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Alsipaper

Popular Science (September 1940): "Paper Made from Clay"

USP # 3,266,636 ~ Inorganic Film Products & Method of Making Same

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USP # 4,118,247 ~ Suspensions of Reactive Acidic Clay Pigments

Tomoe Engineering: Bentonite Paper Products

Popular Science (September 1940)

"Paper Made from Clay"

Paper from clay, a remarkable new product for household, industrial, and war use, has just been developed at the Massachusetts Institute of Technology. While various kinds of it may be applied in familiar ways -- as in transparent wrapping sheets and milk containers -- the "mineral paper" is far more than a substitute for wood pulp or linen paper.

In printing, its ultrafine texture imparts new clarity and detail to half-tone illustrations. Waterproof and nonabsorbent, it gives a much higher gloss than common paper. Unaffected by age, it may be employed for permanent records.

Its fibers can be made into filter cloth invaluable to chemical industries, because of its resistance to corrosive acids and alkalies. A flexible sheet form can be wrapped around electric cables for insulation.

For mica, a strategic war material used in electric parts of autos, planes, and radios, the United States depends almost entirely on imports from abroad. Since the new clay paper has the same chemical composition and electrical insulating qualities, stiff sheets of it should make an admirable substitute.

Called alsifilm, the new paper takes its name from the first letters of aluminum and silica. These are the constituents of Wyoming bentonite, a type of clay that serves as raw material for light-brown "mineral paper". Another kind of bentonite, from California, yields white paper.

Ground to fine powder, the clay is suspended in water while grit and foreign matter settle out. Evaporated to a jellylike mass, the residue then is chemically treated according to the desired use. Ultramicroscopic mineral fibers mat together during the process, as fibers of ordinary paper do.

U.S. Patent #3,266,636

Inorganic Film Products & Method of Making Same

(Cl. 18-57) ~ (December 16, 1941)

Ernst A. Hauser

This invention relates to flexible, coherent, self-supporting solid bodies such as films, filaments, coatings and the like formed of colloidal, crystalline inorganic hydrous oxides which contain structural water and are capable of swelling when brought into contact with water to form plastic hydro-gels and exhibit base exchange properties, and to the process of making such bodies.

It is known that certain organic materials are capable of forming coherent, self-supporting flexible films or sheets upon being deposited in a thin layer from a solution or suspension by evaporation of the solvent or vehicle. Typical examples are rubber, cellulose derivatives and resins. The formation of such films may be explained by the theory that the film-forming materials are composed of large, long-chain molecules which felt together when the diluting vehicle is removed.

Now I have found that a somewhat similar result may be obtained with certain inorganic materials such as highly hydrated colloidal clays, e.g., bentonite. It is of course known that a film or thin layer of finely divided inorganic materials may be deposited on solid surfaces. For example, a suspension of chalk in water may be deposited as a film on a solid surface and dried, resulting in a coating of the chalk on the solid surface. If a sufficiently thick deposit is produced it may be removed as a self-supporting rigid cake, but so far as I am aware no one heretofore has produced self-supporting coherent flexible films of inorganic materials without an organic binder.

The ability of inorganic materials to form self-supporting coherent flexible films apparently depends upon their ability to form gels due to the presence of strongly hydrated colloidal matter. I have found that when a sol (water dispersion) of such a colloidal strongly hydrated inorganic material, such as a water suspension of a highly hydrated colloidal bentonite, is deposited as a thin coating on a solid surface and dried, the resulting film may be removed from the surface and is coherent, self-supporting and flexible and may have sufficient strength to permit its use for a variety of purposes.

Ultramicroscopic investigation has shown that during the evaporation of the vehicle of such as inorganic sol it passes through the gel stage, with the particles still in random arrangement (after the Brownian motion has ceased) and finally, as the particles are forced closer and closer together by the removal of the vehicle, they line up and produce relatively long filaments or fibers and fiber bundles which interweave and interfelt to form a coherent film. Under magnification some of the films have somewhat the appearance of a woven fabric. This formation of fibers probably is due to the fact that when colloidal particles of an isometric shape and possessing a sufficient polarity are brought sufficiently close together by removal of the suspending medium they attach to each other to form the fibers or fibrous crystals which have been observed. X-ray analysis of the film shows only part of the lines characteristic of the x-ray diffraction powder diagram of the material, e.g., montmorillonite, of which the film is formed and whereas a picture obtained by exposing the film edgewise shows an x-ray diffraction pattern which also lacks certain lines found in the powder diagram of the material, the two film diagrams when superimposed or combined give a complete pattern which matches the powder pattern of the material. This observed characteristic of the films is believed to be capable of serving to identify films in accordance with the invention.

In order to form such films, the particles of solid material which are capable of being hydrated and of swelling in water preferably are of colloidal dimensions. In general the smaller are the individual particles and the more nearly monodisperse the system the stronger and more flexible and less brittle will be the film produced although useful films may be made from materials with the particles in the upper range of colloidal dimensions and with somewhat polydisperse systems, containing, for example, particles ranging in size from 0.1 to 0.5 micron. By colloidal dimensions I mean particle sizes less than 1 micron. The particles within a given batch of material will of course vary in size but it is preferred that the bulk of the particles shall be of a particle size of the order of 0.01 to 0.1 micron.

A suitable method for the preparation of the films is as follows:

Bentonite (a hydrous aluminum or magnesium or aluminum magnesium silicate) of commercial grade which may have been partially purified to free it of coarse grained impurities in any suitable manner such as air sifting is suspended in water and allowed to settle for several days and the liquid is decanted from the deposited sludge. A suspension containing 1 to 2% of solids is suitable for this purpose. This sludge

consists largely of particles of greater than colloidal size, and consists mainly of quartz, calcium carbonate, feldspar and the like. The decanted suspension which may be taken off in fractions at different levels is then subjected to the action of a super-centrifuge, for example a centrifuge having a cylindrical tube about 2 inches in diameter operated at about 25,000 revolutions per minute. The suspension is flowed in at the bottom and out at the top resulting in a deposition of heavier or coarser particles on the wall of the tube near the bottom and smaller particles near the top of the tube. The overflow contains still smaller particles and may be subjected to further centrifuging for the recovery thereof. The deposit on the wall of the tube may be separated into two or more fractions according to the particle size or distance from the bottom of the tube, resuspended in water and centrifuged again. By this procedure one may obtain a substantially monodisperse sol of any desired average particle size. The particle size range within the fraction should be relatively small, e.g., not more than about 10 millimicrons in a product having an average particle size of up to say 100 millimicrons. The larger the average particle size of particle the greater may be the actual difference in particle size but the relative difference in particle size, i.e., the ratio of the difference to the average particle size should be small, e.g., not more than about one-fourth of the average particle size.

The suspension passed through the centrifuge should be quite dilute. In general the finer the average size of the particles in suspension the more dilute should be the suspension. A concentration of 0.5% to 1% is suitable for the crude suspension obtained by stationary settling of a suspension of bentonite containing particles of all sizes up to about 1 micron.

Films of the resulting refined material may be produced in a variety of ways. For instance the suspension may be deposited as a film or layer on a suitable removable liner within the centrifuge cylinder, the liner and film removed, laid flat and dried and the films stripped off of the liner. Foils of aluminum, copper, brass, etc., are suitable for the liner or one may use other materials with or without a coating such as paraffin to prevent adhesion of the film.

Similar films may be formed by flowing a dilute suspension or sol, e.g., 1 or 2% on a suitable surface, such as glass, and allowing to dry and stripping of the resulting film. Continuous films and filament may be produced in the ways commonly employed with other film and filament forming materials. For example, a drying cylinder may be revolved in contact with the suspension. It is also possible to employ the material in such a concentration that it is more or less gelatinous or pasty by spreading it in substantially uniform thickness on a suitable surface. It will be apparent that films of any desired thickness may be produced and that by selecting the average size of the particles in suspension, films of different grades as to strength, flexibility, degree of transparency, etc., may be produced. Films made from suspensions of large particle size tend to lack flexibility or to be brittle. Certain impurities in the suspension tend to interfere with the formation of fibrous structure and produce weak spots in the resulting films.

