделательной машине изготавливают бумагу аналогично примеру 1. Полученную бумагу подвергают тонированию в ванне, содержащей 40 мл прямого красителя, коричневого светопрочного концентраций 1 г/л, 100 мл NaCl, концентраций 10 г/л, 12 мл Na₂CO₃ (10 г/л) и 848 мл дистиллированной воды. Тонирование проводят при температуре 50°C в течение 30 с. Бумагу высушивают на воздухе и затем подвергают старению.

Результаты испытаний бумаги по примерам 1-5 приведены в таблице.

Волокнистая масса для изготовления реставрационной бумаги обеспечивает получение бумаги с широким спектром белизны и оттенков желтизны. Полученная бумага хорошо сопротивляется старению, о чем свидетельствует показатель излома, который практически не меняется в период искусственного старения, в то время как из приведенных ранее работ и результатов испытаний бумаги по прототипу следует, что этот показатель уменьшается значительно (в прототипе в 2-3 раза). Повышение долговечности бумаги подтверждается также меньшим снижением белизны после искусственного старения. Так белизна тонированного реставрационного материала по прототипу снижается от 49 до 45,4% (на 3,6%), тогда как у реставрационного материала при близкой белизне по прототипу 49,5 имеет место снижение белизны после старения на 0,8% (пример 3).

| Состав волокна по примерам | Белизна бумаги, % | | Желтизна бумаги, % | | Излом бумаги, число двойных перегибов | |
|-------------------------------|----------------------|-------------------|-----------------------|-------------------|---|-------------------|
| | исход- ной | после старения | исходной | после старения | исходной | после старения |
| 1 | 58,0 | 56,7 | 10,2 | 12,8 | 67,0 | 65,0 |
| 2 | 74,0 | 70,3 | 9,0 | 12,6 | 37,0 | 36,0 |
| 3 | 49,5 | 48,7 | 10,6 | 12,6 | 147,0 | 143,0 |
| 4 | 76,3 | 69,8 | 11,6 | 14,5 | 46,0 | 20,0 |
| Прототип | | | | | | |
| а) исходная | 81,3 | 78,8 | 8,3 | 11,8 | 83,0 | 42,0 |
| б) тонированная | 49,0 | 45,4 | 12,4 | 16,8 | 61,0 | 23,0 |

Формула изобретения

Волокнистая масса для изготовления реставрационной бумаги, содержащая сульфатную хвойную беленую целлюлозу и облагороженную низкозольную хвойную целлюлозу, отличающаяся тем, что, с целью повышения долговечности бумаги, она содержит в качестве облагороженной низкозольной хвойной целлюлозы сульфатную небеленую хвойную целлюлозу с зольностью 0,05-0,8% при следующем соот-

5 Из примера 4 видно, что использование небеленой сульфатной целлюлозы с зольностью выше 0,8% не приводит к желаемому результату, т.е. падение показателей белизны, желтизны и излома при хранении бумаги более интенсивное, чем при использовании сульфатной небеленой целлюлозы с содержанием золы в пределах от 0,05 - до 0,8%.

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Падение желтизны реставрационного материала по прототипу составляет 4,4%, тогда как у материала из предлагаемой бумажной массы желтизна 15 после старения падает на 2-2,9%, что свидетельствует о долговечности предлагаемого реставрационного материала.

20 Кроме того, предлагаемая композиция позволяет упростить технологию получения реставрационного материала, так как исключается операция тонирования при сохранении колористических свойств материала.

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ношении компонентов мас.%: сульфатная беленая хвойная целлюлоза 50-95 и сульфатная небеленая хвойная целлюлоза с зольностью 0,05-0,8% 5-50.

Источники информации, принятые во внимание при экспертизе

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Patent Translate

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DESCRIPTION SU979564

Pulp for making restoration paper

The enriched low-ash softwood pulp contains sulfate unbleached softwood pulp with an ash content of 0.05-0.8% in the following ratio of components, wt.-%: Sulfated bleached softwood pulp 50-95 and sulfate unbleached softwood pulp with ash, 8% 5-50. The boundary values of the content of sulfate and unbleached pulp introduced into the paper composition are determined by the limits of coloristic properties, paper subject to natural aging. The introduction of less than 5% sulfate unbleached pulp into the paper pulp composition does not practically change the whiteness and yellowness of the paper, and the content of more than 50% of the pulp in the paper pulp composition reduces the whiteness of the paper to 45%, which is practically not typical for old papers. As an enriched low-ash pulp, the proposed paper pulp contains cellulose subjected to acid treatment. The content of mineral impurities in the cellulose in the range of 0.05-0.8% is due to the impossibility of obtaining an ash content of less than 0.05% under industrial conditions, and an ash content of more than 0.8% . negatively affects paper trading. The pH of the aqueous extract of softwood sulphate pulp should be in the range of 7.2-8.5. these boundaries are optimal from the point of view of achieving a minimum aging rate.

To give the paper the necessary physical and mechanical properties, chemical additives of various kinds, fillers, sizing agents and coagulating substances are introduced into the paper pulp composition. A prerequisite for the manufacture of restoration types of paper is the process of ebb in a neutral or semi-alkaline environment. , Example 1. In fiber pulp, May su, containing, wt.-%: GOST .5186-74 sulfate unbleached pulp GOST .5186-74 (grade EK-2) 20 with an ash content of 0.45% and 8.1 aqueous extract pH and GOST 3914-60 bleached bleached pulp (mark AC-1) 80, grinded separately to .46ShR, a mineral filler is introduced - chalk in the amount of 10% by weight of the fiber, rosin glue in the amount of 1% by weight of the fiber. The pH value to 7.2 is regulated by the introduction of sodium aluminate and aluminum sulfate. On an experimental machine, paper 6 was cast with a weight of 80 g / m. The paper in its original state and after accelerated thermal aging (72 h at) is subjected to tests for optical and physico-mechanical properties.

6 Example 2 Into the pulp, containing, wt.-%: Sulfate unbleached pulp with an ash content of 0.05-5 (water extract 7.2) and sulfate bleached pulp 95, milled separately to, a mineral filler is introduced - kaolin in an amount of 20% by weight of fiber and rosin glue in an amount of 2% by weight of fiber. The coagulant used is the acetic acid salt of the condensation product of dicyandiamide and formaldehyde in an amount of 1% by weight of fiber. The pH value is regulated by the introduction of aluminum sulfate. From the prepared pulp, paper is obtained with a mass of 60 g / m and it is tested, as in example 1. PRI me R 3, In the pulp containing, wt.% Sulfate and bleached pulp with an ox content of 0.8% 50 (pH of an aqueous extract of 8.5). bleached sulphate pulp 50, ground separately, is added chalk in an amount of 5% by weight of fiber. a and rosin glue in an amount of 2% by weight of fiber. The pH is adjusted to 8.0. Sodium aluminate is used as a coagulite. From the prepared pulp, a paper of mass 6 O g / m is obtained and tested as in Example 1.

Example 4 (control). Into pulp containing May. %: sulfate unbleached pulp (grade NS-1) with an ash content of 1.5% 30 (pH of aqueous extract 7.0) and sulfate bleached pulp (grade AC-1) 70, milled separately to 48, introduce a mineral filler - kaolin in an amount of 10% by weight of fiber and rosin glue in an amount of 1%. The value of pR is regulated using aluminum sulfate to a value of 7.0. Sodium aluminate is used as a coagulant. From the prepared pulp get paper mass of 80 test, as in example 1. Example 5 (prototype). A composition is prepared containing, in wt.-%: Sulfate bleached pulp 75 and sulfite bleached enriched jcellulose 25. Paper is made on papermaking MaBmHe in the same manner as in Example 1. The resulting paper is subjected to thinning in a bath containing 40 MP of direct dye, brown lightfast concentration of 1 g / l, 100 ml of NaCl, concentration of 10 g / l, 12 ml (10 g / l) and 848 ml of distilled water. Toning is carried out at a temperature for 30 s.

The paper is dried in air and then aged.

The test results of the paper according to examples 1-5 are shown in the table.

The pulp for the manufacture of restoration paper provides paper with a wide range of whiteness and shades of yellowness. The resulting paper resists aging well, as evidenced by the kink index, which practically does not change during artificial aging, while from the previous works and the results of testing the paper on the prototype it follows that this figure decreases significantly (in the prototype by 2-3 times) The increased durability of the paper is also confirmed by a lower decrease in whiteness after artificial aging. So the whiteness of the tinted restoration material according to the prototype decreases from 49 to 45.4% (by 3.6%), while the restoration material with a close whiteness according to the prototype 49.5 has a decrease in whiteness after aging by 0.8% (example 3)

From example 4 it is seen that the use of unbleached sulfate pulp with an ash content above 0.8% does not lead to KejriaeMOMy result, that is, the decrease in whiteness, yellowness and kink during paper storage is more intense than when using sulfate unbleached pulp with ash content in ranging from 0.05 to 0.8%.

The fall in the yellowness of the restoration material according to the prototype is 4.4%, while in the case of material from the proposed paper pulp, the yellowness 15 after aging drops by 2-2, (indicates the durability of the proposed restoration material).

20 In addition, the proposed composition allows to simplify the technology of obtaining restoration material, as the operation of tinting while maintaining color

25 material properties.



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(54) 발명의 명칭 복합체 조성물 및 복합체

(57) 요약

본 발명의 복합체 조성물은 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하는 복합체 조성물로서, 상기 섬유상 필러의 평균 섬유 지름이 4~1000nm인 것을 특징으로 한다. 상기 섬유상 필러는 셀룰로오스 섬유인 것이 바람직하다. 또, 셀룰로오스 섬유는 셀룰로오스 원료를 화학 처리 및 기계적 처리 중 적어도 한쪽에 의해 미세하여 얇어진 섬유인 것이 바람직하고, 포함되는 셀룰로오스 문자 중의 수산기의 일부가 알데히드기 및 카르복실기 중 적어도 한쪽으로 산화되어 있는 것이 바람직하다. 본 발명의 복합체는 이와 같은 복합체 조성물을 성형해서 이루어진 것이다.

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특허청 구의 범위

청구항 1

평균 섬유 지름이 4~1000nm인 셀룰로오스 섬유와,

상기 셀룰로오스 섬유와 혼합된, 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하는 복합체 조성물로서,

상기 셀룰로오스 섬유는 셀룰로오스 원료에 대하여 공산화제를 작용시킴으로써 미세화시키고, 셀룰로오스 분자 중의 수산기의 일부를 알데히드기 및 카르복실기 중 적어도 한쪽으로 산화하여 이루어진 것임을 특징으로 하는 복합체 조성물.

청구항 2

청구항 1에 있어서,

상기 알데히드기 및 상기 카르복실기 양의 총합은 상기 셀룰로오스 섬유의 중량에 대해 0.2~2.2mmol/g인 복합체 조성물.

청구항 3

청구항 1에 있어서,

상기 셀룰로오스 섬유는 추가로 셀룰로오스 원료를 기계적 처리함으로써 미세화시킨 것인 복합체 조성물.

청구항 4

청구항 1에 있어서,

상기 셀룰로오스 섬유는 천연 셀룰로오스를 상기 셀룰로오스 원료로서 준비하고, N-옥실 화합물을 산화 촉매로서 이용함과 함께, 수중에서 상기 천연 셀룰로오스에 대하여 상기 공산화제를 작용시킴으로써 상기 천연 셀룰로오스를 산화하여 얻어진 것인 복합체 조성물.

청구항 5

청구항 1에 있어서,

상기 셀룰로오스 섬유는 I형 결정 구조를 가지는 복합체 조성물.

청구항 6

청구항 1에 있어서,

상기 수지는 가소성 수지 및 경화성 수지 중 적어도 한쪽인 복합체 조성물.

청구항 7

청구항 1에 있어서,

상기 수지는 에폭시 수지를 포함하는 것인 복합체 조성물.

청구항 8

청구항 1에 있어서,

상기 수지는 폐놀 수지를 포함하는 것인 복합체 조성물.

청구항 9

청구항 1에 있어서,

상기 수지는 커플링제 및 이 커플링제의 가수분해물 중 적어도 한쪽을 포함하는 것인 복합체 조성물.

청구항 10

청구항 9에 있어서,

상기 커플링제는 알록시실란 또는 알록시티탄인 복합체 조성물.

청구항 11

청구항 1에 있어서,

상기 금속 산화물의 평균 입경이 1~1000nm인 복합체 조성물.

청구항 12

청구항 1에 있어서,

상기 금속 산화물은 이산화규소인 복합체 조성물.

청구항 13

청구항 1에 있어서,

상기 박편상 무기 재료는 운모, 베미큘라이트, 몬모릴로나이트, 철 몬모릴로나이트, 바이델라이트, 사포나이트, 헥토라이트, 스티븐사이트, 논트로나이트, 마가디아이트, 일러라이트, 카네마이트, 스멕타이트 및 충상 티탄산 중에서 선택되는 1종 이상인 복합체 조성물.

청구항 14

청구항 1에 있어서,

상기 복합체 조성물에서의 상기 셀룰로오스 섬유의 함유율은 0.1~99.9중량%인 복합체 조성물.

청구항 15

청구항 1에 있어서,

두께 30μm에서의 전광선 투과율이 80% 이상인 복합체 조성물.

청구항 16

청구항 1에 있어서,

30°C 내지 180°C에서의 열팽창 계수가 50ppm/°C 이하인 복합체 조성물.

청구항 17

청구항 1 내지 청구항 16 중 어느 한 항에 기재된 복합체 조성물을 성형해서 이루어지며, 두께가 10~2000μm인 것을 특징으로 하는 복합체.

청구항 18

청구항 17에 있어서,

30°C 내지 150°C에서의 열팽창 계수가 0.4~50ppm/°C인 복합체.

청구항 19

청구항 17에 있어서,

습도 팽창 계수가 100ppm/습도% 이하인 복합체.

영 세 시

기 술 문 앙

[0001] 본 발명은 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하는 복합체 조성물 및 복합체에 관한 것이다.

제 1 기술 분야

[0002] 수지의 열선행착 계수의 저감, 또는 탄성률, 휨 강도 등의 기계적 강도를 올리기 위해서 구상 필러나 섬유상 필러를 배합하는 것이 널리 행해지고 있다. 근래, 종래의 마크로필러를 대신하는 재료로서 실리카 미립자나 금속 미립자 등의 구상의 미립자나, 막대 모양의 워스커 타입의 나노사이즈 필러에 관한 연구가 한창이다. 그렇지만 이들 필러에 대하여 섬유상의 나노 재료에 대한 연구는 보고가 적다.

[0003] 근래, 셀룰로오스를 이용한 플라스틱 대체품이 많이 보고되고 있다. 예를 들면, 고압 호모지나이저로 불리는 극히 높은 압력을 부여할 수 있는 장치를 이용하여 셀룰로오스의 피브릴상 물질을 고도로 미세화해 얻어진 셀룰로오스의 마이크로피브릴을 충전재로서 이용한 복합체, 그 외 마이크로플루이저법, 글라인더법, 동결 건조법, 강선 탄력 혼련법, 볼밀 분쇄법에 의해 다운사이징한 셀룰로오스의 마이크로피브릴을 충전재로서 이용한 복합체를 들 수 있다. 이를 충전재를 이용하면 비교적 강도가 높은 성형체가 얻어진다는 보고가 되고 있다(예를 들면, 특허문헌 1 참조).

[0004] 그렇지만, 종래의 마이크로피브릴화 방법에서는 다운사이징 처리에 다대한 에너지를 필요로 하여 비용적으로 불리한 동시에, 얻어지는 미세화 섬유의 섬유 지름에도 비교적 넓은 분포가 존재해 미세화의 정도도 불완전하다. 경우에 따라서는 $1\mu\text{m}$ 이상의 굽은 섬유도 약간 남는 경우가 있기 때문에, 마이크로피브릴 섬유 지름이나 밀도에서 특히 넓은 분포가 존재해 성형품의 강도에서 절대값의 저하나 격차가 생기는 경우가 있다.

[0005] 또, 특허문헌 2에 기재되어 있듯이 균이 생성되는 박테리아 셀룰로오스를 이용하여 투명하고 저선행착률을 가지는 섬유 강화 복합 재료가 얻어지는 것이 알려져 있다. 그렇지만, 전술한 기계적으로 셀룰로오스 마이크로피브릴을 얻는 경우와 마찬가지로, 생산 속도가 늦고 공업적 관점으로부터 생각하면 반드시 유리하다고는 말할 수 없다.

[0006] 또, 셀룰로오스는 섬유 표면에 수산기를 다수 가지기 때문에 친수성이 높고, 흡수시에 치수나 물성이 크게 변화된다. 이 때문에, 흡수시에는 복합 재료의 치수나 물성도 크게 변화해 복합 재료의 용도가 한정된다는 문제가 존재하고 있다.

성형기술 분야

특허문헌

[0007] (특허문헌 0001) 일본 공개특허 2003-201695호 공보

(특허문헌 0002) 일본 공개특허 2005-60680호 공보

발명의 내용

제 1 개혁하는 과제

[0008] 본 발명의 목적은 저열행착 계수, 고강도, 고투명성, 저습도 행착 계수(고내수성)를 가지는 복합체 조성물 및 그 성형체인 복합체를 생산 효율적으로 제공하는 것에 있다.

과제의 해결 수단

[0009] 상기 목적을 달성하기 위해서, 본 발명은

섬유상 필러와,

- [0011] 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하는 복합체 조성물로서,
- [0012] 상기 섬유상 필러의 평균 섬유 지름이 4~1000nm인 것을 특징으로 하는 복합체 조성물이다.
- [0013] 또, 본 발명의 복합체 조성물에서는 상기 섬유상 필러는 셀룰로오스 섬유인 것이 바람직하다.
- [0014] 또, 본 발명의 복합체 조성물에서는 상기 셀룰로오스 섬유는 셀룰로오스 원료를 화학 처리 및 기계적 처리 중 적어도 한쪽에 의해 미세화하여 얻어진 섬유인 것이 바람직하다.
- [0015] 또, 본 발명의 복합체 조성물에서는 상기 셀룰로오스 섬유는 포함되는 셀룰로오스 분자 중의 수산기의 일부가 알데히드기 및 카르복실기 중 적어도 한쪽으로 산화되어 있는 것이 바람직하다.
- [0016] 또, 본 발명의 복합체 조성물에서는 상기 셀룰로오스 섬유는 천연 셀룰로오스를 원료로 하고, N-옥실 화합물을 산화 촉매로서 이용하는 동시에, 수중에서 상기 원료에 공산화제를 작용시킴으로써 상기 원료를 산화하여 얻어진 것이 바람직하다.
- [0017] 또, 본 발명의 복합체 조성물에서는 상기 수지는 가소성 수지 및 경화성 수지 중 적어도 한쪽인 것이 바람직하다.
- [0018] 또, 본 발명의 복합체 조성물에서는 상기 수지는 에폭시 수지를 포함하는 것이 바람직하다.
- [0019] 또, 본 발명의 복합체 조성물에서는 상기 수지는 폐놀 수지를 포함하는 것이 바람직하다.
- [0020] 또, 본 발명의 복합체 조성물에서는 상기 수지는 커플링제 및 이 커플링제의 가수분해물 중 적어도 한쪽을 포함하는 것이 바람직하다.
- [0021] 또, 본 발명의 복합체 조성물에서는 상기 커플링제는 알콕시실란 또는 알콕시티탄인 것이 바람직하다.
- [0022] 또, 본 발명의 복합체 조성물에서는 상기 금속 산화물의 평균 입경이 1~1000nm인 것이 바람직하다.
- [0023] 또, 본 발명의 복합체 조성물에서는 상기 금속 산화물은 이산화규소인 것이 바람직하다.
- [0024] 또, 본 발명의 복합체 조성물에서는 상기 박편상 무기 재료는 운모, 베미큘라이트, 몬모릴로나이트, 철 몬모릴로나이트, 바이엘라이트, 사포나이트, 헥토라이트, 스티븐사이트, 녹트로나이트, 마가디아이트, 일러라이트, 카네마이트, 스黠타이트 및 층상 티탄산 중에서 선택되는 1종 이상인 것이 바람직하다.
- [0025] 또, 본 발명의 복합체 조성물에서는 상기 복합체 조성물에서의 상기 섬유상 필러의 함유율은 0.1~99.9중량%인 것이 바람직하다.
- [0026] 또, 본 발명의 복합체 조성물에서는 두께 30μm에서의 전광선 투과율이 80% 이상인 것이 바람직하다.
- [0027] 또, 본 발명의 복합체 조성물에서는 30°C 내지 180°C에서의 열팽창 계수가 50ppm/°C 이하인 것이 바람직하다.
- [0028] 상기 목적을 달성하기 위해서, 본 발명은 상기 복합체 조성물을 성형해서 이루어지며, 두께가 10~2000μm인 것을 특징으로 하는 복합체이다.
- [0029] 또, 본 발명의 복합체에서는 30°C 내지 150°C에서의 열팽창 계수가 0.4~50ppm/°C인 것이 바람직하다.
- [0030] 또, 본 발명의 복합체에서는 습도 팽창 계수가 100ppm/습도% 이하인 것이 바람직하다.

발명을 실시하기 위한 구체적인 내용

- [0031] 이하, 본 발명의 복합체 조성물 및 복합체의 바람직한 실시형태에 대해서 상세하게 설명한다.
- [0032] 본 발명의 복합체 조성물은 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함한다. 그리고, 본 발명의 복합체는 이 복합체 조성물을 소정의 형상으로 성형함으로써 제조된 것이다.
- [0033] <복합체 조성물>
- [0034] (섬유상 필러)
- [0035] 우선, 섬유상 필러에 대해서 설명한다.
- [0036] 본 발명에 이용되는 섬유상 필러의 평균 섬유 지름은 4~1000nm이고, 4~300nm인 것이 바람직하며, 4~200nm인 것

이 보다 바람직하다. 또한, 평균 섬유 지름이 상기 상한값을 웃돌면 투명성이 악화되는 동시에 기계적인 강도의 향상이 보여지지 않는다. 한편, 평균 섬유 지름이 상기 하한값을 밀돌아도 상관없지만, 그러한 섬유상 필러를 얻는 것은 곤란하다.

[0037] 본 발명에 이용되는 섬유상 필러의 길이에 대해서는 특별히 한정되지 않지만, 섬유상 필러의 평균 길이가 100nm 이상이면 보강 효과가 얻어지기 쉬워 강도의 향상이 도모된다.

[0038] 여기서, 섬유상 필러의 평균 섬유 지름의 측정은 이하와 같이 하여 실시할 수 있다.

[0039] 우선, 고형분율로 0.05~0.1중량%인 섬유상 필러의 분산체를 조제하고, 이 분산체를 카본막 피복 그리드 상에 캐스트하여 TEM 관찰용 시료로 한다. 또, 큰 섬유 지름의 섬유상 필러를 포함하는 경우에는 유리 상에 캐스트하여 SEM 관찰용 시료로 해도 된다.

[0040] 현미경 관찰시에는 구성하는 섬유상 필러의 크기(섬유 지름)에 따라 5000배, 10000배 혹은 50000배 중 어느 하나의 배율로 전자 현미경 화상을 취득한다. 이때에 얻어진 화상 내에 종횡 임의의 화상 폭의 축을 상정했을 경우에 적어도 축에 대해 20개 이상의 섬유상 필러가 축과 교차하도록 시료 조건 및 관찰 조건(배율 등)을 설정한다.

