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(71) Applicant: **Toray Industries, Inc.**
Tokyo, 103-8666 (JP)

(72) Inventors:
- **SHIKURI, Ryuji**
  Anpachi-gun, Gifu 503-2395 (JP)
- **ISHII, Koki**
  Anpachi-gun, Gifu 503-2395 (JP)
- **SHIBANO, Takuya**
  Anpachi-gun, Gifu 503-2395 (JP)

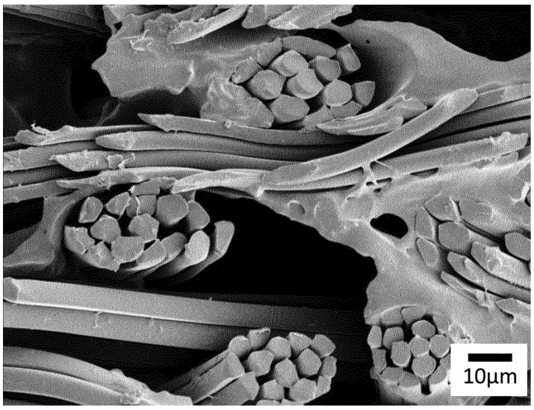
(74) Representative: **Mewburn Ellis LLP**
Aurora Building
Counterslip
Bristol BS1 6BX (GB)

(54) SHEET-SHAPED ARTICLE AND MANUFACTURING METHOD THEREFOR

(57) A purpose of the present invention is to provide a sheet-shaped article and a manufacturing method therefor, said sheet-shaped article demonstrating both a supple texture and superior wear resistance. In order to achieve this purpose, a sheet-shaped article according to the present invention is a sheet-shaped article that includes, in a fibrous base material, a polymer elastic body with a hydrophilic group, said fibrous base material comprising extremely fine fibers with an average individual fiber fineness of 0.1μm to 10μm, wherein the sheet-shaped article has N-acylurea bonding or isourea bonding within the polymer elastic body, and a monovalent positive ion-including inorganic salt is present at a rate of 0.1mass% to 5mass% with regard to the mass of the polymer elastic body.

[Fig 1]

[Fig 1]



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Description

TECHNICAL FIELD

[0001] The present invention relates to a sheet-shaped article and a method for manufacturing the sheet-shaped article, and particularly preferably to a sheet-shaped article having a raised nap and a method for manufacturing the sheet-shaped article.

BACKGROUND ART

[0002] Sheet-shaped articles mainly including a fibrous substrate and polyurethane such as a nonwoven fabric have superior characteristics not shared with natural leather, and are widely used for various applications such as artificial leather. In particular, sheet-shaped articles using a polyester-based fibrous substrate have superior lightfast, so that their usage as clothing, chair covering, and automobile interior material has increasingly been extended year by year.

[0003] In order to manufacture such a sheet-shaped article, a combination of steps has been generally adopted, including: impregnating a fibrous substrate with a polyurethane-containing organic solvent solution; and then immersing the resulting fibrous substrate in an aqueous solution containing water or an organic solvent in which polyurethane is not dissolved, thereby subjecting the polyurethane to wet coagulation. In this case, a water miscible organic solvent such as N,N-dimethylformamide is used as the organic solvent that is a solvent for polyurethane. However, since the organic solvents are highly harmful to the environment in general, a procedure without using any organic solvent has been strongly sought in manufacturing the sheet-shaped article.

[0004] As a specific solution, a method has been considered in which a water-dispersible polyurethane prepared by dispersing a polyurethane resin into water is used as an alternative for the conventional organic solvent-based polyurethane. So far, in order to obtain a sheet-shaped article with a supple texture by using a water-dispersible polyurethane, for example, a method has been proposed in which a thickener is added to a solution containing a water-dispersible polyurethane, and a fibrous substrate impregnated with the solution is treated with hot water, thereby reducing the domain size of polyurethane and reducing retaining forces of entangled portions of fibers by the water-dispersible polyurethane (Patent Document 1).

[0005] In addition, a method has been proposed in which a water-dispersible polyurethane having a thermal gelation property with a specific composition is used, polyurethane does not strongly retain ultrafine fibers in a fibrous substrate, and soaks into the ultrafine fibers in the fibrous substrate while an appropriate fiber space is maintained, and then coagulates, thereby obtaining a high-quality leather-like sheet-shaped article superior in flexibility and satisfactory sense (Patent Document 2).

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0006]

Patent Document 1: WO 2015/129602 A
Patent Document 2: Japanese Patent Laid-open Publication No. H10-199699

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] However, in the method disclosed in Patent Document 1, although the hardness of the texture can be improved to obtain a supple texture, polyurethane does not sufficiently function as a binder, and the wear resistance is insufficient.

[0008] Meanwhile, in the method disclosed in Patent Document 2, although a strong retaining of the water-dispersible polyurethane with respect to the fibers during coagulation by dry heat can be alleviated to a certain extent, it is insufficient and it is not possible to obtain a satisfactory texture, as compared with the case where the solvent-based polyurethane is wet-coagulated.

[0009] Therefore, in view of the background of the related art described above, an object of the present invention is to provide a sheet-shaped article having both a supple texture and superior wear resistance, and a method for manufacturing the sheet-shaped article.

SOLUTIONS TO THE PROBLEMS

[0010] A sheet-shaped article manufactured by impregnating a fibrous substrate with a water-dispersible polyurethane dispersion in which a water-dispersible polyurethane has been dispersed in the liquid and coagulating the polyurethane tends to have a hard texture. As one of the main reasons lies in a difference in the form of coagulation between the case of using the organic solvent-based polyurethane and the case of using the water-dispersible polyurethane.

[0011] The coagulated form of the organic solvent-based polyurethane liquid is a coagulated form obtained by replacing the solvent for a polyurethane molecule, which has been dissolved in the organic solvent, by water, and is generally obtained by using a so-called wet coagulation process. Regarding this polyurethane, when a film was formed and the structure after coagulation was observed, a porous film having a low density was formed in the organic solvent-based polyurethane film coagulated by the wet coagulation process. This low-density porous structure causes the contact area between fibers and the polyurethane at the time of coagulation to be reduced even in the case where the polyurethane is soaked in a fibrous substrate, and thus a soft sheet-shaped article is considered to be obtained.

[0012] Meanwhile, for a water-dispersible polyurethane, there is an often used method, i.e., a so-called dry coagulation process including disintegrating the hydration state of a water-dispersible polyurethane dispersion mainly by heating to cause polyurethane emulsions to be aggregated to one another for coagulation. Regarding this polyurethane, when a film was formed and the structure after coagulation was observed, a nonporous film having a high density was formed in the film of the water-dispersible polyurethane coagulated by the dry coagulation process. This enhances the adhesion between a fibrous substrate and the polyurethane, thereby strongly retaining entangled portions of fibers. Accordingly, it is considered that this makes the texture hard.

[0013] As a result of repeated studies by the inventors to achieve the above object, the inventors have found that a specific amount of a monovalent positive ion-including inorganic salt and a crosslinker is used in coagulation of a hydrophilic group-having polymer elastic body, whereby it is possible to manufacture not only a sheet-shaped article in consideration of the environment, but also a sheet-shaped article having superior texture and wear resistance as compared with a conventional sheet-shaped article. Thus, the present invention has been completed.

[0014] That is, the present invention is intended to solve the above-described problems, and the sheet-shaped article of the present invention is a sheet-shaped article including a fibrous substrate including ultrafine fibers with an average individual fiber fineness of 0.1 μm or more and 10 μm or less, the fibrous substrate containing a hydrophilic group-having polymer elastic body, in which an inside of the polymer elastic body has N-acylurea bonding and/or isourea bonding, and a monovalent positive ion-including inorganic salt is present at a rate of 0.1 mass% or more and 5 mass% or less, with regard to a mass of the polymer elastic body.

[0015] According to a preferred embodiment of the sheet-shaped article of the present invention, the monovalent positive ion-including inorganic salt is sodium chloride and/or sodium sulfate.

[0016] According to a preferred embodiment of the sheet-shaped article of the present invention, the polymer elastic body contains a polyether diol as a constituent.

[0017] According to a preferred embodiment of the sheet-shaped article of the present invention, the polymer elastic body includes a hydrophilic group-having polymer elastic body A containing a polyether diol as a constituent, and a hydrophilic group-having polymer elastic body B containing a polycarbonate diol as a constituent.

[0018] According to a preferred embodiment of the sheet-shaped article of the present invention, a bending resistance as specified in JIS L 1096: 2010 (a 45° cantilever method) is 50 mm or more and 180 mm or less, and an abrasion loss after 20,000 times of rubbing by a Martindale abrasion test as specified in JIS L 1096: 2010 is 10 mg or less.

[0019] Further, a method for manufacturing a sheet-shaped article includes: impregnating a fibrous substrate including ultrafine fibers with an average individual fiber fineness of 0.1 μm or more and 10 μm or less with an aqueous dispersion containing a hydrophilic group-having polymer elastic body, a monovalent positive ion-including inorganic salt, and a crosslinker; and subjecting the fibrous substrate to a heat treatment at a temperature of 100°C or more and 180°C or less, in which a content of the monovalent positive ion-including inorganic salt in the aqueous dispersion is 10 mass% or more and 50 mass% or less with regard to a mass of a solid content of the hydrophilic group-having polymer elastic body.

[0020] According to a preferred embodiment of the method for manufacturing a sheet-shaped article of the present invention, the monovalent positive ion-including inorganic salt is sodium chloride and/or sodium sulfate.

[0021] According to a preferred embodiment of the method for manufacturing a sheet-shaped article of the present invention, the crosslinker is a carbodiimide-based crosslinker.

[0022] According to a preferred embodiment of the method for manufacturing a sheet-shaped article of the present invention, the hydrophilic group-having polymer elastic body contains a polyether diol as a constituent.

[0023] According to a preferred embodiment of the method for manufacturing a sheet-shaped article of the present invention, a hydrophilic group-having polymer elastic body X and a hydrophilic group-having polymer elastic body Y having compositions different from each other are contained in the aqueous dispersion liquid, and the hydrophilic group-having polymer elastic body Y is coagulated after the hydrophilic group-having polymer elastic body X is coagulated.

EFFECTS OF THE INVENTION

[0024] According to the present invention, a sheet-shaped article having both a supple texture and superior wear resistance is obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025]

Fig. 1 is an example of a cross-sectional micrograph of a bonded portion between a polymer elastic body and a fiber in a sheet-shaped article of the present invention.

Fig. 2 is an example of a cross-sectional micrograph of a bonded portion between a polymer elastic body and a fiber in a sheet-shaped article of the related art.

EMBODIMENTS OF THE INVENTION

[0026] The sheet-shaped article of the present invention is a sheet-shaped article including a fibrous substrate including ultrafine fibers with an average individual fiber fineness of 0.1 μm or more and 10 μm or less, the fibrous substrate containing a hydrophilic group-having polymer elastic body, in which an inside of the polymer elastic body has N-acylurea bonding and/or isourea bonding, and a monovalent positive ion-including inorganic salt is present at a rate of 0.1 mass% or more and 5 mass% or less, with regard to a mass of the polymer elastic body. Here, "0.1 mass% or more and 5 mass% or less with regard to the mass of the polymer elastic body" means that the mass of the monovalent positive ion-including inorganic salt is 0.1 or more and 5 or less with regard to 100 mass of the polymer elastic body. That is, in this case, the total mass of the polymer elastic body and the monovalent positive ion-including inorganic salt is 100.1 or more and 105 or less. The same applies to the description of other contents "with regard to the mass of the polymer elastic body" in the present specification. Hereinafter, this constituent element will be described in detail, but the present invention is not limited to the scope described below at all as long as it is not beyond the gist of the present invention.

[Ultrafine Fiber]

[0027] As the ultrafine fiber used in the present invention, a polyester-based resin can be used. Specific examples of the polyester-based resin include polyethylene terephthalate, polybutylene terephthalate, and polytrimethylene terephthalate. The polyester-based resin can be obtained from, for example, a dicarboxylic acid and/or an ester-forming derivative thereof and a diol.