Films made from bentonite after being dried in the air at atmospheric temperatures contain a considerable amount of water, e.g., 8% and are capable of swelling in water. This is particularly true of the natural clays which contain alkali metal. The clays in which the alkali metal has been replaced by hydrogen, e.g., the hydrogen clays lose this property of swelling in water upon being air-dried. After the non-hydrogen clay films have been heated to 110°C or higher they are dehydrated and also lose proportionally this property of swelling in water. After slow dehydration the films may be heated to white heat without being destroyed. Such heating yields a product which is very similar in appearance and in dielectric properties to mica. A useful product of this character may be made by heating the film to about 300°C and simultaneously subjecting it to heavy pressure, say 1000 pounds per square inch. If several of the films, before being dehydrated are laid together and then subjected to heating and heavy pressure a product resembling mica is produced.

Before being dehydrated by heating, the films, as stated above, swell in water but they are resistant to oils, acid, alkalies and other strong electrolytes and may be heated to white heat without being destroyed. Depending on the purity of the clay, the size of the particles and the thickness of the film it may vary from being substantially opaque through all degrees of transparency to substantial transparency.

The utility of the films has not been fully investigated but certain uses are evident, e.g., as a substitute for

paper where resistance to the action of certain corrosive chemicals is required and as an insulating flexible sheet material in place of mica, synthetic resins, and impregnated paper or fabric. As stated above a plurality of sheets subjected to high pressure and temperature strongly resembles mica in appearance and dielectric properties. The films are non-flammable, may be written or printed upon and are capable of withstanding high temperatures. A useful product may be made by coating or impregnating a plurality of the films with a solution or melt of a heat hardenable synthetic resin, superposing the so treated films and heating and pressing them to form a laminated structure having high dielectric properties.

The film may be deposited on a surface such as that of a corrodable metal, e.g., iron to serve as a base or priming coat for anti-corrosion paint.

I have successfully used a sol of bentonite having an average particle size of about 14 millimicrons and produced excellent flexible, self-supporting translucent film having a thickness of about one-thousandth of an inch. I have given that particle size range as from 10 millimicrons to 1 micron but as stated I prefer the smaller particles. A more practical range of particle size is from 0.05 to 0.1 micron.

In the above-described process I have referred only to the preparation of suspensions or sols suitable for the production of film, by centrifuging. It is, however, possible to produce such a suspension of bentonite by settling. Thus by settling a suspension of bentonite in water for a week or more and then drawing off only the top-most layer of liquid I may obtain directly a sol which is capable of producing a self-supporting film.

The suspensions used for the production of film vary considerably in concentration. I have found pure clay suspensions of a concentration as low as 1.5% to be capable of forming a gel. On the other hand, I have produced gels capable of being spread to a film containing as high as 10% of solids.

It will be apparent that a great variety of specific procedures may be employed for refining the bentonite to the desired particle size and up to the desired particle size range within a given suspension. It is also apparent that a variety of methods may be used for forming the suspension into films.

In the foregoing I have referred particularly to bentonite as a specific example of materials capable of forming films. Within the genus of swellable, readily hydratable colloidal anisometric (polar) inorganic materials are other materials such as halloysite, gibbsite, and vanadium pentoxide. Lime and silica gel may be expected to produce films. The absorption of water by the particles apparently is not analogous to the absorption of water by a sponge nor is it a chemical combination. Rather, it appears to be an absorption of water into a molecular structure. Montmorillonite, the basic constituent of bentonite, has been found to give excellent results. By the term "self-supporting" in the description of the coherent, self-supporting, flexible solid body, I mean bodies which in the absence of any physical support and in sizes of say up to 1 foot, maximum dimension, are capable of being handled, e.g., picked up between thumb and forefinger without tearing or breaking.

I claim:

1. A coherent, self-supporting, flexible solid body, the continuous structure at least of which consists of a colloidal crystalline, inorganic hydrous oxide which contains structural water, is capable of swelling when brought into contact with water to form a plastic hydro-gel and exhibits base exchange properties.
2. A body as defined in claim 1 in which the hydrous oxide is a colloidal clay.
3. A body as defined in claim 1 in which the hydrous oxide is montmorillonite.
4. A body as defined in claim 1 in which the hydrous oxide is a silicate of the group consisting of aluminum silicate, magnesium silicate and aluminum magnesium silicate.
5. A body as defined in claim 1 in the form of a film.
6. A coherent, self-supporting, flexible solid body as defined in claim 1 in the form of a film characterized by a partial Debye Scherrer powder x-ray diagram of the mineral comprising the film when the film is

radiated normal to a surface thereof, and a partial fiber diagram corresponding to the mineral component of the film when the film is irradiated parallel to said surface, both diagrams combined and the fiber diagram rotated corresponding to a complete Debye Scherrer powder pattern of said mineral.

7. As a new product a plurality of superposed, adherent self-supporting flexible coherent films consisting essentially of a colloidal, crystalline inorganic hydrous oxide which contains structural water, is capable of swelling when brought into contact with water to form a plastic hydrogel and exhibits base exchange properties.

8. Method which comprises forming a structurally compact film, filament, coating or the like of an aqueous suspension of a colloidal, crystalline, inorganic hydrous oxide which contains structural water, is capable of swelling when brought into contact with water to form a plastic hydro-gel and exhibits base exchange properties, and drying the same by exposing at least half of the surface area thereof to a drying atmosphere, said film, filament or coating being coherent, flexible and self-supporting.

US Patent # 2,266,637

Waterproofing & Flexibilizing Clay Films

(Cl. 25-156) ~ (December 16, 1941)

Ernst A. Hauser

In my application Serial No. 212,398, filed June 7, 1938, I have described the production of flexible, coherent, self-supporting solid bodies such as films, filaments and the like from natural crystalline inorganic hydrous oxides containing structural water and capable of swelling when brought into contact with water to form plastic hydro-gels and exhibiting base exchange properties such as hydrous aluminum and magnesium silicates, e.g., bentonite. According to said application the material is refined by suspending it in water and centrifuging or settling to separate gritty material, probably consisting of quartz, and coarse particles substantially exceeding colloidal size so as to produce a product consisting principally of particles of the substantially pure material of colloidal dimensions. It is further indicated in said application to be desirable to produce a suspension of the smaller particle sizes such as 0.01 to 0.5 microns in which the particles are nearly of the same size, i.e., substantially monodisperse.

I have now found that it is possible to produce self-supporting films, filaments and the like from sols and gels which although of colloidal dimensions are not substantially monodisperse. According to my present experience, self-supporting films, filaments, etc., can be made from any sol or gel of the specified materials of any polydisperse or monodisperse character so long as the particles are of colloidal dimensions. By the term "self-supporting" in the description of the coherent, self-supporting, flexible, solid bodies, I mean bodies which in the absence of any physical support and in sizes of say up to 1 foot maximum dimension, are capable of being handled, e.g., picked up between thumb and finger, without tearing or breaking.

The hydrous oxide may be found in the natural state in sufficient purity that no refining is necessary. Such material may be simply suspended in water and used directly. In the case of a magnesium silicate bentonite which is commercially available and contains practically no particles over 1 micron in diameter, it may be suspended in water, allowed to settle for a short time to remove any coarse particles, concentrated to a gel and used. The refining of the hydrous oxide may of course be carried out in any suitable way such as by the use of any suitable suspending liquid other than water or by wind sifting and the refined material then suspended in water to swell the particles and form the gel.

It will be further understood that whether the sol or gel is used as the film forming material, the gel stage immediately precedes the solid state. If the sol is applied to a surface as a coating, it passes through the gel state to the solid state by drying. The sol is quite dilute and highly fluid and will produce only a relatively thin deposit of solid material. If a small amount of electrolyte is added to a sol, it will form a gel which may be used for the production of films but here again the high dilution of the gel or the low

concentration of solids must be considered. If the addition of electrolyte to the sol is carried so far as to cause precipitation the resulting suspension is practically useless for the production of films. But a gel produced by concentration and containing a sufficiently high concentration of solids, e.g., 3% or higher or such a gel after slight or incipient flocculation without precipitation by the addition of electrolyte may be used directly for the production of films, filaments, or the like. The air-dried film, filament or the like, however prepared, generally contains 6-10% of water.

In bentonite, the essential ingredient appears to be the mineral montmorillonite which constitutes 75% or more of bentonites which are found to be suitable for the production of films, filaments, and the like.