[0041] 그리고, 이 조건을 만족하는 관찰 화상에 대해 1매의 화상당 종횡 2개씩의 무작위인 축을 끌어 각 축에 교차하는 섬유상 필러의 섬유 지름을 눈으로 봐서 읽어낸다. 또한, 시료 표면에 대해서 서로 중복하지 않도록 관찰 위치를 옮기면서 최저 3매의 관찰 화상을 취득해 각 화상에 대해서 각각 상기와 같이 하여 섬유 지름을 읽어낸다. 이에 의해, 최저 20개×2×3=120개의 섬유상 필러에 대해서 섬유 지름의 정보가 얻어진다. 이와 같이 하여 얻어진 섬유 지름의 데이터에 기초하여 평균 섬유 지름을 산출한다.

[0042] 본 발명에 이용되는 섬유상 필러는 어떠한 섬유여도 되지만, 바람직하게는 셀룰로오스 섬유로 구성된 것이다.

[0043] 셀룰로오스 섬유로는 천연 셀룰로오스 섬유, 재생 셀룰로오스 섬유 등을 들 수 있다. 한편, 셀룰로오스 섬유 이외의 섬유로는 예를 들면, 키친 섬유, 키토산 섬유 등을 들 수 있다.

[0044] 이 중, 천연 셀룰로오스 섬유로는 침엽수나 광엽수로부터 얻어지는 정제 펄프, 코튼 런터나 코튼 런트로부터 얻어지는 셀룰로오스 섬유, 바로니아나 시오그사 등의 해초로부터 얻어지는 셀룰로오스 섬유, 호야로부터 얻어지는 셀룰로오스 섬유, 박테리아를 생산하는 셀룰로오스 섬유 등을 들 수 있다. 한편, 재생 셀룰로오스 섬유로는 천연 셀룰로오스 섬유를 일단 용해한 후, 셀룰로오스 조성인 채로 섬유상으로 재생한 것을 들 수 있다.

[0045] 또, 본 발명에 이용되는 셀룰로오스 섬유는 고결정성인 것이 바람직하게 이용된다. 이와 같은 셀룰로오스 섬유는 특히 선행창률이 작고, 기계적 강도가 높아지기 때문에 섬유상 필러로서 바람직하게 이용된다. 또한, 이러한 관점으로부터 본 발명에 이용되는 셀룰로오스 섬유로는 재생 셀룰로오스 섬유보다도 천연 셀룰로오스 섬유가 바람직하다.

[0046] 또, 본 발명에 이용되는 셀룰로오스 섬유로는 공지의 어떠한 방법으로 얻어진 것이어도 되고, 그 제법은 특별히 한정되지 않지만, 일례로서 셀룰로오스 원료(천연 셀룰로오스 또는 재생 셀룰로오스)를 매체 교반 밀 처리장치, 진동 밀 처리 장치, 고압 호모지나이저 처리 장치, 초고압 호모지나이저 처리 장치 등의 각종 미세화 장치에 의해 기계적으로 미세화한 것이 이용된다. 또, 다른 방법으로서 일렉트로스피닝법, 스팀제트법, APEX(등록 상표) 기술(Polymer Group. Inc.)법 등에 의해 얻어진 셀룰로오스 섬유를 이용할 수도 있다. 그렇지만, 에너지 효율 등을 고려하면, 셀룰로오스 원료로는 이하에 나타내는 화학적인 처리를 수반하는 방법에 의해 얻어진 셀룰로오스 섬유가 가장 바람직하다.

[0047] 이하에서 설명하는 셀룰로오스 섬유의 제작 방법은 셀룰로오스 원료에 화학적 처리를 실시한 후, 기계적 처리에 제공함으로써 분산매 중에 분산시켜 셀룰로오스 섬유(나노 셀룰로오스 섬유)를 제작하는 방법이다.

[0048] 구체적으로는 [1] 천연 셀룰로오스를 원료로 하고, 수중에서 N-옥실 화합물을 산화 촉매로 하여 공산화제를 작용시킴으로써 천연 셀룰로오스를 산화하여 반응물 섬유를 얻는 산화 반응 공정과, [2] 불순물을 제거하고 물을 함침시킨 반응물 섬유를 얻는 정제 공정과, [3] 물을 함침시킨 반응물 섬유를 분산매에 분산시키는 분산 공정을 가진다. 이하에 각 공정에 대해서 상세하게 설명한다.

[1] 산화 반응 공정

[0050] 우선, 산화 반응 공정에서는 수중에 셀룰로오스 원료를 분산시킨 분산액을 조제한다. 여기서, 이용되는 셀룰로오스 원료에는 미리 고해(叩解) 등의 표면적을 높이는 처리를 실시한 것이 바람직하게 이용된다. 이에 의해 반

응 효율을 높일 수 있어 생산성을 높일 수 있기 때문이다. 또, 셀룰로오스 원료로는 단리, 정제 후 네바드라이로 보존하고 있던 것을 사용하는 것이 바람직하다. 이에 의해, 셀룰로오스 원료를 구성하는 마이크로피브릴의 수렴체가 팽윤하기 쉬운 상태가 되기 때문에 역시 반응 효율을 높여 미세화 처리 후의 수 평균 섬유 지름을 작게 할 수 있다.

[0051] 또한, 본 공정에서의 셀룰로오스 원료의 분산매로서 물을 이용했을 경우, 분산액(반응 수용액) 중의 셀룰로오스 농도는 시약의 충분한 확산이 가능한 농도이면 임의이지만, 통상 분산액의 중량에 대해서 5중량% 이하이다.

[0052] 또, 셀룰로오스의 산화 촉매로서 사용 가능한 N-옥실 화합물은 다수 보고되고 있다. 예를 들면, 「Cellulose」 Vol. 10, 2003년, 제335~341페이지에서의 I.Shibata 및 A.Isoyai에 의한 「TEMPO 유도체를 이용한 셀룰로오스의 촉매 산화: 산화 생성물의 HPSEC 및 NMR 분석」이라는 제목의 기사에 기재된 TEMPO(2,2,6,6-테트라메틸-1-페페리딘-N-옥실), 4-아세트아미드-TEMPO, 4-카르복시-TEMPO 및 4-포스포노옥시-TEMPO의 각종 N-옥실계 화합물 촉매는 수중에서의 상온에서의 반응 속도에서 바람직하게 이용된다. 또한, 이들 N-옥실 화합물의 첨가는 촉매량으로 충분하고, 바람직하게는 0.1~4mmol/l, 보다 바람직하게는 0.2~2mmol/l의 범위에서 반응 수용액에 첨가된다.

[0053] 또, 공산화제로는 예를 들면, 차아할로겐산 또는 그의 염, 아할로겐산 또는 그의 염, 과할로겐산 또는 그의 염, 과산화수소 및 과유기산 등을 들 수 있지만, 특히 알칼리 금속 차아할로겐산염, 구체적으로는 차아염소산 나트륨이나 차아브롬산 나트륨 등이 바람직하게 이용된다. 차아염소산 나트륨을 사용하는 경우 브롬화 알칼리 금속, 예를 들어 브롬화 나트륨의 존재 하에서 반응을 진행시키는 것이 반응 속도에 있어서 바람직하다. 이 브롬화 알칼리 금속의 첨가량은 N-옥실 화합물에 대해서 바람직하게는 약 1~40배 몰량, 보다 바람직하게는 약 10~20배 몰량이 된다.

[0054] 또, 반응 수용액의 pH는 약 8~11의 범위에서 유지되는 것이 바람직하다. 수용액의 온도는 약 4~40°C의 범위에서 임의이지만, 반응은 실온에서 실시하는 것이 가능하고, 특히 온도 제어는 필요로 하지 않는다.

[0055] 공산화제에 의해 셀룰로오스 분자에는 수산기를 치환하도록 카르복실기가 도입되지만, 본 발명에 사용되는 미세 셀룰로오스 섬유를 얻음에 있어서는 셀룰로오스 원료의 종류에 따라 필요하게 되는 카르복실기 양이 상이하기 때문에 그것에 따라 공산화제의 첨가량이나 공산화제를 작용시키는 시간을 설정하면 된다. 구체적으로는 카르복실기 양이 많을수록 최종적으로 얻어지는 셀룰로오스 섬유의 최대 섬유 지름 및 수 평균 섬유 지름은 작아지므로, 그것을 고려해 설정하면 된다.

[0056] 예를 들면, 셀룰로오스 원료로서 목재 펄프 및 면계 펄프를 이용하는 경우, 필요하게 되는 카르복실기 양은 셀룰로오스 원료에 대해서 0.2~2.2mmol/g이며, 셀룰로오스 원료로서 박테리아 셀룰로오스(BC)나 호야로부터의 추출 셀룰로오스를 이용하는 경우, 필요하게 되는 카르복실기 양은 0.1~0.8mmol/g가 된다. 이와 같이 셀룰로오스 원료의 종류에 따라서 공산화제의 첨가량과 반응 시간을 제어함으로써 각 셀룰로오스 원료에 최적인 카르복실기 양을 도입할 수 있다.

[0057] 또한, 이상과 같은 카르복실기의 도입량에 근거하면, 공산화제의 첨가량을 유도할 수 있고, 일례로서 셀룰로오스 원료 1g에 대해서 약 0.5~8mmol의 공산화제를 첨가하는 것이 바람직하고, 반응 시간은 약 5~120분, 길어도 240분 이내로 하는 것이 바람직하다.

[0058] 또, 본 산화 반응 공정을 거친으로써, 셀룰로오스 분자에는 카르복실기가 도입되지만, 산화 처리의 진행 정도에 따라서는 알데히드기가 도입되는 경우도 있다. 따라서, 본 산화 반응 공정 종료 후 셀룰로오스 분자의 수산기는 알데히드기 및 카르복실기 중 적어도 한쪽으로 치환되어 있게 된다.

[2] 정제 공정

[0060] 정제 공정에 있어서는 반응 슬러리 중에 포함되는 반응물 섬유와 물 이외의 화합물, 구체적으로는 미반응 차아염소산이나 각종 부생성물 등과 같은 화합물을 계외로 제거하는 것을 목적으로 한다. 반응물 섬유는 통상 이 단계에서는 나노 섬유(nanofiber) 단위까지 뿐만 아니라 흩어지게 분산되어 있는 것은 아니기 때문에, 통상의 정제법, 즉 세정과 여과를 반복함으로써 고순도(99중량% 이상)화를 도모할 수 있다.

[0061] 본 정제 공정에서의 정제 방법은 원심 탈수를 이용하는 방법과 같이 상술한 목적을 달성할 수 있는 장치(예를 들면, 연속식 디켄더)이면 어떠한 장치를 이용해도 상관없다. 이렇게 하여 얻어지는 반응물 섬유는 쥐어짠 상태의 고형분(셀룰로오스) 농도로서 대략 10~50중량%의 범위에 있다. 또한, 이후의 공정에서 나노 섬유 단위로 분산시키는 것을 고려하면, 50중량%보다 높은 고형분 농도로 하는 것은 분산에 극히 높은 에너지가 필요해지기 때문에 바람직하지 않다.

- [0062] [3] 분산 공정
- [0063] 상술한 공정에 있어서는 물을 함침시킨 반응물 섬유가 얻어지지만, 이것을 용매 중에 분산시켜 분산 처리를 실시함으로써 본 발명에 이용되는 미세 셀룰로오스 섬유가 분산체 상태로 얻어진다.
- [0064] 여기서, 분산매로서의 용매는 통상은 물이 바람직하지만, 물 이외에도 목적에 따라 물에 가용되는 알코올류(메탄올, 에탄올, 이소프로판올, 이소부탄올, sec-부탄올, tert-부탄올, 메틸셀로솔브, 에틸셀로솔브, 에틸렌글리콜, 글리세린 등), 에테르류(에틸렌글리콜 디메틸에테르, 1,4-디옥산, 테트라히드로푸란 등), 켐톤류(아세톤, 메틸에틸케톤), N,N-디메틸포름아미드, N,N-디메틸아세트아미드, 디메틸설폭시드 등이어도 된다. 또, 이들 혼합물도 바람직하게 사용할 수 있다.
- [0065] 또, 상술한 반응물 섬유 용매에 의해 회석, 분산시킬 때에는 조금씩 용매를 가해 분산시켜 나간다는 단계적인 분산을 실시함으로써, 효율적으로 나노 섬유 레벨의 섬유의 분산체를 얻을 수 있다. 또한, 조작상 문제로부터 분산 공정 후에는 분산체가 접성이 있는 상태 혹은 겔상이 되도록 분산 조건을 선택하면 된다.
- [0066] 여기서, 분산 공정에서 사용되는 분산기로는 다양한 것을 사용할 수 있다. 구체예를 나타내면, 반응물 섬유에서의 반응의 진행도(알데히드기나 카르복실기로의 변환량)에도 의존하지만, 바람직하게 반응이 진행되는 조건 하에서는 스크류형 믹서, 페들 믹서, 디스퍼터형 믹서, 터빈형 믹서 등의 공업 생산기로서의 범용 분산기로 충분히 미세 셀룰로오스 섬유의 분산체를 얻을 수 있다.
- [0067] 또, 호모 믹서, 고압 호모지나이저, 초고압 호모지나이저, 초음파 분산 처리, 비터, 디스크형 리파이너, 코니칼형 리파이너, 더블 디스크형 리파이너, 그라인더와 같은 고속 회전 하에서 강력한 고해 능력을 가지는 장치를 사용함으로써, 보다 효율적이면서 고도의 다운사이징이 가능해진다. 나아가, 이를 장치를 사용함으로써 알데히드기나 카르복실기의 도입량이 비교적 작은 경우(예를 들면, 알데히드기나 카르복실기의 셀룰로오스에 대한 총 합량으로서 0.1~0.5mmol/g)에도, 고도로 미세화된 미세 셀룰로오스 섬유의 분산체를 제공할 수 있다.
- [0068] 다음에, 미세 셀룰로오스 섬유를 분산매 중에 분산시킨 분산체로부터 미세 셀룰로오스 섬유를 회수하는 방법에 대해서 설명한다.
- [0069] 구체적으로는 상술한 미세 셀룰로오스 섬유의 분산체를 건조시킴으로써 미세 셀룰로오스 섬유를 회수할 수 있다.
- [0070] 여기서 건조에는 예를 들면, 분산매가 물인 경우에는 동결 건조법, 분산매가 물과 유기용매의 혼합액인 경우에는 드럼 드라이어에 의한 건조나 경우에 따라서는 스프레이 드라이어에 의한 분무 건조를 바람직하게 사용할 수 있다.
- [0071] 또, 상술한 미세 셀룰로오스 섬유의 분산체 중에는 바인더로서 수용성 고분자(폴리에틸렌옥사이드, 폴리비닐알코올, 폴리아크릴아미드, 카르복시메틸 셀룰로오스, 히드록시에틸 셀룰로오스, 히드록시프로필 셀룰로오스, 메틸 셀룰로오스, 전분, 천연 검류 등), 당류(글루코오스, 프룩토오스, 만노오스, 갈락토오스, 트레할로오스 등)를 첨가하도록 해도 된다. 이를 바인더 성분은 극히 비점이 높고 게다가 셀룰로오스에 대해서 친화성을 가지기 때문에 이를 성분을 분산체 중에 첨가함으로써, 드럼 드라이어나 스프레이 드라이어와 같은 범용의 건조법으로 건조시켰을 경우에도, 재차 분산매 중에 분산시켰을 때의 응집이 방지되어 나노 섬유로서 분산된 미세 셀룰로오스 섬유의 분산체를 확실히 얻을 수 있다. 이 경우에는 분산체 중에 첨가되는 바인더의 양은 반응물 섬유에 대해서 10~80중량%의 범위에 있는 것이 바람직하다.
- [0072] 또한, 회수된 미세 셀룰로오스 섬유는 다시 분산매(물이나 유기용매 혹은 이들 혼합액) 중에 혼입하고 적당한 분산력을 가함으로써(예를 들면, 상술한 분산 공정에서 사용되는 각종 분산기를 이용한 분산을 실시함), 미세 셀룰로오스 섬유의 분산체로 할 수 있다.
- [0073] 본 발명에 사용되는 미세 셀룰로오스 섬유는 셀룰로오스의 수산기의 일부가 카르복실기 또는 알데히드기로 산화되어 있고, 또한 셀룰로오스 I형 결정 구조를 가지는 것이 바람직하다. 또한, 미세 셀룰로오스 섬유가 I형 결정 구조를 가지는 것은 천연 유래의 셀룰로오스 고체 원료를 표면 산화하여 미세화시킨 섬유인 것을 의미한다.
- [0074] 또, 미세 셀룰로오스 섬유가 I형 결정 구조를 가지는 것은 그 광각 X선 회절상 측정에 의해 얻어지는 회절 프로파일에 있어서, $2\theta=14\sim17^\circ$ 부근과 $2\theta=22\sim23^\circ$ 부근의 두 개의 위치에 전형적인 피크를 가지는 것에 기초하여 동정(同定)할 수 있다. 또한 미세 셀룰로오스 섬유의 셀룰로오스에 알데히드기 혹은 카르복실기가 도입되어 있는 것은 수분을 완전히 제거한 샘플에 대한 전반사식 적외 분광 스펙트럼(ATR)에서 카르보닐기에 기인하는 흡수

(1608cm⁻¹ 부근)가 존재함으로써 확인할 수 있다. 특히, 셀룰로오스에 산 형의 카르복실기(-COOH)가 도입되어 있는 경우에는 상기 측정에서 1730cm⁻¹에 흡수가 존재한다.

[0075] 미세한 셀룰로오스 섬유는 상술한 이유에 의해 셀룰로오스에 존재하는 카르복실기와 알데히드기 양의 총합이 많으면 많을수록, 보다 미소한 섬유 지름으로서 안정하게 존재할 수 있다. 예를 들면 목재 펄프나 면 펄프의 경우, 미세한 셀룰로오스 섬유에 존재하는 카르복실기와 알데히드기 양의 총합(이하, 생략해서 「총합량」이라고 함)이 셀룰로오스 섬유의 중량에 대해 0.2~2.2mmol/g, 바람직하게는 0.5~2.2mmol/g, 더욱 바람직하게는 0.8~2.2mmol/g이면, 나노 섬유로서의 안정성이 뛰어난 셀룰로오스 섬유가 얻어진다. 또, BC나 호야로부터의 추출 셀룰로오스와 같은 마이크로피브릴의 섬유 지름이 비교적 굵은 셀룰로오스의 경우(평균 섬유 지름이 수 10nm 수준)에는 총합량은 0.1~0.8mmol/g, 바람직하게는 0.2~0.8mmol/g이면, 나노 섬유로서의 안정성이 뛰어난 셀룰로오스 섬유가 얻어진다. 또한, 총합량이 상기 하한값보다도 작은 경우에는 종래 알려져 있는 미세화된 셀룰로오스 섬유와의 물성상 차이(예를 들면, 분산체에서의 분산 안정화 효과)도 작아지는 동시에 미소한 섬유 지름의 섬유로서 얻어지기 어려워지기 때문에 바람직하지 않다.

[0076] 또한, 비이온성 치환기인 알데히드기에 대해 카르복실기가 도입됨으로써 전기적인 반발력이 생겨난다. 이에 의해, 마이크로피브릴이 응집을 유지하지 않고 뿐뿐이 흩어지려고 하는 경향이 증대하기 때문에 나노 섬유의 분산체로서의 안정성은 보다 증대한다. 예를 들면 목재 펄프나 면 펄프의 경우, 미세한 셀룰로오스 섬유에 존재하는 카르복실기의 양이 셀룰로오스 섬유의 중량에 대해 0.2~2.2mmol/g, 바람직하게는 0.4~2.2mmol/g, 더욱 바람직하게는 0.6~2.2mmol/g이면, 나노 섬유로서의 안정성이 극히 뛰어난 셀룰로오스 섬유가 얻어진다. 또, BC나 호야로부터의 추출 셀룰로오스와 같은 마이크로피브릴의 섬유 지름이 비교적 굵은 셀룰로오스의 경우에는 카르복실기의 양은 0.1~0.8mmol/g, 바람직하게는 0.2~0.8mmol/g이면 나노 섬유로서의 안정성이 뛰어난 셀룰로오스 섬유가 얻어진다.

[0077] 여기서, 셀룰로오스 섬유의 중량에 대한 셀룰로오스의 알데히드기 및 카르복실기의 양(mmol/g)은 이하의 수법에 의해 평가한다.

[0078] 건조 중량을 정칭한 셀룰로오스 시료를 이용해 농도가 0.5~1중량%인 슬러리를 60ml 조제하고 0.1M의 염산 수용액에 의해 pH를 약 2.5로 한 후, 0.05M의 수산화나트륨 수용액을 적하하여 슬러리의 전기 전도도 측정을 실시한다. 이 측정은 pH가 약 11이 될 때까지 계속한다. 전기 전도도의 변화가 완만한 약산의 중화 단계에서 소비된 수산화나트륨 양(V)으로부터 아래 식을 이용해 관능기량을 산출한다. 여기서 산출된 관능기량을 「관능기량 1」이라고 한다. 이 관능기량 1이 카르복실기의 양을 나타낸다.

$$\text{관능기량}(\text{mmol/g}) = V(\text{ml}) \times 0.05 / \text{셀룰로오스의 중량(g)}$$

[0080] 다음에, 셀룰로오스 시료를 아세트산에 의해 pH 4~5로 조제한 2% 아염소산 나트륨 수용액 중에서 추가로 48시간 상온에서 산화하여, 상기 수법에 의해 다시 관능기량을 산출한다. 여기서 산출된 관능기량을 「관능기량 2」라고 한다. 그리고, 이 산화에 의해 추가된 관능기량(= 관능기량 2 - 관능기량 1)을 산출한다. 이 관능기량이 알데히드기의 양을 나타낸다.

[0081] (수지)

[0082] 본 발명에서 이용되는 수지로는 공지의 것을 이용할 수 있고, 특별히 한정되지는 않지만 각종 경화성 수지, 각종 가소성 수지, 각종 수용성 수지 등을 포함하는 것을 들 수 있다.

[0083] 수용성 수지로는 물에 용해되는 것이면 특별히 한정되지 않고, 열가소성 수지, 경화성 수지, 천연 고분자 등을 들 수 있지만, 바람직하게는 폴리비닐알코올, 폴리에틸렌옥시드, 폴리아크릴아미드, 폴리비닐피롤리돈과 같은 합성 고분자, 전분류, 알긴산류와 같은 다당류, 목재의 구성 성분인 헤미셀룰로오스, 젤라틴, 니카와, 카제인을 비롯한 단백질과 같은 천연 고분자 등을 들 수 있다.

[0084] 또, 열가소성 수지로는 특별히 한정되는 것은 아니지만, 예를 들면 염화비닐 수지, 아세트산비닐 수지, 폴리스티렌, ABS 수지, 아크릴 수지, 폴리에틸렌, 폴리에틸렌 테레프탈레이트, 폴리에틸렌 나프탈레이트, 폴리프로필렌, 불소 수지, 폴리아미드 수지, 열가소성 폴리아미드 수지, 폴리아세탈 수지, 폴리카보네이트, 폴리젖산, 폴리글리콜산, 폴리-3-히드록시 부티레이트, 폴리히드록시 발리레이트, 폴리에틸렌 아디페이트, 폴리카프로락톤, 폴리프로필락톤 등의 폴리에스테르, 폴리에틸렌글리콜 등의 폴리에테르, 폴리글루타민산, 폴리리진 등의 폴리아미드 등을 들 수 있다.

