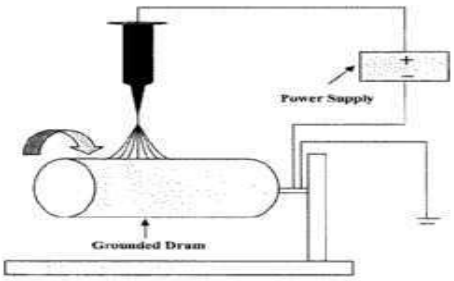
JAPANESE [JP,2007-154335,A]

(54) WATER-REPELLENT MEMBRANE, METHOD FOR PRODUCING WATER-REPELLENT MEMBRANE, METHOD FOR FORMING WATER-REPELLENT MEMBRANE ON SURFACE OF ARTICLE, AND ARTICLE OBTAINED BY THE METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for readily producing a super-water-repellent membrane by electrospinning method.
SOLUTION: The water-repellent membrane is produced by dissolving a polymer in a two or more-mixed solvent having difference in the boiling points to provide 17.5-35 wt.% solution, and laminating nanofibers formed by the electrospinning method under a condition of 15 kV applied voltage and 5-15 cm distance between a syringe and an electrode.



DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Field of the Invention]
[0001]
The present invention relates to the goods obtained by manufacturing method of the water repellent film which consists of a fiber (this is called "nanofiber" on these Descriptions) of the diameter of a nano order created by an electro spinning process, manufacturing method for the same, the method of forming a water-repellent membrane in an article surface, and this method.
[Background of the Invention]

[0002]
As a method of producing nanofiber, the electro spinning process is known from the former. According to the electro spinning process, application in various fields, such as a separator etc. of a culture medium with a biological fibrous body which could produce the fibrous body of the diameter of a nano order comparatively easily, and was created, the hemostatic material in a medical field, and a cell, is expected.
[0003]
An electro spinning process is a nano spinning method which applies the high tension of not less than 2 kV to the polymer solution put into the syringe, disperses a solution in electric field, and produces nanofiber. Since the thickness of that a spinning process is easy and a fiber can control even a nonwoven fabric from a thin film, it is observed as a nano spinning method nearest to practical use. It is possible for the diameter of a fiber and fiber form to change with the concentration and the solution scattering ranges of the kind of polymer, or a molecular weight and a solution, and to produce a fiber with a thickness of several micrometers from tens of nanometers in this method.
[0004]
In order to manufacture such a pole microfilament object large scale and at high speed, the voltage of 5-50 kV is applied, The interval of the nozzle of a syringe and an electrode shall be not less than 5 mm, the pump which pressurizes and supplies the stored liquefied polymeric material is used, and the method of manufacturing the polymer web which has the form with which the fiber which has a diameter for several nanometers - thousands of nm was laminated by three-dimensional network structure is proposed (Patent document 1). A polymer solution is maintained from 40 degrees C to the temperature requirement below the boiling point of a solvent for the same purpose, and the method of the nozzle which carries out the increase in discharge quantity is also proposed (Patent document 2). In this advanced technology, 20 g of polyacrylonitrile (molecular weight 150,000), Shall dissolve in 80 g of N.N-dimethylformamide, shall consider it as 20wt% of a polymer solution, the height between a nozzle and a collector shall be 20 cm, using an aluminum plate as a collector, and the voltage of 10 kV is applied, A polymer solution is made to discharge with the discharge velocity of 180microl/min from the nozzle of electro spinning equipment, and the polymer web of 50-micrometer thickness is made to generate on an aluminum plate, moving the aluminum plate which is a collector by 4 m/min. It is checked that this web is a polymer web of the film state which a fiber and droplet mixed as a result of a transmission electron microscope photograph.
Silk fibroin and silklike material are used as a polymer, and, naturally, the method of creating the single filament fiber with desired thickness not existing is also proposed by carrying out electro spinning (Patent document 3). In this method, the nonwoven fabric according [the silk concentration in a solution] to an ultrafine fiber (tens of nm - hundreds of nm) at 8 to 10 % by weight is obtained using 10-30 kV.
[Patent document 1] JP,2002-201559,A
[Patent document 2] JP,2002-249966,A
[Patent document 3] JP,2004-068161,A
[Description of the Invention]
[Problem to be solved by the invention]
[0005]
Since according to creation of the polymer fiber by an electro spinning process nanofiber can be produced comparatively easily and various polymers can be applied, development has been proceeding actively also about the applicable field recently, but development of the material and use which were further rich in functionality is desired.
[Means for solving problem]
[0006]
When creating the polymer fiber according [the inventors] to an electro spinning process, the

nanofiber film produced under the specific condition found out that ultra water repellency was shown in a surprising thing, and resulted in the present invention.
In the present invention, "water-repellency" means that an angle of contact will be not less than 120 degrees, and "super-water-repellency" says that an angle of contact will be not less than 150 degrees. It is thought that it is revealed with unevenness of the surface of the nanofiber formed of super-****** of the present invention and an electro spinning process or a nano particle. Such a phenomenon is seen also in a nature, for example, the surface of the flower of a lotus has the unevenness which consists of a minute organization which was able to do it as the crystal of the wax of a nano order, and shows water repellence (the lotus effect).
To everything but a lotus The plant in which super-**** is shown exists in a nature. For example, if silver ragwort observes the surface with an electron microscope, it turns out that it is covered with many fibers (Fig.10). For the rugged structure by this fiber, silver ragwort shows super-****.
The present invention makes the surface of goods water repellence using this "effect of the surface structure of silver ragwort."
[0007]
In order to create the water-repellent membrane of the present invention, in an electron spinning process, it is required to adjust polymer solution concentration, the distance of a syringe and an electrode, and impressed electromotive force to a specific range.
The present invention consists of the following composition.
(1) Dissolve in the mixed solvent which consists of volatile solvents, and a polymer is used as 17.5 - 35wt% of a solution, A manufacturing method of the water repellent film making the nanofiber formed [impressed electromotive force] in the distance of 15 kV, a syringe, and an electrode of a bottom [of 5-15 cm] of condition electro spinning process laminate from this polymer solution.
(2) A manufacturing method of (1) with which a volatile solvent consists of a TETORAHA hydronaliumfranc.
(3) A manufacturing method of (1) with which a volatile solvent consists of N.N-dimethylformamide.
(4) A manufacturing method of (1) whose volatile solvents are two or more kinds of mixed solvents in which volatility differs.
(5) (Four) manufacturing methods with which a mixed solvent consists of a TETORAHA hydronaliumfranc and N.N-dimethylformamide.
(6) A manufacturing method of either (1) thru/or (5) whose polymer is a water-repellent material.
(7) A manufacturing method of either (1) thru/or (5) whose polymer is polystyrene.
The water repellent film manufactured by the manufacturing method of either (8), (1) to (7).
How to make water repellence the article surface characterized by making a water repellent film form in an article surface directly by the method of of either (9), (1) to (7).
Goods which have the water repellence acquired by the method of of (10) and (9).
[Effect of the Invention]
[0008]
According to the present invention, ultra water repellency can be easily given to goods by enforcing an electro spinning process under a specific condition by making the ultra-water-repellency film which can create an ultra-water-repellency film easily, and is applied form in the surface of direct goods.
[Best Mode of Carrying Out the Invention]
[0009]
The water-repellent membrane of the present invention can be manufactured by enforcing an electro spinning process under a specific condition by laminating nanofiber or the nano particle which has minute unevenness on the surface, and forming a film in it.
The above-mentioned minute unevenness is considered to be formed by rapid evaporation of the solvent in a polymer when flying in the direction of an electrode, while a polymer solution