Films, filaments, coatings, etc., may be made by customary means, e.g., by extrusion, spraying, electro-deposition, or spreading. The films, etc., may be formed on a suitable surface and removed therefrom and may be dried and baked and heated to high temperatures and/or subjected to pressure to produce certain effects. The films, etc., produced as described in said application are, as stated therein, self-supporting and capable of being handled and used for many purposes but they are relatively fragile and moreover unless they have been heated to about 600°C or higher are not entirely water resistant and such heating tends to render them quite brittle.

In a companion application Serial No. 257,248, filed February 18, 1939, I have described and claimed the production of various articles such as films, coatings, filaments, etc., of the type generally regarded as being obtainable by suitable manipulation of liquid or plastic, i.e., flowable or moldable composition, consisting of or comprising an ingredient capable of solidifying and acting as a binder, from mixtures of the natural crystalline inorganic hydrous oxide capable of forming plastic hydro-gels with other materials such as finely divided organic fibrous materials, e.g., paper pulp, jute, silk, cotton, synthetic fibers and the like, inorganic fibrous materials, e.g., asbestos, rock wool, glass wool and the like, powdered and flake materials, e.g., ground mica and metal flakes or powders, e.g., aluminum and copper powders, also dyes and pigments such as titanium dioxide, lithopone, carbon black, etc., and water emulsions of materials such as asphaltum, nitrocellulose and waxes.

An object of the present invention is to render all such films, filaments, etc, whether formed of the substantially pure hydrous oxide or of mixtures thereof with other finely divided materials, more water resistant and to improve their softness, flexibility and crease resistance.

For the purpose of illustration bentonite will be referred to hereinafter as an example of a suitable hydrous oxide and the invention will be described more particularly with reference to the production of films.

For rendering the films water resistant either the formed film after air drying or drying up to a temperature of about 120°C may be treated with suitable agents to be described below or said agents may be added to and mixed with the sol or gel prior to the formation of the film. At 432°C the film is dehydrated but is still capable of regaining water very slowly and theoretically at least is still capable of responding to the action of the treating agents. By water resistant I mean that the film is rendered capable of being soaked or even boiled in water for a long period of time, say one hour or more, without any apparent change in the physical character of the film such as swelling or disintegration.

The amount of treating agent required is small. When applying the treating agent to the formed (air dried) film the optimum conditions for treatment must be determined in each instance depending on the thickness and other physical characteristics of the film, the concentration and temperature of the treating agent and the effect desired. For example in treating air-dried bentonite films 2-3 mils in thickness with a saturated solution of lead acetate, a plurality of films were immersed in the solution at room temperature and samples were withdrawn every 2 or 3 minutes, dried at room conditions for several hours and then placed in boiling water to test the effect of the treatment. By this procedure it was found that 30-45 minutes was required to produce the maximum effect. Samples treated for a somewhat shorter time were water resistant in that they did not swell when boiled in water but they were quite fragile and some of them disintegrated in the boiling water. This test indicates that the lead acetate treatment produces the double effect of rendering the films water resistant and stronger.

A similar test with saturated lead acetate solution at 55°C showing that 20-25 minutes treatment was

sufficient. In general the treatment time varies inversely with the temperature of the treating agent. Also in general the more concentrated the treating agent the shorter is the treating time and of course the thinner the film the shorter is the treating time. Only a very small quantity of the treating agent is consumed in the treatment.

When the treating agent is added to the gel before the film is formed, tests with lead acetate have shown that quantities of the order of 10% are sufficient to give satisfactory results.

The electrical properties of the films, which are an important consideration, since the electrical properties of the films indicate a valuable use of them, are greatly improved by the treatment. As has been indicated above, the treatment which renders the films waterproof, when properly applied, also serves to improve their tensile strength.

In addition to rendering the films water resistant, it is desirable for certain purposes also to improve their flexibility or crease resistance. A film is considered to be sufficiently crease resistant for many practical purposes when it can be creased once without breaking. The above described treatment for rendering films water resistant generally also renders the films somewhat more brittle and the treatment to be described hereinafter is particularly important for certain purposes.

I have found that while certain chemical treating agents serve to improve the water resistance of the films, others serve to improve the flexibility of the films. The agents for flexibilizing the films may be applied before or after the treatment for rendering the films water resistant and in some instances, when the two treating agents are compatible, the film, after it is formed, may be treated with the two agents simultaneously.

Heating the films before the chemical treatment for rendering them water resistant, provided the heating is not so high as to render the treatment ineffective, appears to be without effect but heating the films after the treatment greatly improves the electrical properties of the films. Heating the so treated films to only a little above 100°C, say 105°C, serves to expel absorbed water from the film which once removed does not return upon exposure of the films to the atmosphere. The same effect is obtained more slowly by extended exposure to normal room temperatures. The air dried films before any treatment contain 6-10% moisture depending on the conditions under which they are dried. After treatment with lead acetate and air-drying they contain about 2.6% moisture and after heating at 105°C about 0.3% moisture. Boiling the films in water after the chemical treatment to render them water resistant renders them tougher and stronger.

As has been indicated both the agents for improving water resistance and the agent for flexibilizing the films may be applied separately and when compatible may be applied together to the film and if done carefully some of the agents for improving water resistance may be added to the gel before the film is formed.

A variety of treating agents have been tested and found to be suitable.

Consideration of the character and effects of the treating agents which are operable compared to other chemicals which are not operable indicates that the molecules or the active ions of the treating agents must, in both cases, be of such a character as to be able to enter the lattice structure of the material or to neutralize the electric surface charge of the clay particles. In the case of the agents serving to render the films water resistant the action of the agent if it is present in the form of a true solution appears to consist of a base exchange reaction between the exchangeable cation of the silicate and the cation of the treating agent. If it is a colloidal dispersion the action appears to be caused by electric neutralization of surface charges. In the case of the agents which serve to render the films more flexible the theory may be advanced that the molecules of the treating agent enter the lattice structure of the silicate and serve to lubricate it. It appears that the operability of the agents for rendering the films water resistant depends upon their ability to change the electrokinetic characteristics of the silicate.

The action of the agents which render the films of base exchangeable hydrous oxides resistant to water may be further explained and the agents further characterized as follows. It appears from a comparison of diameters of the cations of effective agents which are capable of the base exchange with the cations of

agents which are capable of base exchange with the exchangeable base of the hydrous oxide but are not effective that the cations which are effective have a fairly definite minimum diameter whereas the non-effective cations have a substantially smaller diameter. The minimum effective diameter depends upon the structure of the hydrous oxide. In the case of montmorillonite, the principal constituent of bentonite, the minimum diameter of the cations of effective agents appears to be about 2.6 Angstrom units or at least about as large as the spacing between the opposite oxygen atoms in the hexagonal silicon-oxygen sheet of the unit crystal of montmorillonite. Such cations apparently enter the films by base exchange and are bound by residual valencies and serve to bind adjacent unit sheet-parcels together whereas smaller cations, even though they may enter the film by base exchange and become fixed in the lattice structure by residual valencies fall into the internal structure of the lattice and remain free-moving in the space available and do not bind the adjacent unit-parcels together.

I have found both inorganic and organic agents to be effective in rendering the films water resistant. Examples of operable agents are concentrated solutions of potassium hydroxide, mercurous nitrate, calcium, barium, strontium, magnesium, manganese, cobalt and lead chlorides (lead chloride is effective only in hot solution), magnesium, cobalt and copper nitrates, zinc, manganese, nickel and copper sulfates, calcium, barium, magnesium, zinc, uranium, copper and lead acetates, iron chlorides and thorium nitrates, chromium and aluminum sulfates, chromium and iron acetates and colloidal iron oxide and aluminum oxide dispersions. Various acids were tried and found to be less effective. The results of extensive testing of compounds indicates that the anions of the compounds used are of secondary importance only and that the prime requisites of the operable compounds are that their cations shall be capable of base exchange with the exchangeable base of the silicate and that the compound shall be sufficiently soluble in water, which solubility may be increased by heating, are effective. The organic compound trimethylbenzyl ammonium hydroxide also was found to be effective. Most of these treating agents for rendering the films water resistant also tend to render the film more brittle which brittleness, however, may be removed by the action of the agents to be disclosed hereinafter for increasing flexibility. Films treated with colloidal ferric oxide or colloidal alumina are rendered water resistant. Colloidal ferric oxide or colloidal alumina when added to a sol or gel of bentonite in sufficient amounts cause incipient flocculation and the film produced from the resulting mixture is water resistant. This fact supports my theory that the anion of the added agent is of secondary importance so far as rendering of the films water insoluble is concerned. It indicates that rendering the films insoluble is essentially an electrokinetic phenomenon and that colloids of opposite charge to those of the film-forming material generally may serve to render the films insoluble in water. In the case of iron oxide and alumina it appears that their positively charged colloidal nuclei have replaced the adsorbed cation of the bentonite.