[0028] Examples of the dicarboxylic acid and/or the ester-forming derivative thereof used for the polyester-based resin include terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, and an ester-forming derivative thereof. Note that the ester-forming derivative referred in the present invention is a lower alkyl ester of a dicarboxylic acid, an acid anhydride, an acyl chloride, and the like. Specifically, a methyl ester, an ethyl ester, a hydroxyethyl ester, and the like are preferably used. A more preferred embodiment of a dicarboxylic acid and/or an ester-forming derivative thereof used in the present invention is a terephthalic acid and/or a dimethyl ester thereof.

[0029] Examples of the diol used in the polyester-based resin include ethylene glycol, 1,3-propanediol, 1,4-butanediol, and cyclohexanedimethanol. Among them, ethylene glycol is preferably used.

[0030] The polyester-based resin may contain particles of metal oxides, pigments, and the like that are usually used, and additives such as a flame retardant and an antistatic agent as long as the effects of the present invention are not impaired.

[0031] The cross-sectional shape of the ultrafine fiber may be either a round cross section or a modified cross section. Examples of the modified cross section include an elliptical shape, a flat shape, a polygonal shape such as a triangular shape, a fan-like shape, and a cross shape.

[0032] In the present invention, it is important that the average individual fiber fineness of the ultrafine fibers is 0.1 μm or more and 10 μm or less. When the average individual fiber fineness of the ultrafine fibers is 10 μm or less, preferably 7 μm or less, and more preferably 5 μm or less, it is possible to cause the sheet-shaped article to be more supple. In a case where the sheet-shaped article has a raised nap, the raised nap quality can be improved. Meanwhile, when the average individual fiber fineness of the ultrafine fibers is 0.1 μm or more, preferably 0.3 μm or more, and more preferably 0.7 μm or more, it is possible to obtain a sheet-shaped article superior in color developability after dyeing. Further, in a case where the sheet-shaped article has a raised nap, when napped by buffing, bundled ultrafine fibers can be easy to disperse and handle.

[0033] The average individual fiber fineness referred to in the present invention is measured by the following method. That is:

(1) A cross section of the resulting sheet-shaped article cut in the thickness direction is observed with a scanning electron microscope (SEM).

(2) The fiber diameters of any 50 ultrafine fibers in the observation plane with respect to 3 sites on each ultrafine fiber cross section are measured. Provided that in the case of utilizing ultrafine fibers with a modified cross section, the cross-section area of single fiber is measured and the diameter of a circle corresponding to the cross-section area is calculated using the following equation. The resulting diameter is defined as the single fiber diameter of the single fiber.

·Single fiber diameter (μm) = (4 × (Cross-section area (μm^2) of single fiber) / π)$^{1/2}$

(3) The total of the diameters obtained at 150 points is averaged and the arithmetic mean value (μm) is rounded off to the first decimal place.

[Fibrous Substrate]

[0034] The fibrous substrate used in the present invention is made of the ultrafine fiber. In this regard, it is allowed that ultrafine fibers of different raw materials are mixed in the fibrous substrate.

[0035] As a specific form of the above fibrous substrate, it is possible to use a nonwoven fabric in which the above ultrafine fibers are interlaced or a nonwoven fabric in which fiber bundles of ultrafine fibers are interlaced. Among them, a nonwoven fabric in which fiber bundles of ultrafine fibers are interlaced is preferably used, from the viewpoints of the strength and texture of a sheet-shaped article. From the viewpoints of flexibility and texture, it is particularly preferable to use a nonwoven fabric in which ultrafine fibers constituting fiber bundles of ultrafine fibers are appropriately spaced from one another to form spaces. As described above, the nonwoven fabric, in which fiber bundles of ultrafine fibers are interlaced, may be obtained by, for example, beforehand interlacing ultrafine fiber-generating fibers and then generating ultrafine fibers. Further, the nonwoven fabric, in which ultrafine fibers constituting fiber bundles of ultrafine fibers are appropriately spaced from one another to form spaces, may be obtained by, for example, using islands-in-the-sea fibers in which a sea component may be removed to make a space between island components.

[0036] The nonwoven fabric may be either a short fiber nonwoven fabric or a long fiber nonwoven fabric. From the viewpoint of the texture and quality of the sheet-shaped article, the short fiber nonwoven fabric is more preferably used.

[0037] In a preferred embodiment, the fiber length of the short fibers in the case of using the short fiber nonwoven fabric is in a range of 25 mm or more and 90 mm or less. When the fiber length is 25 mm or more, more preferably 35 mm or more, and still more preferably 40 mm or more, a sheet-shaped article with superior wear resistance is obtained by interlacing. Further, the fiber length is set to 90 mm or less, more preferably 80 mm or less, and still more preferably 70 mm or less, so that it is possible to obtain a sheet-shaped article having more superior texture and quality.

[0038] In the present invention, when a nonwoven fabric is used as the fibrous substrate, a woven fabric or a knitted fabric may be inserted into or laminated on the nonwoven fabric, or the nonwoven fabric may be lined with a woven fabric or a knitted fabric, for the purpose of improving strength or the like. The average individual fiber fineness of the fibers constituting the woven fabric and the knitted fabric is more preferably 0.3 μm or more and 10 μm or less, because damage during needle punching can be reduced and the strength can be maintained.

[0039] As the fibers constituting the woven fabric and the knitted fabric, it is possible to use a polyester such as polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, or polylactic acid, a synthetic fiber such as a polyamide such as 6-nylon or 66-nylon, a regenerated fiber such as cellulosic polymer, and a natural fiber such as cotton or hemp.

[Polymer Elastic Body]

[0040] In the sheet-shaped article of the present invention, examples of the hydrophilic group-having polymer elastic body include water-dispersible silicone resins, water-dispersible acrylic resins, water-dispersible urethane resins, and copolymers thereof. Among them, water-dispersible polyurethane resins are preferably used from the viewpoint of texture.

[0041] As the water-dispersible polyurethane resin, a resin obtained by a reaction of a polymeric polyol having a number average molecular weight of preferably 500 or more and 5000 or less, an organic polyisocyanate, and a chain extender is preferably used. Further, in order to enhance the stability of the water-dispersible polyurethane dispersion, it is preferable to use an active hydrogen component-containing compound having a hydrophilic group in combination. The number average molecular weight of the polymeric polyol is set to 500 or more, and more preferably 1500 or more, so that it is possible to easily prevent the texture from becoming hard. Further, the number average molecular weight is set to 5000 or less, and more preferably 4000 or less, so that it is possible to easily maintain the strength of the polyurethane as a binder. Hereinafter, a case where a water-dispersible polyurethane resin is used as the polymer elastic body will be described.

(1)Reaction Components of Water-dispersible Polyurethane Resin

[0042] First, reaction components of the water-dispersible polyurethane resin will be described.

(1-1) Polymeric Polyol

[0043] Examples of the polymeric polyol that can be used in the sheet-shaped article of the present invention include polyether polyol, polyester polyol, and polycarbonate polyol.

[0044] Examples of the polyether polyol include polyols obtained by adding and polymerizing a monomer such as ethylene oxide, propylene oxide, butylene oxide, styrene oxide, tetrahydrofuran, epichlorohydrin, or cyclohexylene using a polyhydric alcohol or a polyamine as an initiator, and polyols obtained by ring-opening polymerization of the monomer using a protic acid, a Lewis acid, a cationic catalyst, or the like as a catalyst. Specific examples thereof include polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and copolymerized polyol obtained by combining these glycols.

[0045] Examples of the polyester polyol include polyester polyols obtained by condensing various low-molecular-weight polyols with a polybasic acid, and polyols obtained by ring-opening polymerization of lactones.

[0046] Examples of the low-molecular-weight polyols include one or more selected from linear alkylene glycols such as ethylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1.8-octanediol, 1,9-nonanediol, and 1,10-decanediol; branched alkylene glycols such as neopentyl glycol, 3-methyl-1,5-pentanediol, 2,4-diethyl-1,5-pentanediol, and 2-methyl-1,8-octanediol; alicyclic diols such as 1,4-cyclohexanediol; and aromatic dihydric alcohols such as 1,4-bis(β-hydroxyethoxy)benzene. Adducts obtained by adding various alkylene oxides to bisphenol A can also be used as low-molecular-weight polyols.

[0047] Examples of the polybasic acid include one or more selected from the group consisting of succinic acid, maleic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and hexahydroisophthalic acid.

[0048] Examples of the polycarbonate polyol include compounds obtained by reacting a polyol with a carbonate compound such as a dialkyl carbonate or a diaryl carbonate.

[0049] As the polyol as a raw material for manufacturing the polycarbonate polyol, the polyols exemplified in the raw materials for manufacturing the polyester polyol can be used. As the dialkyl carbonate, a dimethyl carbonate, a diethyl carbonate, or the like can be used, and as the diaryl carbonate, a diphenyl carbonate or the like can be listed.

[0050] In the sheet-shaped article of the present invention, the polymer elastic body preferably contains a polyether diol as a constituent. In the present specification, the term "contain as a constituent" refers to containing as a monomer component or an oligomer component constituting the polymer elastic body. The polyether diol has a high degree of freedom of the ether bond, and thus has a low glass transition temperature and a weak cohesive force. Accordingly, a polyurethane having superior flexibility is easily obtained.

[0051] In the sheet-shaped article of the present invention, the polymer elastic body preferably includes a hydrophilic group-having polymer elastic body A containing a polyether diol as a constituent, and a hydrophilic group-having polymer elastic body B containing a polycarbonate diol as a constituent. Both the hydrophilic group-having polymer elastic body A containing a polyether diol as a constituent superior in flexibility and the hydrophilic group-having polymer elastic body B containing a polycarbonate diol as a constituent superior in durability against external stimuli such as light and heat are contained in the sheet-shaped article, whereby a sheet-shaped article superior in flexibility and durability is easily obtained.

(1-2) Organic Diisocyanate

[0052] Examples of the organic diisocyanate used in the present invention include a C6-20 aromatic diisocyanate (excluding carbon atoms in an NCO group; the same applies to the following), a C2-18 aliphatic diisocyanate, a C4-15 alicyclic diisocyanate, a C8-15 aroaliphatic diisocyanate, a modified product of these diisocyanates (e.g., a carbodiimide-modified product, a urethane-modified product, a uretdione-modified product), or a mixture of two or more kinds thereof.

[0053] Specific examples of the C6-20 aromatic diisocyanate include 1,3- and/or 1,4-phenylene diisocyanate, 2,4- and/or 2,6-tolylene diisocyanate, 2,4'- and/or 4,4'-diphenylmethane diisocyanate (hereinafter, abbreviated as MDI), 4,4'-diisocyanatobiphenyl, 3,3'-dimethyl-4,4'-diisocyanatobiphenyl, 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane, and 1,5-naphthylene diisocyanate.

[0054] Specific examples of the C2-18 aliphatic diisocyanate include ethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, dodecamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, lysine diisocyanate, 2,6-diisocyanatomethylcaproate, bis(2-isocyanatoethyl)carbonate, and 2-isocyanatoethyl-2,6-diisocyanatohexaate.

[0055] Specific examples of the C4-15 alicyclic diisocyanate include isophorone diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, cyclohexylene diisocyanate, methylcyclohexylene diisocyanate, bis(2-isocyanatoethyl)-4-cyclohexylene-1,2-dicarboxylate, and 2,5- and/or 2,6-norbornane diisocyanate.

[0056] Specific examples of the C8-15 aroaliphatic diisocyanate include m- and/or p-xylylene diisocyanate, and $\alpha,\alpha,\alpha',\alpha'$-tetramethylxylylene diisocyanate.

[0057] Among them, a preferred organic diisocyanate is an alicyclic diisocyanate. A particularly preferred organic diisocyanate is dicyclohexylmethane-4,4'-diisocyanate.

