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(54) **SHEET-LIKE MATERIAL AND METHOD FOR PRODUCING SAME**

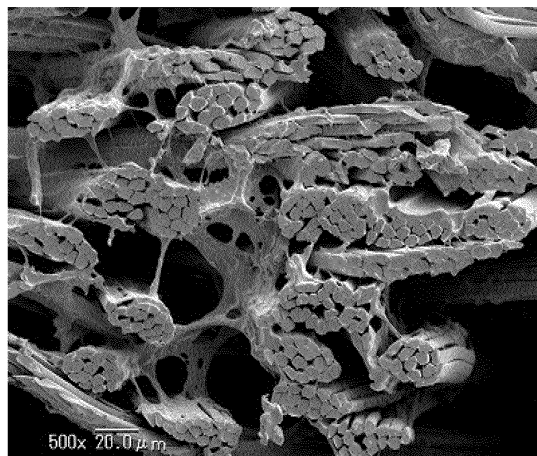
(57) The invention relates to an environmentally friendly production method for a sheet-like article that does not use an organic solvent in the production process and provides a sheet-like article that compares favorably in terms of a uniform feel with artificial leather products produced from an organic solvent based polyurethane and in particular has good surface quality and texture and also provides a production method therefor.

The present invention aims to provide a sheet-like article comprising a fibrous base material formed of ultrafine fibers and/or ultrafine fiber bundles provided with, as a binder, a polymer elastomer having a hydrophilic group, any thickness-directional cross section of the sheet-like article containing regions occupied by the polymer elastomer, the regions including independent regions each with a cross-sectional area of 50 μm^2 or more, the total area of the independent regions accounting for 0.1% or more and 5.0% or less of the cross-sectional area of the artificial leather in an observation view field.

The production method for the sheet-like article according to the present invention provides a production process for a sheet-like article including a fibrous base material formed of ultrafine fibers and, as a binder, a polymer elastomer having a hydrophilic group, the process

including a step for adding an aqueous resin dispersion liquid containing a water-dispersed polymer elastomer and a viscosity improver to a fibrous base material and a step for coagulating the polymer elastomer in hot water at a temperature of 50°C to 100°C.

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Description

Technical Field

5 **[0001]** The invention relates to an environmentally friendly production method for a sheet-like article that does not use an organic solvent in the production process and particularly relates to a sheet-like article that has good surface quality and texture and to a production method therefor.

Background Art

10 **[0002]** Sheet-like articles made up mainly of a fibrous base material, such as nonwoven fabric, and polyurethane have excellent features that natural leathers do not have, and are widely utilized in various uses such as artificial leather. In particular, a sheet-like article that employs a polyester-based fibrous base material is excellent in light resistance, and therefore its use has spread year by year to products such as clothing, chair upholstery, automotive interior finishing material uses, etc.

15 **[0003]** To produce such a sheet-like article, a generally adopted method is a combination of processes in which a fibrous base material is impregnated with an organic solvent solution of polyurethane and then the fibrous base material obtained is immersed in water or an aqueous solution of an organic solvent that is a non-dissolving medium for polyurethane, so as to cause polyurethane to undergo wet coagulation. Here, examples of the organic solvent for polyurethane include water-miscible solvents such as N,N-dimethyl formaldehyde. However, since organic solvents are generally high in harmfulness to the human body and the environment, the production of a sheet-like article strongly requires a technique that does not use an organic solvent.

20 **[0004]** Specific proposed solutions to this problem include the adoption of water-dispersed polyurethane, which is prepared by adding a hydrophilic group into the molecular chain of polyurethane and dispersing the polyurethane resin in water, instead of the conventional method of using organic solvent based polyurethane.

25 **[0005]** However, sheet-like articles that are produced by impregnating a fibrous base material with a dispersion liquid of a water-dispersible polyurethane, which is prepared by dispersing a water-dispersible polyurethane in a liquid, and subsequently coagulating the polyurethane tend to have the problem of stiff texture.

30 **[0006]** One of the major reasons is the difference between them in terms of the coagulation technique used. Specifically, the method involving the coagulation of a polyurethane solution in an organic solvent uses the so-called wet coagulation technique in which polyurethane molecules dissolved in an organic solvent are coagulated by substituting water for solvent. When applied to polyurethane, the technique produces low-density, porous film. Accordingly, if polyurethane is coagulated after penetrating into the fibrous base material, the contact area between the fiber and polyurethane decreases, leading to a soft sheet-like article.