Examples of agents capable of improving the flexibility of the films are ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, methyl acetate, ethyl acetate, isopropyl acetate, butyl acetate, cellosolve acetate, methyl cellosolve acetate, ethylene glycol, propylene glycol, methyl isobutyl ketone, diisobutyl ketone, and butyl carbinol. A consideration of these compounds and a comparison thereof with other compounds which are not effective leads to the generalization that those organic compounds which are at least partially soluble in water and do not contain an aromatic ring or a side chain in the middle of the molecule are effective. In other words, the solubility and the configuration of the molecule of the treating agent appear to determine its ability to soften the film. The molecule of the treating agent apparently must be free of any group which results in steric hindrance and prevents the molecule from entering the aluminum silicate lattice.

A film treated with lead acetate to produce water resistance after drying for several days at 105°C was found to have an electrical resistance of the order 10^{13} ohms per cm^3 and a breakdown resistance of 2000-3000 volts per mil. On exposure to the atmosphere after the heating to 105°C the electrical resistance of the film remained unchanged.

Films may be softened without being rendered water resistant by applying only the above described treatment for the latter purpose but the resulting films are water soluble or swellable if immersed in pure water.

Various combinations of the two treatments may be applied. The preferred treatment is to first waterproof the film and then improve its flexibility but it is possible to reverse the order of these steps.

I claim:

1. Process which comprises forming a coherent self-supporting flexible solid body consisting essentially of a crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought in contact with water to form a plastic hydro-gel and exhibiting base exchange properties and rendering said solid body insoluble in water by the action of a soluble electrolyte salt containing a cation capable of base exchange with said hydrous oxide, the exchanging cation being less hydrated than the exchanged cation.
2. Process as defined in claim 1 in which the electrolyte salt is added to the hydrous oxide prior to formation of the solid body.
3. Process as defined in claim 1 in which the solid body is contacted with a solution of the electrolyte salt.
4. Process as defined in claim 1 in which the solid body is contacted with a solution of a water-soluble salt of a metal capable of base exchange with said hydrous oxide.
5. Process which comprises forming a coherent self-supporting flexible solid body consisting essentially of a crystalline inorganic hydrous oxide containing structural water and capable swelling when brought in contact with water to form a plastic hydro-gel and exhibiting base exchange properties and rendering said solid body insoluble in water by the action of a colloidal dispersion, the disperse phase of which carries a charge opposite to the surface charge of said hydrous oxide.
6. Process as defined in claim 5 in which the colloidal dispersion is added to the hydrous oxide prior to formation of the solid body.
7. Process as defined in claim 5 in which the solid body is contacted with the colloidal dispersion.
8. Process as defined in claim 5 in which the solid body is contacted with a colloidal dispersion of alumina.
9. Method of improving the flexibility of a coherent, self-supporting, flexible solid body consisting essentially of a crystalline inorganic hydrous oxide having a lattice structure and containing structural water and capable of swelling when brought in contact with water to form a plastic hydro-gel and exhibiting base-exchange properties which comprise treating said solid body with an organic compound which is soluble in water and capable of entering the lattice structure of said hydrous oxide.
10. Method as defined in claim 9 in which said organic compound is free of any aromatic ring and any aliphatic side chain intermediate the ends of the molecule.
11. Method which comprises forming a coherent, flexible self-supporting solid body consisting essentially of a crystalline inorganic hydrous oxide having a lattice structure and containing structural water and capable of swelling when brought in contact with water to form a plastic hydro-gel and exhibiting base exchange properties, rendering said solid body insoluble in water by the action of a cation capable of base exchange with the hydrous oxide and rendering said solid body more flexible by the action of an organic molecule capable of entering the lattice structure of said hydrous oxide.
12. As a new product, a water insoluble flexible structure the continuous phase of which consists of a naturally crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought in contact with water to form a plastic hydro-gel and exhibiting base exchange properties, said structure having incorporated therein a cation capable of base exchange with the hydrous oxide.
13. A coherent, self-supporting, flexible and water insoluble solid body of a crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought in contact with water to form a plastic hydro-gel and exhibiting base exchange properties, said solid body having incorporated therein a cation capable of base exchange with hydrous oxide and, in the air-dried condition, being incapable of absorbing water and reverting to a hydro-gel.

14. A coherent, self-supporting, flexible solid body, the continuous phase of which consists of a crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought into contact with water to form a plastic hydro-gel and exhibiting base exchange properties and possessing at least one hexagonal type of silicon-oxygen sheet, said solid body containing base exchange cations having an ionic radius of at least 1.28 Angstrom units.

15. A coherent, self-supporting, flexible solid body as defined in claim 14 in which the base exchange cations are less hydrated than the cation of the hydrous oxide.

16. A coherent, self-supporting, flexible solid body as defined in claim 14 in which the cations are those of a water-soluble amine.

17. A coherent, self-supporting, flexible solid body, the continuous phase of which consists of a crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought into contact with water to form a plastic hydro-gel and exhibiting base exchange properties and possessing at least one hexagonal type of silicon-oxygen sheet, said solid body being insoluble in water and flexible due to the presence within the crystalline structure thereof, of base exchange cations having anionic radius greater than 1.28 Angstrom units, and an inorganic compound.

18. A coherent, self-supporting, flexible solid body, the continuous phase of which consists of a crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought into contact with water to form a plastic hydro-gel and exhibiting base exchange properties and possessing at least one hexagonal type of silicon-oxygen sheet, said unit parcels being held together by cations having an ionic diameter at least as large as the free space between opposing oxygen atoms on the surface of the hexagonal silicon-oxygen sheets of the unit parcels, said solid body containing also a lubricating organic compound.

19. A new product as defined in claim 12 in which the solid body is a film.

20. A solid body as defined in claim 13 in the form of a film.

21. A solid body as defined in claim 14 in the form of a film.

22. A solid body as defined in claim 17 in the form of a film.

23. A solid body as defined in claim 18 in the form of a film.

U.S. Patent # 2,266,638

Flexible Body

(Cl. 106-287) ~ (December 16, 1941)

Ernst A. Hauser

In my application Serial # 212,398, filed June 7, 1938, I have described the production of coherent, self-supporting, flexible solid bodies such as films, filaments and the like from natural crystalline inorganic hydrous oxides containing structural water and capable of swelling when brought in contact with water to form plastic hydro-gels and exhibiting base exchange properties such as hydrous aluminum and magnesium silicates, i.e., bentonite. According to said application the material is refined by suspending it in water and centrifuging or settling to separate gritty material, probably consisting principally of quartz, and coarse particles substantially exceeding colloidal size so as to produce a product consisting principally of particles of the substantially pure material of colloidal dimensions. It is further indicated in said application to be desirable to produce a suspension of the smaller particle sizes such as 0.01 to 0.5 micron in which the particles are nearly of the same size, i.e., substantially monodisperse.

I have now found that it is possible to produce coherent, self-supporting flexible films, filaments and the like from sols and gels of such hydrous oxides which although of colloidal dimensions are not substantially monodisperse. According to my present experience self-supporting films, filaments, etc., can be made from any sol or gel of the specified materials of any polydisperse or monodisperse character so long as the particles are of colloidal dimensions. It is further indicated in said application to be desirable to produce a suspension of the smaller particle sizes such as 0.01 to 0.5 micron in which the particles are nearly of the same size, i.e., substantially monodisperse.

I have now found that it is possible to produce coherent, self-supporting, flexible films, filaments and the like from sols and gels of such hydrous oxides which although of colloidal dimensions are not substantially monodisperse. According to my present experience, self-supporting films, filaments, etc., can be made from any sol or gel of the specified materials of any polydisperse or monodisperse character so long as the particles are of colloidal dimensions.

The hydrous oxide may be found in the natural state in sufficient purity that no refining is necessary. Such material may be simply suspended in water and used directly. In the case of a magnesium silicate bentonite which is commercially available and contains practically no particles over 1 micron in diameter, it may be suspended in water, allowed to settle for a short time to remove any coarse particles, concentrated to a gel and used. The refining of the hydrous oxide may of course be carried out in any suitable way such as by the use of any suitable suspending liquid other than water or by wind sifting and the refined material then suspended in water to swell the particles and form the gel.