(1-3) Chain Extender

[0058] Examples of the chain extender used in the present invention include water, a low-molecular-weight diol such as "ethylene glycol, propylene glycol, 1,3-butylene glycol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, or neopentyl glycol", an alicyclic diol such as "1,4-bis(hydroxymethyl)cyclohexane", an aromatic diol such as "1,4-bis(hydroxyethyl)benzene", an aliphatic diamine such as "ethylenediamine", an alicyclic diamine such as "isophoronediamine", an aromatic diamine such as "4-4-diaminodiphenylmethane", an aroaliphatic diamine such as "xylenediamine", an alkanolamine such as "ethanolamine", hydrazine, a dihydrazide such as "adipic acid dihydrazide", and a mixture of two or more kinds thereof.

[0059] Among them, preferred chain extenders are water, low molecular weight diols, and aromatic diamines, and more preferred examples thereof include water, ethylene glycol, 1,4-butanediol, 4,4'-diaminodiphenylmethane, and a mixture of two or more kinds thereof.

(2) Additives of Water-dispersible Polyurethane Resin

[0060] In the present invention, for the reasons described later, it is important to add a monovalent positive ion-including inorganic salt to a solution containing water-dispersible polyurethane. In addition, a colorant such as titanium oxide, various stabilizers such as a UV absorber (e.g., a benzophenone-based or benzotriazole-based UV absorber) and an antioxidant [e.g., a hindered phenol such as 4,4-butylidene-bis(3-methyl-6-1-butylphenol); an organic phosphite such as triphenylphosphite or trichloroethylphosphite], an inorganic filler (e.g., calcium carbonate), and the like may be added, if necessary.

(3) Structure of Water-dispersible Polyurethane Resin

[0061] In the water-dispersible polyurethane used in the present invention, examples of the component for imparting a hydrophilic group include a hydrophilic group-containing active hydrogen component. Examples of the hydrophilic group-containing active hydrogen component include a compound containing a nonionic group and/or an anionic group and/or a cationic group and active hydrogen.

[0062] Examples of the compound having a nonionic group and active hydrogen include compounds containing two or more active hydrogen components or two or more isocyanate groups and having a polyoxyethylene glycol group with a molecular weight of 250 to 9000 or the like in a side chain, and triols such as trimethylol propane and trimethylol butane.

[0063] Examples of the compound having an anionic group and active hydrogen include carboxyl group-containing compounds such as 2,2-dimethylol propionic acid, 2,2-dimethylol butanoic acid and 2,2-dimethylol valeric acid and derivatives thereof, sulfonic group-containing compounds such as 1,3-phenylenediamine-4,6-disulfonic acid and 3-(2,3-dihydroxypropoxy)-1-propanesulfonic acid and derivatives thereof, and salts obtained by neutralizing these compounds with a neutralizer.

[0064] Examples of the compound containing a cationic group and active hydrogen include tertiary amino group-containing compounds such as 3-dimethylaminopropanol, N-methyldiethanolamine, and N-propyldiethanolamine, and derivatives thereof.

[0065] The hydrophilic group-containing active hydrogen component can also be used in the form of salt neutralized with a neutralizer.

[0066] As the hydrophilic group-containing active hydrogen component used in the polyurethane molecule, 2,2-dimethylol propionic acid, 2,2-dimethylol butanoic acid, and neutralized salts thereof are preferably used from the viewpoints of the mechanical strength and dispersion stability of the water-dispersible polyurethane resin.

[0067] In the present invention, the hydrophilic group in the hydrophilic group-having polymer elastic body is a group having active hydrogen. Specific examples of the hydrophilic group include a hydroxyl group, a carboxyl group, a sulfonic acid group, and an amino group.

[0068] In the present invention, an inside of the hydrophilic group-having polymer elastic body has N-acylurea bonding and/or isourea bonding. Here, the term "inside of the polymer elastic body has N-acylurea bonding and/or isourea bonding" means that the polymer elastic body has N-acylurea bonding and/or isourea bonding.

[0069] In the present invention, the hydrophilic group-having polymer elastic body has N-acylurea bonding and/or isourea bonding. When a water-dispersible polyurethane resin is used as the hydrophilic group-having polymer elastic body, the N-acylurea bonding and/or the isourea bonding can be formed, for example, by reacting a hydroxyl group and/or a carboxyl group present as the hydrophilic group-containing active hydrogen component with a carbodiimide-based crosslinker. As a result, a three-dimensional crosslinked structure by N-acylurea bonding and/or isourea bonding, which is superior in physical properties, such as lightfast, heat resistance and wear resistance, and flexibility, is imparted into the molecule of the hydrophilic group-having polymer elastic body, and physical properties such as wear resistance can be dramatically improved while maintaining the flexibility of the sheet-shaped article. The presence of the N-acylurea group or the isourea group in the polymer elastic body can be analyzed by performing a mapping process such as TOF-SIMS analysis on the cross section of the sheet-shaped article.

[0070] The number average molecular weight of the hydrophilic group-having polymer elastic body used in the present invention is preferably 20,000 or more from the viewpoint of resin strength, and is preferably 500,000 or less from the viewpoint of viscosity stability and workability. The number average molecular weight is more preferably 30,000 or more and 150,000 or less.

[0071] The number average molecular weight of the hydrophilic group-having polymer elastic body can be determined by gel permeation chromatography, and is measured under, for example, the following conditions:

- Instrument: HLC-8220, manufactured by Tosoh Corporation
- Column: TOSOH TSKgel α-M
- Solvent: N,N-dimethylformamide (DMF)
- Temperature: 40°C
- Calibration: polystyrene

[0072] The hydrophilic group-having polymer elastic body used in the present invention appropriately retains fibers in the sheet-shaped article, and is preferably present in the fibrous substrate from the viewpoint of providing at least one raised nap surface of the sheet-shaped article, which is a preferred embodiment.

[Sheet-shaped Article]

[0073] In the sheet-shaped article of the present invention, a monovalent positive ion-including inorganic salt is present in the polymer elastic body at a rate of 0.1 mass% or more and 5 mass% or less, with regard to a mass of the polymer elastic body. The presence of the monovalent positive ion-including inorganic salt in the polymer elastic body means that the polymer elastic body contains a monovalent positive ion-including inorganic salt. When the content is 0.1 mass% or more, an effect of inhibiting fusion of the polymer elastic body by the inorganic salt can be sufficiently obtained, and a supple sheet-shaped article can be obtained. Meanwhile, when the content is 5 mass% or less, a sufficient film strength of the polymer elastic body can be obtained, and the polymer elastic body is superior in physical properties. The presence of the inorganic salt in the polymer elastic body can be analyzed by performing a mapping process such as TOF-SIMS analysis on the cross section of the sheet-shaped article.

[0074] In the sheet-shaped article of the present invention, the monovalent positive ion-including inorganic salt is preferably sodium chloride and/or sodium sulfate. The significance of using these monovalent positive ion-including inorganic salts is as described later.

[0075] In the sheet-shaped article of the present invention, it is preferable that a bending resistance as specified in JIS L 1096: 2010 (a 45° cantilever method) is 50 mm or more and 180 mm or less, and an abrasion loss after 20,000 times of rubbing by a Martindale abrasion test as specified in JIS L 1096: 2010 is 10 mg or less. When the bending resistance is within the above range, a sheet-shaped article having moderate flexibility and repulsive feeling is easily obtained. Further, when the abrasion loss after 20,000 times of rubbing by the Martindale abrasion test is 10 mg or less, it is possible to suppress fall-off of fluff in actual use, deterioration of appearance, and the like.

[Method for Manufacturing Sheet-shaped Article]

[0076] Next, a method for manufacturing a sheet-shaped article of the present invention will be described.

[0077] The method for manufacturing a sheet-shaped article of the present invention is a method for manufacturing a sheet-shaped article, including: impregnating a fibrous substrate including ultrafine fibers having an average individual fiber fineness of 0.1 μm or more and 10 μm or less with an aqueous dispersion containing a hydrophilic group-having polymer elastic body, a monovalent positive ion-including inorganic salt, and a crosslinker; and subjecting the fibrous substrate to a heat treatment at a temperature of 100°C or more and 180°C or less, in which a content of the monovalent positive ion-including inorganic salt in the aqueous dispersion is 10 mass% or more and 50 mass% or less with regard to a mass of a solid content of the hydrophilic group-having polymer elastic body.

[0078] Direct fiber spinning and ultrafine fiber-generating fibers may be used as a production unit of ultrafine fibers used in the present invention. Among them, ultrafine fiber-generating fibers are used in a preferred embodiment. Examples of the ultrafine fiber-generating fibers employed include: islands-in-the-sea fibers in which a sea component and an island component are made of two thermoplastic resin components with different solvent solubilities are used as a sea component and an island component, and only the sea component is dissolved and removed using a solvent to yield ultrafine fibers as the island component; or peelable composite fibers or multi-layer composite fibers in which two thermoplastic resin components are alternately arranged to make a fiber cross section radiated or layered, and each component is peeled or split into ultrafine fibers. Since the product quality can be uniform, the sea-island composite fibers are preferably used.

[0079] Examples of the sea component of the islands-in-the-sea fibers include a polyolefin such as polyethylene or polypropylene, polystyrene, sodium sulfoisophthalate, a copolymerized polyester obtained by copolymerizing polyethylene glycol, polylactic acid, or polyvinyl alcohol, or a copolymer thereof.

[0080] An ultrafine fiber-generating process (sea-removing process) for the islands-in-the-sea fibers may be carried out by immersing the islands-in-the-sea fibers in a solvent and by squeezing them. As the solvent for dissolving the sea component, it is possible to use an organic solvent such as toluene or trichlorethylene, an alkaline aqueous solution such as sodium hydroxide, or hot water.

[0081] The ultrafine fiber-generating process may be implemented by using a machine such as a continuous dyeing machine, a vibro washer type sea remover, a jet dyeing machine, a wins dyeing machine, or a jigger dyeing machine.

[0082] The sea component may be dissolved and removed at any of the timing before or after the polymer elastic body is imparted. In a case where the sea-removing process is carried out before the polymer elastic body is imparted, the ultrafine fibers can be strongly retained by the structure of the polymer elastic body directly and tightly attached to the ultrafine fibers. Thus, this allows the wear resistance of the sheet-shaped article to be more favorable. Meanwhile, in a case where the sea-removing process is carried out after the polymer elastic body is imparted, a space caused by removing the sea component occurs between the polymer elastic body and the ultrafine fibers. Accordingly, the polymer elastic body does not directly retain the ultrafine fibers, so the texture of the sheet-shaped article becomes more supple.

[0083] It is preferable that the mass ratio between the sea component and the island component in the islands-in-the-sea fibers used in the present invention is in a range of sea component : island component = 10 : 90 to 80 : 20. When the mass ratio of the sea component is 10 mass% or more, the island component tends to be made sufficiently ultrafine. When the mass ratio of the sea component is 80 mass or less, the proportion of the eluted component is small and the productivity is thus improved. The mass ratio between the sea component and the island component is more preferably in a range of the sea component : the island component = 20 : 80 to 70 : 30.

[0084] When the ultrafine fiber-generating fibers represented by the islands-in-the-sea fibers are stretched in the present invention, an unstretched yarn may be once wound and then stretched in another time or an unstretched yarn may be withdrawn and stretched continuously as they are. Either method can be adopted. The stretching may be conducted, if appropriate, by a one-to-three stretching step using wet heat or dry heat or both. Next, the stretched islands-in-the-sea fibers may be preferably crimped and cut into a predetermined length to obtain raw stock for a nonwoven fabric. A usual method can be used for the crimping and/or cutting.

[0085] It is preferable that a buckling crimp is given to a composite fiber such as islands-in-the-sea fibers used in the present invention. This is because the buckling crimp can cause interlacing between the fibers to be improved when a short fiber nonwoven fabric is formed, thereby achieving high density and high degree of interlacing. To give a buckling crimp to a composite fiber, a usual stuffing box-type crimper is preferably used. To obtain a preferable crimp retention coefficient in the present invention, the processed fiber fineness, the crimper temperature, the crimper load, the pushing pressure, and the like are adjusted, if appropriate, in a preferred embodiment.