- [0085] 한편, 경화성 수지로는 예를 들면, 폐놀 수지, 우레아 수지, 멜라민 수지, 불포화 폴리에스테르 수지, 에폭시 수지, 아크릴 수지, 옥세탄 수지, 디알릴 프탈레이트 수지, 폴리우레탄 수지, 규소 수지, 말레이미드 수지, 열경화성 폴리이미드 수지 등을 들 수 있다.
- [0086] 이 중, 아크릴 수지로는 아크릴산, 메타크릴산, 메틸 아크릴레이트, 메틸 메타크릴레이트와 같은 알킬 아크릴레이트 또는 알킬 메타크릴레이트 외, 환상 아크릴레이트 또는 메타크릴레이트, 히드록시에틸 아크릴레이트 등을 1종 이상 포함하는 수지를 들 수 있다.
- [0087] 또, 폐놀 수지는 분자 내에 폐놀성 수산기를 1개 이상 가지는 유기 화합물이다. 예를 들면, 노볼락이나 비스페놀류, 나프톨이나 나프톨을 분자 내에 가지는 수지, 파라크실릴렌 변성 폐놀 수지, 디메틸렌에테르형 레졸, 메틸올형 폐놀 등의 레졸 수지를 들 수 있다. 또, 이를 수지를 추가로 메틸올화시킨 화합물, 폐놀성 수산기를 1개 이상 포함하는 리그닌이나 리그닌 유도체, 리그닌 분해물, 또한 리그닌이나 리그닌 유도체, 리그닌 분해물을 변성한 것 혹은 이것들을 석유 자원으로부터 제조된 폐놀 수지와 혼합한 것을 포함하는 수지를 들 수 있다.
- [0088] 또, 에폭시 수지는 적어도 1개의 에폭시기를 가지는 유기 화합물이다. 예를 들면, 비스페놀 A형 에폭시 수지, 비스페놀 F형 에폭시 수지, 비스페놀 S형 에폭시 수지 등의 비스페놀형 에폭시 수지, 이를 비스페놀형 에폭시 수지의 수첨화물(水添化物), 디시클로펜타디엔 골격을 가지는 에폭시 수지, 트리글리시딜 이소시아누레이트 골격을 가지는 에폭시 수지, 카르드 골격을 가지는 에폭시 수지, 폴리실록산 구조를 가지는 에폭시 수지, 지환식 다관능 에폭시 수지, 수첨 비페닐 골격을 가지는 지환식 에폭시 수지, 수첨 비스페놀 A 골격을 가지는 지환식 에폭시 수지 등을 들 수 있다.
- [0089] 또, 본 발명에서 이용되는 수지는 각종 커플링제여도 된다.
- [0090] 커플링제로는 공지의 것을 이용할 수 있지만, 실란계 커플링제, 티탄계 커플링제, 지르코늄계 커플링제, 알루미늄계 커플링제 등을 들 수 있고, 이를 중에서도 실란계 커플링제 또는 티탄계 커플링제가 바람직하게 이용된다. 이것들은 비교적 입수가 용이하고, 무기 재료와 유기 재료의 계면에서의 접착성이 높기 때문에 복합체 조성물에 포함되는 커플링제로서 매우 적합하다.
- [0091] 또, 상기 커플링제 가운데 실란계 커플링제는 적어도 규소 원자를 1개 이상, 관능기로서 알콕시기를 1개 이상 포함하고 있는 것이 바람직하다. 또, 그 이외의 관능기로는 에폭시기 혹은 에폭시 시클로헥실기, 아미노기, 수산기, 아크릴기, 메타크릴기, 비닐기, 폐닐기, 스티릴기, 이소시아네이트기 등을 들 수 있다. 또한, 본 발명에 있어서는 커플링제와 동등한 효과가 얻어지는 것으로부터, 알콕시기를 4개 포함하는 테트라알콕시실란도 실란 커플링제에 포함된다.
- [0092] 실란계 커플링제의 구체예로는 테트라알콕시실란 화합물, 메틸트리알콕시실란, 디메틸디알콕시실란과 같은 알킬기 함유 알콕시실란 화합물, 3-글리시독시프로필 트리알콕시실란, 3-글리시드프로필메틸 디알콕시실란, 2-(3,4-에폭시시클로헥실)에틸 트리알콕시실란 등의 에폭시실란 화합물, 3-아미노프로필 트리알콕시실란, N-페닐-3-아미노프로필 트리알콕시실란과 같은 아미노알콕시실란 화합물, 3-아크릴옥시프로필 트리알콕시실란, 메타크릴옥시프로필 트리알콕시실란, 3-메타크릴옥시프로필메틸 디알콕시실란, 3-메타크릴옥시프로필 트리알콕시실란과 같은 (메타)아크릴알콕시실란 화합물, 비닐트리알콕시실란과 같은 비닐알콕시실란 화합물, 폐닐트리알콕시실란, 디페닐디알콕시실란, 4-히드록시페닐 트리알콕시실란과 같은 폐닐기 함유 트리알콕시실란 화합물, 3-이소시아네이트프로필 트리알콕시실란과 같은 스티릴기 함유 알콕시실란 화합물 등이 예시된다. 이를 중에서도, 테트라알콕시실란 화합물, 알킬기 함유 알콕시실란 화합물, 폐닐기 함유 알콕시실란 화합물이 내수성을 높이는 효과가 높아 바람직하다.
- [0093] 한편, 티탄계 커플링제의 구체예로는 알콕시실란 화합물과 동일한 치환기를 가지는 알콕시티탄 화합물을 들 수 있다. 예를 들면, 이소프로필 트리이소스테아로일 티타네이트, 이소프로필 트리도데실벤젠설헬포닐 티타네이트, 이소프로필 트리스(디옥틸파이로포스페이트) 티타네이트, 테트라이소프로필 비스(디옥틸포스페이트) 티타네이트, 테트라옥틸 비스(디트리테일포스페이트) 티타네이트, 이소프로필 트리옥타노일 티타네이트, 이소프로필 디메타크릴 이소스테아로일 티타네이트, 이소프로필 이소스테아로일 디아크릴티타네이트, 이소프로필 트리(디옥틸포스페이트) 티타네이트, 이소프로필 트리크실페닐 티타네이트, 이소프로필 트리(N-아미노에틸-아미노에틸) 티타네이트, 디쿠밀페닐옥시아세테이트 티타네이트, 디이소스테아로일 에틸렌티타네이트, 비스(디옥틸파이로포스페이트) 에틸렌티타네이트, 비스(디옥틸파이로포스페이트) 옥시아세테이트 티타네이트, 테트라(2,2-디알릴옥시메틸-1-부틸) 비스(디-트리테일) 포스페이트 티타네이트 등을 들 수 있다.
- [0094] 또, 커플링제 대신에 상술한 바와 같이 커플링제의 가수분해물을 이용해도 된다. 커플링제 또는 그 가수분해물

의 선택은 분산매 등과의 상용성, 가수분해물의 안정성 등을 감안해 적당히 실시하면 된다. 또한, 커플링제의 가수분해물은 아세트산 수용액 등의 산성 수용액을 커플링제와 교반 혼합함으로써 용이하게 작성할 수 있다. 또, 커플링제의 가수분해물로는 가수분해성기(알록시드기)를 가수분해한 것이 아니더라도 분자 구조가 커플링제의 가수분해물과 동일하면 어떠한 방법으로 제작된 것이어도 된다.

[0095] 또한, 상술한 수용성 수지, 열가소성 수지, 경화성 수지 및 커플링제는 각각 개별적으로 이용할 수도, 또는 2 이상을 조합해 이용할 수도 있다.

(금속 산화물)

[0097] 본 발명에서 이용되는 금속 산화물은 그 종류가 특별히 한정되는 것은 아니지만, SiO_2 (실리카), Al_2O_3 (알루미나), TiO_2 (티타니아), ZrO_2 (지르코니아) 등의 단일 금속의 산화물을 비롯해 $\text{SiO}_2\text{-}\text{Al}_2\text{O}_3$ (무라이트 등), $\text{SiO}_2\text{-}\text{TiO}_2$, $\text{SiO}_2\text{-}\text{ZrO}_2$, 스페넬 등의 복합 산화물, 티타니아 내포 실리카, 지르코니아 내포 실리카 등을 들 수 있다.

[0098] 이와 같은 금속 산화물은 어떠한 형태를 이루고 있어도 되지만, 바람직하게는 입자상으로 된다. 이 경우, 금속 산화물의 입자를 1종의 산화물 미립자로 구성할 뿐만 아니라, 2종 이상의 산화물을 미립자를 혼합한 혼합물로 구성해도 된다. 이와 같은 산화물 미립자는 졸겔법, 습식법, 기상법, 건식법 등의 방법에 의해 얻을 수 있다.

[0099] 상기 금속 산화물 중에서도 특히 SiO_2 , Al_2O_3 혹은 이들의 복합 산화물을 이용하는 것이 바람직하다. 이것들은 비교적 저렴할 뿐만 아니라, 복합체의 기계적 강도, 내열성, 내마모성의 향상을 도모할 수 있다.

[0100] 특히, 복합체의 내마모성을 향상시키기 위해서는 금속 산화물로서 Al_2O_3 의 미립자를 이용하는 것이 바람직하다. 이 미립자는 가장 저렴하며, 또한 산 및 알칼리에 의한 부식에 강하기 때문에 복합체의 화학적 안정성을 높일 수 있다.

[0101] 또한, 복합체가 전자 부품 등의 용도에 제공되는 경우에는 금속 산화물로서 SiO_2 의 미립자(실리카 미립자)를 이용하는 것이 바람직하다. 이 미립자는 저유전율이기 때문에 복합체의 유전율을 저하시켜 전자 부품에서의 전송 지연 등을 억제할 수 있다.

[0102] 실리카 미립자로는 건조한 분말상의 실리카 미립자, 용매에 분산된 콜로이달 실리카(실리카졸)를 들 수 있다. 분산성의 점에서 물 또는 유기용매, 혹은 이를 혼합 용매에 분산된 콜로이달 실리카(실리카졸)를 이용하는 것이 바람직하다. 용매로는 예를 들면, 물, 메탄올, 에탄올, 이소프로필 알코올, 부틸 알코올, n-프로필 알코올 등의 알코올류, 케톤류, 에스테르류, 글리콜 에테르류를 들 수 있지만, 섬유상 필러의 분산의 용이함으로부터 적당한 용매를 선택할 수 있다.

[0103] 이와 같은 금속 산화물의 평균 입경은 1~1000nm가 바람직하고, 투명성과 작업성의 벨런스의 점에서 보다 바람직하게는 1~50nm, 더욱 바람직하게는 5~50nm, 가장 바람직하게는 5~40nm가 된다. 또한, 상기 하한값 미만에서는 제작된 복합체 조성물의 점도가 극단적으로 증대할 우려가 있다. 한편, 상기 상한값을 넘으면 복합체의 투명성이 현저하게 악화될 우려가 있으므로 바람직하지 않다.

[0104] 또, 금속 산화물로서 실리카 미립자를 이용하는 경우, 파장 400~500nm의 광선 투과율을 저하시키지 않기 위해 1차 입경이 200nm 이상인 실리카 미립자의 비율을 5% 이하로 억제한 실리카 미립자를 이용하는 것이 바람직하고, 그 비율을 0%로 하는 것이 보다 바람직하다. 실리카 미립자의 충전량을 올리기 위해서 평균 입경이 상이한 실리카 미립자를 혼합해 이용해도 된다. 또, 실리카 미립자로서 일본 특개 평7-48117호 공보에 나타내는 바와 같은 다공질 실리카졸이나, 알루미늄, 마그네슘, 아연 등과 규소의 복합 금속 산화물을 이용해도 된다.

(박편상 무기 재료)

[0106] 본 발명에서 이용되는 박편상 무기 재료로는 예를 들면, 천연물 또는 합성물로 이루어진 점토 광물을 들 수 있다. 구체적으로는 운모, 베미큘라이트, 몬모릴로나이트, 철 몬모릴로나이트, 바이델라이트, 사포나이트, 헥토라이트, 스티븐사이트, 논트로나이트, 마가디아이트, 일러라이트, 카네마이트, 층상 티탄산, 스黠타이트 등으로 이루어진 군으로부터 선택되는 적어도 1종을 들 수 있다.

[0107] 박편상 무기 재료는 형상이 비늘 조각상인 것으로서 대표적으로는 입자 1개의 두께가 약 1~10nm, 어스펙트비가 바람직하게는 20~수천, 보다 바람직하게는 20~수백인 비늘 조각상의 입자가 된다. 이와 같은 비늘 조각상의 점토 입자가 복합체 중에 어떠한 층에도 겹침으로써, 가스가 통과하는 경로가 길어져 결과적으로 복합체의 가스

배리어성이 향상된다.

[0108] 또, 복합체 조성물 중의 박편상 무기 재료의 충간에는 필요에 따라 소수성을 가지는 양이온 물질을 포함하도록 해도 된다. 일반적으로 점토 광물은 충간에 친수성의 교환성 양이온을 포함하고 있다. 본 발명에서는 점토 광물인 박편상 무기 재료의 충간에 존재하는 친수성의 교환성 양이온을 소수성의 양이온으로 물질 교환해 유기화시킬 수 있다. 소수성의 양이온 물질로는 예를 들면, 디메틸디스테아릴 암모늄염, 트리메틸스테아릴 암모늄염 등의 제4급 암모늄염이나, 벤질기나 폴리옥시에틸렌기를 가지는 암모늄염을 이용하거나 포스포늄염이나 피리디늄염이나 이미다졸륨염을 사용해 점토의 이온 교환성을 이용하여 유기화할 수도 있다.

[0109] 또한, 본 발명의 복합체 조성물은 전술한 수지, 금속 산화물 및 박편상 무기 재료 가운데 어느 하나를 포함하고 있어도 되고, 2 이상을 포함하고 있어도 된다. 예를 들면, 본 발명의 복합체 조성물은 섬유상 필러와 수지와 금속 산화물과 박편상 무기 재료를 포함하는 것이어야 된다.

[0110] 본 발명의 복합체 조성물에서는 섬유상 필러의 함유율이 0.1~99.9중량%인 것이 바람직하고, 0.1~75중량%인 것이 보다 바람직하다. 또한, 섬유상 필러의 함유율은 특별히 한정되는 것은 아니고, 복합체 조성물을 성형했을 때에 필요해지는 특성에 따라 적절히 조정된다. 복합체 조성물에서 섬유상 필러의 특성을 보다 반영시키고 싶은 경우에는 섬유상 필러의 함유율을 증가시키고, 수지의 특성을 보다 반영시키고 싶은 경우에는 수지의 함유율을 증가시키면 된다.

[0111] 또, 본 발명의 복합체 조성물을 이용하여 광학 용도에 이용되는 복합체를 제조하는 경우에는 복합체 조성물의 30~180°C의 평균 열팽창 계수(평균 선행창 계수)가 50ppm/°C 이하인 것이 바람직하고, 보다 바람직하게는 30ppm/°C 이하, 더욱 바람직하게는 20ppm/°C 이하가 된다.

[0112] 또, 본 발명의 복합체 조성물은 두께 30μm에서의 전광선 투과율이 80% 이상인 것이 바람직하고, 90% 이상인 것이 보다 바람직하다. 이에 의해, 최종적으로 투명성이 높고, 광학 용도에 적절한 복합체가 얻어진다.

<복합체>

[0114] 본 발명의 복합체 조성물을 소정의 형상으로 성형함으로써, 본 발명의 복합체가 얻어진다.

[0115] 본 발명의 복합체는 예를 들면, 태양 전지용 기판, 유기 EL용 기판, 전자 페이퍼용 기판, 액정 표시 소자용 플라스틱 기판으로서 이용되지만, 이 경우 등에 있어서는 전광선 투과율이 70% 이상인 것이 바람직하고, 보다 바람직하게는 80% 이상이며, 더욱 바람직하게는 88% 이상이다.

[0116] 또, 본 발명의 복합체를, 예를 들면 광학 용도, 즉 투명판, 광학 렌즈, 액정 표시 소자용 플라스틱 기판, 컬러 필터용 기판, 유기 EL 표시 소자용 플라스틱 기판, 태양 전지 기판, 터치 패널, 광학 소자, 광도파로, LED 봉지재 등으로서 이용하는 경우 등에 있어서는 30~150°C의 평균 열팽창 계수(평균 선행창 계수)가 50ppm/°C 이하인 것이 바람직하고, 보다 바람직하게는 30ppm/°C 이하이다. 특히 시트상 액티브 매트릭스 표시 소자 기판에 이용하는 경우에는 상기 평균 열팽창 계수가 30ppm/°C 이하인 것이 바람직하고, 보다 바람직하게는 20ppm/°C 이하가 된다. 상기 상한값을 넘으면, 제조 공정에서 흙이나 배선의 단선 등의 문제가 생길 우려가 있기 때문이다. 또한, 하한값은 특별히 설정되지는 않지만, 일례로서 0.4ppm/°C가 된다.

[0117] 또, 본 발명의 복합체를, 예를 들면 액정 표시 소자용 플라스틱 기판, 컬러 필터용 기판, 유기 EL 표시 소자용 플라스틱 기판, 태양 전지 기판, 터치 패널 등으로서 이용하는 경우 등에 있어서는 습도 팽창 계수는 바람직하게는 100ppm/습도% 이하이고, 보다 바람직하게는 50ppm/습도% 이하이며, 더욱 바람직하게는 30ppm/습도% 이하이다. 나아가서는, 본 발명 복합체의 흡수시에서의 팽윤율(팽윤 배율)은 바람직하게는 50배 이하, 보다 바람직하게는 30배 이하, 더욱 바람직하게는 10배 이하가 된다.

[0118] 또, 본 발명의 복합체를 판상으로 성형했을 경우, 그 두께는 10~2000μm인 것이 바람직하고, 10~500μm인 것이 보다 바람직하며, 20~200μm인 것이 더욱 바람직하다. 기판의 두께가 이 범위 내에 있으면, 본 발명의 복합체는 투명 기판으로서 필요하고 또한 충분한 기계적 강도와 광투과성을 겸비한 것이 된다. 또, 기판의 두께를 상기 범위 내로 함으로써, 평탄성이 뛰어나고, 유리 기판과 비교하여 기판의 경량화를 도모할 수 있다.

[0119] 본 발명의 복합체 조성물을 광학 시트로서 이용하는 경우, 평활성 향상을 위해서 양면에 수지의 코트층을 마련해도 된다. 코트하는 수지로는 뛰어난 투명성, 내열성, 내약품성을 가지고 있는 것이 바람직하고, 구체적으로는 다관능 아크릴레이트나 에폭시 수지 등을 들 수 있다. 코트층의 평균 두께는 0.1~50μm인 것이 바람직하고, 0.5~30μm인 것이 보다 바람직하다.

- [0120] 또, 본 발명의 복합체 조성물로부터 얻은 광학 시트를 특히 표시 소자용 플라스틱 기판으로서 이용하는 경우에 필요에 따라 수증기나 산소에 대한 가스 배리어층이나 투명 전극층을 마련해도 된다.
- [0121] 본 발명의 복합체 조성물이 경화성 수지를 포함하는 경우, 경화성 수지의 경화 방법은 특별히 한정되지 않지만, 산 무수물이나 지방족 아민 등의 가교제, 또는 양이온계 경화 촉매, 혹은 음이온계 경화 촉매 등의 경화 촉진제를 이용할 수 있다.
- [0122] 이중, 양이온계 경화 촉매로는 예를 들면 가열에 의해 양이온 중합을 개시시키는 물질을 방출하는 것(예를 들면 오늄염계 양이온 경화 촉매 또는 알루미늄 칼레이트계 양이온 경화 촉매)나, 활성 에너지선에 의해 양이온 중합을 개시시키는 물질을 방출시키는 것(예를 들면 오늄염계 양이온계 경화 촉매 등)을 들 수 있다. 구체적으로는 방향족 설포늄염으로는 삼신화학공업제의 SI-60L, SI-80L, SI-100L, 아사히전화공업제의 SP-66이나 SP-77 등의 헥사플루오로안티모네이트염 등을 들 수 있고, 알루미늄 칼레이트로는 에틸아세트아세테이트 알루미늄디이소프로필레이트, 알루미늄 트리스(에틸아세트아세테이트) 등을 들 수 있고, 3불화붕소아민 착체로는 3불화붕소 모노에틸아민 착체, 3불화붕소 이미다졸 착체, 3불화붕소페리딘 착체 등을 들 수 있다.
- [0123] 한편, 음이온계 경화 촉진제로는 예를 들면 1,8-디아자-비시클로(5,4,0)운데센-7, 트리에틸렌디아민 등의 3급 아민류, 2-에틸-4-메틸이미다졸이나 1-벤질-2-페닐이미다졸 등의 이미다졸류, 트리페닐포스핀, 테트라페닐포스포늄 테트라페닐보레이트 등의 인화합물, 4급 암모늄염, 유기 금속염류 및 이들 유도체 등을 들 수 있고, 이들 중에서도 투명성이 뛰어난 것으로부터 인화합물이나 1-벤질-2-페닐이미다졸 등의 이미다졸류가 바람직하다. 이들 경화 촉진제는 단독으로 이용해도 2종 이상을 병용해도 된다.
- [0124] 본 발명의 복합체 조성물에서는 필요에 따라 열가소성 또는 열경화성 올리고머나 폴리머를 병용할 수 있다. 또, 본 발명의 복합체 조성물 중에는 필요에 따라 특성을 해치지 않는 범위에서 소량의 산화 방지제, 자외선 흡수제, 염안료, 다른 무기 필러 등의 충전제 등을 포함하고 있어도 된다.
- [0125] 본 발명의 복합체 조성물은 임의의 방법에 의해 각 성분을 혼합함으로써 제조된다. 예를 들면, 섭유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 그대로 혼합하는 방법을 들 수 있다. 또, 필요에 따라서 가열하면서 혼합하도록 해도 된다.
- [0126] 또, 용매(분산매)를 이용해 섭유상 필러의 균일 분산액을 조제하고, 후에 탈용매를 실시하는 방법을 이용하면, 섭유상 필러의 분산성 및 금속 산화물이나 박편상 무기 재료의 분산성이 뛰어난 균일한 복합체 조성물을 얻을 수 있다.
- [0127] 이용하는 용매로는, 예를 들면 섭유상 필러의 분산성을 유지할 수 있고, 또한 수지, 금속 산화물 및 박편상 무기 재료를 용해 또는 분산시킬 수 있는 용매가 바람직하다. 이와 같은 용매로는 예를 들면, 물, 메틸알코올, 에틸알코올, 이소프로필알코올, 에틸렌글리콜, 프로필렌글리콜, 디에틸렌글리콜, 디옥산, 아세톤, 메틸에틸케톤, 메틸셀로솔브, 테트라하드로푸란, 펜타에리트리톨, 디메틸설클록시드, 디메틸포름아미드, N-메틸-2-피롤리돈 등을 들 수 있고, 이것들을 단독 혹은 2종류 이상 혼합해 이용할 수도 있다. 또, 원래 분산매의 분극률을 목적으로 하는 분산매의 극성으로 서서히 변화시켜 섭유상 필러를 상이한 극성의 분산매에 분산시키는 것도 가능하다.
- [0128] 나아가 본 발명의 복합체 조성물을 이용하여 태양 전지용 기판, 유기 EL용 기판, 전자 페이퍼용 기판, 액정 표시 소자용 플라스틱 기판 등의 소정의 두께를 가지는 시트를 얻는 방법은 일반적인 시트 형성 방법이면 되고, 특별히 한정되지 않는다. 예를 들면 섭유상 필러와 수지, 금속 산화물 및 박편상 무기 재료를 포함하는 복합체 조성물을 그대로 시트화하는 방법이나, 섭유상 필러의 분산매를 유연(流延)하고 용매를 제거하여 섭유상 필러의 시트를 얻고, 후에 수지를 함침시키는 방법, 또는 섭유상 필러와 수지, 금속 산화물 및 박편상 무기 재료와 용매를 포함하는 용액을 유연한 후, 용매를 제거하여 시트를 얻는 방법 등을 들 수 있다.
- [0129] 그와 같은 프로세스에 있어서 바람직한 태양의 하나로는 섭유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 미리 용매 중에 분산시켜 분산액을 조제한 후, 얻어진 분산액을 여과지, 멤브레인 필터 또는 초망 등에 유연하고, 용매 등의 그 외 성분을 여별 및/또는 건조시켜 복합체 조성물로 이루어진 시트를 얻는 방법이다. 또한, 상기 여별 건조 공정에서는 작업 효율을 높이기 위해 감압 하, 가압 하에서 실시해도 상관없다. 또, 연속적으로 형성하는 경우에는 제지 업계에서 사용되는 초지기를 이용해 박층 시트를 연속적으로 형성하는 방법도 포함된다.
- [0130] 유연하여 시트를 제작하는 경우, 여별 및/또는 건조 후에 형성된 시트가 용이하게 박리될 수 있는 기재 상에 제작되는 것이 바람직하다. 이와 같은 기재로는 금속제 또는 수지제인 것을 들 수 있다. 금속제 기재로는 스테인

레스제 기재, 황동제 기재, 아연제 기재, 구리제 기재, 철제 기재 등을 들 수 있고, 수지제 기재로는 아크릴성 기재, 불소계 기재, 폴리에틸렌테레프탈레이트제 기재, 염화비닐제 기재, 폴리스티렌성 기재, 폴리염화비닐리멘제 기재 등을 들 수 있다.