It will be further understood that whether the sol or the gel is used as the film forming material the gel stage immediately precedes the solid state. If the sol is applied to a surface as a coating it passes through the gel state to the solid state by drying. The sol is quite dilute and highly fluid and will produce only a relatively thin deposit of solid material. If a small amount of electrolyte is added to a sol, it will form a gel which may be used for the production of films but here again the high dilution of the gel or the low concentration of solids must be considered. If the addition of electrolyte to the sol is carried so far as to cause precipitation or flocculation the resulting suspension is practically useless for the production of films. But a gel produced by concentration and containing a sufficiently high concentration of solids, e.g., 3% or higher or such a gel after slight or incipient flocculation without precipitation by the addition of electrolyte may be used directly for the production of films, filaments, and the like. The air-dried film, filament, or the like, however prepared, generally contains 6-10% of water.

In bentonite, the essential ingredient appears to be the mineral montmorillonite which generally constitutes 75% or more of bentonites which are found to be suitable for the production of films, filaments, or the like.

The present invention is more particularly concerned with the use of the natural crystalline inorganic hydrous oxides capable of forming plastic hydro-gels in combination with other materials for the production of various coherent, self-supporting and flexible articles such as films, coatings, filaments, etc., of the type generally regarded as being obtainable by suitable manipulation of liquid or plastic, i.e., flowable or moldable, compositions consisting or comprising an ingredient capable of solidifying and of acting as a matrix.

In accordance with my present invention, the sol or gel of the hydrous oxide may be mixed with a variety of water-insoluble solid materials including organic fibrous materials such as paper pulp, jute, silk, cotton, synthetic fibers, etc., inorganic fibrous materials such as asbestos, rock wool, glass wool, etc., powdered or flake materials such as ground mica, metal flakes or powders, e.g., aluminum and copper powders, dyes and pigments such as titanium dioxide, lithopone, carbon black, etc., and with water emulsions of plastic water-insoluble materials such as asphaltum, nitrocellulose and waxes. In certain instances, the hydrous oxide itself may serve as the emulsifying agent, as for example, in the case of asphalt and waxes. Fibrous materials either individually dispersed or in the form of a more or less loosely matted fabric generally serve to strengthen the films, filaments, etc., especially with respect to tear resistance...

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I claim:

1. A flexible, coherent, self-supporting solid body comprising an inert water-insoluble finely divided material incorporated into a coherent and self-supporting flexible matrix of a natural crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought in contact with water to form a plastic hydro-gel and exhibiting base-exchange properties, the weight of hydrous oxide being at least equal to the weight of the finely divided material.
2. A flexible, coherent, self-supporting solid body as defined in claim 1 in which the hydrous oxide is montmorillonite.
3. A flexible, coherent, self-supporting solid body as defined in claim 1 in which the hydrous oxide is a member of the group consisting of aluminum silicates, magnesium silicates and magnesium aluminum silicates.
4. A flexible, coherent, self-supporting solid body comprising a finely divided fibrous material formed by drying a colloidal suspension of a natural crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought in contact with water to form a plastic hydro-gel and exhibiting base-exchange properties, the weight of the hydrous oxide being at least equal to the weight of the finely divided material.
5. Solid body as defined in claim 1 in which the inert finely divided material is an organic fibrous material.
6. Solid body as defined in claim 1 in which the inert finely divided material is an inorganic fibrous material.
7. Solid body as defined in claim 1 in which the inert finely divided material is a metal powder.
8. A flexible, coherent, self-supporting solid body formed of a mixture of a colloidal suspension of a natural crystalline inorganic hydrous oxide containing structural water and capable of swelling when brought in contact with water to form a plastic hydro-gel and exhibiting base-exchange properties and an emulsion of an organic material, said solid body comprising finely divided particles of the organic material dispersed in a matrix of the hydrous oxide and the weight of the hydrous oxide being at least equal to the weight of organic material.
9. Solid body as defined in claim 1 in which the finely divided material is a pigment.
10. Solid body as defined in claim 1 in which the finely divided material is a dye.
11. Solid body as defined in claim 1 in which the finely divided material is in the form of flakes.
12. Solid body as defined in claim 1 in the form of a film.
13. Solid body as defined in claim 4 in the form of a film.
14. A flexible, coherent, self-supporting solid body as defined in claim 1 in which the inert, water-insoluble, finely divided material is a fibrous material in the form of a fabric.

Ernst A. Hauser

<http://www.tomo-e.co.jp/english/chemical/index.html>

Moisture Preventive Sealing Material

Tomoe Engineering supplies moisture preventive sealing material, mainly made from plastic bentonite, to be applied to contacting surfaces between concrete layers as well as between concrete and an H-steel.

Recently Tomoe Engineering launched Tomoe K-seal to the market-the bentonite concrete moisture barrier that prevents rainwater from penetrating into concrete. This is a new sealing material, on which rain protective coating is prepared: it exhibits sealing ability almost eternally owing to its high elasticity and resistance against rainwater.

In addition to the above products, the department supplies the following sealing materials for civil engineering and construction industries.

- Kuniseal C-31: plastic bentonite sealing material
- Kuniseal AB2505: modified sealing material of an asphalt/bentonite consolidation
- Kuniseal TP-50: plastic bentonite impregnated sealing tape

United States Patent 6,045,657
(April 4, 2000)

Clay Compositions & Their Use in Paper Making

Adrian S. A llen

Abstract -- Paper making processes, including microparticulate processes, which utilise bentonite are provided with bentonite in the form of a concentrate, or a dilute dispersion made by diluting the concentrate, wherein the concentrate is a dispersion of 15 to 40% by weight bentonite in water containing citrate and has a viscosity below 5000 cps and is a stable fluid. The concentrates are novel. They are preferably made by mixing alkaline earth bentonite with water and sodium citrate.

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Assignee: Ciba Specialty Chemicals Water Treatments Limited (West Yorkshire, GB)

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Intern'l Class: D21H 017/69; D21H 017/68; C04B 033/02; C04B 033/04

Field of Search: 162/158,181.1,181.7,181.8,183 106/486,416,DIG. 4,400 501/144,145,146,147

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Description

This invention relates primarily to paper making processes that utilise bentonite and to novel fluid bentonite concentrates suitable for use in these processes. The invention also relates to other processes in which such concentrates are useful.

There are many paper making processes which comprise providing a cellulosic suspension at a paper mill, mixing an activated bentonite dispersion into the cellulosic suspension and draining the suspension to form a wet sheet, which is then dried to provide paper (including paper board). In some instances the bentonite is added at the thick stock stage (for instance for stickies control) and the suspension is diluted to a thin stock before drainage, but in other processes the bentonite dispersion is added at the thin stock stage. It can be added before a polymeric retention aid, but there is particular interest in microparticulate processes, wherein the cellulosic suspension is subjected to shearing after adding the polymeric retention aid, and the bentonite is then added to the sheared suspension prior to drainage.

It is necessary that the bentonite should be in a highly swollen, activated, form and in practice this means that it should be in the form of a monovalent salt of bentonite such as sodium bentonite. Although there are some naturally occurring sources of sodium bentonite, most natural bentonites are alkaline earth bentonites, generally calcium or magnesium bentonites. The normal practice is to activate the alkaline earth bentonite by ion exchanging the calcium or magnesium for sodium or other alkali metal or ammonium ion. Generally this is done by exposing the bentonite to an aqueous solution of sodium carbonate, although some other activating materials are known, for instance as described in JP-A-64-45754.

Because of the high viscosifying effect of activated bentonite, it is not convenient to transport or handle a simple dispersion of activated bentonite in water which has a solids content of greater than around 5%. It is not convenient to supply such a dilute composition to the mill and so the normal way of supplying bentonite to a paper mill is in solid form. The mill mixes bentonite powder with water and optionally activating chemicals generally to form an activated dispersion having a solids content of around 3 to 5% and this is then generally diluted to around 0.05 to 1% prior to addition to the cellulosic suspension. This necessitates that the mill should be equipped with apparatus for handling and mixing the powder and the dilute dispersion.