[0086] The crimp retention coefficient of the ultrafine fiber-generating fibers subjected to a buckling crimp is preferably in a range of 3.5 or more and 15 and less and more preferably in a range of 4 or more and 10 or less. In a case where the crimp retention coefficient is 3.5 or more, the stiffness of nonwoven fabric in the thickness direction when the nonwoven fabric is formed is increased. This makes it possible to maintain interlacing performance during an interlacing step such as needle punching. In addition, when the crimp retention coefficient is 15 or less, crimps are not too strong and the fiber-opening performance for fiber web is superior during carding.

[0087] As used herein, the crimp retention coefficient is expressed by the following equation.

- Crimp retention coefficient = $(W/L-L_0)^{1/2}$
- W: Crimp disappearance load (load when a crimp is maximally stretched: mg/dtex)
- L: Fiber length (cm) under crimp disappearance load
- L_0: Fiber length (cm) at 6 mg/dtex. Here, 30.0 cm is marked.

[0088] As a measurement method, a load of 100 mg/dtex is first applied to a sample. Next, the load is incremented by 10 mg/dtex. Then, the resulting crimp state is checked. The load is increased until the crimp is maximally stretched. When the crimp is in a maximally stretched state, the marking length (the distance from 30.0 cm) is measured.

[0089] The single fiber fineness of each composite fiber used in the present invention is preferably in a range of 2 dtex or more and 10 dtex or less, and more preferably in a range of 3 dtex or more and 9 dtex or less from the viewpoint of interlacing performance in a needle punching step or the like.

[0090] Each composite fiber that can be used in manufacturing the sheet-shaped article of the present invention preferably has a contraction rate, at a temperature of 98°C, of 5% or more and 40% or less and more preferably 10% or more and 35% or less. When the contraction rate is within this range, hydrothermal treatment can cause the fiber density to increase, thereby realizing a touch inspiring real leather.

[0091] Specifically, in the method for measuring the contraction rate, a load of 50 mg/dtex is first applied to a composite fiber bundle. Next, 30.0 cm is marked (L_0). Thereafter, 10-min treatment in hot water at a temperature of 98°C is carried out, lengths (L_1) before and after the treatment are measured, and $(L_0-L_1)/L_0 \times 100$ is calculated. The measurement is performed three times, and the average value of the measurements is defined as the contraction rate.

[0092] In the present invention, the number of fibers in the ultrafine fiber bundle is preferably 8 fibers/bundle or more and 1000 fibers/bundle or less, and more preferably 10 fibers/bundle or more and 800 fibers/bundle or less. When the number of fibers is 8 fibers/bundle or more, the ultrafine fibers tend to have sufficient compactness. For example, the mechanical property such as abrasion tends to increase. When the number of fibers is 1000 fibers/bundle or less, the fiber-opening performance at the time of napping is improved, the fiber distribution on the raised nap surface becomes uniform, and a favorable product quality is easily obtained.

[0093] As a method for producing a nonwoven fabric that can be used for a fibrous substrate constituting a sheet-shaped article of the present invention, it is possible to use a method for interlacing a composite fiber web by needle punching or water-jet punching, spun bonding, melt-blowing, or papermaking. Among them, it is preferable to use a method undergoing treatment such as needle punching or water-jet punching so as to provide the previously mentioned ultrafine fiber bundle form.

[0094] The nonwoven fabric may be prepared such that a nonwoven fabric and a woven or knitted fabric are layered and integrated as described above. It is preferable to use a method for integrating them by needle punching or water-jet punching.

[0095] The number of needle barbs (notches) of a needle used for the needle punching is preferably 1 or more and 9 or less. The number of needle barbs is preferably set to 1 or more, the fibers can be interlaced efficiently. Meanwhile, the number of needle barbs is preferably set to 9 or less, so that damage on the fibers can be reduced.

[0096] The number of composite fibers hooked by the barbs is determined depending on the shape of the barbs and the diameter of the composite fibers. Due to this, each barb of a needle used during the needle punching step is preferably shaped such that the kick-up is 0 μm or more and 50 μm or less, the undercut angle is 0° or more and 40° or less, the throat depth is 40 μm or more and 80 μm or less, and the throat length is 0.5 mm or more and 1.0 mm or less.

[0097] In addition, the number of punching is preferably 1000 sites/cm^2 or more and 8000 sites/cm^2 or less. The number of punching is preferably set to 1000 sites/cm^2 or more, so that the compactness can be obtained, and the finishing can be achieved with high precision. Meanwhile, the number of punching is preferably set to 8000 sites/cm^2 or less, so that it is possible to prevent deterioration of processability, damage on the fibers, and a decrease in the strength.

[0098] Further, when water-jet punching is carried out, it is preferable that water is in a pillar-shaped stream state. Specifically, water is jetted from nozzles with a diameter of 0.05 mm or more and 1.0 mm or less at a pressure of 1 MPa to 60 MPa in a preferred embodiment.

[0099] The apparent density of the nonwoven fabric after needle punching or water-jet punching is preferably 0.15 g/cm^3 or more and 0.45 g/cm^3 or less. The apparent density is preferably set to 0.15 g/cm^3 or more, whereby the sheet-shaped article is likely to have sufficient shape stability and dimension stability. Meanwhile, the apparent density is preferably set to 0.45 g/cm^3 or less, so that a sufficient space for imparting polyurethane can be easily maintained.

[0100] From the viewpoint of compactness, the nonwoven fabric thus obtained may be contracted and further highly compacted by dry heat or wet heat or by both in a preferred embodiment. Further, the nonwoven fabric may be compressed in the thickness direction by calendaring or the like.

[0101] The sea-removing process for removing the sea component of the islands-in-the-sea fibers in the case of using the islands-in-the-sea fibers may be carried out before or/and after the aqueous dispersion containing the hydrophilic group-having polymer elastic body is imparted to the fibrous substrate. In a case where the sea-removing process is carried out before the aqueous dispersion is imparted, there is a tendency of forming a structure of the polymer elastic body directly and tightly attached to the ultrafine fibers, causing the ultrafine fibers to be strongly retained. Thus, this allows the wear resistance of the sheet-shaped article to be more favorable.

[0102] Meanwhile, the ultrafine fibers and an inhibitor such as a cellulose derivative or polyvinyl alcohol (hereinafter, sometimes abbreviated as PVA) are imparted before the aqueous dispersion is imparted, and then the aqueous dispersion is imparted, whereby the adhesion between the ultrafine fibers and the polymer elastic body can be reduced, and a more supple texture can be achieved.

[0103] The inhibitor may be added either before or after the sea-removing process of a fiber having an islands-in-the-sea structure. The inhibitor is imparted before the sea-removing process, so that the shape retention capacity of the fibrous substrate can be enhanced even when the basis weight of the fiber decreases and the tensile strength of the sheet decreases. Thus, a thin sheet can also be stably processed, and the thickness retention of the fibrous substrate in the step of the sea-removing process can be increased. Consequently, it is possible to prevent the fibrous substrate from being highly compacted. Meanwhile, the inhibitor is imparted after the sea-removing process, so that it is possible to allow the fibrous substrate to be highly compacted. Therefore, appropriate adjustment is carried out according to the purpose in a preferred embodiment.

[0104] As the inhibitor, PVA is preferably used because it has a high reinforcing effect on the fibrous substrate and is hardly eluted in water. Among the PVAs, highly saponified polyvinyl alcohol that is more poorly soluble in water is used in a more preferred embodiment, from the viewpoint that it is possible to cause the inhibitor to be hardly eluted at the time of imparting the aqueous dispersion containing the hydrophilic group-having polymer elastic body, and inhibit the adhesion between the ultrafine fibers and the polymer elastic body.

[0105] The highly saponified polyvinyl alcohol has a saponification degree of preferably 95% or more and 100% or less, and more preferably 98% or more and 100% or less. The saponification degree is set to 95% or more, so that it is possible to reduce elution at the time of imparting the hydrophilic group-having polymer elastic body dispersion.

[0106] The polymerization degree of PVA is preferably 500 or more and 3500 or less, and more preferably 500 or more and 2000 or less. The polymerization degree of PVA is set to 500 or more, so that it is possible to reduce the elution of highly saponified polyvinyl alcohol at the time of imparting the polymer elastic body dispersion. The polymerization degree of PVA is set to 3500 or less, so that the viscosity of the highly saponified polyvinyl alcohol liquid does not become excessively high, and it is possible to stably impart the highly saponified polyvinyl alcohol to the fibrous substrate.

[0107] The amount of PVA imparted to the fibrous substrate with regard to the fiber mass of the fibrous substrate is 0.1 mass% or more and 50 mass% or less, and preferably 1 mass% or more and 45 mass% or less. The amount of PVA imparted is set to 0.1 mass% or more, so that it is possible to obtain a sheet-shaped article with favorable flexibility and texture. The amount of PVA imparted is set to 50 mass% or less, so that it is possible to obtain a sheet-shaped article with favorable processability and more favorable physical characteristics such as wear resistance.

[0108] In the method for manufacturing a sheet-shaped article of the present invention, a fibrous substrate is impregnated with an aqueous dispersion containing a hydrophilic group-having polymer elastic body, a monovalent positive ion-including inorganic salt, and a crosslinker, and then heat treatment is performed at a temperature of 100°C or more and 180°C or less.

[0109] In the method for manufacturing a sheet-shaped article of the present invention, the hydrophilic group-having polymer elastic body is imparted to the fibrous substrate. When a nonwoven fabric is used as the fibrous substrate, the hydrophilic group-having polymer elastic body can be imparted to both a nonwoven fabric made of composite fibers and a nonwoven fabric in which fibers are made ultrafine.

[0110] In the method for manufacturing a sheet-shaped article of the present invention, a dry-heat coagulation method in which heat treatment is performed at a temperature of 100°C or more and 180°C or less is used for coagulation after imparting the hydrophilic group-having polymer elastic body. In another coagulation method, for example, a hot water coagulation method in which the hydrophilic group-having polymer elastic body is coagulated in hot water, the polymer elastic body is diffused into hot water and partially falls off, whereby there is a concern about processability. Further, in an acid coagulation method in which the hydrophilic group-having polymer elastic body is coagulated by an acid, it is necessary to neutralize an acidic solution remaining in the sheet, which is not preferable in processing operability. Meanwhile, the dry-heat coagulation method used in the present invention is a very simple procedure of heat-treating a sheet impregnated with the hydrophilic group-having polymer elastic body using a hot-air dryer or the like, and is a procedure superior in processability without concern of falling off of the polymer elastic body.

[0111] In the method for manufacturing a sheet-shaped article of the present invention, the heating temperature in dry heat coagulation is 100°C or more and 180°C or less. The heating temperature is set to 100°C or more, so that it is possible to cause the hydrophilic group-having polymer elastic body to rapidly coagulate, and reduce uneven distribution of the polymer elastic body on the lower surface of the sheet due to its own weight. Further, in the present invention, it is necessary to use a crosslinker in combination. The temperature is set to the above temperature, so that the crosslinking reaction can be sufficiently promoted, and the physical properties can be improved. In addition, the heating temperature is set to 180°C or less, so that it is possible to suppress the heat deterioration of the polymer elastic body. From the viewpoint of curing the polymer, the heating temperature is more preferably 120°C or more and 160°C or less. Within such a temperature range, the wear resistance and heat resistance are easily improved.

[0112] The concentration of the aqueous dispersion of the hydrophilic group-having polymer elastic body (the content of the polymer elastic body with regard to the aqueous dispersion of the hydrophilic group-having polymer elastic body) is preferably 10 mass% or more and 50 mass% or less, and more preferably 15 mass% or more and 40 mass% or less, from the viewpoint of the storage stability of the aqueous dispersion of the hydrophilic group-having polymer elastic body.

[0113] In addition, the aqueous dispersion of the hydrophilic group-having polymer elastic body used in the present invention may contain a water-soluble organic solvent in an amount of 40 mass% or less with regard to the aqueous dispersion of the hydrophilic group-having polymer elastic body in order to improve storage stability and film formability. The content of the water-soluble organic solvent is preferably 1 mass% or less in view of protecting a film-forming environment, and the like.