evaporates a solvent in an electro spinning process, but. When such minute unevenness especially used the mixed solvent of volatile high solvent;DMF (153 degrees C of boiling points), and volatile low solvent;THF (66 degrees C of boiling points), it turned out that it can form easily.
[0010]
The raw material of the water repellent film of the present invention is a polymer usually used by an electro spinning process, A FIBURO asbestos mixing silklike polymer (SLPF), silk (N. Clavipes silk, B.Mori silk, silk fibroin), Poly fluoridation vinylidene (PVDF), polytrimethylene terphthalate (PTT), Polyurethane, polystyrene, a polypyrrolidone (tic [AISOTA], atactic), Polyacrylonitrile (PAN), polybenzonitrile (PBI), Polycaprolactam (PCL), polyepsilon caprolactam, l-lactide epsilon caprolactam copolymer, Poly (D, L-lactic acid), poly (L-lactic acid), nylon 6, PA-66, an ethylene-vinylalcohol copolymer, Cellulose acetate, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), An ethylene-vinyl acetate copolymer (PEVA), polyethylene phthalate (PET), Polymethacrylate (PMMA), polyvinyl phenol (PVP), polyacrylamide (PAAm), PLGA, poly 2-hydroxyethyl methacrylate (HEME), collagen, polyvinylidene fluoride (PVDF), polyether imide (PEI), Poly ferrocenyl dimethylsilane (PFDMS) etc. can use it.
Various functions can also be given besides water repellence by choosing the material which has various functions.
For example, there is the following as a material in which a deodorizing function is expected.
A benzoquinone compound (it is an effect to mercaptans or disulfide), aramid, Meta-aramid, polybenzimidazole, polybenzooxazol, polyimide, polyamidoimide, polyether ketone, polyvinyl alcohol, starch, polyacrylonitrile, a sodium hexametaphosphate, polyethyleneimine (hydrogen-sulfide-odor deodorization)
As a thing effective in basic malodorous component removal,
Malic acid, citrate content polymer, polyacrylic acid, and poly phosphoric acid (ammonia smell removal), Titanium oxide, aluminum sulfate content polymer, zinc oxide content polymer, iron phthalocyanine content polymer, the nature argillite content polymer of hydrous-silicic-acid magnesium (gas removals, such as ammonia, lower fatty acid, pyridine, and trimethylamine), aluminosilicate content polymer
Others
precious-metals oxide oxidative decomposition catalyst content polymer (manganese oxide and cobalt oxide --) Nickel oxide, cobalt oxide, copper oxide, chrome oxide It reaches. The composite metal oxide, Ruthenium compound content polymer, such as transition element content compound (cupric nitrate, copper sulfate, cupric chloride) content polymer, photocatalyst (titanium oxide, zinc oxide, iron oxide, etc.) content polymer, and ruthenium tetroxide, silicic acid magnesium aluminate content polymer
Polymer containing the following compound
An iron tetracarboxyphthalocyanine content compound, oxy many chlorides, a ruthenium compound, An aluminum content compound phyllosilicate, calcium phosphate, metal 2 Russia Nin, 3-aminopropyl bird hydro-Silang, gamma aminopropyl triethoxysilane, Aminopropyl trimethoxysilane, salicylic acid, benzoic acid, sodium alkylsulfate, Alkyl benzylammonium salt, phytic acid, inositol hexalin acid ester, Alkali carbonate metal salt, ammonium carbonate, a calcium chloride, calcium acetate, Sodium hypochlorite, 2-hydroxyl methylamino ethanol, the hexahydro 1 and 3, 5-triethyl S-triazine, a benzoquinone derivative, trunk chloro fin sodium, the 2-methoxy- 1, 4-benzoquinone
the 2-methyl 1, 4-benzoquinone, a benzoquinone derivative - liquid support nature -- high support nature - silicon-oxide powder or calcium oxide powder, hydroxylamine, hydrazine, a semicarbazide, a hydrazine derivative, ethylenediamine, triethanolamine, and phosphoric acid and ethylenediamine
The reactant of phosphoric acid, triethanol, aliphatic aldehyde, the amine supported by the fine-pores surface of activated carbon, a Schiff base, ethylenediamine, triethanolamine, a hydrazine system compound, and a long-chain aliphatic compound, the reactant of a hydrazine system