It is known to make aqueous dispersions of bentonite having a higher solids content. The first disclosure of this in connection with the production of bentonite for paper making is in EP-A-485,124 wherein the bentonite is dispersed at high solids, for instance up to 27 to 30%, as a slurry in an aqueous solution of sodium chloride or other inorganic electrolyte. optionally some sodium polyacrylate can be used. The bentonite which is dispersed in this manner is preferably a commercial (typically calcium) bentonite containing sodium carbonate activator. Thus the activation of the bentonite is completed when the slurry is diluted with water to make a flowable dilute dispersion.

U.S. Pat. No. 5,266,538 is another disclosure of making concentrated bentonite slurries for paper making, again concentrating primarily on the use of sodium chloride or other inorganic electrolyte for depressing the viscosity of the slurry. In this publication, however, the bentonite is always introduced in sodium form. Various electrolytes are exemplified. Amongst these, there is an example of forming 25% bentonite gel with 2.5 or 5% sodium citrate in water. It is shown that these gels have viscosities respectively of 40,000 and 5,500 cps (Brookfield, 20 rpm) and that they gel on standing for 24 hours. The preferred material is said to be sodium chloride.

U.S. Pat. No. 5,391,228 repeats much of the disclosure of U.S. Pat. No. 5,266,538 but adds disclosure of a process in which calcium bentonite and sodium carbonate are slurried in aqueous sodium chloride (i.e., similar to the preferred process in EP 485,124). It also mentions the use of sodium salts such as sodium chloride or several others (including sodium citrate) in combination with a dispersant salt which is usually sodium silicate or tetra sodium pyrophosphate or sodium polyacrylate (again as suggested in EP 485,124).

There has been some commercial use of bentonite concentrates made in sodium chloride or other inorganic electrolytes but this use has demonstrated some practical difficulties. One difficulty is that it can be difficult to achieve a dispersion which is wholly stable against hard settling, i.e., there is a risk that, if any settling does occur, it may create a hard precipitate which is difficult to redisperse. However even when the concentrated slurry is formulated so as to eliminate this problem, it is found necessary to interpose an extra activation period during the dilution of the concentrate and prior to addition to the cellulosic suspension. Thus, it is necessary to dilute the concentrate with water and then allow this to mix or stand for a sufficient period to allow activity to recover, prior to addition of the diluted dispersion to the cellulosic suspension. The reason for this is that the sodium chloride or other electrolytes which have been preferred (from the point of view of convenience and efficiency of dispersion formation) all have the disadvantage that the sodium chloride or other electrolyte seems to cause salting out and double layer compression in the bentonite structure because of the high ionic strength. Thus it is necessary to give prolonged mixing with dilution water to allow the bentonite to try to recover to as highly an activated condition as is possible.

Unfortunately, however, full recovery of performance does not seem to be possible and it is a fact that the performance of dilute activated bentonite dispersions made by dilution of a concentrated slurry has proved to be inferior to the performance of a dilute activated bentonite dispersion made by direct dispersion of the corresponding bentonite powder (and activator) in water.

It would be desirable to be able to provide a bentonite concentrate which has the advantages of high solids content and fluidity and stability with the potential for giving activity in use equivalent to the optimum activity which is obtainable from the corresponding dry bentonite. In particular, it would be desirable to be able to provide paper making processes in which the mill can be supplied with a concentrate but can then easily and conveniently use that concentrate under conditions whereby performance is substantially equivalent to the performance previously obtainable using the corresponding bentonite supplied to the mill in powder form.

The normal way of providing bentonite (either for supply as powder or as a concentrate) comprises digging the bentonite out of the ground, wet mulling it with sodium carbonate or other activator, drying the mixture, grinding it, air classifying it and then supplying the resultant powder either direct to the user or to the slurring facility where it is converted into a concentrate. It would be desirable to simplify this procedure.

In one aspect of the invention we make paper by a process comprising forming a cellulosic suspension, mixing an activated bentonite dispersion into the cellulosic suspension, draining the cellulosic suspension to form a wet sheet and drying the sheet, and in this process the activated bentonite dispersion added to the cellulosic suspension is either a stable fluid bentonite concentrate or is a dilute bentonite dispersion made by diluting the concentrate with water, and the concentrate is a dispersion of 15 to 40% by weight of bentonite in water containing citrate in a fluid stabilising and activating amount which is such that the concentrate has a viscosity (Brookfield, 20 rpm, spindle 4) of below 5,000 cps.

The invention also includes the novel concentrate which is a dispersion of 15 to 40% by weight of bentonite in water containing citrate in a fluid stabilising and activating amount which is such that the concentrate has a viscosity (Brookfield, 20 rpm, spindle 4) of below 5,000 cps.

The concentrate can be made using natural sodium bentonite or previously activated bentonite, but is particularly preferred that the concentrate should be formed from alkaline earth bentonite (in practice calcium and/or magnesium bentonite) by blending the alkaline earth bentonite with water and alkali metal or ammonium citrate (in practice sodium citrate) as activator and stabiliser. Thus by this technique it is possible simultaneously to activate the bentonite and convert it into a stable concentrate.

Accordingly, another aspect of the invention comprises blending alkaline earth bentonite with water and sodium citrate (or other alkali metal or ammonium citrate) and thereby forming a concentrate of 15 to 40% by weight activated bentonite in water containing citrate.

The paper making processes of the invention have several advantages compared to known processes of

making paper using bentonite. In particular, by the invention it is now possible to obtain performance in such processes equivalent to that which is obtainable using the corresponding bentonite in powder form but without the inconvenience of having to handle powder. Thus, for the first time, we are now providing a bentonite concentrate which, when diluted into the cellulosic suspension, gives performance substantially equivalent to the corresponding powder and considerably improved compared to the corresponding concentrate made using the previously preferred activator and stabiliser, namely sodium chloride.

A further advantage is that the concentrate can be used without undergoing a prior dilution activation stage. Thus whereas the prior concentrates made using sodium chloride had to be diluted in water and then allowed to stand to activate or recover their activity, the concentrates of the invention can, without significant loss of performance, either be mixed direct into the cellulosic suspension (i.e., without any prior dilution) or can be converted to a dilute bentonite dispersion by diluting the concentrate substantially immediately before mixing the dilute bentonite dispersion with the cellulosic suspension. For instance the concentrate can be diluted in line as it is being fed towards or into the cellulosic suspension, without any significant holding stage between the dilution and the addition of the diluted dispersion to the cellulosic suspension.

Accordingly, in preferred processes the undiluted concentrate is mixed into the cellulosic suspension or the concentrate is diluted with water to form a dilute bentonite dispersion which is then mixed substantially immediately with the cellulosic suspension. If there is predilution, preferably the diluted bentonite dispersion is mixed into the cellulosic suspension in less than 5 minutes and often less than 2 minutes from the start of dilution. If there is predilution, the dilution is preferably in line and does not involve any significant holding tank or stage prior to addition to the cellulosic suspension. This is in contrast to the preferred concentrates that are described in EP 485,124 and U.S. Pat. Nos. 5,266,538 and 5,391,228 as being used in paper making, since all such concentrates would necessarily have involved a considerable holding stage in an attempt at recovering activity, and the recovered activity would still have been inferior to the activity of the corresponding powder or the activity of the bentonite in the invention.

For instance, in paper making, performance can be indicated by a simple test such as drainage time. The dry weight of bentonite required to give a particular drainage time in a particular test using the slurries of the invention is usually no more than, and often is about the same as, when the same bentonite had been activated from powder using sodium carbonate in conventional manner, whereas the dosage of bentonite required to give the same performance when the bentonite is provided as a slurry in aqueous sodium chloride is often at least 25% or 30% more, frequently at least 60% more, and often double. Thus the use of slurries in accordance with the invention can result in a saving of at least 25% and often at least 50% in the amount of bentonite that is required to give any particular performance result, compared to slurries made using sodium chloride.

Another advantage of the invention arises in paper making processes and other environments where the performance of conventional activated bentonites (eg obtained by activation from powder using sodium carbonate in conventional manner) is depressed by the pH or the osmotic pressure of hardness salts. Thus conventional bentonites tend to be less effective when the cellulosic suspension has pH below about 6.5, for instance in the range 4.2 to 5.5, than when the suspension has a higher pH, for instance 7 to 7.5. Surprisingly the activated bentonites obtained in the invention can perform very well in such suspensions without any significant loss of activity. Thus the use of the slurries in acidic suspensions can give a large improvement in the paper making process compared to the use of known bentonites.