[0114] In the method for manufacturing a sheet-shaped article of the present invention, the aqueous dispersion of the hydrophilic group-having polymer elastic body contains a monovalent positive ion-including inorganic salt. The monovalent positive ion-including inorganic salt is contained, thereby making it possible to impart thermosensitive coagulability to the aqueous dispersion of the hydrophilic group-having polymer elastic body. In the present invention, the thermosensitive coagulability refers to a property of decreasing fluidity of the aqueous dispersion of the hydrophilic group-having polymer elastic body and coagulating the aqueous dispersion after a certain temperature (thermosensitive coagulation temperature) is reached at the time of heating the aqueous dispersion of the hydrophilic group-having polymer elastic body.

[0115] In the method for manufacturing a sheet-shaped article of the present invention, the aqueous dispersion of the hydrophilic group-having polymer elastic body is imparted to the fibrous substrate, and the resulting product is dry-heat coagulated by heat treatment at a temperature of 100°C or more and 180°C or less so as to impart the polymer elastic body to the fibrous substrate.

[0116] In a case where the hydrophilic group-having polymer elastic body does not have thermosensitive coagulability, migration occurs in which the hydrophilic group-having polymer elastic body migrates to the sheet surface along with evaporation of moisture. Further, coagulation proceeds in a state in which the polymer elastic body is unevenly distributed around the fiber as moisture evaporates, whereby the polymer elastic body covers the periphery of the fiber and strongly restricts the movement. As a result, the texture of the sheet-shaped article becomes significantly hard.

[0117] The thermosensitive coagulation temperature of the aqueous dispersion of the hydrophilic group-having polymer elastic body is preferably 55°C or more and 80°C or less, more preferably 60°C or more and 70°C or less. The thermosensitive coagulation temperature is set to 55°C or more, so that the stability of the aqueous dispersion of the hydrophilic group-having polymer elastic body during storage is improved, and the adhesion of the polymer elastic body to a machine during operation or the like can be suppressed. The thermosensitive coagulation temperature is set to 80°C or less, so that the migration phenomenon of the polymer elastic body to the surface layer of the fibrous substrate can be suppressed. Further, the coagulation of the polymer elastic body proceeds before moisture evaporates from the fibrous substrate, so that a structure similar to that obtained by wet coagulation of a solvent-based polymer elastic body, i.e., a structure in which the polymer elastic body does not strongly retain fibers can be formed, thereby achieving favorable flexibility, repulsive feeling, and heat resistance.

[0118] In the present invention, regarding an inorganic salt used as a thermosensitive coagulant, it is important to use a monovalent positive ion-including inorganic salt. The monovalent positive ion-including inorganic salt is preferably sodium chloride and/or sodium sulfate. In the conventional procedure, a divalent positive ion-including inorganic salt such as magnesium sulfate or calcium chloride has been preferably used as the thermosensitive coagulant. These inorganic salts greatly affect the stability of the aqueous dispersion of the hydrophilic group-having polymer elastic body even when added in a small amount. Depending on the kind of the polymer elastic body, it is difficult to strictly control the thermosensitive gelation temperature by adjusting the additive amount of the polymer elastic body. In addition, there has been a problem such as concern about gelation at the time of adjusting or storing the aqueous dispersion of the hydrophilic group-having polymer elastic body. Meanwhile, the monovalent positive ion-including inorganic salt having a small ionic valence has a small influence on the stability of the aqueous dispersion. Thus, the additive amount is adjusted, as a result of which the thermosensitive coagulation temperature of the aqueous dispersion can be strictly controlled while ensuring the stability of the aqueous dispersion.

[0119] Further, in the present invention, it is important that the content of the monovalent positive ion-including inorganic salt in the aqueous dispersion is 10 mass% or more and 50 mass% or less with regard to the solid content of the hydrophilic group-having polymer elastic body. When the content is 10 mass% or more, ions present in a large amount in the aqueous dispersion of the hydrophilic group-having polymer elastic body uniformly act on the polymer elastic body particles, as a result of which coagulation can be rapidly completed at a specific thermosensitive coagulation temperature. Thus, a more remarkable effect can be obtained by allowing the coagulation of the polymer elastic body to proceed in a state where a large amount of moisture is contained in the fibrous substrate as described above. As a result, it is possible to form a structure very similar to that obtained by wet coagulation of the solvent-based polymer elastic body and to achieve favorable flexibility and repulsive feeling. Furthermore, the content is set as described above, as a result of which the inorganic salt serves as an inhibitor in the fusion of the polymer elastic body particles, and it is also possible to prevent the polymer elastic body from being hardened due to the continuous film formation. Meanwhile, the content is set to 50 mass% or less, as a result of which it is possible to cause a continuous film structure of an appropriate polymer elastic body to be remained, and suppress a decrease in physical properties. In addition, it is possible to maintain the stability of the aqueous dispersion of the hydrophilic group-having polymer elastic body.

[0120] The sheet-shaped article of the present invention preferably has a L value retention of 90% to 100% when the napped surface of the sheet-shaped article is placed on a hot plate heated to 150°C and pressed at a pressing load of 2.5 kPa for 10 seconds (hereinafter, sometimes simply abbreviated as L value retention). In particular, when the L value retention is 90% or more, more preferably 92% or more, and still more preferably 95% or more, the sheet-shaped article has high heat resistance.

[0121] In the present invention, the "napped surface of the sheet-shaped article" refers to a surface obtained by napping the sheet-shaped article. In addition, the L value is an L value defined by the International Commission on Illumination (CIE). The L value retention in the present invention is an index indicating that a rate of change in brightness under heating and pressing conditions is small, that is, to what extent a sheet-shaped article having a dark color before heating and pressing does not become bright after heating and pressing.

[0122] In the present invention, the L value retention refers to a value measured and calculated by the following procedure.

(1) The sheet-shaped article is cut, and the L value of the cut test piece is measured using a color difference meter (e.g., "CR-410", manufactured by Konica Minolta, Inc.).
(2) The test piece is placed on a hot plate (e.g., "CHP-250 DN", manufactured by AS ONE Corporation) heated to 150°C with the napped surface of the test piece facing down.
(3) An indenter adjusted to have a pressing load of 2.5 kPa is placed on the test piece, and held for 10 seconds.
(4) The indenter on the test piece is removed, and the L value of the napped surface of the test piece is measured with the color difference meter.
(5) The L value retention is calculated by the following equation.

$$\text{L value retention (\%)} = (\text{L value measured by (1)})/(\text{L value measured by (4)}) \times 100$$

[0123] Examples of the method for setting the L value retention to the above range include a method in which uneven distribution (migration) of polyurethane to the surface of the sheet-shaped article due to moisture evaporation is suppressed by setting the thermosensitive coagulation temperature to a range of 55 to 80°C, and deterioration of polyurethane due to hot pressing is suppressed, and/or a method in which heat treatment (curing treatment) is performed at a temperature of 120°C or more and 160°C or less in a drying step in dry heat coagulation.

[0124] In the method for manufacturing a sheet-shaped article of the present invention, it is important that an aqueous dispersion of a hydrophilic group-having polymer elastic body contains a crosslinker. The content of the crosslinker is preferably 1 mass% or more, and more preferably 2 mass% or more, with regard to the mass of the solid content of the polymer elastic body. The content of the crosslinker is set to 1 mass% or more, so that more three-dimensional network structures can be introduced into the polymer elastic body by the crosslinker, and physical properties such as wear resistance can be further improved. In addition, the content of the crosslinker is preferably 10 mass% or less and more preferably 7 mass% or less, with regard to the mass of the solid content of the polymer elastic body. The content of the crosslinker is set to 10 mass% or less, whereby fusion inhibition of the polymer elastic body by an excess of the crosslinker hardly occurs, and deterioration of physical properties such as wear resistance is easily suppressed. Further, the monovalent positive ion-including inorganic salt described above is used in combination, the sheet-shaped article is made supple by controlling the adhesive structure between the polymer elastic body and the fiber, and at the same time, high physical properties and high heat resistance of the sheet-shaped article are easily achieved.

[0125] The crosslinker is preferably a carbodiimide-based crosslinker because the polymer elastic body obtained after the reaction is superior in lightfast, heat resistance, and wear resistance, and has favorable flexibility, and the L value retention of the napped surface before and after hot pressing is low.

[0126] In the method for manufacturing a sheet-shaped article of the present invention, the polymer elastic body contains a polyether diol as a constituent in a preferred embodiment. The reason is as described in the section of (1-1) Polymeric Polyol.

[0127] Further, in the method for manufacturing a sheet-shaped article of the present invention, a hydrophilic group-having polymer elastic body X and a hydrophilic group-having polymer elastic body Y having compositions different from each other are contained in the aqueous dispersion, and the hydrophilic group-having polymer elastic body Y is coagulated after the hydrophilic group-having polymer elastic body X is coagulated. This is a preferred embodiment. The content of the monovalent positive ion-including inorganic salt is adjusted, as a result of which it is possible to adjust each thermosensitive coagulation temperature so that the hydrophilic group-having polymer elastic body B is coagulated after the hydrophilic group-having polymer elastic body A is coagulated, and to control the distribution of the two kinds of polymer elastic bodies in the sheet-shaped article. Thus, for example, when the hydrophilic group-having polymer elastic body X is a polymer elastic body having superior flexibility such as a polyether-based polymer elastic body, and the hydrophilic group-having polymer elastic body Y is a polycarbonate-based polymer elastic body having superior physical properties such as durability, a sheet-shaped article having superior flexibility and physical properties is easily obtained.

[0128] A step of removing PVA from the fibrous substrate to which the hydrophilic group-having polymer elastic body has been imparted may be included, if necessary. A supple sheet-shaped article is obtained by removing PVA from the fibrous substrate to which the hydrophilic group-having polymer elastic body has been imparted. The method for removing PVA is not particularly limited. For example, the sheet is immersed in hot water at a temperature of 60°C or more and 100°C or less and then squeezed using a mangle or the like, if necessary, to dissolve and remove PVA. This is a preferred embodiment.

[0129] In the present invention, at least one surface of the sheet-shaped article may be subjected to a napping treatment to form a raised nap on the surface. The method for forming the raised nap is not particularly limited, and various methods usually performed in the art such as buffing with sandpaper or the like can be used. When the length of the raised nap is too short, it is difficult to obtain an elegant appearance, and when the length of the raised nap is too long, pilling tends to occur. Therefore, the length of the raised nap is preferably 0.2 mm or more and 1 mm or less.

[0130] Further, in one embodiment of the present invention, prior to the napping, a lubricant such as silicone may be imparted to the sheet-shaped article. When a lubricant is imparted, napping can be made easy by surface grinding. This is preferable because the surface quality is very favorable. In addition, an antistatic agent may be imparted before the napping. When an antistatic agent is imparted, grinding powder generated from a sheet-shaped article by grinding is unlikely to be deposited on a sandpaper. This is thus a preferred embodiment.

[0131] In one embodiment of the present invention, the sheet-shaped article may be dyed. As the dyeing method, various methods usually used in the art may be adopted. Since the sheet-shaped article may be made supple by adding a softening effect at the same time of dyeing of the sheet-shaped article, a method using a jet dyeing machine is preferable.

[0132] Although depending on the kind of fiber, the dyeing temperature is preferably set to 80°C or more and 150°C or less. The dyeing temperature is set to 80°C or more, and more preferably 110°C or more, so that it is possible to efficiently dye the fiber. Meanwhile, the dyeing temperature is set to 150°C or less, and more preferably 130°C or less, so that it is possible to prevent deterioration of the polymer elastic body.

[0133] A dye used in the present invention may be selected according to the kind of fibers included in the fibrous substrate, and is not particularly limited. For example, any disperse dye may be used in the case of a polyester-based fiber. In the case of a polyamide-based fiber, an acidic dye or a gold-containing dye may be used. In the case of dyeing with a disperse dye, reduction cleaning may be performed after the dyeing.