compound and aromatic compounds, cevadine acid dihydrazide
Dodecanedioic acid dihydrazide, dihydrazide isophthalate, aniline, The organosilicon compound, 3-aminopropyl trihydroxy silane containing aromatic amine and an amino group, gamma-aminopropyl triethoxysilane, gamma-aminopropyl trimethoxysilane, The combination of the compound which has the 1st class amino group, and the nature argillite of a magnesium silicate, Chitosan, polyacrylic acid hydrazide, organic acid, vitamin C, flavonoid, Malonic ester, tartrate, mandelic acid ester species, activated carbon, Ascorbic acid, sulfamic acid, a glycine, Zarko Singh, 2-aminoethanol, Organic acid ester species, a phytic acid metal complex compound, an amino compound, an amide compound, A benzoquinone derivative, an amino compound, a hydrazine derivative, an organosilicon compound silanol group, Type hydrogen, a peroxide, quinolinol, a quinoline metal complex and gluconate, and an alkaline agent, Malonic ester, tartrate, a phytic acid metal complex compound, fatty acid soap and a deodorizer bubble, an amino ethanol derivative, a triazine derivative, an amide oxime system complex compound, a benzoquinone derivative, amine, an acid gas adsorptivity amino group content organosilicon compound, a hydrazine derivative, Aromatic amine is intercalated between the layers of a poly amino compound, the nature argillite of a magnesium silicate, and stratified slightly soluble phosphate salt.
Polymer containing the following microorganism
A microorganism, the Thiobacillus thio pulse and phosphoric acid alkali salt of Enterobacter, punishment -- lath Subtilis KUBOTA and Bacillus:Bacillus subcillus -- Bacillus natto, bacillus core GYURASU, a Bacillus macerans, Enterobacter : Enterobacter SAKAZAKI, the Enterobacter AGURONE lance, Streptococcus group: A Streptococcus faecalis, streptococcus Clemeau Rith, Streptococcus Lactis, Alcaligenes:Alcaligenes faecalis, Alcaligenes DENITORIFIKANSU KURESHIERA group: KURESHIERA NYUMONI
Polymer containing the following substance
A beta-vulgaris-rubra extract, a cacao extract, a coffee parsley extract, a green tea extract, SHISOEKISU, a persimmon extract, and Japanese butterbur -- an extract, a sea paste extract, and a varnished conk extract -- A mushroom extract, polyphenol, flavonoid, a terpene, A polyphenol compound, catechin, flavonoids, polyphenol, Tannic acid, polyphenol of an apple, catechin, epicatechin, phlorizin, Chlorogenic acid, a pro anthocyanidin, a coumarin, folic acid, abietic acid, Hinokitiol, guava tea, dried myrica, Terminalia chebula Retzus (chebulae fructus), SHIBAIKA tea, RENSEISOU, the Puer tea, corni fructus, Mallotus japonicus, cinnamon, Tara, Activated carbon, silica gel, calcium hydroxide, citrate, sodium subsulfite, potassium permanganate, urease inhibitor, areca powder, and a flavonoid content wood extract (a surfactant --) Those with a perfume **** thing, a life-prolonging grass (Isodon japonicus, Isodon trichocarpus) extract, A diterpene derivative, enmain, nodosin, trichorabdal A, trichorabdal B, trichorabdal C, trichorabdal H, oridonin, effusanin A, effusanin B. longikaurin A, longikaurin B, longikaurin D, lasiokaurin and trichoranin (naming schedule) -- "-- semelle -- it is a blend (a Japan cedar --) about the extract extracted from the plant of 30 kinds of NAKU":domestic production Phytoncide, such as a hinoki, Sasa Veitchii Rehder, an aloe, and a physalis radix, a betaine (Japanese horseradish), Amino acid (Japanese horseradish), organic fatty acids (Japanese horseradish), fructose (Japanese horseradish), Polyphenol from the Rosaceae unripe fruit, a green tea flavonoid coumarin, Folic acid, abietine, hinokitiol, a zinc oxide, magnesium oxide, Titanium oxide, alumina, activated carbon, triclosan, isopropylmethyl phenol, A benzalkonium chloride, chlorhexidine glyconate, halo carbane, The Para zinc phenolsulfonate, citrate, an aluminum salt, a hydroxyaluminium chloride, Ethyl alcohol, lauric acid (dodecanoic acid) (straight chain saturated fatty acid, glyceryl mono- KAPURI rate, etc.), alpha, omega-alkane dicarboxylic acid (malonic acid, succinic acid, guru slack acid, etc.) (with mixture with wool low acid), benzyl alcohol, benzyl acetate, cinnamyl acetate, styryl carbinol citronellol, Geraniol, chitosan, antibacterial zeolite (if the fine particles of specific particle diameter are used) (ammonium ion and an antibacterial metal replaced), Natural essential oils, such as a fennel, caryophylli flos, a mentha herb, and a eucalyptus, a ginseng, The common plants, such as an

aloe, sage brush, a loquat, a beefsteak plant, and a Geranium thunbergii Sieb. etZucc., Organic acid, chitosan, benzyl alcohol, benzyl acetate, natural essential oils, Plants, such as organic acid zinc salt, a sage, and a rosemary, thru/or a natural extract, the extract of a tamarind husk, Tocotrienol, the N-methacryloiloxy-ethyl N, N-dimethylannmonium and an alpha-N-methyl carboxy betaine butyl methacrylate copolymer, cow's milk, acid foods (a pickled plum, lemon, etc.), and fiber foodstuffs (lettuce and a cabbage --) The protein of flavonoid, chlorophyll, and cyanobacteriums, such as a dried seaweed, vitamins, Polysaccharide, a mineral, a chlorella hot water extract, a dill seed, a parsley seed, A fennel seed, an anise seed, star anise fruits, a cumin seed, an AOSHISO seed, A cinnamon bark, a basil leaf, a nutmeg seed, a rosemary leaf, a cardamom seed, a juniper sap fruit, a peppermint leaf, a coriander seed, a caraway seed, a terpene, terpene alcohol, an oxide compound. Green tea, oolong tea, a persimmon leaf, an apple extract, Aspalathus linears crown, a dehydrated carrot leaf, Dehydrated vegetables with many fiber components, the high dehydrated vegetables of sugar content, the extract of natural-plants yucca, saponin and punishment -- the deodorizing component from lath Subtilis, glyoxal, and the Theaceae plant -- A chlorophyllin system color, a porphyrin system color, zeolite, silica gel, Organic system flavonoid, anionic system deodorant finish liquid, a zinc oxide, a zirconium compound, a mineral silicate, an alumino mineral silicate, SiO2 and MOn/2 and Al2O3, and HaMb(PO4) andnH2O (a+4b=3c) (M -- a zirconium --) The inorganic cation exchanger which consists of quadrivalent metal phosphate which made univalent or divalent metal ion, such as titanium and tin, support, A hydrotalcite, an amine compound, ethylenediamine, diamino propylamine, polyamine compound, xylenediamine, a phenylenediamine, and aromatic polyamine (silicon --) The hydrazine, the hydroxylamine, the hydrazine compound, adipic acid dihydrazide (alkylene dicarboxylic acid dihydrazide, aromatic-dicarboxylic-acid dihydrazide, etc. of the carbon numbers 6-12), polyacrylic acid hydrazide which add inorganic system compounds, such as zinc, copper, zeolite, and activated carbon. Zirconium hydroxide, zirconium oxide, titanium oxide, a ceramic system deodorizer, A carboxylic acid group and a sulfonic group are introduced into a polyamide fiber or polyester fiber, The fiber, precious-metals zeolite catalyst which replaced hydrogen ions, such as this carboxylic acid group, with metal ion, Pulverization of a metallic oxide, amphoteric metal hydroxide, and a formless silicon dioxide and formless zinc oxides (zinc hydroxide etc.) is carried out, What carried out water jet confounding of an inorganic system ion adsorption type deodorizer, and mixed span bond non-**** and cellulose fiber sheet of a synthetic fiber, and was made into compound non-****, What immersed acid type a part or all of the carboxyl group in the aqueous solution containing a divalent copper compound, and was converted into the copper salt type by pH of the specific range, A mineral silicate, an alumino mineral silicate, a modacrylic fiber, metal phthalocyanines, No metal phthalocyanine derivative, the copolymer which becomes a vinyl monomer which has an acidic group, and its vinyl monomer from a copolymerizable monomer, Acrylate fiber, hydrazine compound, essential oil ingredient, organic acid, metallic-oxide, photocatalyst, polytetrafluoroethylene resin, polyethylene, polyvinyl chloride, apatite, calcium phosphate, metal-phthalocyanines polycarboxylic acid, and Tripoli phosphoric acid 2 hydrogen aluminum, Chlorinated isocyanuric acid, halogenation hydantoin, polyester, Polypropylene, polyethylene, polybutadiene, styrene, butadiene, A styrene-sulfonic-acid salt, an acrylonitrile butadiene series copolymer, SBR, SB, HS, NBR, a styrene-sulfonic-acid salt, acrylic acid, Polytetrafluoroethylene, polyolefin, a glyoxal, vinyl acetate, Gellant gum, gelatin, pectin, locust bean gum, xanthan gum, Sodium alginate, a cellulosic, agar, galla GINAN, glucose acid, Succinic acid, adipic acid, phthalic acid, magnesium sulfate, an aluminium nitrate, Potassium bisulfate, acrylamide, methylenebis acrylamide, Polymer with a carboxyl group, polymer with a sulfonic group, a silicon dioxide, A zinc oxide, a vanadium oxide, CMC, starch, CMS (carboxy methyl starch), All [PORUNE / HEC (hydroxyethyl cellulose), HPC (hydroxypropylcellulose) tetraalkylsilane, a halo silane, disiloxane disilazane, a silanol, an alpha pinene, and], limonene, terpene hydrocarbon, hinokitiol, tannin, catechin, A sodium perborate hydrate, sodium perborate 4 hydrate, a cyanate, dichloro isocyanuric acid soda, Trichloro