[0131] 실시예

[0132] 다음에, 본 발명의 구체적 실시예에 대해서 설명한다.

[0133] [미세 셀룰로오스 섬유의 제작 A]

[제작예 A)

[0135] 우선, 주로 1000nm를 넘는 섬유 지름의 셀룰로오스 섬유로 이루어지고, 건조 중량으로 2g 상당분의 미건조 펄프와 0.025g의 TEMPO(2,2,6,6-테트라메틸-1-피페리딘-N-옥실)과 0.25g의 브롬화나트륨을 물 150mℓ에 분산시켜 분산액을 조제했다.

[0136] 다음에, 이 분산액에 대해서 13중량% 차아염소산 나트륨 수용액을 1g의 펄프에 대해서 차아염소산 나트륨의 양이 2.5mmol가 되도록 가해 반응을 개시했다. 반응중에는 분산액 중에 0.5M의 수산화나트륨 수용액을 적하여 pH를 10.5로 유지하도록 했다. 그 후, pH에 변화가 보여지지 않게 된 시점에서 반응 종료라고 보고 반응물을 유리 필터로 여과하고, 여과물을 충분한 양의 물로 세정하는 동시에 여과를 5회 반복했다. 이에 의해, 고형분 농도 25중량%의 물을 포함하는 반응물 섬유를 얻었다.

[0137] 다음에, 얻어진 반응물 섬유에 물을 가해 2중량% 슬러리를 조제했다. 그리고 이 슬러리에 대해서 회전 칼날식 믹서로 약 5분간 처리를 실시했다. 처리에 수반해 현저하게 슬러리의 점도가 상승했기 때문에 조금씩 물을 가해서 가 고형분 농도가 0.2중량%가 될 때까지 믹서에 의한 분산 처리를 계속했다. 이에 의해 셀룰로오스 나노 섬유 분산액을 얻었다.

[0138] 이 셀룰로오스 나노 섬유 분산액을 친수 처리를 완료한 카본막 피복 그리드 상에 캐스트한 후, 2% 우라닐아세테이트로 네가티브 염색했다. 그리고, 캐스트한 셀룰로오스 나노 섬유 분산액을 TEM으로 관찰했는데 최대 섬유 지름이 10nm, 수 평균 섬유 지름이 6nm였다.

[0139] 또, 캐스트한 셀룰로오스 나노 섬유 분산액을 견조시켰는데, 투명한 막상 셀룰로오스가 얻어졌다. 이 막상 셀룰로오스에 대해서 광각 X선 회절상을 얻었는데, 막상 셀룰로오스가 셀룰로오스 I형 결정 구조를 가지는 셀룰로오스 나노 섬유로 이루어진 점이 분명해졌다.

[0140] 또, 동일한 막상 셀룰로오스에 대해서 전반사식 적외 분광 분석을 실시해 ATR 스펙트럼을 얻었다. ATR 스펙트럼의 패턴에서는 카르보닐기의 존재가 확인되어 상술한 방법에 의해 평가한 셀룰로오스 중의 알데히드기의 양 및 카르복실기의 양은 각각 0.31mmol/g 및 0.97mmol/g였다.

[0141] [복합체의 제작 A]

(실시예 1A)

[0143] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 10중량부)을 감압 여과해 물을 제거하고 메탄올로 5회 치환했다. 다음에, 셀룰로오스 나노 섬유 메탄올 분산액을 감압 여과해 메탄올을 제거하고, 추가로 열 양이온 촉매(SI-100L)를 1중량부 함유하는 치환식 에폭시 모노머 90중량부로 치환하는 작업을 5회 반복했다. 그리고, 얻어진 셀룰로오스 나노 섬유 분산 에폭시 수지(셀룰로오스 고형분량 10중량%)를 주형하고 100℃에서 2시간 가열한 후, 추가로 150℃에서 2시간 가열해 경화시켰다. 이에 의해, 두께 1mm의 복합체를 얻었다. 얻어진 복합체를 폭 10mm로 절단하고, 휨 강도 측정용 테스트 피스를 제작했다. 이 테스트 피스에 대해서 휨 강도를 측정하면 48N였다.

(실시예 2A)

[0145] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 15중량부)을 감압 여과해 물을 제거하고 추가로 동결 견조함으로써 셀룰로오스 나노 섬유를 얻었다. 다음에, 페놀 노볼락 수지 85중량부, 헥사메틸렌테트라민 15중량부에 셀룰로오스 나노 섬유를 15중량부 첨가해 얻어진 혼합물을 믹서로 3분간 혼합했다. 또한 혼합물을 100℃의 2개의 가열 룰에 의해 혼련하여 열경화성 수지 성형 재료를 얻었다. 얻어진 성형 재

료를 압축 성형에 의해 125°C에서 2시간 가열한 후, 추가로 150°C에서 2시간 가열해 경화시켰다. 이에 의해, 두께 1mm의 복합체를 얻었다. 얻어진 복합체를 폭 10mm로 절단해 휨 강도 측정용 테스트 피스를 제작했다. 이 테스트 피스에 대해서 휨 강도를 측정하면 60N였다.

[0146] (실시예 3A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)에 테트라에톡시실란을 셀룰로오스 나노 섬유 고형분 중량과 동일한 중량 첨가하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수를 측정했는데, 전광선 투과율은 90%, 열선팽창 계수는 11ppm/°C, 습도 팽창 계수는 26ppm/습도%였다.

[0148] (실시예 4A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)에 페닐트리에톡시실란을 셀룰로오스 나노 섬유 고형분 중량과 동일한 중량 첨가하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수를 측정했는데, 전광선 투과율은 89%, 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 23ppm/습도%였다.

[0150] (실시예 5A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)에 3-글리시독시프로필 트리에톡시실란을 셀룰로오스 나노 섬유 고형분 중량과 동일한 중량 첨가하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수를 측정했는데, 전광선 투과율은 89%, 열선팽창 계수는 11ppm/°C, 습도 팽창 계수는 25ppm/습도%였다.

[0152] (실시예 6A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)에 티탄알록사이드를 셀룰로오스 나노 섬유 고형분 중량과 동일한 중량 첨가하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수를 측정했는데, 전광선 투과율은 88%, 열선팽창 계수는 12ppm/°C, 습도 팽창 계수는 27ppm/습도%였다.

[0154] (실시예 7A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 에폭시 수지(데나콜 EX-214L, 나가세켐텍스사제) 80중량부와 테트라메틸에틸렌디아민 5중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 80%, 열선팽창 계수는 15ppm/°C, 습도 팽창 계수는 110ppm/습도%, 팽윤율은 16배였다.

[0156] (실시예 8A)

제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 에폭시 수지(데나콜 EX-1410L, 나가세켐텍스사제) 110중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50μm의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 80%, 열선팽창 계수는 14ppm/°C, 습도 팽창 계수는 61ppm/습도%, 팽윤율은 1.8배였다.

[0158] (실시예 9A)

[0159] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 에폭시 수지(테나콜 EX-1410L, 나가세켐텍스사제) 110중량부와 테트라메틸에틸렌디아민 5중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50 μm 의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 80%, 열선팽창 계수는 12ppm/°C, 습도 팽창 계수는 90ppm/습도%, 팽윤율은 3.1배였다.

[0160] (실시예 10A)

[0161] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 에폭시 수지(테나콜 EX-1610L, 나가세켐텍스사제) 110중량부와 테트라메틸에틸렌디아민 5중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50 μm 의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 80%, 열선팽창 계수는 13ppm/°C, 습도 팽창 계수는 76ppm/습도%, 팽윤율은 2.4배였다.

[0162] (실시예 11A)

[0163] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 레졸형 폐놀수지(PR-967, 스미토모베이클라이트제) 100중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 25 μm 의 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 50%, 습도 팽창 계수는 50ppm/습도%, 팽윤율은 1.2배였다. 또한, 본 샘플은 물렸기 때문에, 열팽창 계수 측정용 샘플을 얻을 수 없었다.

[0164] (실시예 12A)

[0165] 제작예 A에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 레졸형 폐놀수지(PR-967, 스미토모베이클라이트제) 300중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 58 μm 의 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 40%, 열선팽창 계수는 20ppm/°C, 습도 팽창 계수는 45ppm/습도%, 팽윤율은 1.2배였다.

[0166] (비)교예 1A)

[0167] 아황산 표백 침엽수 펄프를 물에 팽윤 후, 빙서로 세세하게 분산했다. 얻어진 단섬유 펄프 분산액을 감압 여과해 물을 제거하고 메탄올로 5회 치환했다. 다음에, 단섬유 펄프 메탄올 분산액을 감압 여과해 메탄올을 제거하고 열양이온 촉매(SI-100L)를 1중량부 함유하는 지환식 에폭시 모노머 90중량부로 치환하는 작업을 5회 반복했다. 그리고, 얻어진 단섬유 펄프 분산 애폭시 수지(셀룰로오스 고형분량 10중량%)를 주형에 100°C에서 2시간 가열한 후, 추가로 150°C에서 2시간 가열해 경화시켰다. 이에 의해, 두께 1mm의 복합체를 얻었다. 얻어진 복합체를 폭 10mm로 절단해 휨 강도 측정용 테스트 피스를 제작했다. 이 테스트 피스에 대해서 휨 강도를 측정하면 28N였다.

[0168] 또한, 단섬유 펄프 메탄올 분산액을 SEM으로 관찰했는데, 최대 섬유 지름이 70 μm , 수 평균 섬유 지름이 40 μm 였다.

[0169] (비)교예 2A)

[0170] 아황산 표백 침엽수 펄프를 물에 팽윤 후, 빙서로 세세하게 분산했다. 얻어진 단섬유 펄프 분산액을 감압 여과해 물을 제거하고, 추가로 동결 건조함으로써 미세 셀룰로오스 섬유를 얻었다. 다음에, 폐놀 노볼락 85중량부, 헥사메틸렌테트라민 15중량부에 미세 셀룰로오스 섬유를 15중량부 첨가해 얻어진 혼합물을 빙서로 3분간 혼합했다. 또한, 혼합물을 100°C의 2개의 가열 롤에 의해 혼련하여 열경화성 수지 성형 재료를 얻었다. 얻어진 성형 재료를 압축 성형에 의해 125°C에서 2시간 가열한 후, 추가로 150°C에서 2시간 가열해 경화시켰다. 이에 의해, 두께 1mm의 복합체를 얻었다. 얻어진 복합체를 폭 10mm로 절단해 휨 강도 측정용 테스트 피스를 제작했다. 이 테스트 피스에 대해서 휨 강도를 측정하면 40N였다.

[0171] 또한, 단섬유 펄프 메탄올 분산액을 SEM으로 관찰했는데, 최대 섬유 지름이 70 μm , 수 평균 섬유 지름이 40 μm 였다.

다.

[0172] (비)교예 3A)

[0173] 제작예 A에서 얻어진 셀룰로오스 나노 섬유 분산액(고형분량 0.15중량%)을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 이 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 125ppm/습도%, 팽윤율은 140배였다.

[0174] [미세 셀룰로오스 섬유의 제작 B]

[0175] (제작예 B)

[0176] 우선, 주로 1000nm를 넘는 섬유 지름의 셀룰로오스 섬유로 이루어지고, 건조 중량으로 2g 상당분의 미건조 필프와 0.025g의 TEMPO(2,2,6,6-테트라메틸-1-페페리딘-N-옥실)과 0.25g의 브롬화나트륨을 물 150mℓ에 분산시켜 분산액을 조제했다.

[0177] 다음에, 이 분산액에 대해서 13중량% 차아염소산 나트륨 수용액을 1g의 필프에 대해서 차아염소산 나트륨의 양이 2.5mmol가 되도록 가해 반응을 개시했다. 반응 중에는 자동 적정 장치를 이용해 0.5M의 수산화나트륨 수용액을 적하해 pH를 10.5로 유지하도록 했다. 그 후, pH에 변화가 보여지지 않게 된 시점에서 반응 종료라고 보고 0.5M의 염산 수용액으로 pH 7로 중화했다. 그리고, 반응물을 여과하고 여과물을 충분한 양의 물로 세정하는 동시에 여과를 6회 반복했다. 이에 의해, 고형분 농도 2중량%의 물을 포함하는 반응물 섬유를 얻었다.

[0178] 다음에, 얻어진 반응물 섬유에 물을 가해 0.2중량%의 반응물 섬유 분산액을 조제했다.

[0179] 이 반응물 섬유 분산액을 고압 호모지나이저(APV GAULIN LABORATORY제, 15MR-8TA형)를 이용해 압력 200bar(20MPa)로 20회 처리했다. 이에 의해, 투명한 셀룰로오스 나노 섬유 분산액을 얻었다.

[0180] 이 셀룰로오스 나노 섬유 분산액을 친수 처리를 완료한 카본막 피복 그리드 상에 캐스트 후, 2% 우라닐아세테이트로 네가티브 염색했다. 그리고, 캐스트한 셀룰로오스 나노 섬유 분산액을 TEM으로 관찰했는데, 최대 섬유 지름이 10nm, 수 평균 섬유 지름이 8nm였다.

[0181] 또, 캐스트한 셀룰로오스 나노 섬유 분산액을 건조시켰는데, 투명한 막상 셀룰로오스가 얻어졌다. 이 막상 셀룰로오스에 대해서 광각 X선 회절상을 얻었는데, 막상 셀룰로오스가 셀룰로오스 I형 결정 구조를 가지는 셀룰로오스 나노 섬유로 이루어진 것이 분명해졌다.

[0182] 또, 동일한 막상 셀룰로오스에 대해서, 전반사식 적외 분광 분석을 실시해 ATR 스펙트럼을 얻었다. ATR 스펙트럼의 패턴으로부터는 카르보닐기의 존재가 확인되어 상술한 방법에 의해 평가한 셀룰로오스 중의 알데히드기 양 및 카르복실기 양은 각각 0.31mmol/g 및 1.7mmol/g였다.

[0183] [복합체의 제작 B]

[0184] (실시예 1B)

[0185] 제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 20, 입자 지름 10~20nm, 무수 규산 함유량 20~21wt%, 낮산화학공업사제) 1중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 87%, 30°C~180°C의 범위에서의 열선팽창 계수는 9ppm/°C, 습도 팽창 계수는 70ppm/습도%, 팽윤율은 2배였다.

[0186] (실시예 2B)

[0187] 제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 N, 입자 지름 10~20nm, 무수 규산 함유량 20~21wt%, 낮산화학공업사제) 1중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오

분에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 30°C~180°C의 범위에서의 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 61ppm/습도%, 팽윤율은 1.6배였다.

[0188] (실시예 3B)

제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 0, 입자 지름 10~20nm, 무수 규산 함유량 20~21wt%, 낫산화학공업사제) 1중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 90%, 30°C~180°C의 범위에서의 열선팽창 계수는 11ppm/°C, 습도 팽창 계수는 65ppm/습도%, 팽윤율은 1.7배였다.

[0189] (실시예 4B)

제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 XS, 입자 지름 4~6nm, 무수 규산 함유량 20~21wt%, 낫산화학공업사제) 1중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 89%, 30°C~180°C의 범위에서의 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 68ppm/습도%, 팽윤율은 1.9배였다.

[0190] (실시예 5B)

제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액 100중량부(고형분량 0.2g)와 콜로이달 실리카(스노우텍스 CM, 입자 지름 20~30nm, 무수 규산 함유량 30~31wt%, 낫산화학공업사제) 0.7중량부(고형분량은 0.2g)를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 88%, 30°C~180°C의 범위에서의 열선팽창 계수는 11ppm/°C, 습도 팽창 계수는 70ppm/습도%, 팽윤율은 1.9배였다.

[0191] (비)교예 1B)

제작예 B에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 진공 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 투명한 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 30°C~180°C의 범위에서의 열선팽창 계수는 10ppm/°C, 습도 팽창 계수는 115ppm/습도%, 팽윤율은 100배였다.

[0192] [미세 셀룰로오스 섬유의 제작 C]

[0193] (제작예 C)

우선, 주로 1000nm를 넘는 섬유 지름의 섬유로 이루어지고, 건조 중량으로 2g 상당분의 미건조 펄프와 0.025g의 TEMPO(2,2,6,6-테트라메틸-1-페페리딘-N-옥실)과 0.25g의 브롬화나트륨을 물 150mL에 분산시켜 분산액을 조제했다.

다음에, 이 분산액에 대해서 13중량% 차아염소산 나트륨 수용액을 1g의 펄프에 대해서 차아염소산 나트륨의 양이 2.5mmol가 되도록 가해 반응을 개시했다. 반응 중에는 자동 적정 장치를 이용해 0.5M의 수산화나트륨 수용액을 적하해 pH를 10.5로 유지하도록 했다. 그 후, pH에 변화가 보여지지 않게 된 시점에서 반응 종료라고 보고 0.5M의 염산 수용액으로 pH 7로 중화했다. 그리고, 반응물을 여과하고 여과물을 충분한 양의 물에 의해 세정하는 동시에, 여과를 6회 반복했다. 이에 의해, 고형분량 2중량%의 물을 포함하는 반응물 섬유를 얻었다.

[0200] 다음에, 얻어진 반응물 섬유에 물을 가해 0.2중량%의 반응물 섬유 분산액을 조제했다.

- [0201] 이 반응물 섬유 분산액을 고압 호모지나이저(APV GAULIN LABORATORY제, 15MR-8TA형)를 이용해 압력 20MPa로 10회 처리했다. 이에 의해, 투명한 셀룰로오스 나노 섬유 분산액을 얻었다.
- [0202] 이 셀룰로오스 나노 섬유 분산액을 친수 처리를 완료한 카본막 피복 그리드 상에 캐스트 후, 2% 우라닐아세테이트로 네가티브 염색했다. 그리고, 캐스트한 셀룰로오스 나노 섬유 분산액을 TEM으로 관찰했는데, 최대 섬유 지름이 10nm, 수 평균 섬유 지름이 6nm였다.
- [0203] 또, 캐스트한 셀룰로오스 나노 섬유 분산액을 건조시켰는데, 투명한 막상 셀룰로오스가 얻어졌다. 이 막상 셀룰로오스에 대해서 광각 X선 회절상을 얻었는데, 막상 셀룰로오스가 셀룰로오스 I형 결정 구조를 가지는 셀룰로오스 나노 섬유로 이루어진 것이 분명해졌다.
- [0204] 또, 동일한 막상 셀룰로오스에 대해서, 전반사식 적외 분광 분석을 실시해 ATR 스펙트럼을 얻었다. ATR 스펙트럼의 패턴으로부터는 카르보닐기의 존재가 확인되어 상술한 방법에 의해 평가한 셀룰로오스 중의 알데히드기의 양 및 카르복실기의 양은 각각 0.31mmol/g 및 1.7mmol/g였다.
- [0205] [복합체의 제작 C]
- [0206] (실시예 1C)
- [0207] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액과 합성 스멕타이트(루센타이트 SW F)를 셀룰로오스 나노 섬유와 합성 스멕타이트의 중량비가 25 대 75가 되도록 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 50μm의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 91%이며, 30°C~180°C의 범위에서의 선팽창 계수는 4ppm/°C, 팽윤율은 15배였다.
- [0208] (실시예 2C)
- [0209] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액과 합성 스멕타이트(루센타이트 SW F)를 셀룰로오스 나노 섬유와 합성 스멕타이트의 중량비가 55 대 45가 되도록 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 20μm의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 91%이며, 30°C~180°C의 범위에서의 선팽창 계수는 5ppm/°C, 팽윤율은 48배였다.
- [0210] (실시예 3C)
- [0211] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액과 합성 사포나이트(스멕톤 SA)를 셀룰로오스 나노 섬유와 합성 사포나이트의 중량비가 25 대 75가 되도록 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 47μm의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 90%이며, 30°C~180°C의 범위에서의 선팽창 계수는 3.2ppm/°C, 팽윤율은 12배였다.
- [0212] (실시예 4C)
- [0213] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액과 합성 사포나이트(스멕톤 SA)를 셀룰로오스 나노 섬유와 합성 사포나이트의 중량비가 50 대 50이 되도록 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 41μm의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 90%이며, 30°C~180°C의 범위에서의 선팽창 계수는 5.8ppm/°C, 팽윤율은 32배였다.
- [0214] (실시예 5C)
- [0215] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 박편상 무기 재료(루센트 SWF, 코프케미컬사제) 100중량부와 에폭시 수지(테나콜 EX-214L, 나가세켐텍스사제) 600중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 24μm의 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 열선팽창 계수는 14ppm/°C, 습도 팽창 계수는 60ppm/습도%, 팽윤율은 2.1배였다.