35 **[0007]** For coagulation of water-dispersed polyurethane, on the other hand, the wet heat coagulation technique is mainly used, in which heating is performed to destroy the hydrated state of the dispersion liquid of water-dispersed polyurethane to cause the aggregation of emulsion particles of polyurethane to achieve coagulation. The resulting polyurethane film has a high-density, nonporous film structure. Consequently, strong contact is developed between the fibrous base material and polyurethane to maintain strong entanglement of fibers, leading to stiff texture.

40 **[0008]** To improve the texture attributed to the use of water-dispersed polyurethane, that is, to prevent the polyurethane from holding the fiber entanglement, a technique has been proposed which allows the polyurethane in the fibrous base material to have a porous structure.

45 **[0009]** Specifically, there is a proposed method in which the structure of polyurethane in a fibrous base material, such as nonwoven fabric, is made porous by adding to the fiber base material a water-dispersed polyurethane liquid that contains a foaming agent and causing the foaming agent to foam by heating (refer to Patent document 1). In this proposal, water-dispersed polyurethane is made porous so that the contact area between the fiber and the polyurethane decreases to weaken the force to hold fiber entanglement, thereby providing a sheet-like article having a good texture with soft feel. However, such texture still tends to be poor in softness compared to products produced from a base material containing a solution of polyurethane in an organic solvent.

50 **[0010]** To develop a porous polyurethane structure in a fibrous base material, there is another proposed technique in which a dispersion liquid of water-dispersed polyurethane containing an association type viscosity improver is added to a fibrous base material, which is then subjected to wet-heat coagulation, thereby producing a porous structure from water-dispersed polyurethane (see Patent document 2). In this proposal, too, water-dispersed polyurethane is made porous so that the contact area between the fiber and the polyurethane decreases to weaken the force to hold fiber entanglement, thereby providing a sheet-like article having a good texture with soft feel. However, such texture still tends to be poor in softness compared to products produced from a base material containing a solution of polyurethane in an organic solvent.

Prior Art Documents

Patent Documents

5 [0011]

[Patent document 1] Japanese Unexamined Patent Publication (Kokai) No. 2011-214210

[Patent document 2] Japanese Patent No. 4042016

10 Problems to be Solved by the Invention

[0012] Thus, in view of the prior art background, an object of the present invention is to provide a sheet-like article that can be produced from an environment-friendly production process, compares favorably in terms of a uniform feel with artificial leather products produced from organic solvent based polyurethane, and has elegant surface quality and good texture, and also relates to a production method therefor.

[0013] Another object of the present invention is to provide a sheet-like article that contains a porous polyurethane structure produced from water-dispersed polyurethane and has fold and crease recoverability and flexibility equivalent to those of artificial leather products produced from solvent based polyurethane, and also relates to a production method therefor.

20 Means of Solving the Problems

[0014] The present invention aims to meet the above objectives and the sheet-like article according to the invention includes a fibrous base material formed of ultrafine fibers and/or ultrafine fiber bundles that contains, as a binder, a polymer elastomer having a hydrophilic group, any thickness-directional cross section of the sheet-like article containing regions occupied by the polymer elastomer, the regions including independent regions each with a cross-sectional area of $50 \mu\text{m}^2$ or more, the total area of the independent regions accounting for 0.1 % or more and 5.0% or less of the cross-sectional area of the artificial leather in an observation view field.

[0015] In a preferred embodiment of the sheet-like article according to the present invention, 1% or more and 35% or less of the circumferences of the cross sections of the ultrafine fibers and/or ultrafine fiber bundles observed in a cross section made by cutting the sheet-like article in the thickness direction are covered by film of the polymer elastomer.

[0016] Another preferred embodiment of the sheet-like article according to the present invention is a sheet-like article as described in either claim 1 or 2, wherein the polymer elastomer has a crosslinked structure formed by using a crosslinking agent.

[0017] The present invention aims to meet the above objectives and the production method for the sheet-like article according to the present invention provides a production process for a sheet-like article including a fibrous base material formed of ultrafine fibers and, as a binder, a polymer elastomer having a hydrophilic group, the process including a step for adding an aqueous resin dispersion liquid containing a water-dispersed polymer elastomer and a viscosity improver to a fibrous base material and a step for coagulating the polymer elastomer in hot water at a temperature of 50°C to 100°C .

[0018] In a preferred embodiment of the production method for the sheet-like article according to the present invention, the aqueous resin dispersion liquid shows non-Newtonian characteristics.

[0019] In a preferred embodiment of the production method for the sheet-like article according to the present invention, the viscosity improver is a nonionic type viscosity improver.

[0020] In a preferred embodiment of the production method for the sheet-like article according to the present invention, the aqueous resin dispersion liquid shows thixotropy.