isocyanuric acid soda, a chlorine dioxide, sodium hypochlorite, Calcium hypochlorite, sodium nitrate, slaked lime, ascorbic acid, 1,3,5-tris-(beta-oxyethyl)-hexahydrotriazine, Kolin, glucoheptonic acid iron, soda ash, ferrous sulfate, a magnesium silicate, Mannan oligosaccharide, undecylenic acid polyoxyalkylene ester, Palm oil fatty acid, an amide propylbetaine, naphthalene, camphor, PARAJI chlorobenzene, A polyethylene glycol, stearic acid, sodium lauryl sulfate, Chlorinated isocyanuric acid, a parlor palm, a banyan, OPOPONAKKUSU resin, Mill resin, olibanum resin, the Sitrah base, a floral base, a musk base, Glyoxal, carboxymethyl cellulose, bentonite, methyl salicylate, Timor, aniline, menthol, eugenol, sepiolite, a carmine pigment, an anthraquinone compound, carboxylate, etc. can be used.

[0011]

Dissolve the above-mentioned polymer, as a solvent which dissolves a fiber material, if it is a low thing of high volatility of the boiling point, will not ask a kind, but. Hexafluoro 2-propanol, $CaCl_2$ / ethanol / water, DMAA, TFA/MC, DMF, THF, THF/DMF, DMAc, DMF/THF/isopropanol, chloroform/methanol, acetone, Although dimethylformaldehyde, methylene chloride, dichloromethane, the product from Gyi, IPA/water (7:3), ethanol, hexafluoro 2-propanol, DMF / dimethylacetone, etc. are mentioned, The mixed solvent of the low solvent of high volatility of the boiling point and the volatile solvent in which the boiling point is higher than it is preferable like DMF/THF.

[0012]

What is necessary is just to arrange to electrode vicinity between the syringe in an electro spinning process, and an electrode, in order to make the water repellent film of the present invention form on the surface of goods. If a fiber is made to form by an electro spinning process, carrying out rotation and movement for goods, a water-repellent membrane can also be made to form uniformly on the surface of [whole] goods.

If goods are conductive construction material, the goods themselves can be used as an electrode. As goods which form a water repellent film by the present invention, construction material, such as clothes, building materials, and daily needs, is not asked.

[Working example]

[0013]

With the equipment shown in Fig.1, polystyrene (average molecular weight Mw=208,000) to the mixed solvent of a tetrahydrofuran (THF) and N.N-dimethylformamide (DMF), The solution in which it was made to dissolve in 17.5 - 35wt% of the range was used, the distance between the impressed electromotive force of 15 kV and a syringe electrode was adjusted to 5-15 cm, on the cylindrical cathode drum, nanofiber was made to laminate and the water repellent film was formed. the mixed solvent in which Fig.2 set the mixture ratio of DMF/THF to 3:1, 2:2, and 1:3 for polystyrene -- respectively -- 30wt% -- the dissolved solution is used and the nanofiber which created the distance between the impressed electromotive force of 15 kV, a syringe, and an electrode on 10-cm conditions is photoed with an electron microscope.

In 500 times, although a difference is not looked at by the fiber, if it expands by 10,000 times, what dissolved the mixture ratio of DMF/THF in the solvent set to 3:1 and 2:2 can observe that minute unevenness is formed in the fiber surface. If it separates from this range as shown in Fig.3, unevenness will become coarse or unevenness will no longer be formed.

Thus, the result of having measured the angle of contact of the created fiber film is shown in Fig.4. By the film consisting of the fiber in which the minute unevenness shown in Fig.3 was formed, the angle of contact has become largely, and especially the film that formed the distance between a syringe and an electrode as 10-15 cm exceeds 150 degrees, and shows ultra water repellency.

[0014]

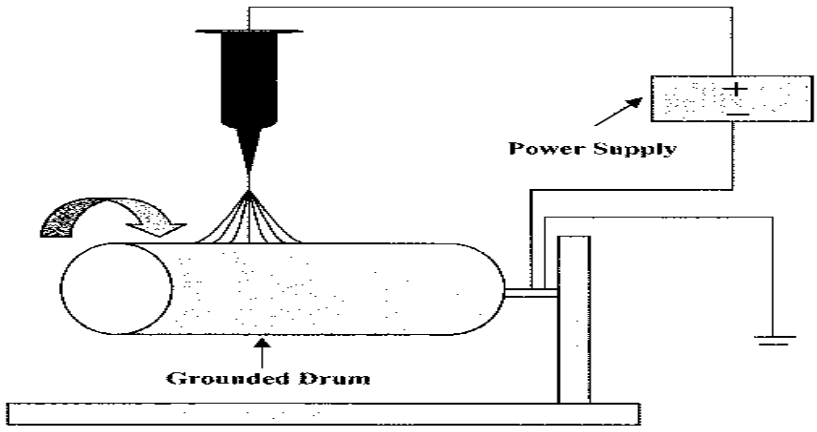
[The example 1 of an experiment]

The solution which dissolved polystyrene in the THF independent solvent is used, and the electron microscope photograph of the film which formed the distance between a syringe and an electrode as

5-30 cm is shown in Fig.5.
The film in which concentration was formed from the dilute solution has many ratios of a nano particle, when concentration becomes high, the ratio of a fiber becomes high and the diameter of a fiber is also known by that it is thick. Fig.6 is the electron microscope photograph which photoed the surface of each nano particle or nanofiber.
It turns out that a surface concave part is sparse as concentration becomes high.