[0216] (실시예 6C)

[0217] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 박편상 무기 재료(루센트 SWF, 코프케미컬사제) 100중량부와 에폭시 수지(테나콜 EX-214L, 나가세켐텍스사제) 200중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 50 μm 의 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 92%, 열선팽창 계수는 13ppm/°C, 습도 팽창 계수는 57ppm/습도%, 팽윤율은 1.7배였다.

[0218] (실시예 7C)

[0219] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 박편상 무기 재료(스멕톤 SA, 쿠니미네공업사제) 100중량부와 에폭시 수지(테나콜 EX-214L, 나가세켐텍스사제) 600중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 30 μm 의 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 열선팽창 계수는 15ppm/°C, 습도 팽창 계수는 92ppm/습도%, 팽윤율은 3.4배였다.

[0220] (실시예 8C)

[0221] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액(고형분 100중량부)과 박편상 무기 재료(스멕톤 SA, 쿠니미네공업사제) 100중량부와 에폭시 수지(테나콜 EX-214L, 나가세켐텍스사제) 200중량부를 혼합하고 실온에서 30분간 교반했다. 얻어진 혼합 용액을 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시키고, 추가로 120°C의 오븐 중에서 건조시켰다. 이에 의해, 두께 58 μm 의 필름을 얻었다. 얻어진 필름에 대해서 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 측정했는데, 전광선 투과율은 91%, 열선팽창 계수는 13ppm/°C, 습도 팽창 계수는 71ppm/습도%, 팽윤율은 2.4배였다.

[0222] (비)교예 1C)

[0223] 제작예 C에서 얻어진 고형분 농도 0.2중량%의 셀룰로오스 나노 섬유 분산액을 실온에서 30분간 교반하고 이형 처리한 살레에 따라 온도 50°C의 오븐에서 수분을 증발시켜 두께 18 μm 의 투명한 필름을 얻었다. 얻어진 필름의 전광선 투과율, 열선팽창 계수, 습도 팽창 계수 및 팽윤율을 평가했다. 전광선 투과율은 90%이며, 30°C~180°C의 범위에서의 열선팽창 계수는 12ppm/°C, 습도 팽창 계수는 200ppm/습도%, 팽윤율은 185배였다.

[0224] [복합체의 평가]

[0225] 특성 평가 방법은 이하와 같다.

[0226] (a) 휨 강도

[0227] 휨 강도 측정용 테스트 피스의 휨 강도는 JIS K 7171에 준거해 신전간(伸展間) 거리 36mm, 크로스 헤드 속도 1 mm/분, 23°C, 상대 습도 60% 하에서 휨 강도 측정 장치((주)오리엔테크사제, UCT-30T형 텐시론)를 이용해 측정했다.

[0228] (b) 열선팽창 계수

[0229] 열응력 뒤틀림 측정 장치(세이코전자(주)제, TMA/SS120C형)를 이용하여, 질소 분위기 하, 1분간 5°C의 비율로 온도를 30°C에서 150°C까지 상승시킨 후, 일단 0°C까지 냉각하고, 다시 1분간 5°C의 비율로 온도를 상승시켜 30°C~150°C 일 때의 값을 측정해 구했다. 하중을 5g로 하고 인장 모드로 측정을 실시했다.

[0230] 또한, 실시예 1B~5B 및 비교예 1B에 대해서는 1분간 5°C의 비율로 온도를 30°C에서 200°C까지 상승시킨 후, 일단 0°C까지 냉각하고, 다시 1분간 5°C의 비율로 온도를 상승시켜 30°C~180°C 일 때의 값을 측정해 구했다.

[0231] 또한, 실시예 1C~8C 및 비교예 1C에 대해서는 1분간 5°C의 비율로 온도를 30°C에서 200°C까지 상승시킨 후, 일단 -50°C까지 냉각하고, 다시 1분간 5°C의 비율로 온도를 상승시켜 30°C~180°C 일 때의 값을 측정해 구했다.

[0232] (c) 전광선 투과율

[0233] 분광 광도계(시마즈제작소제, U3200)로 전광선 투과율을 측정했다.

- [0234] 또한, 실시예 1C~8C 및 비교예 1C에 대해서는 헤이즈미터(일본전색사제, NDH-2000)에 의해 전광선 투과율을 측정했다.
- [0235] (d) 습도 팽창 계수
- [0236] 얻어진 필름에 치수 측정의 기준이 되는 2점을 그려 실온 23°C, 습도 60%의 분위기 하에 24시간 방치하고, 그 후 100°C의 건조기에 3시간 넣어 건조했다.
- [0237] 건조 후 즉시 미리 그린 2점간의 거리를 3차원 측장기로 측정해, 이 거리를 2점간 거리의 기준으로 했다. 그 후, 건조 후의 필름을 재차 실온 23°C, 습도 60%의 분위기 하에 24시간 방치한 후, 미리 그린 2점간 거리를 3차원 측장기로 측정해 기준 거리로부터의 치수 변화율을 산출했다. 또한, 건조 후 외관의 습도를 0%로 하고, 습도 0%에서 60% 범위에서의 습도 1%당 습도 팽창 계수를 산출했다.
- [0238] (e) 팽윤율
- [0239] 얻어진 필름을 23°C의 순수에 1시간 담궈 합침 전후의 필름 두께 변화율을 측정했다. 그리고 팽윤율을 합침 후 필름 두께의 합침 전 필름 두께에 대한 배율로서 산출했다.
- [0240] 상기 측정 결과를 표 1~3에 나타낸다.

| 제조조건 및 특성 | 실시예 | | | | | | | | | | | | 비교예 단위 |
|-----------|----------------------------|-----|-----|------|------|------|------|------|------|------|------|------|-----------|
| | 1.A | 2.A | 3.A | 4.A | 5.A | 6.A | 7.A | 8.A | 9.A | 10.A | 11.A | 12.A | |
| 예주식 수식 | 지판식 예 쪽시수지 | 90 | | | | | | | | | | | 90 |
| | 대나클 EX-214L | | | | | | | 80 | | | | | |
| | 대나클 EX-1410 | | | | | | | 110 | 110 | | | | |
| | 대나클 EX-1610 | | | | | | | | | 110 | | | |
| 배수지 | 페놀노블락 | | | | | | | | | | | | 85 |
| | 리플 | | | | | | | | | | | | |
| 커플링제 | 테트라 에톡시 실란 페닐트리 에톡시 실란 | | | | | | | | | | | | |
| | 나-글리시디록시프로필 드리아에톡시 실란 | | | | | | | | | | | | |
| | 타판 알록사이드 | | | | | | | | | | | | |
| 박판상 무기재료 | 두체트 SWF | | | | | | | | | | | | |
| | 스펙톤 SA | | | | | | | | | | | | |
| 금속설파를 | 스노우택스20 | | | | | | | | | | | | |
| | 스노우택스N | | | | | | | | | | | | |
| | 스노우택스O | | | | | | | | | | | | |
| | 스노우택스XS | | | | | | | | | | | | |
| | 스노우택스CM | | | | | | | | | | | | |
| 속비 | 셀룰로오스 나노섬유 | 10 | 15 | 160 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 미세화 윌로 | | | | | | | | | | | | |
| 기교재 | SI-14QL | 1 | | | | | | | | | | | 1 |
| | 테트라메틸 에틸렌디아민 | | | | | | | | | | | | |
| 두께 | 액사페닐렌데드라인 | 15 | | | | | | | | | | | 15 |
| | mm | 1 | 1 | 0.63 | 0.03 | 0.03 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 1 |
| 활간도 | N | 48 | 60 | — | — | — | — | — | — | — | — | — | 0.03 |
| | 전광선투과율 % | — | — | 96 | 60 | 38 | 88 | 80 | 80 | 80 | 50 | 40 | — |
| | 열선방정계수 ppm/ ^o C | — | — | 11 | 10 | 11 | 12 | 15 | 14 | 12 | 13 | — | 31 |
| | 습도방정계수 ppm/%습도 % | — | — | 26 | 23 | 25 | 22 | 110 | 61 | 90 | 76 | 50 | 20 |
| | 평점률 | — | — | — | — | — | — | 16 | 1.8 | 3.1 | 2.4 | 1.2 | 140 |

[0241]

[0242]

표 1로부터 알 수 있는 바와 같이, 실시예 1A, 2A에서 얻어진 테스트 피스(본 발명의 복합체 조성물을 이용해 얻어진 복합체)는 모두 비교예 1A에서 얻어진 종래의 섬유상 필러를 포함하는 테스트 피스와 비교하면 기계적 강도 및 치수 안정성이 높고 각종 특성이 뛰어난 것이 확인되었다.

[0243]

또, 실시예 3A~12A에서 얻어진 필름(본 발명의 복합체 조성물을 이용해 얻어진 복합체)은 섬유상 필러와 수지 또는 커플링제(또는 커플링제의 가수분해물)를 포함하는 복합체 조성물로부터 형성된 필름이지만, 이것들은 습도 팽창 계수(흡수 치수 변화율) 및 열선팽창 계수가 비교적 작고, 또한 투명성이 뛰어난 것이 확인되었다.

| 제조조건 및 특성 | | 실시예 1B | 실시예 2B | 실시예 3B | 실시예 4B | 실시예 5B | 비교예 1B |
|------------|-------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| 예폭시 수지 | 지환식 예폭시수지 | | | | | | |
| | 데나콜 EX-214L | | | | | | |
| | 데나콜 EX-1410 | | | | | | |
| | 데나콜 EX-1610 | | | | | | |
| 페놀 수지 | 페놀노블락 | | | | | | |
| | 레졸 | | | | | | |
| 커플링제 | 테트라 에톡시 실란 | | | | | | |
| | 페닐트리 에톡시 실란 | | | | | | |
| | 3-글리시도시프로필 트리에톡시 실란 | | | | | | |
| | 티탄 알콕사이드 | | | | | | |
| 박편상 무기재료 | 투센트 SWF | | | | | | |
| | 스맥톤 SA | | | | | | |
| 금속산화물 | 스노우텍스20 | 100 | | | | | |
| | 스노우텍스N | | 100 | | | | |
| | 스노우텍스O | | | 100 | | | |
| | 스노우텍스XS | | | | 100 | | |
| | 스노우텍스CM | | | | | 100 | |
| 셀룰로오스 나노섬유 | | 100 | 100 | 100 | 100 | 100 | 100 |
| 미세화 필프 | | | | | | | |
| 촉매 | SI-100L | | | | | | |
| | 테트라메틸 에틸렌디아민 | | | | | | |
| 기교재 | 헥사메틸렌테트라민 | | | | | | |
| 두께 | mm | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| 휨강도 | N | — | — | — | — | — | — |
| 전광선투과율 | % | 87 | — | 90 | 89 | 88 | 91 |
| 열선팽창계수 | ppm/ $^{\circ}\text{C}$ | 9 | 10 | 11 | 10 | 11 | 10 |
| 습도팽창계수 | ppm/습도 % | 70 | 61 | 65 | 68 | 70 | 115 |
| 팽창률 | 배 | 2 | 1.6 | 1.7 | 1.9 | 1.9 | 160 |

[0244]

[0245] 표 2로부터 알 수 있는 바와 같이, 실시예 1B~5B에서 얻어진 필름(본 발명의 복합체 조성물을 이용해 얻어진 복합체)은 모두 비교예 1B에서 얻어진 필름과 비교하면 팽윤율이 작고, 내수성이 뛰어난 것이 확인되었다.

| 제조조건 및 특성 | | 실시예 1C | 실시예 2C | 실시예 3C | 실시예 4C | 실시예 5C | 실시예 6C | 실시예 7C | 실시예 8C | 비교예 1C |
|------------|---------------------|-------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 에폭시 수지 | 지환식 에폭시수지 | | | | | | | | | |
| | 데나콜 EX-214L | | | | | 600 | 200 | 600 | 200 | |
| | 데나콜 EX-1410 | | | | | | | | | |
| | 데나콜 EX-1610 | | | | | | | | | |
| 페놀 수지 | 페놀노불락 | | | | | | | | | |
| | 레졸 | | | | | | | | | |
| 커플링제 | 테트라 에톡시 실란 | | | | | | | | | |
| | 페닐트리 에톡시 실란 | | | | | | | | | |
| | 3-글리시도시프로필 트리에톡시 실란 | | | | | | | | | |
| | 티탄 일콕사이드 | | | | | | | | | |
| 박편상 무기재료 | 루센트 SWF | 75 | 45 | | | 100 | 100 | | | |
| | 스맥론 SA | | | 75 | 50 | | | 100 | 100 | |
| 금속산화물 | 스노우텍스20 | | | | | | | | | |
| | 스노우텍스N | | | | | | | | | |
| | 스노우텍스O | | | | | | | | | |
| | 스노우텍스XS | | | | | | | | | |
| | 스노우텍스CM | | | | | | | | | |
| 셀룰로오스 나노섬유 | | 25 | 55 | 25 | 50 | 100 | 100 | 100 | 100 | 100 |
| 미세화 필프 | | | | | | | | | | |
| 촉매 | SI-100L | | | | | | | | | |
| | 테트라메틸 에틸렌디아민 | | | | | | | | | |
| 가교제 | | | | | | | | | | |
| 두께 | mm. | 0.06 | 0.02 | 0.047 | 0.041 | 0.024 | 0.05 | 0.03 | 0.058 | 0.018 |
| | N | — | — | — | — | — | — | — | — | — |
| 휨강도 | % | 91 | 91 | 90 | 90 | 91 | 92 | 91 | 91 | 90 |
| | ppm/ $^{\circ}$ C | 4 | 5 | 3.2 | 5.3 | 14 | 13 | 15 | 13 | 12 |
| 전광선투과율 | ppm/습도 % | — | — | — | — | 60 | 57 | 52 | 51 | 200 |
| | 습도팽창계수 | ppm/ $^{\circ}$ C | 15 | 48 | 12 | 32 | 2.1 | 1.7 | 3.4 | 2.4 |
| 팽창률 | | | | | | | | | | |

[0246]

[0247] 표 3으로부터 알 수 있는 바와 같이, 실시예 1C~8C에서 얻어진 필름(본 발명의 복합체 조성물을 이용해 얻어진 복합체)은 모두 비교예 1C에서 얻어진 필름과 비교하면 팽윤율이 작고, 내수성이 뛰어난 것이 확인되었다. 또, 실시예 1C~8C에서 얻어진 필름은 열선팽창 계수가 비교적 작은 것으로부터 열에 의한 치수 안정성도 뛰어나고, 또한 투명성도 높은 것이 확인되었다.

[0248] 또한, 각 실시예 및 각 비교예에서 사용된 주된 원료는 이하와 같다.

[0249] 에폭시 수지

[0250] : 세록사이드 2021 다이셀화학제

[0251] : 데나콜 EX-214L 나가세캡텍스사제

[0252] : 데나콜 EX-1410L 나가세캡텍스사제

[0253] : 데나콜 EX-1610L 나가세캡텍스사제

[0254] 페놀 수지

[0255] : 레졸형 페놀 수지 PR-967 스미토모베이클라이트제

[0256] 열양이온 촉매

[0257] : SI-100L 삼신화학제

[0258] 페놀 노불락 수지

[0259] : PR-HF-6 스미토모베이클라이트제

[0260] 커플링제

[0261] : 테트라에톡시실란 와코우순약제

[0262] : 폐널트리에톡시실란 아즈막스제

[0263] : 3-글리시도시프로필 트리에톡시실란 신에츠화학제

[0264] : 티탄알록사이드 KR-ET 아지노모토파인테크노제

[0265] 가교재(헥사메틸렌테트라민)

[0266] : 우로트로핀 스미토모정화사제

[0267] 금속 산화물

[0268] : 콜로이달 실리카 스노우텍스 20 낫산화학공업사제

[0269] : 콜로이달 실리카 스노우텍스 N 낫산화학공업사제

[0270] : 콜로이달 실리카 스노우텍스 O 낫산화학공업사제

[0271] : 콜로이달 실리카 스노우텍스 XS 낫산화학공업사제

[0272] : 콜로이달 실리카 스노우텍스 CM 낫산화학공업사제

[0273] 박편상 무기 재료

[0274] : 스멕톤 SA 쿠니미네공업제

[0275] : 루센타이트 SWF 코프케미컬

[0276] 산업상 이용 가능성

[0277] 본 발명의 복합체 조성물은 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개를 포함하고, 상기 섬유상 필러의 평균 섬유 지름이 4~1000nm이다. 이 때문에, 이 복합체 조성물을 성형해서 이루어지는 복합체에는 섬유상 필러와 수지, 금속 산화물 및 박편상 무기 재료 중 적어도 1개가 기계적 및 화학적인 작용을 가져온다. 그 결과, 저열팽창 계수, 고강도, 고투명성, 저습도 팽창 계수(고내수성, 고치수 안정성)를 가지는 복합체가 얻어진다. 따라서, 본 발명의 복합체는 자동차 외장 및 대쉬보드 등의 자동차 부품, 철도, 항공기, 선박 등의 수송용 기기의 부품, 주택이나 오피스에서의 세시, 벽판 및 상판 등의 건재, 기둥 혹은 철근 콘크리트에서의 철근과 같은 구조 부재, 전자 회로, 표시체의 기판 등의 전자 부품, PC 및 휴대 전화 등의 가전 제품의 케이스(하우징), 문구 등의 등의 사무용 기기, 가구, 일회용 용기 등의 생활 용품, 스포츠 용품, 완구 등의 가정 내에서 사용되는 소품, 간판, 표지 등의 야외 설치물, 방탄 방패, 방탄 조끼 등의 충격 흡수 부재, 헬멧 등의 호신 용구, 인공 뼈, 의료용품, 연마제, 방음벽, 방호벽, 진동 흡수 부재, 공구, 판 스프링 등의 기계 부품, 악기, 패킹재 등에 사용할 수 있다. 따라서, 본 발명의 복합체 조성물 및 복합체는 산업상 이용 가능성을 가진다.



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DESCRIPTION KR101335758

Composite composition and composite {COMPOSITE COMPOSITIONS AND COMPOSITES}

[0001]

The present invention relates to a composite composition and composite comprising at least one of a fibrous filler and a resin, metal oxide, and flaky inorganic material.

[0002]

It is widely practiced to blend a spherical filler or a fibrous filler in order to reduce the thermal expansion coefficient of the resin or to increase the mechanical strength such as elastic modulus and flexural strength.

In recent years, studies on nanoparticles of spherical fine particles such as silica fine particles and metal fine particles, and rod-shaped whisker-type fillers as materials that replace conventional macro fillers are in full swing. However, there have been few reports of fibrous nanomaterials for these fillers.

[0003]

Recently, many plastic substitutes using cellulose have been reported. For example, a complex using microfibrils of cellulose obtained by highly miniaturizing the fibril-like material of cellulose using a device capable of applying extremely high pressure called a high pressure homogenizer, and other microfluidizer methods, A composite using microfibrils of cellulose downsized by a grinder method, freeze drying method, steel wire elastic kneading method, or ball mill grinding method as a filler. It has been reported that a molded article having a relatively high strength can be obtained by using these fillers (for example, see Patent Document 1).

[0004]

However, the conventional microfibrillation method requires a great deal of energy for the downsizing treatment, which is disadvantageous in terms of cost, and also has a relatively wide distribution in the fiber diameter of the resulting micronized fiber, resulting in incomplete degree of micronization. In some cases, coarse fibers of 1 μm or more may remain a little, so a particularly wide distribution exists in the diameter and density of the microfibril fibers, resulting in an absolute value decrease or a gap in the strength of the molded article.

[0005]

Further, as described in Patent Document 2, it is known that a fiber-reinforced composite material having a transparent and low linear expansion coefficient is obtained using bacterial cellulose from which bacteria are produced. However, as in the case of mechanically obtaining the cellulose microfibrils described above, the production speed is slow and cannot be said to be necessarily advantageous from an industrial point of view.

[0006]

Moreover, since cellulose has many hydroxyl groups on the fiber surface, hydrophilicity is high, and dimensions and physical properties are greatly changed upon absorption. For this reason, there exists a problem that the size and physical properties of the composite material are greatly changed during absorption, and the use of the composite material is limited.

Japanese Patent Application Publication No. 2003-201695 Japanese Patent Application Publication No. 2005-60680

An object of the present invention is to provide a composite composition having a low coefficient of thermal expansion, high strength, high transparency, and a low humidity expansion coefficient (high water resistance) and a composite that is a molded product thereof efficiently.

In order to achieve the above object, the present invention is a composite composition comprising at least one of a fibrous filler, a resin, a metal oxide and a flaky inorganic material, characterized in that the average fiber diameter of the fibrous filler is 4 to 1000 nm. It is a composite composition. Moreover, in the composite composition of this invention, it is preferable that the said fibrous filler is a cellulose fiber. Moreover, in the composite composition of the present invention, it is preferable that the cellulose fiber is a fiber obtained by refining a cellulose raw material by at least one of chemical treatment and mechanical treatment. Further, in the composite composition of the present invention, it is preferable that the cellulose fiber is partially oxidized to at least one of an aldehyde group and a carboxyl group in the cellulose molecule contained therein. In the composite composition of the present invention, it is preferable that the cellulose fiber is obtained by using natural cellulose as a raw material, using an N-oxyl compound as an oxidation catalyst, and oxidizing the raw material by activating a co-oxidizing agent on the raw material in water. Moreover, in the composite composition of the present invention, it is preferable that the resin is at least one of a plastic resin and a curable resin. Moreover, it is preferable that the said resin contains an epoxy resin in the composite composition of this invention. Moreover, it is preferable that the said resin contains a phenol resin in the composite composition of this invention. Further, in the composite composition of the present invention, the resin preferably contains at least one of a coupling agent and a hydrolyzate of the coupling agent. Further, in the composite composition of the present invention, it is preferable that the coupling agent is alkoxy silane or alkoxy titanium. Moreover, in the composite composition of the present invention, it is preferable that the average particle diameter of the metal oxide is 1 to 1000 nm. Further, in the composite composition of the present invention, it is preferable that the metal oxide is silicon dioxide. Further, in the composite composition of the present invention, the flaky inorganic material is mica, vermiculite, montmorillonite, iron montmorillonite, videlite, saponite, hectorite, stephensite, nontronite, margadialite, illite, kanehite. It is preferable that it is at least one selected from smectite and layered titanic acid.

Further, in the composite composition of the present invention, the content of the fibrous filler in the composite composition is preferably 0.1 to 99.9% by weight. Moreover, in the composite composition of the present invention, it is preferable that the total light transmittance at a thickness of 30 µm is 80% or more. In addition, in the composite composition of the present invention, it is preferable that the coefficient of thermal expansion at 30 °C to 180 °C is 50 ppm / °C or less. In order to achieve the above object, the present invention is made by molding the composite composition, it is a composite characterized in that the thickness is 10 ~ 2000 µm. In addition, in the composite of the present invention, it is preferable that the coefficient of thermal expansion at 30 °C to 150 °C is 0.4 to 50 ppm / °C. Moreover, in the composite of the present invention, it is preferable that the coefficient of humidity expansion is 100 ppm / % humidity or less.

[0031] Hereinafter, preferred embodiments of the composite composition and the composite of the present invention will be described in detail.

[0032] The composite composition of the present invention includes at least one of a fibrous filler and a resin, a metal oxide, and a flaky inorganic material. In addition, the composite of the present invention is produced by molding the composite composition into a predetermined shape.

[0033] <Composite composition>

[0034] (Fibrous filler)

[0035] First, the fibrous filler will be described.