[0021] In a preferred embodiment of the production method for the sheet-like article according to the present invention, the viscosity improver contained in the aqueous resin dispersion liquid is a polysaccharide viscosity improver.

[0022] In a preferred embodiment of the production method for the sheet-like article according to the present invention, the viscosity improver is guar gum.

[0023] In a preferred embodiment of the production method for the sheet-like article according to the present invention, the aqueous resin dispersion liquid contains a thermosensitive coagulant.

[0024] In a preferred embodiment of the production method for the sheet-like article according to the present invention, the aqueous resin dispersion liquid contains a crosslinking agent. Advantageous Effect of the Invention

[0025] According to the present invention, a porous structure can be developed from water-dispersed polyurethane using an environment-friendly production process to achieve fold and crease recoverability and flexibility closely equivalent to those of products produced from a fibrous base material containing organic solvent based polyurethane, making it possible to provide a sheet-like article containing raised hairs with a uniform length similar to those in artificial leather produced from organic solvent based polyurethane and having elegant surface quality with a dense fiber feel and good

texture with high flexibility and crease recoverability.

Brief Description of the Drawings

[0026]

[Fig. 1] Fig. 1 is a SEM photograph given as a substitute for a drawing of a cross section of the artificial leather prepared in Example 13 of the present invention.

[Fig. 2] Fig. 2 is a SEM photograph given as a substitute for a drawing of a cross section of the artificial leather prepared in Comparative example 4 of the present invention.

[Fig. 3] Fig. 3 is a SEM photograph given as a substitute for a drawing for showing an outline of the method for calculating the proportion accounted for by nonporous polymer elastomer masses each with a size of $50\text{ }\mu\text{m}^2$ or more.

[Fig. 4] Fig. 4 is a reference SEM photograph given as a substitute for a drawing for showing the method for calculating the polymer elastomer coverage in a cross section of an ultrafine fiber.

Description of Preferred Embodiments

[Regarding the sheet-like article]

[0027] The sheet-like article according to the present invention is described first.

[0028] The sheet-like article according to the present invention is produced from a fibrous base material, such as nonwoven fabric, formed of ultrafine fibers and contains, as a binder, a polymer elastomer formed of resin having a hydrophilic group, such as water-dispersed polyurethane.

[0029] As the fiber that constitutes the fibrous base material, it is possible to employ a fiber made up of a melt-spinnable thermoplastic resin such as polyesters, including polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, and polylactic acid, polyamides, including 6-nylon and 66-nylon, and others including acryl, polyethylene, polypropylene, and thermoplastic cellulose fibers. Particularly, it is preferable to use polyester fibers from the viewpoint of strength, dimensional stability, and light resistance. Furthermore, the fibrous base material may be composed of a mixture of fibers of different materials.

[0030] As for the cross-sectional shape of the ultrafine fibers, a circular cross section is suitable though fibers having cross sections of non-circular shapes such as an ellipse, flat shape, polygon such as triangle, fan, and cross may also be adopted.

[0031] The average single fiber diameter of the ultrafine fibers constituting a fibrous base material is preferably 0.1 to $7\text{ }\mu\text{m}$. Controlling the average single fiber diameter at preferably $7\text{ }\mu\text{m}$ or less, more preferably $6\text{ }\mu\text{m}$ or less, and still more preferably $5\text{ }\mu\text{m}$ or less, makes it possible to obtain a sheet-like article having high softness and good raised hair quality. On the other hand, controlling the average single fiber diameter at preferably $0.1\text{ }\mu\text{m}$ or more, more preferably $0.3\text{ }\mu\text{m}$ or more, still more preferably $0.7\text{ }\mu\text{m}$ or more, and particularly more preferably $1\text{ }\mu\text{m}$ or more, ensures high post-dyeing color development performance, high fiber dispersibility during hair raising treatment by grinding with sandpaper or the like, and easy untangling.

[0032] As for the configuration of a fibrous base material formed of ultrafine fibers, it is possible to adopt a fibrous base material in the form of woven, knitted, nonwoven fabric or the like. Among others, the use of nonwoven fabric is preferable because the sheet-like article will have good surface quality after being subjected to surface hair raising treatment.

[0033] As the nonwoven fabric, either short-fiber nonwoven fabric or long-fiber nonwoven fabric may be used, but from the viewpoint of texture and quality, the use of short-fiber nonwoven fabric is preferable.

[0034] The short fibers in the short-fiber nonwoven fabric preferably have a fiber length of 25 mm or more and 90 mm or less, more preferably 35 mm or more and 75 mm or less. Controlling the fiber length at 25 mm or more makes it possible to obtain a sheet-like article having high abrasion resistance attributed to entanglement. Furthermore, controlling the fiber length at 90 mm or less makes it possible to obtain a sheet-like article with improved texture and quality.