The result of having measured the angle of contact of these films is shown in Fig.7. When the distance between a syringe and an electrode set to 10-15 cm, concentration showed the water repellence excellent in less than 25wt%, but there was a problem that a fiber will be too soft, and waterdrop will be sunk and crowded. In order that particles might occupy most, there was a problem that it was weak in strength and weak, like thin ice.
[0015]
[The example 2 of an experiment]
The solution which dissolved polystyrene in the DMF independent solvent is used, and the electron microscope photograph of the film which formed the distance between a syringe and an electrode as 5-30 cm is shown in Fig.8.
The film in which concentration was formed from the dilute solution has many ratios of a nano particle, when concentration becomes high, the ratio of a fiber becomes high and the diameter of a fiber is also known by that it is thick.
The result of having measured the angle of contact of these films is shown in Fig.9. Although the water repellence outstanding in the range whose concentration is 15 - 30wt% is shown when the distance between a syringe and an electrode sets to 10-15 cm,
There was a problem that membranous strength was torn easily low.
[Industrial applicability]
[0016]
The water repellent film of the present invention can make the surface of various goods water repellence easily, and its application range is wide.
[Brief Description of the Drawings]
[0017]
[Drawing 1]The key map of the equipment which enforces an electro spinning process
[Drawing 2]The photograph which photoed the surface of the fiber which dissolved in the DMF/THF mixed solvent and formed PS
[Drawing 3]The photograph which photoed the surface of the fiber which changed and formed the DMF/THF mixture ratio
[Drawing 4]Measured value of the angle of contact of the film which changed and formed the distance between the DMF/THF mixture ratio, a syringe, and an electrode
[Drawing 5]The photograph which photoed the surface of the fiber which dissolved in the THF independent solvent and formed PS, and particles
[Drawing 6]The enlargement which photoed the surface of the fiber which dissolved in the THF independent solvent and formed PS, and particles
[Drawing 7]Measured value of the angle of contact of the film which dissolved in the THF independent solvent and formed PS
[Drawing 8]The photograph which photoed the surface of the fiber which dissolved in the DMF independent solvent and formed PS, and particles
[Drawing 9]Measured value of the angle of contact of the film which dissolved in the DMF independent solvent and formed PS
[Drawing 10]The photograph which photoed the surface structure of silver ragwort

[Translation done.]



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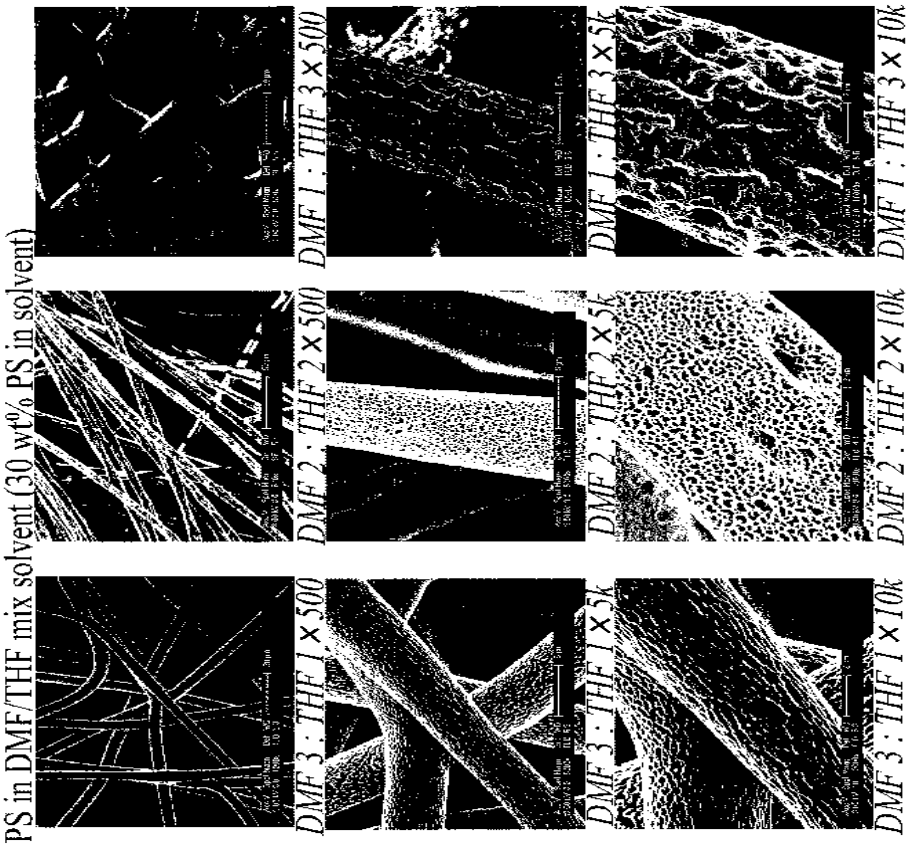
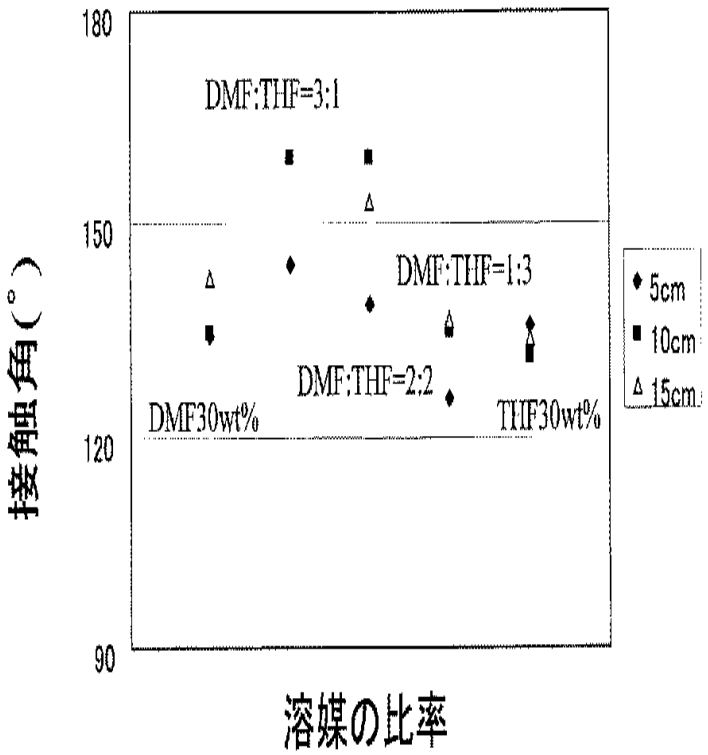
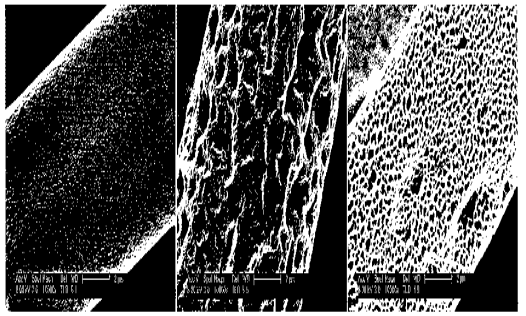
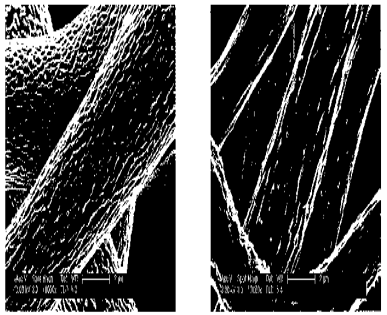