[0036] The average fiber diameter of the fibrous filler used in the present invention is 4 to 1000 nm, preferably 4 to 300 nm, and more preferably 4 to 200 nm. In addition, when the average fiber diameter exceeds the upper limit, transparency is deteriorated and mechanical strength is not improved. On the other hand, although the average fiber diameter may be below the lower limit, it is difficult to obtain such a fibrous filler.

[0037] The length of the fibrous filler used in the present invention is not particularly limited, but when the average length of the fibrous filler is 100 nm or more, a reinforcing effect is easily obtained and strength is improved.

[0038] Here, the measurement of the average fiber diameter of a fibrous filler can be performed as follows.

[0039] First, a dispersion of a fibrous filler having a solid fraction of 0.05 to 0.1% by weight is prepared, and the dispersion is cast on a carbon film-coated grid to prepare a sample for TEM observation. In addition, when a fibrous filler having a large fiber diameter is included, it may be cast on glass and used as a sample for SEM observation.

[0040] Upon observation under a microscope, an electron microscope image is acquired at a magnification of any one of 5000 times, 10000 times, or 50000 times depending on the size (fiber diameter) of the fibrous filler to be constituted. When the axis of arbitrary image width is assumed in the image obtained at this time, sample conditions and observation conditions (magnification, etc.) are set so that at least 20 fibrous fillers intersect the axis.

[0041] Then, for an observed image satisfying this condition, a random axis of two vertical and horizontal axes is pulled per image, and the fiber diameter of the fibrous filler intersecting with each axis is visually read. Further, while moving the

observation positions so as not to overlap each other with respect to the sample surface, at least three observation images are acquired, and the fiber diameters are read for each image as described above. As a result, information on the fiber diameter is obtained for at least $20 \times 2 \times 3 = 120$ fibrous fillers. The average fiber diameter is calculated based on the fiber diameter data thus obtained.

[0042] The fibrous filler used in the present invention may be any fiber, but is preferably composed of cellulose fibers.

[0043] Examples of the cellulose fibers include natural cellulose fibers and regenerated cellulose fibers. On the other hand, examples of fibers other than cellulose fibers include kitchen fibers and chitosan fibers.

[0044] Of these, natural cellulose fibers include purified pulp obtained from coniferous and broad-leaved trees, cellulose fibers obtained from cotton linters and cotton lint, cellulose fibers obtained from seaweeds such as baronia and shiog, cellulose fibers obtained from Hoya, and bacteria And cellulose fibers. On the other hand, as the regenerated cellulose fiber, there is one obtained by dissolving the natural cellulose fiber once and then regenerating it into a fibrous form while maintaining the cellulose composition.

[0045] Moreover, it is preferable that the cellulose fiber used for this invention is highly crystalline. Such cellulose fibers are particularly preferably used as fibrous fillers because of their small linear expansion coefficient and high mechanical strength. Moreover, from this viewpoint, as the cellulose fiber used in the present invention, natural cellulose fiber is preferable to regenerated cellulose fiber.

[0046] Further, the cellulose fibers used in the present invention may be obtained by any known method, and the production method is not particularly limited, but as an example, a cellulose raw material (natural cellulose or regenerated cellulose) is a medium stirring mill processing apparatus and a vibration mill treatment. What is mechanically refined by various refinement apparatuses, such as an apparatus, a high pressure homogenizer processing apparatus, and an ultra high pressure homogenizer treatment apparatus, is used. As another method, the electron spinning method, steam jet method, APEX (registered trademark) technology (Polymer Group. Inc.) can also be used. However, in consideration of energy efficiency and the like, the cellulose fiber obtained by a method involving the following chemical treatment is most preferable as the cellulose raw material.

[0047] The manufacturing method of the cellulose fiber described below is a method of producing cellulose fibers (nanocellulose fibers) by dispersing them in a dispersion medium by performing a chemical treatment on the cellulose raw material and then providing it to a mechanical treatment.

[0048] Specifically, [1] an oxidation reaction process in which natural cellulose is used as a raw material, and an N-oxyl compound is used as an oxidation catalyst in water to act as a oxidizing agent to oxidize natural cellulose to obtain reactant fibers, and [2] to remove impurities It has a purification process for obtaining reactant fibers impregnated with water, and [3] a dispersion process for dispersing reactant fibers impregnated with water in a dispersion medium. Each process is explained in full detail below.

[0049] [1] Oxidation reaction process

[0050] First, in the oxidation reaction step, a dispersion liquid in which cellulose raw materials are dispersed in water is prepared. Here, the cellulose raw material to be used is preferably one that has been subjected to a treatment for increasing the surface area such as beating in advance. This is because the reaction efficiency can be increased and productivity can be increased. Moreover, it is preferable to use what was preserve | saved by Neva dry after isolation | refining and refine | purifying as a cellulose raw material. Thereby, since the convergence body of the microfibrils constituting the cellulose raw material is easily swelled, it is also possible to increase the reaction efficiency and reduce the number average fiber diameter after the refinement treatment.

[0051] In addition, when water is used as the dispersion medium for the cellulose raw material in this step, the cellulose concentration in the dispersion (reactive aqueous solution) is arbitrary as long as it is a concentration capable of sufficiently diffusing the reagent, but is usually 5% by weight or less based on the weight of the dispersion.

[0052] In addition, many N-oxyl compounds that can be used as oxidation catalysts for cellulose have been reported. For example, "Cellulose" Vol. 10, 2003TEMPO (2,2,6,) in an article titled `` Catalytic oxidation of cellulose with TEMPO derivatives: HPSEC and NMR analysis of oxidized products " by I.Shibata and A.Isogai on pages 333-341 Various N-oxyl compound catalysts of 6-tetramethyl-1-piperidine-N-oxyl), 4-acetamide-TEMPO, 4-carboxy-TEMPO and 4-phosphonooxy-TEMPO at room temperature in water It is preferably used in the reaction rate. In addition, the addition of these N-oxyl compounds is sufficient in a catalytic amount, and is preferably added to the reaction aqueous solution in the range of 0.1 to 4 mmol / l, more preferably 0.2 to 2 mmol / l.

[0053] Further, examples of the co-oxidizing agent include hypohalogenic acid or a salt thereof, halogenic acid or a salt thereof, perhalogenic acid or a salt thereof, hydrogen peroxide and perorganic acid, and the like, but in particular, alkali metal hypohalogenates, specifically Sodium hypochlorite, sodium hypobromite, and the like are preferably used. When using sodium hypochlorite, it is preferred in terms of reaction rate to proceed the reaction in the presence of an alkali metal bromide, for example sodium bromide. The amount of the alkali metal bromide added is preferably about 1 to 40 times the molar amount, more preferably about 10 to 20 times the molar amount of the N-oxyl compound.

[0054] Moreover, it is preferable to maintain the pH of the reaction aqueous solution in the range of about 8 to 11. The temperature of the aqueous solution is arbitrary in the range of about 4 to 40 ° C, but the reaction can be carried out at room temperature, and temperature control is not particularly required.

[0055] Although a carboxyl group is introduced to the cellulose molecule by the co-oxidizer to substitute a hydroxyl group, the amount of the oxidizing agent is added depending on the amount of the carboxyl group required depending on the type of the cellulose raw material in obtaining the fine cellulose fibers used in the present invention. It is sufficient to set the time for the co-oxidant to act. Specifically, the larger the amount of carboxyl groups, the smaller the maximum fiber diameter and number average fiber diameter of the finally obtained cellulose fiber, so it may be set in consideration of it.

[0056] For example, when using wood pulp and cotton pulp as the cellulose raw material, the amount of carboxyl groups required is 0.2 to 2.2 mmol / g relative to the cellulose raw material, and bacterial cellulose (BC) or cellulose extracted from Hoya is used as the cellulose raw material. In this case, the required amount of carboxyl groups is 0.1 to 0.8 mmol / g. Thus, by controlling the addition amount and reaction time of the co-oxidizing agent according to the type of the cellulose raw material, it is possible to introduce the optimum amount of carboxyl groups in each cellulose raw material.

[0057] In addition, based on the introduction amount of the carboxyl group as described above, it is possible to induce the amount of the co-oxidant added, and as an example, it is preferable to add about 0.5 to 8 mmol of the co-oxidant per 1 g of the cellulose raw material, and the reaction time is about 5 to 120 It is preferable to make it within 240 minutes even if it is minutes and long.

[0058] In addition, although the carboxyl group is introduced into the cellulose molecule through the oxidation reaction step, an aldehyde group may be introduced depending on the progress of the oxidation treatment. Therefore, after completion of the oxidation reaction process, the hydroxyl group of the cellulose molecule is replaced with at least one of an aldehyde group and a carboxyl group.

[0059] [2] Refining process

[0060] In the purification step, it is an object to remove compounds other than the reactant fibers and water contained in the reaction slurry, specifically, unreacted hypochlorous acid or various by-products. Since the reactant fibers are not normally dispersed in nanofiber units at this stage, high purity (over 99% by weight) can be achieved by repeating a conventional purification method, that is, washing and filtration.

[0061] The purification method in the present purification process may be any apparatus as long as it is a device (for example, a continuous decanter) capable of achieving the above-described object, such as a method using centrifugal dehydration. The reactant fibers thus obtained are in the range of approximately 10 to 50% by weight as the concentration of solid content (cellulose) in the squeezed state. In addition, considering dispersing in units of nanofibers in a subsequent process, it is not preferable to use a solid content concentration higher than 50% by weight because extremely high energy is required for dispersion.

[0062] [3] Dispersion process

[0063] In the above-described step, reactant fibers impregnated with water are obtained, but by dispersing them in a solvent to perform dispersion treatment, fine cellulose fibers used in the present invention are obtained in a dispersed state.

[0064] Here, the solvent as the dispersion medium is usually water, but in addition to water, alcohols (methanol, ethanol, isopropanol, isobutanol, sec-butanol, tert-butanol, methylcellosolve, ethylcello) are soluble in water depending on the purpose. Solvent, ethylene glycol, glycerin, etc.), ethers (ethylene glycol dimethyl ether, 1,4-dioxane, tetrahydrofuran, etc.), ketones (acetone, methyl ethyl ketone), N, N-dimethylformamide, N, N -Dimethylacetamide, dimethyl sulfoxide, etc. may be used. Moreover, these mixtures can also be used preferably.

[0065] In addition, when diluting and dispersing with the above-described reactant fiber solvent, a dispersion of nanofiber level fibers can be efficiently obtained by performing stepwise dispersion in which a solvent is gradually added and dispersed. Further, from the operational problem, after the dispersion step, the dispersion conditions may be selected such that the dispersion becomes a viscous state or a gel.

[0066] Here, various kinds of dispersers used in the dispersing process can be used. Although a specific example is shown, depending on the progress of the reaction in the reactant fibers (the amount of conversion to an aldehyde group or a carboxyl group), preferably under the conditions in which the reaction proceeds, such as a screw mixer, paddle mixer, disper mixer, turbine mixer, etc. A dispersion of fine cellulose fibers can be sufficiently obtained with a general-purpose disperser as an industrial production machine.

[0067] In addition, by using a device having a strong crushing ability under high-speed rotation, such as a homo mixer, a high pressure homogenizer, an ultra high pressure homogenizer, ultrasonic dispersion treatment, a beater, a disc type refiner, a conical type refiner, a double disc type refiner, and a grinder, More efficient and highly downsizing becomes possible. Furthermore, by using these devices, even if the introduction amount of the aldehyde group or the carboxyl group is relatively small (for example, 0.1 to 0.5 mmol / g as the total amount of the aldehyde group or the carboxyl group to cellulose), a dispersion of highly fine-grained fine cellulose fibers can be obtained. Can provide.

[0068] Next, a method for recovering fine cellulose fibers from a dispersion in which fine cellulose fibers are dispersed in a dispersion medium will be described.

[0069] Specifically, the fine cellulose fibers can be recovered by drying the dispersion of the fine cellulose fibers described above.

[0070] Here, for drying, for example, a freeze drying method in the case where the dispersion medium is water, or a drying by a drum dryer when the dispersion medium is a mixture of water and an organic solvent, or in some cases, spray drying by a spray dryer can be preferably used.

[0071] In addition, among the dispersions of the fine cellulose fibers described above, water-soluble polymers as binders (polyethylene oxide, polyvinyl alcohol, polyacrylamide, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, starch, natural gums, etc.) , Sugars (glucose, fructose, mannose, galactose, trehalose, etc.) may be added. Since these binder components have extremely high boiling points and have affinity for cellulose, by adding these components in a dispersion, even when they are dried by a general-purpose drying method such as a drum dryer or spray dryer, agglomeration when dispersed in a dispersion medium again This is prevented, and a dispersion of fine cellulose fibers dispersed as nanofibers can be reliably obtained. In this case, the amount of the binder added in the dispersion is preferably in the range of 10 to 80% by weight relative to the reactant fibers.

[0072] In addition, the recovered fine cellulose fibers are again mixed in a dispersion medium (water, an organic solvent, or a mixture thereof) and an appropriate dispersion force is applied (for example, dispersion is performed using various dispersers used in the dispersion process described above). It can be made into a dispersion of cellulose fibers.

[0073] In the fine cellulose fiber used in the present invention, it is preferable that a part of hydroxyl groups of cellulose is oxidized to a carboxyl group or an aldehyde group, and has a cellulose I-type crystal structure. Further, the fact that the fine cellulose fibers have an I-type crystal structure means that the fibers are finely oxidized by surface oxidation of a naturally occurring cellulose solid raw material.

[0074] In addition, the fine cellulose fibers having an I-type crystal structure have typical peaks at two positions near $2\theta = 14$ ° and $2\theta = 22$ to 23 ° in the diffraction profile obtained by measuring the wide-angle X-ray diffraction image. You can identify based on what you have. In addition, the introduction of an aldehyde group or a carboxyl group into the cellulose of the fine cellulose fiber can be confirmed by the presence of absorption (around 1608 cm⁻¹) due to the carbonyl group in the total reflection infrared spectral spectrum (ATR) of the sample completely removing moisture. In particular, when an acid-type carboxyl group (-COOH) is introduced into cellulose, absorption is present at 1730 cm⁻¹ in the above measurement.

[0075] The finer the cellulose fiber, the more the total amount of carboxyl groups and aldehyde groups present in the cellulose for the above reasons, the more stable the fiber diameter can be. For example, in the case of wood pulp or cotton pulp, the sum of the amount of carboxyl groups and aldehyde groups present in the fine cellulose fibers (hereinafter abbreviated as "total amount") is 0.2 to 2.2 mmol / g, preferably with respect to the weight of the cellulose fibers. If it is 0.5 to 2.2 mmol / g, and more preferably 0.8 to 2.2 mmol / g, cellulose fibers having excellent stability as nanofibers are obtained. Further, in the case of cellulose having a relatively large fiber diameter of microfibrils such as cellulose extracted from BC or Hoya (average fiber diameter is about 10 nm level), the total amount is 0.1 to 0.8 mmol / g, preferably 0.2 to 0.8. If it is mmol / g, cellulose fibers excellent in stability as nanofibers are obtained. In addition, when the total amount is smaller than the lower limit, the difference in physical properties (for example, dispersion stabilization effect in the dispersion) with conventionally known micronized cellulose fibers is also reduced, and at the same time, it is difficult to obtain a fiber with a small fiber diameter. Therefore, it is not preferable.

[0076] In addition, an electric repulsive force is generated by introducing a carboxyl group to the aldehyde group, which is a nonionic substituent. As a result, the tendency for microfibrils to disperse without maintaining agglutination increases, so that the stability of nanofibers as a dispersion increases. For example, in the case of wood pulp or cotton pulp, the amount of carboxyl groups present in the fine cellulose fibers is 0.2 to 2.2 mmol / g, preferably 0.4 to 2.2 mmol / g, more preferably 0.6 to relative to the weight of the cellulose fibers. If it is 2.2 mmol / g, the cellulose fiber with extremely excellent stability as nanofibers is obtained. Further, in the case of cellulose having a relatively large fiber diameter of microfibrils, such as cellulose extracted from BC or Hoya, the amount of carboxyl groups is 0.1 to 0.8 mmol / g, preferably 0.2 to 0.8 mmol / g, which provides excellent stability as nanofibers. Cellulose fibers are obtained.

[0077] Here, the amount (mmol / g) of the aldehyde group and the carboxyl group of cellulose with respect to the weight of the cellulose fiber is evaluated by the following method.

[0078] 60 ml of a slurry having a concentration of 0.5 to 1 wt% was prepared using a cellulose sample with a dry weight, the pH was adjusted to about 2.5 with an aqueous 0.1 M hydrochloric acid solution, and 0.05 M sodium hydroxide aqueous solution was added dropwise to generate the slurry. Conduct conductivity measurement. This measurement continues until the pH is about 11. The amount of functional groups is calculated from the amount of sodium hydroxide (V) consumed in the neutralization step of the weak acid with a slight change in electrical conductivity using the following equation. The functional group amount calculated here is referred to as "functional group amount 1". This functional group amount 1 represents the amount of carboxyl groups.

[0079] Functional group amount (mmol / g) = V (ml) × 0.05 / cellulose weight (g)

[0080] Next, the cellulose sample is oxidized at room temperature for an additional 48 hours in an aqueous 2% sodium chlorite solution prepared with acetic acid at a pH of 4 to 5, and the functional group amount is again calculated by the above method. The functional group amount calculated here is referred to as "functional group amount 2". Then, the functional group amount (= functional group amount 2-functional group amount 1) added by this oxidation is calculated. This functional group amount represents the amount of the aldehyde group.

[0081] (Suzy)

[0082] As the resin used in the present invention, a known one can be used, and although it is not particularly limited, those containing various curable resins, various plastic resins, and various water-soluble resins can be mentioned.

[0083] The water-soluble resin is not particularly limited as long as it is soluble in water, and examples thereof include thermoplastic resins, curable resins, and natural polymers, but are preferably polyvinyl alcohol, polyethylene oxide, polyacrylamide, and polyvinylpyrrolidone. Synthetic polymers, starches, polysaccharides such as alginic acids, natural polymers such as hemicellulose, gelatin, Nikawa, and casein, which are components of wood, and proteins.

[0084] Moreover, although it does not specifically limit as a thermoplastic resin, For example, vinyl chloride resin, vinyl acetate resin, polystyrene, ABS resin, acrylic resin, polyethylene, polyethylene terephthalate, polyethylene naphthalate, polypropylene, fluorine resin, polyamide resin , Polyesters such as thermoplastic polyimide resin, polyacetal resin, polycarbonate, polylactic acid, polyglycolic acid, poly-3-hydroxy butyrate, polyhydroxy volylate, polyethylene adipate, polycaprolactone, polypropyl lactone, And polyethers such as polyether such as polyethylene glycol, polyglutamic acid, and polylysine.

[0085] On the other hand, as the curable resin, for example, phenol resin, urea resin, melamine resin, unsaturated polyester resin, epoxy resin, acrylic resin, oxetane resin, diallyl phthalate resin, polyurethane resin, silicon resin, maleimide resin, And thermosetting polyimide resins.

[0086] Among them, as the acrylic resin, one type of acrylate or methacrylate, hydroxyethyl acrylate, etc., in addition to alkyl acrylate or alkyl methacrylate such as acrylic acid, methacrylic acid, methyl acrylate, and methyl methacrylate. The resin containing the above is mentioned.

[0087] Moreover, the phenol resin is an organic compound having one or more phenolic hydroxyl groups in the molecule. Examples include resins having novolacs or bisphenols, naphthol or naphthol in the molecule, paraxylylene-modified phenolic resins, dimethylene ether-type resols, and methylol-type resol resins. In addition, these resins are further methylolated, lignin or lignin derivatives, lignin decomposition products containing at least one phenolic hydroxyl group, lignin or lignin derivatives, modified lignin decomposition products or phenols prepared from petroleum resources. And resins including those mixed with resins.

[0088] Moreover, the epoxy resin is an organic compound having at least one epoxy group. For example, bisphenol-type epoxy resins such as bisphenol A-type epoxy resins, bisphenol F-type epoxy resins, bisphenol S-type epoxy resins, hydrates of these bisphenol-type epoxy resins, and epoxy having a dicyclopentadiene skeleton Resin, epoxy resin having triglycidyl isocyanurate skeleton, epoxy resin having kard skeleton, epoxy resin having polysiloxane structure, alicyclic polyfunctional epoxy resin, alicyclic epoxy resin having hydrogenated biphenyl skeleton, hydrogenated bisphenol And alicyclic epoxy resins having an A skeleton.

[0089] Moreover, various coupling agents may be sufficient as the resin used by this invention.

[0090] As a coupling agent, a well-known thing can be used, but a silane coupling agent, a titanium coupling agent, a zirconium coupling agent, an aluminum coupling agent, etc. are mentioned, Among these, a silane coupling agent or a titanium coupling agent is preferable. Is used. Since these are relatively easy to obtain and have high adhesion at the interface between the inorganic material and the organic material, they are very suitable as a coupling agent included in the composite composition.

[0091] Moreover, it is preferable that a silane coupling agent contains at least 1 silicon atom and 1 or more alkoxy groups as a functional group among the said coupling agents. Moreover, an epoxy group or epoxy cyclohexyl group, amino group, hydroxyl group, acrylic group, methacryl group, vinyl group, phenyl group, styryl group, isocyanate group etc. are mentioned as other functional groups. Moreover, in this invention, since the effect equivalent to a coupling agent is obtained, the tetraalkoxysilane containing four alkoxy groups is also included in a silane coupling agent.

[0092] Specific examples of the silane coupling agent include an alkyl group-containing alkoxy silane compound such as a tetraalkoxysilane compound, methyltrialkoxysilane, and dimethyldialkoxysilane, 3-glycidoxypropyl trialkoxysilane, and 3-glycidpropylmethyl dialkoxysilane , Epoxy silane compounds such as 2- (3,4-epoxycyclohexyl) ethyl trialkoxysilane, aminoalkoxysilane compounds such as 3-aminopropyl trialkoxysilane, and N-phenyl-3-aminopropyl trialkoxysilane, 3- (Meth) acrylalkoxysilane compounds such as acryloxypropyl trialkoxysilane, methacryloxypropyl trialkoxysilane, 3-methacryloxypropylmethyl dialkoxysilane, and 3-methacryloxypropyl trialkoxysilane, and vinyl trialkoxysilane Phenyl group-containing trialcohols such as vinylalkoxysilane compounds, phenyltrialkoxysilanes, diphenyldialkoxysilanes, and 4-hydroxyphenyl trialkoxysilanes. And styryl group-containing alkoxy silane compounds such as cysilane compounds and 3-isocyanatepropyl trialkoxysilane. Among these, a tetraalkoxysilane compound, an alkyl group-containing alkoxy silane compound, and a phenyl group-containing alkoxy silane compound have a high effect of increasing water resistance, and are preferable.