[0035] In the case of a nonwoven fabric formed of a fibrous base material of ultrafine fibers, the nonwoven fabric preferably has a structure formed of bundles of ultrafine fibers (fiber bundles) that are entangled together. The entanglement of bundles of ultrafine fibers allows the sheet-like article to have improved strength. Such a nonwoven fabric can be produced by entangling ultrafine fiber-developing type fibers first and then converting them into ultrafine fibers.

[0036] In the case of a nonwoven fabric formed of ultrafine fibers or bundles thereof, woven or knitted fabrics may be added into the nonwoven fabric with the aim of, for example, increasing the strength. Fibers constituting such woven or knitted fabrics preferably have an average single fiber diameter of about 0.1 to $10\text{ }\mu\text{m}$.

[0037] For the sheet-like article according to the present invention, useful hydrophilic group containing resins, or elastic polymers, that can be used as a binder include water-dispersed silicone resins, water-dispersed acrylic resins, and

water-dispersed urethane resins, and copolymers thereof, of which water-dispersed polyurethanes are preferable from the viewpoint of texture.

[0038] The polyurethane is preferably a resin produced through reaction among a polymeric polyol having a number average molecular weight of preferably 500 or more and 5,000 or less, an organic polyisocyanate, and a chain extender. In addition, a compound containing an active hydrogen component having a hydrophilic group may be combined to increase the stability of the water-dispersed polyurethane dispersion liquid. The use of a polymeric polyol having a number average molecular weight of 500 or more, more preferably 1,500 or more, prevents the texture from stiffening, and the use of one having a number average molecular weight of 5,000 or less, more preferably 4,000 or less, serves to maintain a strength required for a polyurethane binder.

[0039] Of the polymeric polyols described above, useful polyether based polyols include those produced by addition and polymerization of such monomers as ethylene oxide, propylene oxide, butylene oxide, styrene oxide, tetrahydrofuran, epichlorohydrin, and cyclohexylene, using a polyhydric alcohol, polyamine, or the like as initiator, and those produced by ring opening polymerization of the monomers listed above using a catalyst such as proton acid, Lewis acid, and cationic catalyst. Specific examples include polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and copolymer polyols produced by combination thereof.

[0040] Useful polyester based polyols include, for example, polyester polyols produced by condensation of a low molecular weight polyol and a polybasic acid, and polyols produced by ring opening polymerization of a lactone or the like.

[0041] Such low molecular weight polyols include 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 divalent alcohols such as 1,4-bis(β -hydroxyethoxy) benzene, which may be used singly or as a combination of two or more thereof. Furthermore, an adduct which is formed by adding one of various alkylene oxides to bisphenol A may also be used as the low molecular weight polyol.

[0042] Furthermore, for example, one or a plurality selected from the following can be used as the polybasic acid: succinic acid, maleic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecane dicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and hexahydroisophthalic acid.

[0043] Useful polylactone polyols include those polylactone polyols produced from one or a plurality selected from γ -butyrolactones, γ -valerolactones, and ϵ -caprolactones by ring opening polymerization using a polyhydric alcohol as initiator.

[0044] Useful polycarbonate based polyols include compounds produced through reaction between a polyol and a carbonate compound such as dialkyl carbonate and diaryl carbonate.

[0045] Polyols useful as material for producing a polycarbonate polyol include those polyols listed previously as material for producing polyester polyol. Useful dialkyl carbonates include dimethyl carbonate and diethyl carbonate and useful diaryl carbonates include diphenyl carbonate.

[0046] For the polymer elastomers containing a hydrophilic group to be used for the present invention, suitable components used to add a hydrophilic group to a polymer elastomer include, for example, hydrophilic group-containing active hydrogen components. Such hydrophilic group-containing active hydrogen components include compounds that contain a nonionic group and/or anionic group and/or cationic group and an active hydrogen. Such compounds having a nonionic group and an active hydrogen include those compounds having two or more active hydrogen components or two or more isocyanate groups and having a side chain that contains a polyoxyethylene glycol group with a molecular weight of 250 to 9,000, as well as triols such as trimethylolpropane and trimethylolbutane.

[0047] Such compounds having an anionic group and an active hydrogen include carboxyl group-containing compounds such as 2,2-dimethylol propionic acid, 2,2-dimethylol butane acid, 2,2-dimethylol valeric acid, and derivatives thereof; sulfonic group-containing compounds such as 1,3-phenylene diamine-4,6-disulfone acid, 3-(2,3-dihydroxypropoxy)-1-propane sulfonic acid, and derivatives thereof; and salts produced by neutralizing these compounds with a neutralization agent.