PS concentration: 30 wt%; Voltage: 15 kV; Distance: 10 cm

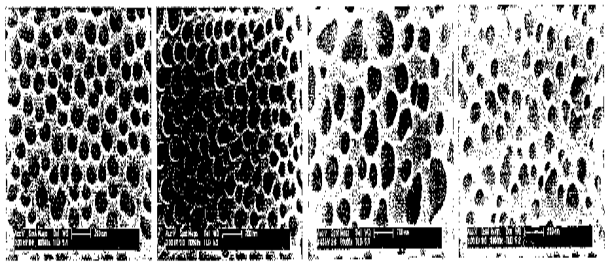


THF:DMF = 4:0　　THF:DMF = 3:1　　THF:DMF = 2:2



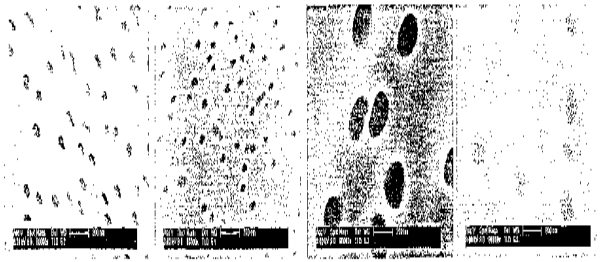
THF:DMF = 1:3　　THF:DMF = 0:4

PS in THF 17.5~25wt%→beads surface



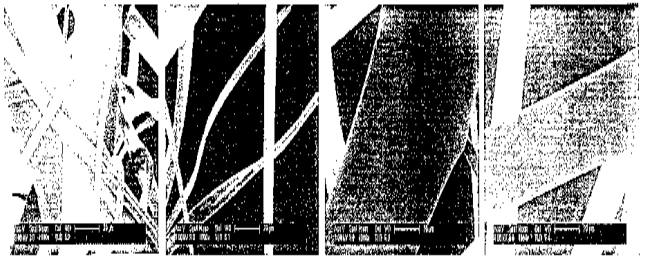
17.5wt% 20wt% 22.5wt% 25wt%

PS in THF 27.5~35wt%→fiber surface

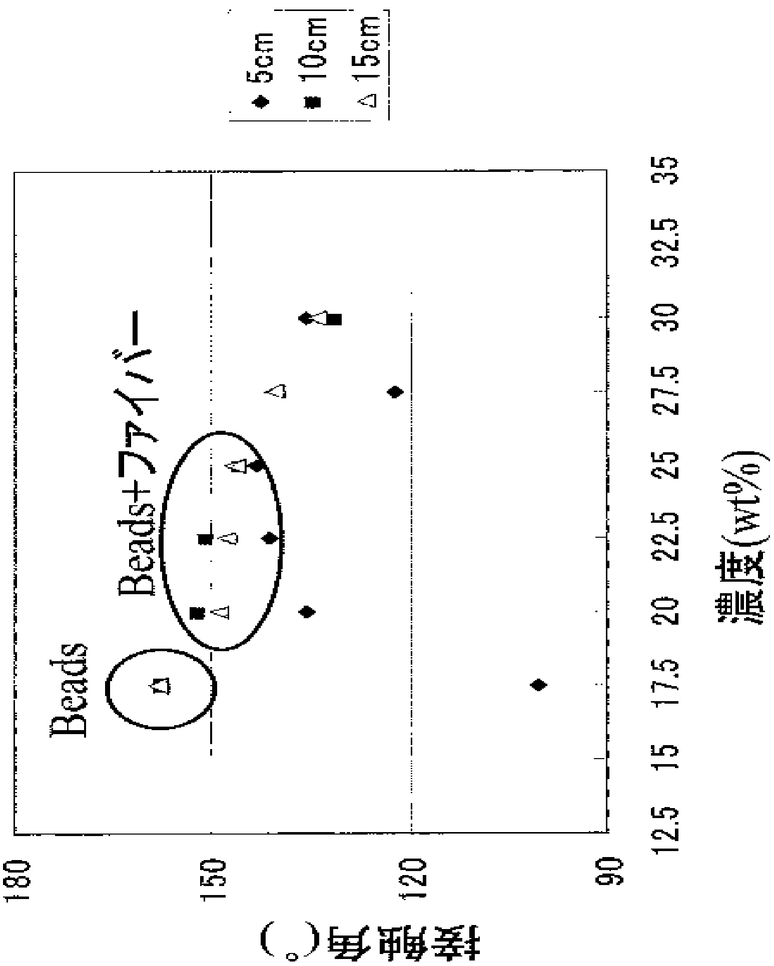


27.5wt% 30wt% 32.5wt% 35wt%

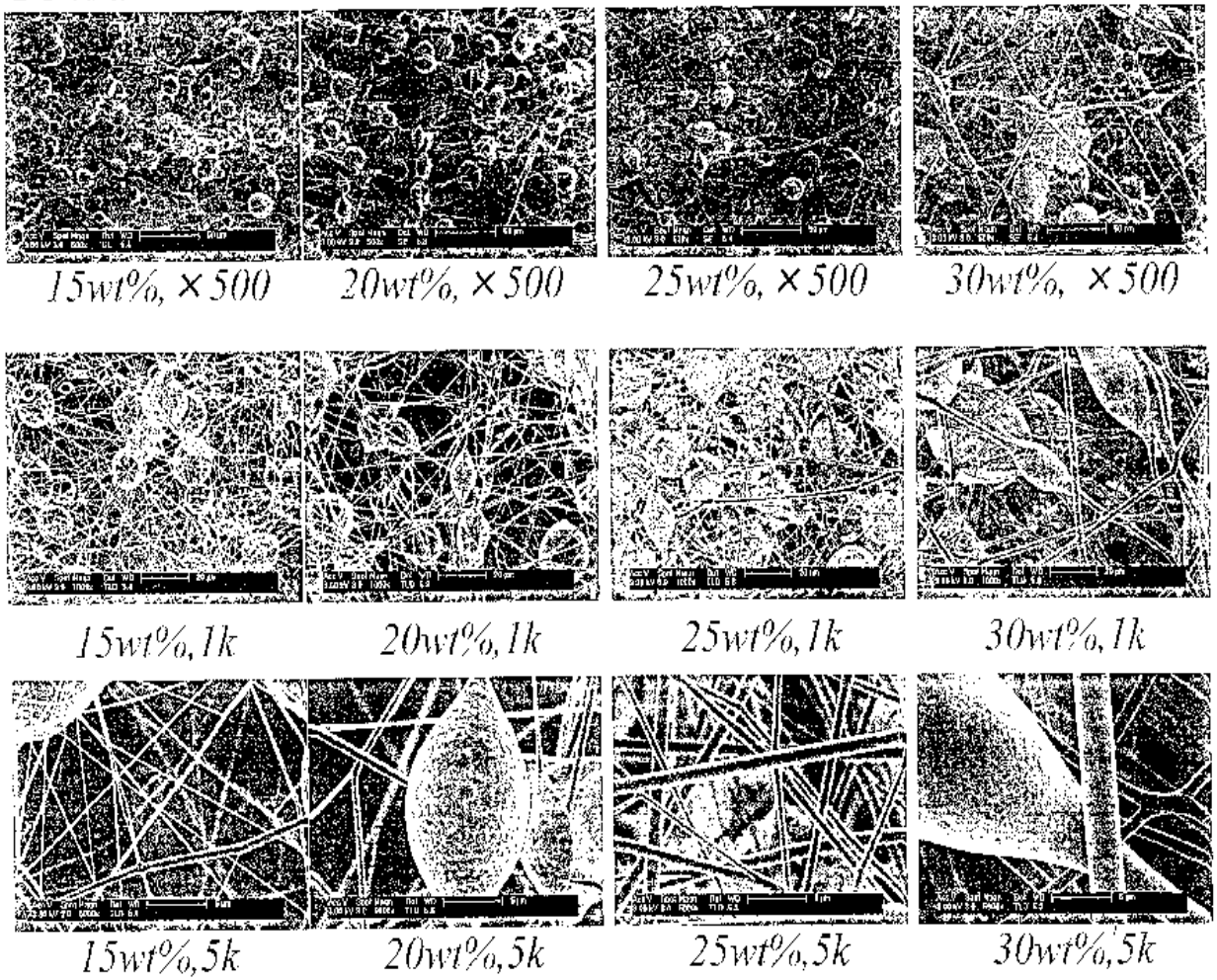
17.5wt% 20wt% 22.5wt% 25wt%



27.5wt% 30wt% 32.5wt% 35wt%


Beads
Beads+ファイバー
5cm
10cm
15cm
接触角(°)
濃度(wt%)
180
150
120
90
12.5
15
17.5
20
22.5
25
27.5
30
32.5
35