[0093] On the other hand, specific examples of the titanium-based coupling agent include an alkoxy titanium compound having the same substituent as the alkoxysilane compound. For example, isopropyl triisostearoyl titanate, isopropyl tridodecylbenzenesulfonyl titanate, isopropyl tri (dioctylpyrophosphate) titanate, tetraisopropyl bis (dioctylphosphite) titanate, Tetraoctyl bis (ditridecylphosphite) titanate, isopropyl trioctanoyl titanate, isopropyl dimethacryl isostearoyl titanate, isopropyl isostearoyl diacrylic titanate, isopropyl tri (di Octyl phosphate) titanate, isopropyl trixylophenyl titanate, isopropyl tri (N-aminoethylaminoethyl) titanate, dicumylphenyloxyacetate titanate, diisostearoyl ethylene titanate, bis (dioctyl Pyrophosphate) ethylene titanate, bis (dioctyl pyrophosphate) oxyacetate titanate And tetra (2,2-diallyloxymethyl-1-butyl) bis (di-tridecyl) phosphite titanate.

[0094] Moreover, you may use the hydrolyzate of a coupling agent as mentioned above instead of a coupling agent. The coupling agent or the hydrolyzate thereof may be appropriately selected in consideration of compatibility with a dispersion medium, stability of the hydrolyzate, and the like. Further, the hydrolyzate of the coupling agent can be easily prepared by stirring and mixing an acidic aqueous solution such as an acetic acid aqueous solution with the coupling agent. Moreover, as a hydrolyzate of a coupling agent, even if it is not hydrolyzed a hydrolyzable group (alkoxide group), it may be manufactured by any method as long as the molecular structure is the same as the hydrolyzate of a coupling agent.

[0095] In addition, the above-mentioned water-soluble resin, thermoplastic resin, curable resin, and coupling agent may be used individually, or two or more may be used in combination.

[0096] (Metal oxide)

[0097] The type of the metal oxide used in the present invention is not particularly limited, but includes oxides of single metals such as SiO₂ (silica), Al₂O₃ (alumina), TiO₂ (titania), ZrO₂ (zirconia), and SiO₂-Al₂O₃ (Mullite Etc.), composite oxides, such as SiO₂-TiO₂, SiO₂-ZrO₂, spinel, titania-containing silica, zirconia-containing silica, etc. are mentioned.

[0098] The metal oxide may have any shape, but is preferably in the form of particles. In this case, not only the particles of the metal oxide are composed of one kind of oxide fine particles, but also may be composed of a mixture of two or more kinds of oxide fine particles. Such oxide fine particles can be obtained by a method such as a sol-gel method, a wet method, a vapor phase method, or a dry method.

[0099] Among the metal oxides, it is preferable to use SiO₂, Al₂O₃ or a composite oxide of these. These are not only relatively inexpensive, but also can improve the mechanical strength, heat resistance and wear resistance of the composite.

[0100] In particular, it is preferable to use fine particles of Al₂O₃ as a metal oxide in order to improve the wear resistance of the composite. These fine particles are the cheapest, and they are resistant to corrosion by acids and alkalis, so that the chemical stability of the composite can be enhanced.

[0101] In addition, when the composite is used for applications such as electronic components, it is preferable to use fine particles of SiO₂ (silica fine particles) as the metal oxide. Since these fine particles have a low dielectric constant, the dielectric constant of the composite can be reduced to suppress transmission delays in electronic components.

[0102] Examples of the silica fine particles include dry powdery silica fine particles and colloidal silica (silicasol) dispersed in a solvent. From the point of dispersibility, it is preferable to use colloidal silica (silicasol) dispersed in water or an organic solvent or a mixed solvent. Examples of the solvent include alcohols such as water, methanol, ethanol, isopropyl alcohol, butyl alcohol, and n-propyl alcohol, ketones, esters, and glycol ethers, but suitable for ease of dispersion of the fibrous filler. Solvents can be selected.

[0103] The average particle diameter of such a metal oxide is preferably 1 to 1000 nm, more preferably 1 to 50 nm, more preferably 5 to 50 nm, and most preferably 5 to 40 nm in terms of balance between transparency and workability. Becomes In addition, there is a possibility that the viscosity of the produced composite composition is extremely increased below the lower limit. On the other hand, if it exceeds the above upper limit, the transparency of the composite may deteriorate significantly, which is not preferable.

[0104] When using silica fine particles as the metal oxide, it is preferable to use silica fine particles in which the proportion of silica fine particles having a primary particle size of 200 nm or more is suppressed to 5% or less in order not to lower the light transmittance at a wavelength of 400 to 500 nm. It is more preferable to set the ratio to 0%. In order to increase the filling amount of the silica fine particles, silica fine particles having different average particle sizes may be mixed and used. As the silica fine particles, a porous silica sol as shown in Japanese Patent Application Laid-Open No. 7-48117, or a composite metal oxide of silicon such as aluminum, magnesium, zinc and the like may be used.

[0105] (Plastic inorganic material)

[0106] The flaky inorganic material used in the present invention includes, for example, clay minerals made of natural or synthetic materials. Specifically, it is selected from the group consisting of mica, vermiculite, montmorillonite, iron montmorillonite, videlite, saponite, hectorite, stevensite, nontronite, margadialite, illite, carnemite, layered titanic acid, smectite, etc. At least 1 type is mentioned.

[0107] The flake-like inorganic material is a scaly flake, typically having a particle size of about 1 to 10 nm, an aspect ratio of preferably 20 to several thousand, and more preferably 20 to hundreds. When such scale-like clay particles overlap any layer in the composite, the path through which the gas passes increases, resulting in improved gas barrier properties of the composite.

[0108] Moreover, you may make it contain the cation substance which has hydrophobicity as needed between the layers of flaky inorganic materials in a composite composition. In general, clay minerals contain hydrophilic, exchangeable cations between layers. In the present invention, the hydrophilic exchangeable cation existing between the layers of the flaky inorganic material, which is a clay mineral, can be organically exchanged with a hydrophobic cation. As the hydrophobic cationic material, for example, quaternary ammonium salts such as dimethyl distearyl ammonium salt and trimethylstearyl ammonium salt, ammonium salts having a benzyl group or polyoxyethylene group are used, or phosphonium salts, pyridinium salts or imidazolium salts It is also possible to organicize using the ion-exchange property of clay.

[0109] In addition, the composite composition of the present invention may contain any of the resins, metal oxides, and flaky inorganic materials described above, or may contain two or more. For example, the composite composition of the present invention may contain a fibrous filler, a resin, a metal oxide, and a flaky inorganic material.

[0110] In the composite composition of the present invention, the content of the fibrous filler is preferably 0.1 to 99.9% by weight, and more preferably 0.1 to 75% by weight. Moreover, the content rate of a fibrous filler is not specifically limited, It is suitably adjusted according to the characteristic required when shape | molding a composite composition. In the composite composition, if the properties of the fibrous filler are to be more reflected, the content of the fibrous filler is increased, and if the properties of the resin are to be further reflected, the content of the resin may be increased.

[0111] In addition, in the case of preparing a composite used for optical use using the composite composition of the present invention, it is preferable that the average thermal expansion coefficient (average linear expansion coefficient) of 30 to 180 ° C of the composite composition is 50 ppm / ° C or less, and more preferably It is 30 ppm / ° C or less, more preferably 20 ppm / ° C or less.

[0112] Moreover, the composite composition of the present invention preferably has a total light transmittance of 80% or more at a thickness of 30 µm, more preferably 90% or more. As a result, a composite having high transparency and suitable for optical use is finally obtained.

[0113] <Composite>

[0114] The composite of the present invention is obtained by molding the composite composition of the present invention into a predetermined shape.

[0115] The composite of the present invention is used, for example, as a substrate for a solar cell, a substrate for an organic EL, a substrate for an electronic paper, or a plastic substrate for a liquid crystal display device, but in this case, the total light transmittance is preferably 70% or more, more preferably Is 80% or more, and more preferably 88% or more.

[0116] In addition, the composite of the present invention can be used, for example, in optical applications, that is, transparent plates, optical lenses, plastic substrates for liquid crystal display elements, substrates for color filters, plastic substrates for organic EL display elements, solar cell substrates, touch panels, and optical elements. , When used as an optical waveguide, LED encapsulant, etc., the average thermal expansion coefficient (average linear expansion coefficient) of 30 to 150 ° C is preferably 50 ppm / ° C or less, and more preferably 30 ppm / ° C or less. Particularly, when used for a sheet-like active matrix display element substrate, the average thermal expansion coefficient is preferably 30 ppm / ° C or less, more preferably 20 ppm / ° C or less. This is because if the above upper limit is exceeded, problems such as warping or disconnection of wiring may occur in the manufacturing process. In addition, although the lower limit is not particularly set, it is 0.4 ppm / ° C as an example.

[0117] Moreover, in the case where the composite of the present invention is used as, for example, a plastic substrate for a liquid crystal display element, a substrate for a color filter, a plastic substrate for an organic EL display element, a solar cell substrate, a touch panel, etc., the humidity expansion coefficient is preferably It is 100 ppm / humidity% or less, More preferably, it is 50 ppm / humidity% or less, More preferably, it is 30 ppm / humidity% or less. Furthermore, the swelling ratio (swelling ratio) at the time of absorption of the composite of the present invention is preferably 50 times or less, more preferably 30 times or less, still more preferably 10 times or less.

[0118] Moreover, when the composite of the present invention is molded into a plate shape, the thickness is preferably 10 to 2000 µm, more preferably 10 to 500 µm, and even more preferably 20 to 200 µm. When the thickness of the substrate is within this range, the composite of the present invention is required as a transparent substrate and also has sufficient mechanical strength and light transmittance. Moreover, by making the thickness of the substrate within the above range, the flatness is excellent, and the weight of the substrate can be reduced compared to the glass substrate.

[0119] When using the composite composition of the present invention as an optical sheet, a coating layer of resin may be provided on both surfaces for improving smoothness. It is preferable to have excellent transparency, heat resistance, and chemical resistance as the resin to be coated, and specific examples thereof include polyfunctional acrylates and epoxy resins. The average thickness of the coat layer is preferably 0.1 to 50 µm, and more preferably 0.5 to 30 µm.

[0120] Moreover, when using the optical sheet obtained from the composite composition of this invention as a plastic substrate for display elements especially, you may provide a gas barrier layer for water vapor and oxygen, or a transparent electrode layer as needed.

[0121] When the composite composition of the present invention contains a curable resin, the curing method of the curable resin is not particularly limited, but a curing accelerator such as a crosslinking agent such as an acid anhydride or an aliphatic amine, or a cationic curing catalyst or anionic curing catalyst may be used. You can.

[0122] Among them, as the cationic curing catalyst, for example, a substance that initiates cationic polymerization by heating is released (for example, an onium salt-based cationic curing catalyst or an aluminum chelate-based cationic curing catalyst) or cationic polymerization by an active energy ray. And those which release substances (for example, onium salt-based cationic curing catalysts). Specifically, examples of aromatic sulfonium salts include hexafluoroantimonate salts such as SI-60L, SI-80L, SI-100L manufactured by Samshin Chemical, and SP-66 and SP-77 manufactured by Asahi Corporation. Examples of the aluminum chelate include ethylacetate aluminum diisopropylate, aluminum tris (ethylacetate), and the like, boron trifluoride amine complex, boron trifluoride monoethylamine complex, boron trifluoride imidazole complex, And a boron trifluoride piperidine complex.

[0123] On the other hand, as an anionic curing accelerator, for example, tertiary amines such as 1,8-diaza-bicyclo (5,4,0) undecene-7 and triethylenediamine, 2-ethyl-4-methylimidazole imidazoles such as sol or 1-benzyl-2-phenylimidazole, phosphorus compounds such as triphenylphosphine, tetraphenylphosphonium tetraphenylborate, quaternary ammonium salts, organic metal salts, and derivatives thereof. , Among these, imidazoles such as phosphorus compounds and 1-benzyl-2-phenylimidazole are preferable from those excellent in transparency. These curing accelerators may be used alone or in combination of two or more.

[0124] In the composite composition of the present invention, a thermoplastic or thermosetting oligomer or polymer can be used in combination, if necessary. In addition, the composite composition of the present invention may contain a small amount of antioxidants, ultraviolet absorbers, salt pigments, fillers such as other inorganic fillers, and the like in a range that does not impair the properties as necessary.

[0125] The composite composition of the present invention is prepared by mixing each component by any method. For example, a method of mixing at least one of a fibrous filler and a resin, a metal oxide, and a flaky inorganic material as it is mentioned. Moreover, you may mix it, heating as needed.

[0126] In addition, if a method of preparing a uniform dispersion of a fibrous filler using a solvent (dispersion medium) and then performing desolvation is used, a uniform composite composition excellent in dispersibility of the fibrous filler and dispersibility of a metal oxide or flaky inorganic material Can get

[0127] As a solvent to be used, for example, a solvent capable of maintaining the dispersibility of the fibrous filler and dissolving or dispersing the resin, metal oxide, and flaky inorganic material is preferable. Examples of such a solvent include water, methyl alcohol, ethyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, diethylene glycol, dioxane, acetone, methyl ethyl ketone, methyl cellosolve, tetrahydrofuran, penta Erythritol, dimethyl sulfoxide, dimethylformamide, N-methyl-2-pyrrolidone, etc. may be mentioned, or these may be used alone or in combination of two or more. Further, it is also possible to disperse the fibrous filler in a dispersion medium of different polarity by gradually changing the polarization rate of the original dispersion medium to the polarity of the desired dispersion medium.

[0128] Furthermore, the method for obtaining a sheet having a predetermined thickness such as a substrate for a solar cell, a substrate for an organic EL, a substrate for an electronic paper, or a plastic substrate for a liquid crystal display device using the composite composition of the present invention may be a general sheet forming method, and is particularly limited. Does not work. For example, a method of directly sheeting a composite composition containing a fibrous filler and a resin, metal oxide, and flaky inorganic material, or softening a dispersion medium of the fibrous filler and removing a solvent to obtain a sheet of the fibrous filler, After that, a method of impregnating the resin or a solution containing a fibrous filler and a resin, a metal oxide, and a flaky inorganic material and a solvent is flexible, and then a solvent is removed to obtain a sheet.

[0129] One of the preferred embodiments in such a process is to prepare a dispersion by dispersing at least one of a fibrous filler, a resin, a metal oxide, and a flaky inorganic material in a solvent in advance, and then dispersing the obtained dispersion into a filter paper, membrane filter or draft net , It is a method of obtaining a sheet made of a composite composition by filtering and / or drying other components such as a solvent. In addition, in the drying process by filtration, it may be carried out under reduced pressure and under pressure in order to increase work efficiency. Moreover, when forming continuously, the method of continuously forming a thin-layer sheet using the paper machine used in the paper industry is also included.

[0130] When manufacturing a sheet by being flexible, it is preferable that the sheet formed after filtration and / or drying is produced on a substrate that can be easily peeled off. As such a base material, what is made of metal or resin is mentioned. Examples of the metal base material include a stainless steel base material, a brass base material, a zinc base material, a copper base material, and an iron base material. The resin base material includes an acrylic base material, a fluorine base material, a polyethylene terephthalate base material, and a vinyl chloride base material. , Polystyrene base materials, polyvinylidene chloride base materials, and the like.

[0131] Example

[0132] Next, specific examples of the present invention will be described.

[0133] [Production A of Micro Cellulose Fiber]

[0134] (Production Example A)

[0135] First, it is mainly composed of cellulose fibers with a fiber diameter exceeding 1000 nm, and 2 g of undried pulp and 0.025 g of TEMPO (2,2,6,6-tetramethyl-1-piperidine-N) in a dry weight. -Oxyl) and 0.25 g of sodium bromide were dispersed in 150 ml of water to prepare a dispersion.

[0136] Next, 13% by weight of sodium hypochlorite aqueous solution was added to this dispersion so that the amount of sodium hypochlorite was 2.5 mmol per 1 g of pulp, and the reaction was started. During the reaction, 0.5M sodium hydroxide aqueous solution was added dropwise to the dispersion to maintain the pH at 10.5. Thereafter, when no change in pH was observed, the reaction was deemed to be complete, and the reaction was filtered through a glass filter, and the filtrate was washed with a sufficient amount of water, and filtration was repeated 5 times. As a result, a reactant fiber containing 25% by weight of solid content was obtained.

[0137] Next, water was added to the obtained reactant fibers to prepare a 2% by weight slurry. Then, the slurry was treated with a rotary blade mixer for about 5 minutes. Since the viscosity of the slurry increased remarkably with the treatment, water was added little by little to continue dispersion treatment with a mixer until the solid content concentration was 0.2% by weight. Thereby, a cellulose nanofiber dispersion was obtained.

[0138] This cellulose nanofiber dispersion was cast on a carbon film-coated grid after hydrophilic treatment, and then negatively dyed with 2% uranyl acetate. And the cast cellulose nanofiber dispersion was observed by TEM, but the maximum fiber diameter was 10 nm and the number average fiber diameter was 6 nm.

[0139] Moreover, the cast cellulose nanofiber dispersion was dried, and transparent membrane-like cellulose was obtained. A wide-angle X-ray diffraction image was obtained for this membrane-like cellulose, and it became clear that the membrane-like cellulose was composed of cellulose nanofibers having a cellulose I-type crystal structure.

[0140] Moreover, total reflection infrared spectroscopy analysis was performed on the same membrane cellulose to obtain an ATR spectrum. In the pattern of the ATR spectrum, the presence of the carbonyl group was confirmed, and the amount of the aldehyde group and the amount of the carboxyl group in cellulose evaluated by the above-described method were 0.31 mmol / g and 0.97 mmol / g, respectively.

[0141] [Production A of Composites]

[0142] (Example 1A)

[0143] The cellulose nanofiber dispersion (solid content 10 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A was filtered under reduced pressure to remove water and replaced with methanol 5 times. Next, the cellulose nanofiber methanol dispersion was filtered under reduced pressure to remove methanol, and the operation of further replacing 90 parts by weight of an alicyclic epoxy monomer containing 1 part by weight of a thermal cationic catalyst (SI-100L) was repeated 5 times. Then, the obtained cellulose nanofiber dispersion epoxy resin (cellulose solid content 10% by weight) was molded and heated at 100 ° C for 2 hours, followed by heating at 150 ° C for 2 hours to cure. Thereby, a composite having a thickness of 1 mm was obtained. The obtained composite was cut to a width of 10 mm, and a test piece for bending strength measurement was produced. When the bending strength was measured for this test piece, it was 48N.

[0144] (Example 2A)

[0145] Cellulose nanofibers were obtained by filtering under reduced pressure the cellulose nanofiber dispersion (solids content: 15 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A and further freeze-drying. Next, the mixture obtained by adding 15 parts by weight of cellulose nanofibers to 85 parts by weight of phenol novolac resin and 15 parts by weight of hexamethylenetetramine was mixed with a mixer for 3 minutes. In addition, the mixture was kneaded by two heating rolls at 100 ° C to obtain a thermosetting resin molding material. The obtained molding material was heated at 125 ° C for 2 hours by compression molding, and then further cured by heating at 150 ° C for 2 hours. Thereby, a composite having a thickness of 1 mm was obtained. The obtained composite was cut to a width of 10 mm to produce a test piece for bending strength measurement. The bending strength of this test piece was 60N.

[0146] (Example 3A)

[0147] To the cellulose nanofiber dispersion (solid content 100 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A, tetraethoxysilane was added in the same weight as the cellulose nanofiber solid content, and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. The total light transmittance, the coefficient of thermal expansion, and the coefficient of humidity expansion were measured for this film. The total light transmittance was 90%, the coefficient of thermal expansion was 11 ppm / ° C, and the coefficient of humidity expansion was 26 ppm / humidity%.

[0148] (Example 4A)

[0149] To the cellulose nanofiber dispersion (solid content 100 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A, phenyltriethoxysilane was added in the same weight as the cellulose nanofiber solid content, and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For this film, the total light transmittance, the coefficient of thermal expansion, and the coefficient of humidity expansion were measured. The total light transmittance was 89%, the coefficient of thermal expansion was 10 ppm / ° C, and the coefficient of humidity expansion was 23 ppm / humidity%.

[0150] (Example 5A)

[0151] 3-glycidoxypropyl triethoxysilane was added to the cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight (100 parts by weight of the solid content) obtained in Production Example A and the same weight as the weight of the cellulose nanofiber solid content and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. The total light transmittance, thermal expansion coefficient, and humidity expansion coefficient were measured for this film. The total light transmittance was 88%, the thermal expansion coefficient was 11 ppm / ° C, and the humidity expansion coefficient was 25 ppm / humidity%.

[0152] (Example 6A)

[0153] Titanium alkoxide was added to the cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight (100 parts by weight of the solid content) obtained in Production Example A, and the same weight as that of the cellulose nanofiber solid content was added, followed by stirring at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For this film, total light transmittance, thermal expansion coefficient, and humidity expansion coefficient were measured. The total light transmittance was 88%, the thermal expansion coefficient was 12 ppm / ° C, and the humidity expansion coefficient was 27 ppm / humidity%.

[0154] (Example 7A)

[0155] Cellulose nanofiber dispersion (solid content of 100 parts by weight) and solid resin concentration of 0.2% by weight obtained in Production Example A were mixed with 80 parts by weight of epoxy resin (Denacol EX-214L, manufactured by Nagase Chemtex) and 5 parts by weight of tetramethylethylenediamine. The mixture was stirred for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 50 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured for this film. The total light transmittance was 80%, the thermal expansion coefficient was 15 ppm / ° C, the humidity expansion coefficient was 110 ppm / humidity%, and the swelling rate was 16 times. .

[0156] (Example 8A)

[0157] Cellulose nanofiber dispersion (solid content 100 parts by weight) and epoxy resin (Denacol EX-1410L, manufactured by Nagase Chemtex) having a solid content concentration of 0.2% by weight obtained in Production Example A were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 50 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured for this film. The total light transmittance was 80%, the thermal expansion coefficient was 14 ppm / ° C, the humidity expansion coefficient was 61 ppm / humidity%, and the swelling ratio was 1.8 times. .

[0158] (Example 9A)

[0159] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and epoxy resin (Denacol EX-1410L, manufactured by Nagase Chemtex) having a solid content concentration of 0.2% by weight obtained in Production Example A were mixed with 5 parts by weight of tetramethylethylenediamine and mixed at room temperature. The mixture was stirred for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 50 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured for this film. The total light transmittance was 80%, the thermal expansion coefficient was 12 ppm / ° C, the humidity expansion coefficient was 90 ppm / humidity%, and the swelling ratio was 3.1 times. .

[0160] (Example 10A)

[0161] Cellulose nanofiber dispersion (solid content of 100 parts by weight) and solid resin concentration of 0.2% by weight obtained in Production Example A were mixed with 110 parts by weight of epoxy resin (Denacol EX-1610L, manufactured by Nagase Chemtex) and 5 parts by weight of tetramethylethylenediamine. The mixture was stirred for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 50 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured for this film. The total light transmittance was 80%, the thermal expansion coefficient was 13 ppm / ° C, the humidity expansion coefficient was 76 ppm / humidity%, and the swelling rate was 2.4 times. .

[0162] (Example 11A)

[0163] Cellulose nanofiber dispersion (solids content of 100 parts by weight) having a solid content concentration of 0.2% by weight obtained in Production Example A was mixed with 100 parts by weight of resol type phenol resin (PR-967, manufactured by Sumitomo Bakelite) and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film having a thickness of 25 µm was obtained. The total light transmittance, humidity expansion coefficient, and swelling rate were measured for this film. The total light transmittance was 50%, the humidity expansion coefficient was 50 ppm /% humidity, and the swelling

rate was 1.2 times. Moreover, since this sample was bitten, a sample for measuring the thermal expansion coefficient could not be obtained.