[0134] In addition, a dyeing auxiliary is used during dyeing in a preferred embodiment. The dyeing auxiliary is used, so that the evenness and reproducibility of dyeing can be improved. Further, in the same bath during dyeing or after dyeing, it is possible to perform treatment using a finishing agent such as a softener such as silicone, an antistatic agent, a water repellent, a flame retardant, a lightfast agent, and/or an antimicrobial agent.

EXAMPLES

[0135] Next, the sheet-shaped article of the present invention will be described more specifically using Examples, but the present invention is not limited to these Examples.

[Evaluation Method]

[0136]

(1) Average Individual Fiber Fineness of Sheet-shaped Article:

A cross section including the fibers of the sheet-shaped article, the cross section being perpendicular to the thickness direction, was observed at a magnification of 3000 times using a scanning electron microscope (SEM, VE-7800, manufactured by KEYENCE CORPORATION), and the diameters of 50 single fibers randomly extracted in a field of view of 30 μm × 30 μm were measured in μm units up to the first decimal place. This operation was performed at 3 locations, the diameters of 150 single fibers in total were measured, and the average value was calculated up to the first decimal place. When fibers with a fiber diameter of more than 50 μm were mixed in, these fibers were determined not to correspond to ultrafine fibers and were excluded from subjects for the average fiber diameter measurement. In addition, when ultrafine fibers had a modified cross section, the cross-section area of each single fiber was first measured as described above, and the diameter when the cross section was assumed to be circular was calculated to determine the diameter of the single fiber. The average value for each diameter population was calculated, and the resulting value was defined as the average individual fiber fineness.

(2) Flexibility of Sheet-shaped Article:

Based on A test (45° cantilever method) described in section 8.21.1 of the chapter 8.21 "Bending Resistance" in JIS L 1096:2010 "Testing methods for woven and knitted fabrics", 5 test pieces of 2 × 45 cm were prepared in the longitudinal direction and in the lateral direction. Each test piece was placed on a horizontal table having a slope at an angle of 45 degrees, and was made to glide. Next, when a middle point at one end of the test piece was in contact with the slope, the scale was read. Then, the values for the five test pieces were averaged.

(3) Evaluation of Wear of Sheet-shaped Article

> Evaluation of wear was performed based on JIS L 1096: 2010. Model 406, manufactured by James H. Heal & Co. Ltd., was used as a Martindale abrasion tester, and ABRASTIVE CLOTH SM 25, manufactured by James H. Heal & Co. Ltd., was used as a standard friction cloth. The sheet-shaped article was abraded 20,000 times with a load of 12 kPa. Thereafter, the appearance of the sheet-shaped article was visually observed to evaluate fuzzballs (pilling). Regarding the evaluation criteria, a sheet-shaped article having no change in appearance from that before abrasion was rated as grade 5, and a sheet-shaped article having a large number of fuzzballs was rated as grade 1. The grades 1 to 5 were divided in increments of 0.5.

The mass of the sheet-shaped article before and after abrasion was used, and the abrasion loss was calculated by the following equation.

$$\text{Abrasion loss (mg)} = \text{mass before abrasion (mg)} - \text{mass after abrasion (mg)}$$

(4) Coagulation Temperature of Aqueous Dispersion of Hydrophilic Group-having Polymer Elastic Body

20 g of the aqueous dispersion liquid containing the hydrophilic group-having polymer elastic body prepared in each Example and each Comparative Example was put into a test tube with an inner diameter of 12 mm; a thermometer was inserted such that the tip was below the liquid level; and the test tube was then sealed and submerged in a hot water bath at a temperature of 95°C such that the liquid level of the aqueous dispersion liquid of the hydrophilic group-having polymer elastic body was below the liquid level of the hot water bath. While the temperature rise inside the test tube was checked by the thermometer, the test tube was lifted, if appropriate, and was swung for 5 sec or less per check so as to examine the presence or absence of fluidity of the aqueous dispersion of the hydrophilic group-having polymer elastic body at its surface. Then, the temperature at which the aqueous dispersion of the hydrophilic group-having polymer elastic body at its surface lost fluidity was defined as the coagulation temperature. This measurement was performed three times per kind of the aqueous dispersion of the hydrophilic group-having polymer elastic body, and the measurement values were averaged.

(5) Kind of Inorganic Salt Contained in Sheet-shaped Article and Content Measurement

> The sheet-shaped article was immersed in dimethylformamide overnight, and the solution from which the polymer elastic body and the inorganic salt had been eluted was concentrated by heating and drying at 140°C for solidification. Distilled water was added to the resulting solid, and only the inorganic salt was eluted. The aqueous solution containing the inorganic salt was heated and dried, and then the amount of the inorganic salt contained in the sheet-shaped article was measured. In addition, the weight of the solidified polymer elastic body was also measured after heating and drying, and the weight of the inorganic salt with regard to the mass of the polymer elastic body was calculated.
>
> The kind of the inorganic salt in the aqueous solution containing the inorganic salt was identified using an ion chromatograph system of ICS-3000 type, manufactured by Dionex Corporation.

(6) Identification of Bonded Species in Polymer Elastic Body

Regarding the polymer elastic body separated from the sheet-shaped article, the bonded species were identified by infrared spectroscopic analysis using FT/IR 4000 series, manufactured by JASCO Corporation.

(7) L Value Retention

Measurement and calculation were performed by the above method using "CHP-250 DN" manufactured by AS ONE Corporation as a hot plate and "CR-410" manufactured by Konica Minolta, Inc. as a color difference meter.

(8) Evaluation of Solution Stability of Aqueous Dispersion of Polymer Elastic Body

> In a step of impregnating a fibrous substrate with an aqueous dispersion of a hydrophilic group-having polymer elastic body, the evaluation is conducted based on the presence or absence of precipitated solids that can be visually confirmed on the bottom and/or wall surface of an impregnation vessel containing the aqueous dispersion

of the polymer elastic body, during processing for 1 hour.
The evaluation results are as follows.

A = no solid precipitates.
B = a solid precipitates.

[Reference Example 1: Preparation of Aqueous Dispersion Wa of Hydrophilic Group-having Polymer Elastic Body a]

[0137] A prepolymer was prepared in a toluene solvent using polytetramethylene ether glycol (designated as PTMG in the table) having a number average molecular weight (Mn) of 2,000 as a polyol, MDI as an isocyanate, and 2,2-dimethylol propionic acid as a component for imparting a hydrophilic group. Ethylene glycol and ethylenediamine as chain extenders, polyoxyethylene nonylphenyl ether as an external emulsifier, and water were added and stirred. Toluene was removed under reduced pressure to obtain an aqueous dispersion Wa of a hydrophilic group-having polymer elastic body a. The polymer elastic body a is a polymer elastic body corresponding to the polymer elastic body A.

[Reference Example 2: Preparation of Aqueous Dispersion Wb of Hydrophilic Group-having Polymer Elastic Body b]

[0138] A prepolymer was prepared in an acetone solvent using polyhexamethylene carbonate (designated as PHC in the table) having Mn of 2,000 as a polyol, hydrogenated MDI as an isocyanate, and a diol compound having polyethylene glycol in a side chain and 2,2-dimethylol propionic acid as components for imparting a hydrophilic group. Ethylene glycol and ethylenediamine as chain extenders and water were added, and the mixture was stirred. Acetone was removed under reduced pressure to obtain an aqueous dispersion Wb of a hydrophilic group-having polymer elastic body b. The polymer elastic body b is a polymer elastic body corresponding to the polymer elastic body B.

[Reference Example 3: Preparation of Aqueous Dispersion Wc Containing Hydrophilic Group-having Polymer Elastic Bodies a and b]

[0139] Regarding the aqueous dispersions Wa and Wb of the polymer elastic bodies in Reference Examples 1 and 2, two kinds of aqueous dispersions were mixed so that the solid content of each polymer elastic body was 20 mass%, thereby obtaining an aqueous dispersion Wc containing hydrophilic group-having polymer elastic bodies a and b with a solid content of 40 mass%.

[Reference Example 4: Preparation of Aqueous Dispersion Wd of Hydrophilic Group-having Polymer Elastic Body d]

[0140] A branched (self-crosslinking) prepolymer was prepared in a toluene solvent using polytetramethylene ether glycol (designated as PTMG in the table) having a number average molecular weight (Mn) of 2,000 as a polyol, HDI biuret as an isocyanate, and 2,2-dimethylol propionic acid as a component for imparting a hydrophilic group. Ethylene glycol and ethylenediamine as chain extenders, polyoxyethylene nonylphenyl ether as an external emulsifier, and water were added and stirred. Toluene was removed under reduced pressure to obtain an aqueous dispersion Wd of a hydrophilic group-having polymer elastic body d.

[Example 1]

(Nonwoven Fabric)

[0141] A copolymerized polyester containing 8 mol% SSIA (sodium 5-sulfoisophthalate) was used as a sea component, and polyethylene terephthalate was used as an island component to obtain islands-in-the-sea fibers with an average individual fiber fineness of 20 μm in which the composite ratio of the sea component : the island component was 20 mass% : 80 mass% and the number of islands was 16 islands/1 filament. The resulting islands-in-the-sea fibers were cut into a fiber length of 51 mm to obtain a staple, which went through a carding machine and a cross wrapper to form a fiber web. This fiber web was subjected to needle punching to manufacture a nonwoven fabric with a basis weight of 700 g/m^2 and a thickness of 3.1 mm. The nonwoven fabric thus obtained was immersed and contracted in hot water at a temperature of 98°C for 2 minutes, and was then dried at a temperature of 100°C for 5 minutes to obtain a nonwoven fabric for fibrous substrate.

(Fiber Reinforcement)

[0142] The above nonwoven fabric for fibrous substrate was impregnated with an aqueous solution containing 10 mass% of PVA (NM-14, manufactured by Nippon Chemical Industrial CO., LTD.) with a saponification degree of 99% and a polymerization degree of 1400, and heated and dried at a temperature of 140°C for 10 minutes to obtain a PVA-imparted sheet in which the amount of PVA imparted per fiber mass of the nonwoven fabric for fibrous substrate was 30 mass%.

(To Make Fibers Ultrafine)

[0143] The resulting PVA-imparted sheet was immersed and treated for 30 minutes in a sodium hydroxide aqueous solution that was heated to a temperature of 95°C and was at a concentration of 8 g/L. Then, a sheet (PVA-imparted ultrafine fiber nonwoven fabric) composed of ultrafine fibers, in which the sea component had been removed from the islands-in-the-sea fibers, was obtained.

(To Impart Polymer Elastic Body)

[0144] 20 mass% of sodium sulfate (designated as "Na_2SO_4" in Table 1) as a thermosensitive coagulant and 3 mass% of a carbodiimide-based crosslinker were added to 100 mass% of the solid content of the hydrophilic group-having polymer elastic body, and the whole of the mixture was adjusted to a solid content of 12 mass% using water, thereby obtaining an aqueous dispersion containing a hydrophilic group-having polymer elastic body. The thermosensitive coagulation temperature was 70°C. The resulting PVA-imparted ultrafine fiber nonwoven fabric was immersed in the aqueous dispersion, and then dried with hot air at a temperature of 150°C for 15 minutes to obtain a 1.9 mm-thick polymer elastic body-imparted sheet in which 25 mass% of polymer elastic body A was imparted with regard to the fiber weight.

(To Remove Reinforcing Resin)

[0145] The resulting polymer elastic body-imparted sheet was submerged and treated for 10 minutes in water heated to 95°C to obtain a sheet from which the imparted PVA had been removed.

(For Cutting in Half and Napping)

[0146] The resulting PVA-removed, polymer elastic body-imparted sheet was cut in half in a direction perpendicular to the thickness direction. The side opposite to the half-cutting surface was subjected to grinding with an endless sandpaper of sandpaper count No. 240 to obtain a sheet-shaped article having a raised nap with a thickness of 0.7 mm.

(For Dyeing and Finishing)

[0147] The resulting sheet-shaped article having a raised nap was dyed with a black dye by using a jet dyeing machine under conditions at a temperature of 120°C. Then, drying was performed with a dryer to obtain a sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 1.2 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 95%, and the napped surface had superior heat resistance.