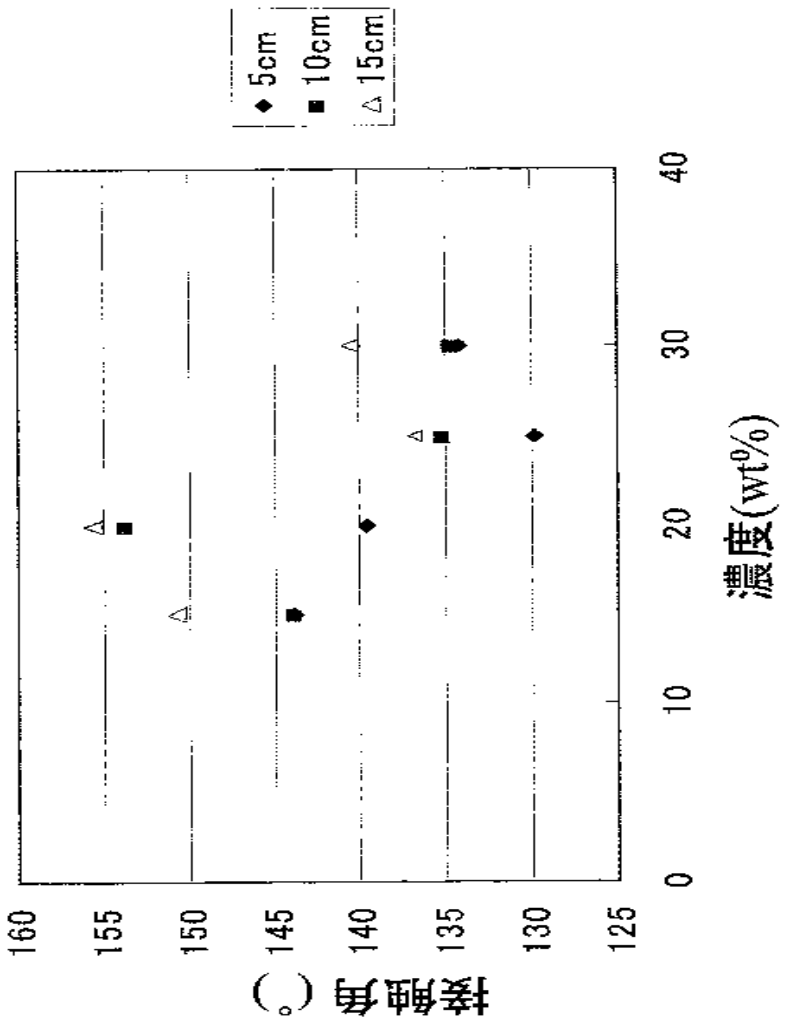
PS in DMF

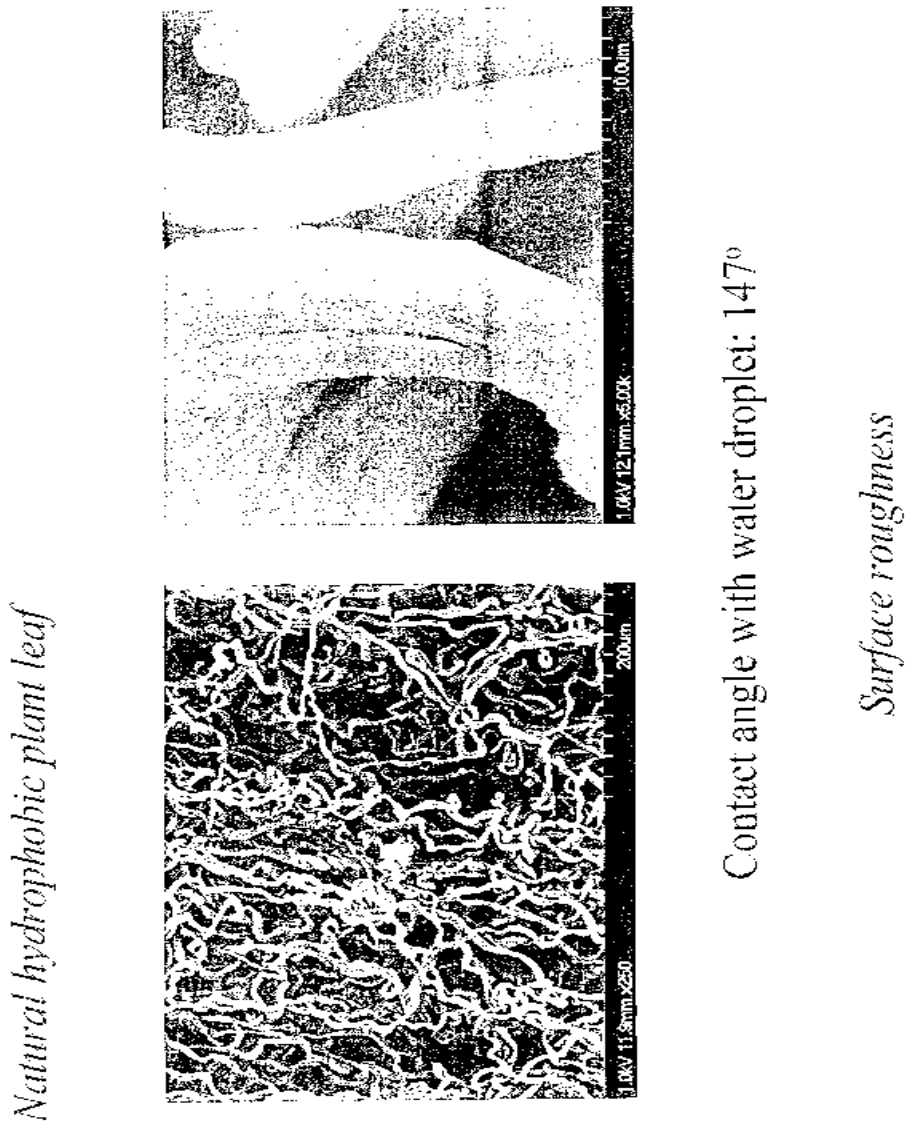


15wt%, × 500 *20wt%, × 500* *25wt%, × 500* *30wt%, × 500*

15wt%, 1k *20wt%, 1k* *25wt%, 1k* *30wt%, 1k*

15wt%, 5k *20wt%, 5k* *25wt%, 5k* *30wt%, 5k*


5cm
10cm
15cm
160
155
150
145
140
135
130
125
0
10
20
30
40
接触角（°）
濃度(wt%)