Conventional activated bentonites also may have inferior performance when the cellulosic suspension is made using relatively hard water, for instance having a hardness above 10.degree. dH and typically in the range 15.degree.dH to 50.degree.dH. Improved performance is obtained using the bentonites obtained in the invention in such hard waters. This improvement may be manifested by improved drainage rates or by reducing scale deposition or both.

A further advantage of the compositions made by activation of alkaline-earth bentonite with sodium citrate is that they can have lower pH (neutral or near neutral) than prevails when activation is by sodium carbonate.

The amounts of citrate and bentonite in the slurry will be inter-related in that greater amounts of citrate will be required with greater amounts of bentonite than with lesser amounts of bentonite. The amount must be sufficient that the concentrate is a stable fluid and, when the bentonite is being activated in the concentrate, that full activation of the bentonite by ion exchange occurs. The amount (calculated as sodium citrate) is usually in the range 1% to 100% based on the dry weight of bentonite. Often it is at least 10% and preferably at least 16%, for instance at least 20%. Often it is below 60%, and frequently not more than 40%.

When the bentonite is introduced as alkaline earth bentonite, it is preferred that sodium citrate is substantially the only activating material in the suspension. Thus if small amounts of other activators (for instance sodium carbonate) are present, preferably their effect on activation is minor relative to the effect of the sodium citrate. Preferably the sodium citrate is the only activator.

Similarly, it is generally preferred that citrate is substantially the only dispersion stabiliser in the concentrate. If other materials are present, preferably their effect is minor compared to that of the citrate. Preferably the citrate is the only dispersion stabiliser.

By saying that the citrate is substantially the only activator and/or dispersion stabiliser, we intend to allow for minor amounts of other components, for instance in a weight amount of not more than 20% and preferably not more than 10% by weight of the citrate. However larger amounts can be used provided they do not detract from the performance of the citrate.

The amount of bentonite in the concentrate should be at least 15% by weight (dry weight bentonite based on the total weight of the concentrated dispersion) since it tends to be uneconomic to provide a concentrate having lower bentonite content. It is not usually more than about 35%, and often not more than 30%, since it becomes more difficult to provide a concentrate of good quality bentonite wherein the concentrate has good fluid stability when the amount of bentonite is very high. However when the bentonite is of rather poor quality, i.e., having rather low swelling potential, then amounts of bentonite above 35%, and in some instances even up to 50%, may be appropriate.

In practice the amount of bentonite is usually at least 20% and often up to 28, 30 or 35% by weight.

The bentonite can be introduced in sodium form, as a result of being a naturally occurring sodium bentonite, or it can be introduced as activated bentonite formed by previously activating alkaline earth metal bentonite with sodium carbonate or other activator, in which event some residual sodium carbonate may be carried into the concentrate. When the bentonite is introduced in sodium form, the citrate can be added in any convenient form, for instance as citric acid or as alkali metal or ammonium citrate, for instance potassium, sodium or ammonium citrate. Generally it is preferred to use sodium citrate or, in some instances, citric acid together with sufficient sodium hydroxide to form sodium citrate. When the bentonite is introduced as alkaline earth metal bentonite, then it is preferred for the citrate to be introduced as sodium citrate.

The amount of citrate which is required to form a stable suspension will depend upon the nature of the bentonite and the nature of its ionic form. There is some evidence indicating that if the bentonite is introduced in sodium form then larger amounts of citrate may be required than when the bentonite is introduced in calcium or magnesium form (i.e., larger amounts may be required to give equivalent fluidity). Also, the amount which is required will vary according to the grade of bentonite and so it is necessary to conduct tests to determine the optimum for any particular grade and chemical type of bentonite. The nature of the water may also influence the amount of citrate.

If the amount of citrate is inadequate then the concentrated dispersion will have too high a viscosity when initially manufactured and/or will not be a stable fluid and/or will be unacceptably thixotropic and/or will form an unacceptable gel on standing. If the amount is too high then the dispersion may become thinner than is desirable and may even become an unstable thin dispersion.

By routine experimentation it is possible to select an amount of citrate, for any particular bentonite and water quality, that is necessary to give a fluid stable dispersion having the desired viscosity. By saying that

the dispersion is a fluid stable dispersion we mean that it does not settle to give a hard, unredispersible, precipitate and does not gel to give an unacceptable gel, and preferably remains as a fluid which is homogeneous or which can easily be made homogeneous by simple stirring. In practice, the compositions of the invention can easily be formulated such that a small amount of supernatant may accumulate on storage but the composition otherwise appears homogeneous. The quoted viscosity is preferably maintained throughout storage and, in any event the suspension should have the quoted viscosity 48 hours after initial manufacture.

Generally the viscosity is below 4000 cps and it can be below 2000 cps. It is usually undesirable for the viscosity to be too low and so should be above 100 cps and generally it is above 500 cps, often above 1000 cps. All viscosity values are measured at room temperature. The suspension can be thixotropic provided it is easily possible to cause it to flow when required. The suspension must be easily miscible with water, by simple stirring.

The amount of citrate, measured as sodium citrate, is usually at least 3% and most usually at least 5% by weight (based on the total weight of the dispersion). When the bentonite is introduced as an alkaline earth bentonite, amounts of 3% or 4% can be adequate, but at least 5% or 6% is usually preferred. When the bentonite is introduced as sodium bentonite, amounts of at least 6% are generally preferred. Irrespective of whether the bentonite is sodium, calcium or magnesium, the amount can be as much as 20% but usually is less than 15% by weight, with preferably not more than 12%. Amounts of 6 to 10% are often suitable.

It will be appreciated that slurries which have been made by activating alkaline earth metal bentonite with sodium citrate can be identified by virtue of the fact that the aqueous medium will contain calcium or magnesium citrate, deriving from the ion exchange of the sodium of the sodium citrate with the calcium or magnesium of the alkaline earth bentonite.

The bentonite can be any of the anionic swelling clays that are conventionally referred to as bentonites. These are usually smectites or montmorillonites, the latter being preferred. Suitable smectite or montmorillonite clays include Wyoming bentonite and Fullers Earth and various clays including those known by the chemical terms hectorite or bentonite.

The stability of the concentrates of the invention should be such that they maintain fluidity (often thixotropic fluidity) for at least a week and preferably several weeks or months, and in particular such that they do not provide a hard sediment (which is difficult to redisperse) during normal storage or transport.

The concentrate can be used in any paper making process where an activated bentonite dispersion is added to the cellulosic stock. For instance it can be used in processes where the bentonite dispersion is added as a pitch dispersant, generally at the thick stock stage (e.g., when the cellulosic suspension contains more than 2% cellulose).

The invention is preferably applied to processes in which the bentonite is incorporated as part of the retention system, either to prepare the cellulosic fibres for retention by a polymer or as part of a microparticulate retention system.

One paper-making process to which the invention can be applied is a process in which bentonite is added to a cellulosic suspension, typically in an amount of 0.02 to 2% dry weight, and a polymeric retention aid is added subsequently, generally after the last point of high shear (for instance in the head box immediately prior to drainage). The polymer can be non-ionic, anionic or cationic. The cellulosic suspension can be made from relatively pure pulp or from pulp having a relatively high cationic demand.

Processes of this type that are of particular value are those in which the pulp has a relatively high cationic demand and the polymer is substantially non-ionic or anionic and the paper product is preferably newsprint or fluting medium. Processes of this type in which the total filler content is relatively low are described in U.S. Pat. No. 4,305,781 and EP-A-17353 to which reference should be made for further details of suitable non-ionic or low ionic polymers and suitable cellulosic suspensions and which is hereby incorporated by reference. More highly ionic or cationic polymers can also be used. These

processes are of particular value when the cellulosic suspension contains de-inked waste. Suitable polymers and fillers (when the pulp is filled) are also described in EP-A-608986 and AU-A-63977/86.

It is particularly preferred to apply the invention to microparticulate paper making processes, namely processes in which polymeric retention aid is added to the cellulosic suspension, the suspension is subjected to shearing, and the bentonite is then added after the shearing, and often after the last point of high shear for instance at the headbox, prior to drainage. The polymer can be anionic or non-ionic but is often cationic. It can be a natural material such as cationic starch but is preferably a synthetic polymer.