[Example 2]

(Nonwoven Fabric)

[0148] This example was performed in a similar manner to Example 1.

(To Make Fibers Ultrafine)

[0149] Next, the resulting nonwoven fabric for fibrous substrate was immersed and treated for 25 minutes in a sodium hydroxide aqueous solution heated to a temperature of 95°C and was at a concentration of 10 g/L and, thereby obtaining a sea-removed sheet from which the sea component of the islands-in-the-sea fibers had been removed.

(To Impart Polymer Elastic Body)

[0150] 15 mass% of sodium chloride (designated as "NaCl" in Table 1) as a thermosensitive coagulant and 5 mass% of a carbodiimide-based crosslinker were added to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a, the whole of the mixture was adjusted to a solid content of 14 mass% using water, thereby obtaining an aqueous dispersion containing a hydrophilic group-having polymer elastic body. The thermosensitive coagulation temperature was 68°C. The resulting sea-removed sheet was immersed in the aqueous dispersion, and then dried with hot air at a temperature of 160°C for 15 minutes to obtain a 1.8 mm-thick polymer elastic body-imparted sheet in which 25 mass% of polymer elastic body was imparted with regard to the fiber weight.

[0151] The cutting in half process and the finishing process were performed in a similar manner to Example 1 to obtain a sheet-shaped article including ultrafine fibers with an average individual fiber fineness of 4.4 μm. The resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 1.8 mass% of sodium chloride was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 94%, and the napped surface had superior heat resistance.

[Example 3]

[0152] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that the aqueous dispersion containing the hydrophilic group-having polymer elastic body was changed (specifically, changed to the aqueous dispersion Wb of the hydrophilic group-having polymer elastic body b) in (To Impart Polymer Elastic Body) of Example 1. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 2.0 mass% of sodium chloride was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 96%, and the napped surface had superior heat resistance.

[Example 4]

[0153] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 2 except that sodium chloride as a thermosensitive coagulant was added in an amount of 40 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 2, and the thermosensitive coagulation temperature was adjusted to 60°C. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 3.5 mass% of sodium chloride was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 92%, and the napped surface had superior heat resistance.

[Example 5]

[0154] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 2 except that the aqueous dispersion liquid containing the hydrophilic group-having polymer elastic body was changed (specifically, changed to the aqueous dispersion Wc containing hydrophilic group-having polymer elastic bodies a and b, 50 mass% of sodium chloride was added as a thermosensitive coagulant, the thermosensitive coagulation temperature of the hydrophilic group-having polymer elastic body a was adjusted to 60°C, and the thermosensitive coagulation temperature of the hydrophilic group-having polymer elastic body b was adjusted to 70°C) in (To Impart Polymer Elastic Body) of Example 2. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 4.8 mass% of sodium chloride was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 97%, and the napped surface had superior heat resistance.

[Example 6]

[0155] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that sodium sulfate as a thermosensitive coagulant was added in an amount of 45 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1, and the thermosensitive coagulation temperature was adjusted to 60°C. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 3.7 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 94%, and the napped surface had superior heat resistance.

[Example 7]

[0156] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that sodium sulfate as a thermosensitive coagulant was added in an amount of 12 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1, and the thermosensitive coagulation temperature was adjusted to 75°C. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 0.7 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 94%, and the napped surface had superior heat resistance.

[Example 8]

[0157] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that a carbodiimide-based crosslinker was added in an amount of 1 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 1.3 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 92%, and the napped surface had superior heat resistance.

[Example 9]

[0158] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that a carbodiimide-based crosslinker was added in an amount of 8 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 1.2 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 96%, and the napped surface had superior heat resistance.

[Example 10]

[0159] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that a carbodiimide-based crosslinker was added in an amount of 0.5 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 1.2 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 91%, and the napped surface had superior heat resistance.

[Example 11]

[0160] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that a carbodiimide-based crosslinker was added in an amount of 12.0 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 1.2 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 90%, and the napped surface had superior heat resistance.

[Example 12]

[0161] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that a blocked isocyanate-based crosslinker was added in an amount of 3 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. Similarly to Fig. 1, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded as shown in Fig. 1, and had a supple texture and superior wear resistance. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 1.2 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 91%, and the napped surface had superior heat resistance.

[Comparative Example 1]

[0162] The process was performed in a similar manner to Example 1 except that calcium chloride was used as a thermosensitive coagulant in (To Impart Polymer Elastic Body) of Example 1, an aqueous dispersion containing a hydrophilic group-having polymer elastic body gelled during processing, and a polymer elastic body-imparted sheet was not able to be obtained.

[Comparative Example 2]

[0163] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that an additive amount of sodium sulfate was 1.0 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. The resulting sheet-shaped article formed a structure in which the entire fiber bundle was covered with the polymer elastic body as shown in Fig. 2, and had superior wear resistance, but had a hard texture. Further, N-acylurea bonding and isourea bonding were present in the polymer elastic body, but sodium sulfate was not present in the sheet-shaped article. Furthermore, the L value retention of the napped surface before and after hot pressing was 87%, and the heat resistance was poor.

[Comparative Example 3]

[0164] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that an additive amount of sodium sulfate was 55 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. In the resulting sheet-shaped article, the resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded, but the size of the lump of the polymer elastic body was very small. The sheet-shaped article was supple, but the wear resistance was poor. Further, it was confirmed that N-acylurea bonding and isourea bonding were present in the polymer elastic body, and 8.0 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 94%, and the napped surface had superior heat resistance.

[Comparative Example 4]

[0165] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 2 except that no crosslinker was added to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 2. The resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded, and was supple but had poor wear resistance. Further, it was confirmed that 2.5 mass% of sodium chloride was contained with regard to the solid content of the polymer elastic body, but N-acylurea bonding and isourea bonding were not able to be confirmed in the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 84%, and the heat resistance was poor.

[Comparative Example 5]

[0166] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that an oxazoline-based crosslinker was added in an amount of 4.0 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. The resulting sheet-shaped article formed a structure in which the fiber and the polymer elastic body were partially bonded, and was supple but had poor wear resistance. Further, it was confirmed that 1.2 mass% of sodium chloride was contained with regard to the solid content of the polymer elastic body, but N-acylurea bonding and isourea bonding were not able to be confirmed in the polymer elastic body. Furthermore, the L value retention of the napped surface before and after hot pressing was 78%, and the heat resistance was poor.

[Comparative Example 6]

[0167] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that calcium chloride was added in an amount of 1.2 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. Similarly to Fig. 2, the resulting sheet-shaped article formed a structure in which the entire fiber bundle was covered with the polymer elastic body as shown in Fig. 2, and had superior wear resistance, but had a hard texture. Further, N-acylurea bonding and isourea bonding were present in the polymer elastic body, but sodium sulfate was not present in the sheet-shaped article. Furthermore, the L value retention of the napped surface before and after hot pressing was 85%, and the heat resistance was poor.

[Comparative Example 7]

[0168] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that "VA-086" (manufactured by Wako Pure Chemical Industries, Ltd., 2,2'-azobis[2-methyl-N-(2-hydroxyester)propionamide] as a foaming agent was added in an amount of 3.0 mass% with regard to 100 mass% of the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. Similarly to Fig. 2, the resulting sheet-shaped article formed a structure in which the entire fiber bundle was covered with the polymer elastic body, but had poor wear resistance and also had a hard texture. Further, N-acylurea bonding and isourea bonding were present in the polymer elastic body, but sodium sulfate was not present in the sheet-shaped article. Furthermore, the L value retention of the napped surface before and after hot pressing was 80%, and the heat resistance was poor.

[Comparative Example 8]

[0169] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that no thermosensitive coagulant was used with regard to the solid content of the aqueous dispersion Wa of the hydrophilic group-having polymer elastic body a in (To Impart Polymer Elastic Body) of Example 1. Similarly to Fig. 2, the resulting sheet-shaped article formed a structure in which the entire fiber bundle was covered with the polymer elastic body, but had poor wear resistance and also had a hard texture. Further, N-acylurea bonding and isourea bonding were present in the polymer elastic body, but sodium sulfate was not present in the sheet-shaped article. Furthermore, the L value retention of the napped surface before and after hot pressing was 87%, and the heat resistance was poor.

[Comparative Example 9]

[0170] A sheet-shaped article having ultrafine fibers with an average individual fiber fineness of 4.4 μm was obtained in a similar manner to Example 1 except that the hydrophilic group-having polymer elastic body d was used in place of the hydrophilic group-having polymer elastic body a and no crosslinker was added in (To Impart Polymer Elastic Body) of Example 1. The resulting sheet-shaped article had favorable wear resistance and formed a structure in which the fiber and the polymer elastic body were partially bonded, but had a hard texture. Further, it was confirmed that 1.2 mass% of sodium sulfate was contained with regard to the solid content of the polymer elastic body, but N-acylurea bonding and isourea bonding were not able to be confirmed in the polymer elastic body. The L value retention of the napped surface before and after hot pressing was 91%, and the heat resistance was favorable.

[Table 1-1]

	Aqueous dispersion containing hydrophilic group-having polymer elastic body					
	Polymer elastic body		Thermosensitive coagulant		Crosslinker	
	Kind	Polyol	Kind	Additive amount (mass%)	Kind	Additive amount (mass%)
Example 1	a	PTMG	Na_2SO_4	20	Carbodiimide-based	3
Example 2	a	PTMG	NaCl	15	Carbodiimide-based	5
Example 3	b	PHC	Na_2SO_4	20	Carbodiimide-based	3
Example 4	a	PTMG	NaCl	40	Carbodiimide-based	5
Example 5	a, b	PTMG/PHC	NaCl	50	Carbodiimide-based	5
Example 6	a	PTMG	Na_2SO_4	45	Carbodiimide-based	3
Example 7	a	PTMG	Na_2SO_4	12	Carbodiimide-based	3
Example 8	a	PTMG	Na_2SO_4	20	Carbodiimide-based	1
Example 9	a	PTMG	Na_2SO_4	20	Carbodiimide-based	8
Example 10	a	PTMG	Na_2SO_4	20	Carbodiimide-based	0.5
Example 11	a	PTMG	Na_2SO_4	20	Carbodiimide-based	12
Example 12	a	PTMG	Na_2SO_4	20	Blocked isocyanate-based	3
Comparative Example 1	a	PTMG	$CaCl_2$	20	Carbodiimide-based	3
Comparative Example 2	a	PTMG	Na_2SO_4	1	Carbodiimide-based	3
Comparative Example 3	a	PTMG	Na_2SO_4	55	Carbodiimide-based	3
Comparative Example 4	a	PTMG	NaCl	15	None	-

(continued)

	Aqueous dispersion containing hydrophilic group-having polymer elastic body					
	Polymer elastic body		Thermosensitive coagulant		Crosslinker	
	Kind	Polyol	Kind	Additive amount (mass%)	Kind	Additive amount (mass%)
Comparative Example 5	a	PTMG	Na_2SO_4	20	Oxazoline-based	4
Comparative Example 6	a	PTMG	$CaCl_2$	1.2	Carbodiimide-based	3
Comparative Example 7	a	PTMG	VA-086	3	Carbodiimide-based	3
Comparative Example 8	a	PTMG	None	-	Carbodiimide-based	3
Comparative Example 9	d	PTMG	Na_2SO_4	20	None	-

[Table 1-2]

	Processability	
	Coagulation method	Solution stability
Example 1	Dry heat	A
Example 2	Dry heat	A
Example 3	Dry heat	A
Example 4	Dry heat	A
Example 5	Dry heat	A
Example 6	Dry heat	A
Example 7	Dry heat	A
Example 8	Dry heat	A
Example 9	Dry heat	A
Example 10	Dry heat	A
Example 11	Dry heat	A
Example 12	Dry heat	A
Comparative Example 1	Dry heat	B
Comparative Example 2	Dry heat	A
Comparative Example 3	Dry heat	A
Comparative Example 4	Dry heat	A
Comparative Example 5	Dry heat	A
Comparative Example 6	Dry heat	A
Comparative Example 7	Dry heat	A
Comparative Example 8	Dry heat	A
Comparative Example 9	Dry heat	A