[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1]
A manufacturing method of a water repellent film which dissolves in a volatile solvent, uses a polymer as a solution, and is characterized by making nanofiber formed [impressed electromotive force] in distance of 5-30 kV, a syringe, and an electrode of a bottom [of 5-30 cm] of condition electro spinning process laminate from this polymer solution.
[Claim 2]
The manufacturing method according to claim 1 whose distance of a syringe and an electrode a volatile solvent is 15-30 cm in a tetrahydrofuran.
[Claim 3]
The manufacturing method according to claim 1 whose distance of a syringe and an electrode a volatile solvent is 15-30 cm in N.N-dimethylformamide.
[Claim 4]
The manufacturing method according to claim 1 whose volatile solvents are two or more kinds of volatile different mixed solvents.
[Claim 5]
The manufacturing method according to claim 4 with which a mixed solvent consists of a tetrahydrofuran and N.N-dimethylformamide.
[Claim 6]
The manufacturing method according to any one of claims 1 to 5 whose polymer is a water-repellent material.
[Claim 7]
The manufacturing method according to any one of claims 1 to 5 whose polymer is polystyrene.
[Claim 8]
A water repellent film manufactured by a manufacturing method described in either of the Claims 1-7.
[Claim 9]
How to make water repellence an article surface characterized by making a water repellent film form in an article surface directly by a method according to any one of claims 1 to 7.
[Claim 10]
Goods which have the water repellence acquired by a method according to claim 9.

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Office européen des brevets

Espacenet

Bibliographic data: CN202344979 (U) — 2012-07-25

Composite material superhydrophobic membrane

No documents available for this priority number.

Inventor(s): WEILIANG LIU; WENHUA XU; LIDONG ZHANG; LI WANG; LI ZHAO ± (LIU WEILIANG, ; XU WENHUA, ; ZHANG LIDONG, ; WANG LI, ; ZHAO LI)

Applicant(s): SHANDONG INST LIGHT INDUSTRY ± (SHANDONG INSTITUTE OF LIGHT INDUSTRY)

Classification: **- international:** ***B32B27/14; B32B27/38; B32B33/00; B32B9/04***
- cooperative:

Application number: CN20112523585U 20111215

Priority number (s): CN20112523585U 20111215

Abstract of CN202344979 (U)

The utility model discloses a composite material superhydrophobic membrane which comprises a resin base layer, a hydrophobic silica nano particle intermediate layer and a low surface energy material surface layer, wherein the resin base layer and the low surface energy surface layer are arranged on two surfaces of the hydrophobic silica nano particle intermediate layer, therefore, organic polymer resin and an inorganic material are well combined, the mechanical property of the membrane is improved due to the introduction of the polymer resin, the surface microscopic roughness of the membrane is increased due to the introduction of hydrophobic nano silica, the surface energy of the membrane is reduced due to the introduction of a low surface energy material, and finally the composite material superhydrophobic membrane with excellent mechanical property is obtained. The composite material superhydrophobic membrane has a surface water contact angle of reaching 151+/-1 DEG, a rolling angle of reaching 6+/-1 DEG, and excellent hydrophobicity and self-cleaning performance.

Last updated: 23.09.2013 Worldwide Database 5.8.11.5; 92p

Espacenet

Bibliographic data: CN102249667 (A) — 2011-11-23

Method for preparing grapheme/ ceramic nanocrystalline particle composite material with electrospinning-hydrothemal method

No documents available for this priority number.

Inventor(s): YUEMING SUN; YUNXI DAI; YINGPING ZHENG; RAO JING; CHUNLONG WANG; QI QI ± (SUN YUEMING, ; DAI YUNXI, ; ZHENG YINGPING, ; JING RAO, ; WANG CHUNLONG, ; QI QI)

Applicant(s): UNIV SOUTHEAST ± (SOUTHEAST UNIVERSITY)

Classification: **- international:** ***C01B31/04; C04B35/10; C04B35/14; C04B35/453; C04B35/46; C04B35/622; D01D5/00***

- cooperative:

Application number: CN2011198809 20110420

Priority number (s): CN2011198809 20110420

Also published as: CN102249667 (B)

Abstract of CN102249667 (A)

The invention discloses a method for preparing grapheme/ ceramic nanocrystalline particle composite material with an electrospinning-hydrothemal method. The method comprises the following steps: firstly, preparing ceramic/ polymer composite fiber by electrospinning; then, dissolving the composite fiber into a solvent for dissolving polymers; dismembering the fiber into tiny ceramic nanocrystalline seeds while the polymers in the composite fiber are dissolved; then, adding graphene oxide; carrying out hydrothermal or solvothermal reaction; and after reaction ends, adding a reducing agent to reduce the graphene oxide into grapheme.; The ceramic/ polymer composite fiber is weaved by the electrospinning, and the hydrolysis speed of the metallorganics of a ceramic material precursor is controlled by controlling the moisture, electrospinning flow rate and the like in the electrospinning environment. The electrospinning method and the hydrothemal method are both simple and easy to implement and can be used for industrially producing and preparing nanofiber materials. The combination of the electrospinning method and the hydrothemal method creates convenience for industrial production of materials.

Last updated: 23.09.2013 Worldwide Database 5.8.11.5; 92p

Espacenet

Bibliographic data: KR101122253 (B1) — 2012-03-20

THE MANUFACTURING METHOD OF SUPERHYDROPHILIC AND SUPERHYDROPHOBIC SILICA COATING LAYER

No documents available for this priority number.

Inventor(s): KIM SANG SUB [KR]; KIM EUN KYEONG [KR]; LEE CHUL SUNG [KR] ± (KIM, SANG SUB, ; KIM, EUN KYEONG, ; LEE, CHUL SUNG)

Applicant(s): INHA IND PARTNERSHIP INST [KR] ± (INHA-INDUSTRY PARTNERSHIP INSTITUTE)

Classification: **- international:** ***B05D1/04; B05D3/00; C09D1/00; C09D183/02***
- cooperative:

Application number: KR20100092411 20100920

Priority number (s): KR20100092411 20100920

Abstract of KR101122253 (B1)

PURPOSE: A manufacturing method of superhydrophobic and super hydrophilic silica coating is provided to form various surface shapes of silica coating layers only by coherence adjustment of mother material. CONSTITUTION: A manufacturing method of superhydrophobic and superhydrophilic silica coating comprises the following steps: manufacturing mother material by mixing polymer and silica precursor solution; forming silica surface by spreading the mother material solution on the mother material using electrospinning method; and calcining the formed silica surface. 0.2~10 weight% of the polymer is used based on the silica precursor solution. The silica precursor solution is tetraethoxysilane, methyltriethoxysilane, or mixture thereof.

Last updated: 23.09.2013 Worldwide Database 5.8.11.5; 92p