The shearing can be due merely to turbulence along a duct but preferably it is caused by passage through a centriscreeen or other cleaning device or a fan pump or a mixing pump or other device for deliberately applying shear. Preferred processes include those commercialised by the applicants under the trade mark Hydrocol and are described in, for instance, EP-B-235,893 and U.S. Pat. Nos. 4,753,710, 4,913,775 and 4,969,976 and EP-B-335,575, all of which are hereby incorporated by reference. The optimum amount of polymeric retentin aid can be determined by routine experimentation and will depend upon the nature of the cellulosic suspension and, inter alia, on whether or not low molecular weight high charge density cationic polymer and/or cationic starch and/or other dry strength resin has been incorporated in the suspension, all as described inthe aforementioned patents.

The polymeric retention aids which are used are usually water soluble, or substantially water soluble polymers of ethylenically unsaturated monomers and usually have molecular weight above 500,000 (measured by gel permeation chromatography) or usually intrinsic viscosity (measured by suspended level viscometer in 1N sodium chloride buffered to pH 7 at 25.degree. C.) of at least 4 dl/g.

Suitable polymers are described in the aforementioned patents.

The amount of the bentonite which is used in all these processes can be within the conventional ranges which are described in the aforementioned patents. As mentioned above, the bentonite can be added into the cellulosic suspension either while it is still in the form of the concentrate or simultaneously with or soon after dilution with water. This dilution can be to, for instance, a solids content in the range 3 to 8% or it can be dilution to a solids content of below 3%, for instance down to 0.1% or even less in some instances.

The invention also includes processes in which the novel concentrate is used for other purposes. For instance it can be used in pulp dewatering, paper sludge dewatering, liquid solid separation processes, effluent clarification, inky waste water clarification all in paper-related industries, and it can be used in other industries. For instance it can be a convenient way of formulating a bentonite slurry which is to be pumped for eventual use in any of the known ways of using bentonite in other industries. It can be used as a convenient way of introducing bentonite into iron ore pelletisation processes where the bentonite is being used in conventional manner as a binder.

The invention also includes a process of making an activated bentonite slurry comprising quarrying raw alkaline earth bentonite and mixing the quarried material with water and sodium citrate and thereby forming a coarse slurry containing at least 10% bentonite and filtering, classifying or cleaning the slurry. The filtering can be any process designed to remove physically large or dense material not suitable for the final process. The size of the filter classification will be selected so that the resultant bentonite particles that are preferably within the size range which is conventional for activating bentonite for the ultimate intended use. The filter may be, for instance, a cyclonic cleaning device or other classifying device or cleaning device.

Having removed the waste material by filtration, the resultant slurry can then be dried in conventional manner to make powdered activated bentonite or it can be supplied to a user as a concentrated dispersion in accordance with the invention. If this is required, then naturally the amount of bentonite which is slurried into the water and sodium citrate should be sufficient to give a concentrated dispersion in accordance with the invention. Thus generally the amount of bentonite which is slurried into the water and sodium citrate is in the range 15 to 40%. The amount of sodium citrate which is required for this process must be sufficient to provide for activation of the alkaline earth bentonite. If it is not necessary for the

slurry to be stable then it can be less than the amount which is required to give fluid stability to the slurry.

This process of making activated bentonite eliminates many of the stages associated with conventional production of activated bentonite. Thus it is now possible to eliminate the conventional stages of wet mulling, drying and grinding and air classifying and, instead, they can be replaced by the simple on-line or batch process of slurring the bentonite into aqueous sodium citrate and filtering (including classifying and cleaning).

Similarly, other concentrates, such as concentrates made using any of fluid stabilisers mentioned in EP 485,124, can be made by the same general technique modified by the use of the stabilisers of EP 485,124 in place of the sodium citrate. Similarly, other materials mentioned in U.S. Pat. Nos. 5,266,538 or 5,391,228 can be used in place of the sodium citrate. However all these modified processes would have the disadvantage that the final product does not have the advantages which are described above in connection with the products made using citrate.

The following are examples.

Example 1 (Comparative)

Dispersion A is made by slurring 5 parts calcium bentonite in 95 parts water.

Dispersion B is made by the conventional activating procedure of slurring a mixture of 4.7 parts calcium bentonite, 0.3 parts sodium carbonate and 95 parts water to give a 5% composition of sodium bentonite, which is then usually further diluted with water prior to use.

Dispersion C is made by slurring 23.5 g calcium bentonite and 1.5 g sodium carbonate (thus providing 25 g sodium bentonite) with 3 g sodium chloride and 72 g water. This 25% slurry then has to be activated in water, typically after dilution to about 5%, prior to use.

Accordingly, the processes using dispersion B are typical of those conducted using conventional powdered bentonite which has to be activated before use, and processes using dispersion C are typical of those using sodium chloride slurries as in the prior art discussed above.

Example 2

25 parts by weight calcium bentonite, 6 parts by weight sodium citrate and 69 parts by weight water are thoroughly mixed together to form a fluid suspension. This is labelled dispersion D. After standing for 48 hours, it had a Brookfield viscosity, measured at 20 rpm of 575 cP.

When the process was repeated using 10 parts sodium citrate and 65 parts water, to make dispersion E, the viscosity after 48 hours was 737 cP.

Dispersion F was formed in similar manner using 9 parts sodium citrate, 66 parts water and 25 parts of a sodium bentonite made by premixing 23.5 parts calcium bentonite and 1.5 parts sodium carbonate.

Dispersion G was made using 25 parts calcium bentonite, 9 parts sodium citrate and 66 parts water.

Example 3

In this example various of the dispersions given above are utilised in a laboratory simulation of processes such as those described in U.S. Pat. No. 4,753,710. A suitable thinstock (usually 0.5% bleached Kraft Furnish) is provided, an appropriate dosage (usually 500 g per ton) of a high molecular weight (typically intrinsic viscosity 6 dl/g) cationic polyacrylamide (usually 40% by weight dimethylaminomethyl acrylate quarternised with methyl chloride and 60% by weight acrylamide) is added, the suspension is sheared for 60 seconds at 1,500 rpm, the required dosage of bentonite dispersion is added, the mixture is subjected to gentle mixing and the Schopper Riegler drainage time is recorded for 700 ml to drain from 1,000 ml of the treated suspension, using a baffled Britt jar.

Each of the following tables represents a different set of experiments. In each set of experiments, the amounts in the column headed "Bentonite" always indicate the dosage of bentonite expressed in dry weight grams per ton paper and the figures in the columns headed by letters B to G show the drainage time using the shown amount of bentonite introduced, respectively, as dispersions B to G. In each instance, for the purposes of this test, the best results are obtained with the lowest drainage time, especially when this is obtained at a low dose of bentonite.

TABLE 1

Bentonite		B	C	F
0	84	84	84	
250	50	77	46	
500	36	78	31	
1000	22	64	20	
2000	14	50	14	
4000	11	35	12	

This demonstrates that the prior art slurries formed in sodium chloride (dispersion C) tend to give poor results compared to conventionally activated powdered bentonite (dispersion B) but the dispersion F of the invention again gives results as good as or a little better than the conventional product B and much better than the prior art concentrate C. Additionally, it has the advantages of ease of manufacture and ease of supply and use compared to processes using dry products (dispersion B).

TABLE 2

Bentonite		G	C
0	52	52	
250	32	48	
500	24	44	
1000	16	40	
2000	11	30	
4000	9	21	

This clearly demonstrates the fact that the sodium citrate slurry concentrate of the inventive gives, at all dosages, a performance which is dramatically better than the performance attainable with the sodium chloride slurry of the prior art.

Example 4

This example demonstrates that it is unimportant in the invention whether or not the bentonite concentrate is diluted before addition to the cellulosic suspension, whereas this makes a critical difference with the prior art concentrates.

Thus, when a 25% slurry in aqueous sodium chloride is diluted first to 5% and then to 0.25%, the drainage time in a test using 2000 g/t bentonite is about 75 seconds compared to 30 seconds for the corresponding bentonite powder. When the dilution is direct from 25% to 0.25%, the drainage time is even worse.

When a 25% slurry in sodium citrate is used, the drainage time at 2000 g/t is about 30, irrespective of the system of dilution.

United States Patent 4,118,247

(October 3, 1978)

Suspensions of Reactive Acidic Clay Pigments

Francis Marchetti, *et al.*

Abstract --- AMP (2-amino, 2-methyl, 1-propanol) or a related amino hydroxy compound is used with a sodium condensed phosphate dispersant in the preparation of stable aqueous suspensions of acidic, acid-treated montmorillonite clay pigment particles. The suspensions are used in the manufacture of carbonless copying paper.



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