[Table 2-1]

	Bending resistance (mm)	Martindale abrasion test		Presence or absence of N-acylurea bonding/isourea bonding
		Abrasion loss (mg)	Pilling Grade	
Example 1	90	6.2	4.5	Presence
Example 2	82	6.5	4.5	Presence
Example 3	100	3.5	4.5	Presence
Example 4	70	5.3	4.5	Presence
Example 5	60	3.2	4.5	Presence
Example 6	80	8.1	4.5	Presence
Example 7	95	6.1	4.5	Presence
Example 8	88	9.1	4.5	Presence
Example 9	82	7.8	4.5	Presence
Example 10	84	9.6	4.0	Presence
Example 11	81	9.5	4.0	Presence
Example 12	96	8.8	4.5	Presence
Comparative Example 1	-	-	-	-
Comparative Example 2	300	7.7	4.5	Presence
Comparative Example 3	100	14.8	2.5	Presence
Comparative Example 4	98	19.0	2.5	None
Comparative Example 5	102	13.3	3.0	None
Comparative Example 6	320	9.0	4.0	Presence
Comparative Example 7	220	14.1	3.0	Presence
Comparative Example 8	348	7.9	3.0	Presence
Comparative Example 9	271	5.1	4.0	None

[Table 2-2]

	Content of monovalent positive ion-including inorganic salt (%)	L value retention (%)
Example 1	1.2	95
Example 2	1.8	94
Example 3	2.0	96
Example 4	3.5	92
Example 5	4.8	97

(continued)

	Content of monovalent positive ion-including inorganic salt (%)	L value retention (%)
Example 6	3.7	94
Example 7	0.7	94
Example 8	1.3	92
Example 9	1.2	96
Example 10	1.2	91
Example 11	1.2	90
Example 12	1.2	91
Comparative Example 1	-	-
Comparative Example 2	0	87
Comparative Example 3	8.0	94
Comparative Example 4	2.5	84
Comparative Example 5	1.2	78
Comparative Example 6	0	85
Comparative Example 7	0	80
Comparative Example 8	0	87
Comparative Example 9	1.2	91

INDUSTRIAL APPLICABILITY

[0171] The sheet-shaped article of the present invention can be fit for furniture, chairs and wall coverings, seats in cabins of vehicles such as cars, trains and aircrafts, skin materials for ceilings and interiors, interior materials with a very elegant appearance, and clothing and industrial materials, and so on.

Claims

1. A sheet-shaped article comprising a fibrous substrate including ultrafine fibers with an average individual fiber fineness of 0.1 μm or more and 10 μm or less, the fibrous substrate containing a hydrophilic group-having polymer elastic body,
   wherein an inside of the polymer elastic body has N-acylurea bonding and/or isourea bonding, and a monovalent positive ion-including inorganic salt is present at a rate of 0.1 mass% or more and 5 mass% or less, with regard to a mass of the polymer elastic body.

2. The sheet-shaped article according to claim 1, wherein the monovalent positive ion-including inorganic salt is sodium chloride and/or sodium sulfate.

3. The sheet-shaped article according to claim 1 or 2, wherein the polymer elastic body contains a polyether diol as a constituent.

4. The sheet-shaped article according to any one of claims 1 to 3, wherein the polymer elastic body includes a hydrophilic group-having polymer elastic body A containing a polyether diol as a constituent, and a hydrophilic group-having polymer elastic body B containing a polycarbonate diol as a constituent.

5. The sheet-shaped article according to any one of claims 1 to 4, wherein a bending resistance as specified in JIS L 1096: 2010 (a 45° cantilever method) is 50 mm or more and 180 mm or less, and an abrasion loss after 20,000 times of rubbing by a Martindale abrasion test as specified in JIS L 1096: 2010 is 10 mg or less.

6. A method for manufacturing a sheet-shaped article, comprising:

impregnating a fibrous substrate including ultrafine fibers with an average individual fiber fineness of 0.1 μm or more and 10 μm or less with an aqueous dispersion containing a hydrophilic group-having polymer elastic body, a monovalent positive ion-including inorganic salt, and a crosslinker; and
subjecting the fibrous substrate to a heat treatment at a temperature of 100°C or more and 180°C or less,
wherein a content of the monovalent positive ion-including inorganic salt in the aqueous dispersion is 10 mass% or more and 50 mass% or less with regard to a mass of a solid content of the hydrophilic group-having polymer elastic body.

7. The method for manufacturing a sheet-shaped article according to claim 6, wherein the monovalent positive ion-including inorganic salt is sodium chloride and/or sodium sulfate.

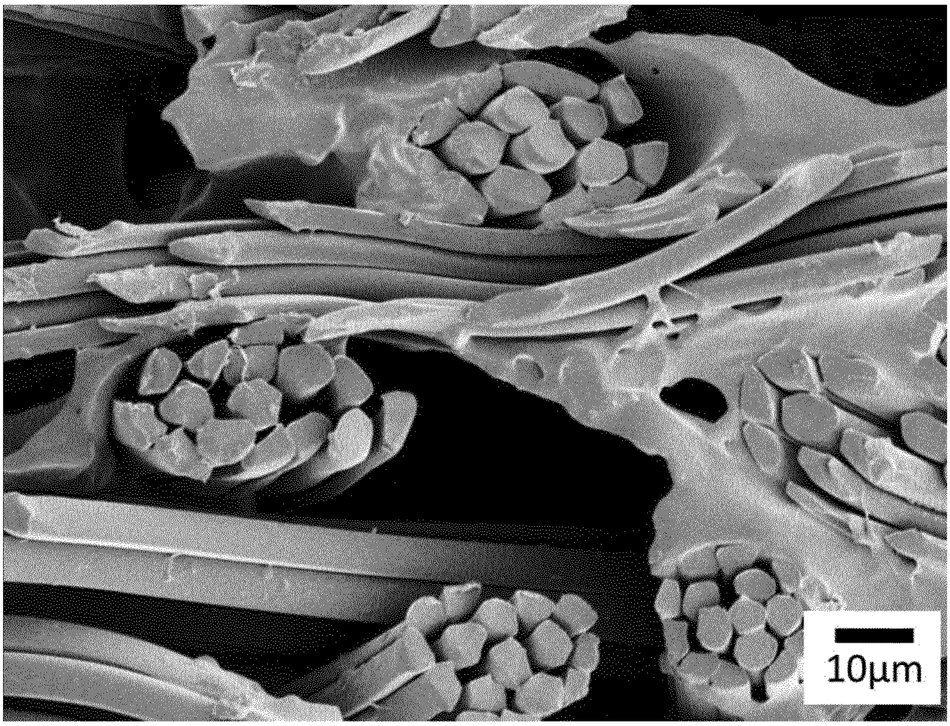
8. The method for manufacturing a sheet-shaped article according to claim 6 or 7, wherein the crosslinker is a carbodiimide-based crosslinker.

9. The method for manufacturing a sheet-shaped article according to any one of claims 6 to 8, wherein the hydrophilic group-having polymer elastic body contains a polyether diol as a constituent.

10. The method for manufacturing a sheet-shaped article according to any one of claims 6 to 9, wherein a hydrophilic group-having polymer elastic body X and a hydrophilic group-having polymer elastic body Y having compositions different from each other are contained in the aqueous dispersion, and the hydrophilic group-having polymer elastic body Y is coagulated after the hydrophilic group-having polymer elastic body X is coagulated.

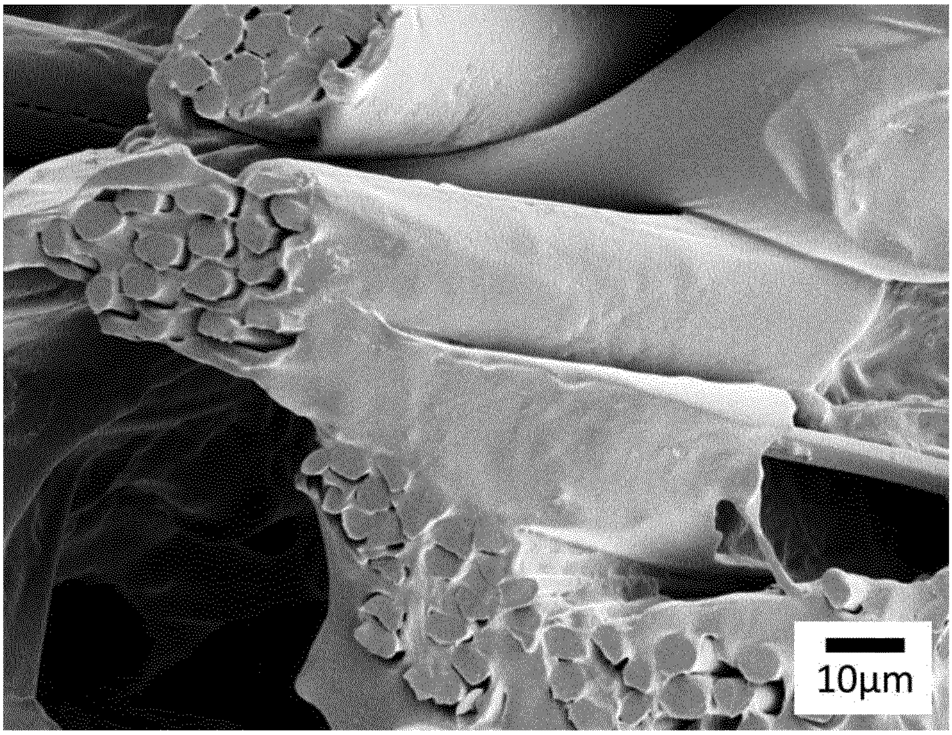
[Fig 1]

[Fig 1]



[Fig 2]

[Fig 2]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/012342

A. CLASSIFICATION OF SUBJECT MATTER
D06N 3/14(2006.01)i; D06M 15/564(2006.01)i
FI: D06N3/14 102; D06M15/564

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D06N1/00-7/06; D06M3/00-15/715; D04H1/00-18/04

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2020
Registered utility model specifications of Japan	1996-2020
Published registered utility model applications of Japan	1994-2020

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus (JDreamIII); JST7580 (JD reamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2015/076204 A1 (TORAY INDUSTRIES, INC.) 28.05.2015 (2015-05-28) claims 1, 7, paragraphs [0011]-[0159], [0169]-[0170], [0202]	1-9
Y	JP 2006-299018 A (MITSUBISHI PENCIL CO., LTD.) 02.11.2006 (2006-11-02) paragraphs [0012], [0016], [0026]	1-9
Y	US 2003/0220462 A1 (PORZIO, Robert Shane, et al.) 27.11.2003 (2003-11-27) paragraphs [0086]-[0161]	1-9
A	JP 2002-294572 A (TORAY INDUSTRIES, INC.) 09.10.2002 (2002-10-09) entire text	1-10

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"&" document member of the same patent family

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Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 62-10127 A (BAYER AG.) 19.01.1987 (1987-01-19) entire text	1-10
A	JP 2015-523429 A (BASF SE) 13.08.2015 (2015-08-13) entire text	1-10
A	CN 101654550 A (FUJIAN POLYTECH GROUP CO., LTD.) 24.02.2010 (2010-02-24) whole document	1-10
A	WO 1996/008524 A1 (STAHL INTERNATIONAL B. V.) 21.03.1996 (1996-03-21) whole document	1-10

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2020/012342

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WO 2015/076204 A1	28 May 2015	US 2016/0289890 A1 claims 1, 7, paragraphs [0020]-[0250], [0262]-[0263], table 3 EP 3073010 A1 CN 105745375 A KR 10-2016-0088330 A	
JP 2006-299018 A	02 Nov. 2006	US 2009/0049625 A1 paragraphs [0029], [0042]-[0043], [0062]-[0063] WO 2006/112452 A1 EP 1873214 A1 CN 101198657 A	
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