[0164] (Example 12A)

[0165] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid resin concentration of 0.2% by weight obtained in Production Example A were mixed with 300 parts by weight of resol type phenolic resin (PR-967, manufactured by Sumitomo Bakelite) and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film with a thickness of 58 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured for this film. The total light transmittance was 40%, the thermal expansion coefficient was 20 ppm / ° C, the humidity expansion coefficient was 45 ppm / humidity%, and the swelling rate was 1.2 times. .

[0166] (Comparative Example 1A)

[0167] After the sulfurous bleached coniferous pulp was swollen in water, it was finely dispersed with a mixer. The obtained short fiber pulp dispersion was filtered under reduced pressure to remove water and replaced with methanol 5 times. Next, the operation of replacing the short-fiber pulp methanol dispersion with reduced pressure by filtration to remove methanol and replacing 90 parts by weight of an alicyclic epoxy monomer containing 1 part by weight of a cationic catalyst (SI-100L) was repeated 5 times. Then, the obtained short-fiber pulp dispersion epoxy resin (cellulose solid content 10% by weight) was molded and heated at 100 ° C for 2 hours, followed by further heating at 150 ° C for 2 hours to cure. Thereby, a composite having a thickness of 1 mm was obtained. The obtained composite was cut to a width of 10 mm to prepare a test piece for bending strength measurement. The bending strength of this test piece was 28N.

[0168] In addition, a single fiber pulp methanol dispersion was observed by SEM, and the maximum fiber diameter was 70 µm and the number average fiber diameter was 40 µm.

[0169] (Comparative Example 2A)

[0170] After the sulfurous bleached coniferous pulp was swollen in water, it was finely dispersed with a mixer. The obtained short-fiber pulp dispersion was filtered under reduced pressure to remove water, and further freeze-dried to obtain fine cellulose fibers. Next, the mixture obtained by adding 15 parts by weight of fine cellulose fibers to 85 parts by weight of phenol novolac and 15 parts by weight of hexamethylenetetramine was mixed with a mixer for 3 minutes. In addition, the mixture was kneaded by two heating rolls at 100 ° C to obtain a thermosetting resin molding material. The obtained molding material was heated at 125 ° C for 2 hours by compression molding, and then further cured by heating at 150 ° C for 2 hours. Thereby, a composite having a thickness of 1 mm was obtained. The obtained composite was cut to a width of 10 mm to produce a test piece for bending strength measurement. When the bending strength was measured for this test piece, it was 40N.

[0171] In addition, a single fiber pulp methanol dispersion was observed by SEM, and the maximum fiber diameter was 70 µm and the number average fiber diameter was 40 µm.

[0172] (Comparative Example 3A)

[0173] The cellulose nanofiber dispersion (solid content 0.15% by weight) obtained in Production Example A was evaporated with moisture in an oven at a temperature of 50 ° C according to a chalet subjected to a release treatment, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured for this film. The total light transmittance was 91%, the thermal expansion coefficient was 10 ppm / ° C, the humidity expansion coefficient was 125 ppm / humidity%, and the swelling rate was 140 times. .

[0174] [Production B of fine cellulose fibers]

[0175] (Production Example B)

[0176] First, it is mainly composed of cellulose fibers with a fiber diameter exceeding 1000 nm, and 2 g of undried pulp and 0.025 g of TEMPO (2,2,6,6-tetramethyl-1-piperidine-N) in a dry weight. -Oxyl) and 0.25 g of sodium bromide were dispersed in 150 ml of water to prepare a dispersion.

[0177] Next, 13% by weight of an aqueous sodium hypochlorite solution was added to this dispersion so that the amount of sodium hypochlorite was 2.5 mmol per 1 g of pulp, and the reaction was started. During the reaction, 0.5M sodium hydroxide aqueous solution was added dropwise using an automatic titrator to maintain the pH at 10.5. Subsequently, when no change in pH was observed, the reaction was considered to be complete, and neutralized to pH 7 with 0.5M aqueous hydrochloric acid. Then, the reaction was filtered and the filtrate was washed with a sufficient amount of water, and filtration was repeated six times. Thereby, a reactant fiber containing water having a solid content concentration of 2% by weight was obtained.

[0178] Next, 0.2% by weight of a reactant fiber dispersion was prepared by adding water to the obtained reactant fiber.

[0179] This reaction fiber dispersion was treated 20 times at a pressure of 200 bar (20 MPa) using a high pressure homogenizer (manufactured by APV GAULIN LABORATORY, type 15MR-8TA). Thereby, a transparent cellulose nanofiber dispersion was obtained.

[0180] This cellulose nanofiber dispersion was cast on a carbon film-coated grid after hydrophilic treatment, and then negatively dyed with 2% uranyl acetate. And the cast cellulose nanofiber dispersion was observed by TEM, but the largest fiber diameter was 10 nm and the number average fiber diameter was 8 nm.

[0181] Moreover, the cast cellulose nanofiber dispersion was dried, and transparent membrane-like cellulose was obtained. A wide-angle X-ray diffraction image was obtained for this membrane-like cellulose, and it became clear that the membrane-like cellulose was composed of cellulose nanofibers having a cellulose I-type crystal structure.

[0182] In addition, the same membrane-like cellulose was subjected to total reflection infrared spectroscopy to obtain an ATR spectrum. The presence of the carbonyl group was confirmed from the pattern of the ATR spectrum, and the amount of the aldehyde group and the amount of the carboxyl group in cellulose evaluated by the method described above were 0.31 mmol / g and 1.7 mmol / g, respectively.

[0183] [Production of Composite B]

[0184] (Example 1B)

[0185] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex 20, particle diameter 10-20 nm, anhydrous silicic acid content 20-21 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2 wt%) Industrial Co.) 1 part by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 87%, and the thermal expansion coefficient in the range of 30 ° C to 180 ° C was 9 ppm / ° C, and the humidity expansion coefficient was 70 ppm /% humidity, and the swelling rate was twice.

[0186] (Example 2B)

[0187] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex N, particle diameter 10-20 nm, anhydrous silicic acid content 20-21 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2% by weight) Industrial Co.) 1 part by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated to moisture in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. The thermal expansion coefficient, humidity expansion coefficient, and swelling rate of the obtained film were measured. The thermal expansion coefficient in the range of 30 ° C to 180 ° C is 10 ppm / ° C, the humidity expansion coefficient is 61 ppm /% humidity, and the swelling rate is 1.6 times.

[0188] (Example 3B)

[0189] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex O, particle diameter 10-20 nm, anhydrous silicic acid content 20-21 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2 wt%) Industrial Co.) 1 part by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated to moisture in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, the total light transmittance, the coefficient of thermal expansion, the coefficient of humidity expansion and the swelling rate were measured. Was 65 ppm /% humidity, and the swelling ratio was 1.7 times.

[0190] (Example 4B)

[0191] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex XS, particle diameter 4-6 nm, anhydrous silicic acid content 20-21 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2% by weight) Industrial Co.) 1 part by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, the total light transmittance, the coefficient of thermal expansion, the coefficient of humidity expansion and the swelling rate were measured. Was 68 ppm /% humidity, and the swelling ratio was 1.9 times.

[0192] (Example 5B)

[0193] 100 parts by weight of a cellulose nanofiber dispersion (solid content 0.2 g) and a colloidal silica (Snowtex CM, particle diameter 20-30 nm, anhydrous silicic acid content 30-31 wt%, Nissan Chemical, obtained in Production Example B with a solid content concentration of 0.2% by weight) Industry Co., Ltd.) 0.7 parts by weight (solid content 0.2g) was mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 88%, and the thermal expansion coefficient in the range of 30 ° C to 180 ° C was 11 ppm / ° C, and the humidity expansion coefficient. Was 70 ppm /% humidity, and the swelling ratio was 1.9 times.

[0194] (Comparative Example 1B)

[0195] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example B was evaporated from the oven at a temperature of 50 ° C according to the chalet subjected to the release treatment, and further dried in a vacuum oven at 120 ° C. Thus, a transparent film having a thickness of 30 µm was obtained. For the obtained film, the total light transmittance, the coefficient of thermal expansion, the coefficient of humidity expansion and the swelling rate were measured. Was 115 ppm / % humidity, and the swelling ratio was 100 times.

[0196] [Production C of fine cellulose fibers]

[0197] (Production Example C)

[0198] First, it is mainly composed of fibers with a fiber diameter of more than 1000 nm, and by dry weight, 2 g equivalent of undried pulp and 0.025 g of TEMPO (2,2,6,6-tetramethyl-1-piperidine-N-Oxyl) and 0.25 g of sodium bromide were dispersed in 150 ml of water to prepare a dispersion.

[0199] Next, 13% by weight of an aqueous sodium hypochlorite solution was added to this dispersion so that the amount of sodium hypochlorite was 2.5 mmol per 1 g of pulp, and the reaction was started. During the reaction, 0.5M sodium hydroxide aqueous solution was added dropwise using an automatic titrator to maintain the pH at 10.5. Subsequently, when no change in pH was observed, the reaction was considered to be complete, and neutralized to pH 7 with 0.5M aqueous hydrochloric acid. Then, the reaction product was filtered and the filtrate was washed with a sufficient amount of water, and filtration was repeated 6 times. Thereby, a reactant fiber containing 2% by weight of water in a solid content was obtained.

[0200] Next, 0.2% by weight of a reactant fiber dispersion was prepared by adding water to the obtained reactant fiber.

[0201] This reactant fiber dispersion was treated 10 times at a pressure of 20 MPa using a high pressure homogenizer (manufactured by APV GAULIN LABORATORY, type 15MR-8TA). Thereby, a transparent cellulose nanofiber dispersion was obtained.

[0202] This cellulose nanofiber dispersion was cast on a carbon film-coated grid that had been subjected to hydrophilic treatment, and then negatively dyed with 2% uranyl acetate. And the cast cellulose nanofiber dispersion was observed by TEM, but the largest fiber diameter was 10 nm and the number average fiber diameter was 6 nm.

[0203] Moreover, the cast cellulose nanofiber dispersion was dried, and transparent membrane-like cellulose was obtained. A wide-angle X-ray diffraction image was obtained for this membrane-like cellulose, and it became clear that the membrane-like cellulose was composed of cellulose nanofibers having a cellulose I-type crystal structure.

[0204] In addition, the same membrane-like cellulose was subjected to total reflection infrared spectroscopy to obtain an ATR spectrum. The presence of the carbonyl group was confirmed from the pattern of the ATR spectrum, and the amount of the aldehyde group and the amount of the carboxyl group in cellulose evaluated by the method described above were 0.31 mmol / g and 1.7 mmol / g, respectively.

[0205] [Production C of Composites]

[0206] (Example 1C)

[0207] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C and synthetic smectite (lucentite SWF) were mixed so that the weight ratio of cellulose nanofiber and synthetic smectite was 25 to 75 and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated from the oven at a temperature of 50 ° C. according to a chalet subjected to a release treatment to obtain a transparent film having a thickness of 50 µm. The total light transmittance, thermal expansion coefficient, and swelling rate of the obtained film were evaluated. The total light transmittance was 91%, the coefficient of linear expansion in the range of 30 ° C to 180 ° C was 4 ppm / ° C, and the swelling rate was 15 times.

[0208] (Example 2C)

[0209] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C and synthetic smectite (lucentite SWF) were mixed so that the weight ratio of cellulose nanofiber and synthetic smectite was 55 to 45, and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated in an oven at a temperature of 50 ° C. according to a chalet subjected to a release treatment to obtain a transparent film having a thickness of 20 µm. The total light transmittance, the coefficient of thermal expansion and the swelling rate of the obtained film were evaluated. The total light transmittance was 91%, the linear expansion coefficient in the range of 30 ° C to 180 ° C was 5 ppm / ° C, and the swelling rate was 48 times.

[0210] (Example 3C)

[0211] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C and synthetic saponite (Smecton SA) were mixed so that the weight ratio of cellulose nanofiber and synthetic saponite was 25 to 75 and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated in an oven at a temperature of 50 ° C. according to a chalet subjected to a release treatment to obtain a transparent film having a thickness of 47 µm. The total light transmittance, the coefficient of thermal expansion and the swelling rate of the obtained film were evaluated. The total light transmittance was 90%, the coefficient of linear expansion in the range of 30 ° C to 180 ° C was 3.2 ppm / ° C, and the swelling rate was 12 times.

[0212] (Example 4C)

[0213] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C and synthetic saponite (Smecton SA) were mixed so that the weight ratio of cellulose nanofiber and synthetic saponite was 50 to 50 and stirred at room temperature for 30 minutes. The obtained mixed solution was evaporated in an oven at a temperature of 50 ° C. according to a chalet subjected to a release treatment to obtain a transparent film having a thickness of 41 µm. The total light transmittance, thermal expansion coefficient, and swelling rate of the obtained film were evaluated. The total light transmittance was 90%, the coefficient of linear expansion in the range of 30 ° C to 180 ° C was 5.8 ppm / ° C, and the swelling rate was 32 times.

[0214] (Example 5C)

[0215] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid flake inorganic material (from Lucent SWF, manufactured by Coff Chemical Co., Ltd.) having a solid content concentration of 0.2% by weight obtained in Production Example C and epoxy resin (Denacol EX-214L, Nagase Chemtex) Co.) 600 parts by weight were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film with a thickness of 24 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient and swelling rate were measured. The total light transmittance was 91%, the thermal expansion coefficient was 14 ppm / ° C, the humidity expansion coefficient was 60 ppm / humidity%, and the swelling ratio was 2.1 times. .

[0216] (Example 6C)

[0217] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid flake inorganic material (from Lucent SWF, manufactured by Coff Chemical Co., Ltd.) having a solid content concentration of 0.2% by weight obtained in Production Example C and epoxy resin (Denacol EX-214L, Nagase Chemtex) Co.) 200 parts by weight were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thus, a film having a thickness of 50 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 92%, the thermal expansion coefficient was 13 ppm / ° C, the humidity expansion coefficient was 57 ppm / humidity%, and the swelling rate was 1.7 times. .

[0218] (Example 7C)

[0219] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid flake inorganic material (Smecton SA, manufactured by Kunimine Industries) with a solid content concentration of 0.2% by weight obtained in Production Example C and epoxy resin (Denacol EX-214L, Nagase) Chemtex Corporation) 600 parts by weight were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film having a thickness of 30 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 91%, the thermal expansion coefficient was 15 ppm / ° C, the humidity expansion coefficient was 92 ppm / humidity%, and the swelling ratio was 3.4 times. .

[0220] (Example 8C)

[0221] Cellulose nanofiber dispersion (solid content: 100 parts by weight) and solid flake inorganic material (Smecton SA, manufactured by Kunimine Industries) with a solid content concentration of 0.2% by weight obtained in Production Example C and epoxy resin (Denacol EX-214L, Nagase) Chemtex Corporation) 200 parts by weight were mixed and stirred at room temperature for 30 minutes. The resulting mixed solution was evaporated in an oven at a temperature of 50 ° C according to a release-treated chalet, and further dried in an oven at 120 ° C. Thereby, a film with a thickness of 58 µm was obtained. For the obtained film, total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate were measured. The total light transmittance was 91%, the thermal expansion coefficient was 13 ppm / ° C, the humidity expansion coefficient was 71 ppm / humidity%, and the swelling rate was 2.4 times. .

[0222] (Comparative Example 1C)

[0223] The cellulose nanofiber dispersion having a solid content concentration of 0.2% by weight obtained in Production Example C was stirred at room temperature for 30 minutes and evaporated moisture in an oven at a temperature of 50 ° C. according to the release-treated chalet to obtain a transparent film having a thickness of 18 µm. The total light transmittance, thermal expansion coefficient, humidity expansion coefficient, and swelling rate of the obtained film were evaluated. The total light transmittance was 90%, the coefficient of thermal expansion in the range of 30 ° C to 180 ° C was 12 ppm / ° C, the coefficient of humidity expansion was 200 ppm /% humidity, and the swelling rate was 185 times.

[0224] [Evaluation of Complexes]

[0225] The characteristic evaluation method is as follows.

[0226] (a) Flexural strength

[0227] The bending strength of the test piece for measuring the bending strength is in accordance with JIS K 7171, the extension distance 36 mm, the cross head speed 1 mm / min, 23 ° C, the bending strength measurement device under 60%

relative humidity (Note) Was measured using Orient Tech Co., Ltd., UCT-30T type tensiron).

[0228] (b) Thermal expansion coefficient

[0229] Using a thermal stress distortion measuring device (TMA / SS120C, manufactured by Seiko Electronics Co., Ltd.), the temperature was increased from 30 ° C to 150 ° C at a rate of 5 ° C for 1 minute under a nitrogen atmosphere, and then 0 After cooling to ° C, the temperature was increased at a rate of 5 ° C for 1 minute to obtain a value measured at 30 ° C to 150 ° C. The load was set to 5 g, and measurement was performed in a tensile mode.

[0230] In addition, for Examples 1B to 5B and Comparative Example 1B, after raising the temperature from 30 ° C to 200 ° C at a rate of 5 ° C for 1 minute, once cooled to 0 ° C, and again at 5 ° C for 1 minute It was obtained by measuring the value at 30 ° C ~ 180 ° C by raising the temperature at a rate.

[0231] In addition, for Examples 1C to 8C and Comparative Example 1C, the temperature was increased from 30 ° C to 200 ° C at a rate of 5 ° C for 1 minute, and then cooled to -50 ° C once again, and then 5 ° C for 1 minute. It was obtained by measuring the value at 30 ° C ~ 180 ° C by raising the temperature in the ratio of.

[0232] (c) Total light transmittance

[0233] The total light transmittance was measured with a spectrophotometer (manufactured by Shimadzu Corporation, U3200).

[0234] In addition, about Example 1C-8C and Comparative Example 1C, the total light transmittance was measured with the haze meter (made by Nippon Color Co., Ltd., NDH-2000).

[0235] (d) Humidity expansion coefficient

[0236] On the obtained film, two points, which are the basis of dimensional measurement, were drawn and left for 24 hours in an atmosphere of 23 ° C at room temperature and 60% humidity, and then dried in a dryer at 100 ° C for 3 hours.

[0237] Immediately after drying, the distance between two points drawn in advance was measured with a three-dimensional measuring instrument, and this distance was used as a reference for the distance between two points. Thereafter, the film after drying was allowed to stand for 24 hours under an atmosphere of 23 ° C and 60% humidity again, and the distance between two points drawn in advance was measured with a 3D measuring instrument to calculate the rate of dimensional change from the reference distance. In addition, the humidity of the exterior after drying was set to 0%, and the coefficient of humidity expansion per 1% of humidity in the range of 0% to 60% of humidity was calculated.

[0238] (e) swelling ratio

[0239] The obtained film was immersed in pure water at 23 ° C for 1 hour to measure the rate of change in film thickness before and after impregnation. And the swelling ratio was calculated as a magnification of the film thickness after impregnation to the film thickness before impregnation.

[0240] The measurement results are shown in Tables 1-3.

[0242] As can be seen from Table 1, the test pieces obtained in Examples 1A and 2A (composites obtained using the composite composition of the present invention) are all mechanical strength compared to the test pieces comprising the conventional fibrous filler obtained in Comparative Example 1A. And high dimensional stability and excellent various properties.

[0243] Further, the films obtained in Examples 3A to 12A (composites obtained using the composite composition of the present invention) are films formed from a composite composition comprising a fibrous filler and a resin or a coupling agent (or a hydrolyzate of the coupling agent), but these are humidity It was confirmed that the expansion coefficient (absorption dimensional change rate) and the thermal expansion coefficient were relatively small and excellent transparency.

[0245] As can be seen from Table 2, it was confirmed that the films obtained in Examples 1B to 5B (composites obtained using the composite composition of the present invention) had a small swelling ratio and excellent water resistance compared to the films obtained in Comparative Example 1B. .

[0247] As can be seen from Table 3, it was confirmed that the films obtained in Examples 1C to 8C (composites obtained using the composite composition of the present invention) had a small swelling ratio and excellent water resistance compared to the films obtained in Comparative Example 1C. . Moreover, it was confirmed that the films obtained in Examples 1C to 8C had relatively low thermal expansion coefficients, and thus excellent dimensional stability due to heat and high transparency.

[0248] In addition, the main raw materials used in each Example and each comparative example are as follows.

[0249] Epoxy resin

[0250] : Seroxide 2021 Daicel Chemical

[0251] : Denacall EX-214L manufactured by Nagase Chemtex

[0252] : Denacall EX-1410L manufactured by Nagase Chemtex

[0253] : Denacall EX-1610L manufactured by Nagase Chemtex

[0254] Phenolic resin

[0255] : Resol type phenol resin PR-967 Sumitomo Bakelite

[0256] Thermo cationic catalyst

[0257] : SI-100L Samshin Chemical

[0258] Phenol novolac resin

[0259] : PR-HF-6 Sumitomo Bakelite

[0260] Coupling agent

[0261] : Tetraethoxysilane Wako Pure Chemicals

[0262] : Phenyltriethoxysilane Azmax product

[0263] : 3-glycidoxypropyl triethoxysilane Shin-Etsu Chemical

[0264] : Titanium alkoxide KR-ET Ajinomoto Fine Technoze

[0265] Crosslinking material (hexamethylenetetramine)

[0266] : Urotropin Sumitomo Purification

[0267] Metal oxide

[0268] : Colloidal silica snowtex 20 manufactured by Nissan Chemical

[0269] : Colloidal silica snowtex N manufactured by Nissan Chemical Industries

[0270] : Colloidal silica snowtex O manufactured by Nissan Chemical

[0271] : Colloidal Silica Snowtex XS Nissan Chemical Industries Co., Ltd.

[0272] : Colloidal silica snowtex CM manufactured by Nissan Chemical Industries

[0273] Flake inorganic material

[0274] : Smecton SA Kunimine Industrial Festival

[0275] : Lucentite SWF Cope Chemical

[0276] Industrial availability

[0277] The composite composition of the present invention includes at least one of a fibrous filler and a resin, a metal oxide, and a flaky inorganic material, and the average fiber diameter of the fibrous filler is 4 to 1000 nm. For this reason, at least one of a fibrous filler, a resin, a metal oxide, and a flaky inorganic material brings mechanical and chemical action to the composite formed by molding this composite composition. As a result, a composite having a low thermal expansion coefficient, high strength, high transparency, and low humidity expansion coefficient (high water resistance, high dimensional stability) is obtained. Accordingly, the composite of the present invention is used in automobile parts such as automobile exteriors and dashboards, parts of transportation equipment such as railroads, aircraft, ships, chassis in houses or offices, building materials such as wall plates and top plates, pillars or reinforced concrete. Structural members such as reinforcing bars, electronic circuits, electronic parts such as substrates for display bodies, cases (housing) of household appliances such as PCs and mobile phones, office equipment such as stationery, household goods such as furniture, disposable containers, sports Household items such as supplies and toys, outdoor installations such as signs and signs, shock-absorbing members such as bulletproof shields, bulletproof vests, protective equipment such as helmets, artificial bones, medical supplies, abrasives, soundproof walls, protective walls, vibrations It can be used for absorbent members, tools, mechanical parts such as leaf springs, musical instruments, packing materials, and the like. Therefore, the composite composition and composite of the present invention have industrial applicability.