[0048] Such compounds containing a cationic group and an active hydrogen include tertiary amino group-containing compounds such as 3-dimethyl aminopropanol, N-methyl diethanolamine, N-propyl diethanolamine, and derivatives thereof.

[0049] These active hydrogen components containing a hydrophilic group may be used in the form of salts after neutralization with a neutralization agent.

[0050] From the viewpoint of mechanical strength and dispersion stability of polyurethane resin, the hydrophilic group-containing active hydrogen component of the polyurethane molecule is preferably 2,2-dimethylol propionic acid, 2,2-dimethylol butanic acid, or a neutralized salt thereof.

[0051] If a hydroxyl group, sulfonic group, carboxyl group, etc., selected particularly from the aforementioned hydrophilic group containing active hydrogen components, are introduced into polyurethane, it serves not only to enhance the hydrophilicity of the polyurethane molecule, but if a crosslinking agent as described later is added, it also serves to improve the physical properties by allowing the polyurethane molecule to form a three dimensional crosslinked structure.

For the production, therefore, it is preferable to use an appropriate one selected from the aforementioned hydrophilic group containing active hydrogen components

[0052] Useful chain extenders include those compounds used in conventional polyurethane production processes and in particular, it is preferable to use a low molecular weight compound containing, in its molecule, two or more active hydrogen atoms that can react with an isocyanate group and having a molecular weight of 600 or less. Specific examples include diols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, 1,4-cyclohexanediol, and xylylene diglycol; triols such as trimethylolpropane and trimethylol butane; diamines such as hydrazine, ethylene diamine, isophorone diamine, piperazine, 4,4'-methylene dianiline, tolylene diamine, xylylene diamine, hexamethylene diamine, and 4,4'-dicyclohexylmethane diamine; triamines such as diethylene triamine; and aminoalcohols such as aminoethyl alcohol and aminopropyl alcohol.

[0053] Useful organic polyisocyanates include aliphatic diisocyanates such as hexamethylene diisocyanate; alicyclic diisocyanates such as isophorone diisocyanate (hereinafter occasionally abbreviated as IPDI), hydrogenated xylylene diisocyanate, and dicyclohexylmethane diisocyanate (hereinafter occasionally abbreviated as MDI); aromatic/aliphatic diisocyanates such as xylylene diisocyanate (hereinafter occasionally abbreviated as XDI) and tetramethyl-m-xylylene diisocyanate; and aromatic diisocyanates such as tolylene diisocyanate (hereinafter occasionally abbreviated as TDI), 4,4'-diphenyl methane diisocyanate (hereinafter occasionally abbreviated as MDI), tolidine diisocyanate, and naphthalene diisocyanate (hereinafter occasionally abbreviated as NDI).

[0054] Introducing a sulfonic group, a carboxyl group, a hydroxyl group, or a primary or secondary amino group into the polyurethane to be used for the present invention and adding a crosslinking agent reactive to these functional group into a dispersion liquid of the polyurethane serve to produce a resin that has an increased molecular weight and an increased crosslink density after reaction. Accordingly, the durability, weather resistance, heat resistance, and wet strength retention rate can be further improved.

[0055] Useful crosslinking agents include those having, in one molecule, two or more reactive groups that can react with the reactive groups introduced into the polyurethane. Specific examples of such crosslinking agents include polyisocyanate based crosslinking agents such as water-soluble isocyanate compounds and blocked isocyanate compounds, melamine based crosslinking agents, oxazoline based crosslinking agents, carbodiimide based crosslinking agents, aziridine based crosslinking agents, epoxy crosslinking agents, and hydrazine based crosslinking agents. These crosslinking agents may be used singly or as a combination of two or more thereof.

[0056] A water-soluble isocyanate based compound contains a two or more isocyanate groups in a molecule, and examples include the aforementioned organic polyisocyanate-containing compounds. Commercial products include the Bayhydur (registered trademark) series and the Desmodur (registered trademark) series manufactured by Bayer MaterialScience.

[0057] A blocked isocyanate based compound contains a two or more blocked isocyanate groups in a molecule. A blocked isocyanate group is produced by blocking an organic polyisocyanate compound as described above with a blocking agent, which is, for example, an alcohol, amine, phenol, imine, mercaptan, pyrazole, oxime, or active methylene. Commercial products thereof include the Elastron (registered trademark) series manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd., the Duranate (registered trademark) series manufactured by Asahi Kasei Chemicals Corporation, and the Takenate (registered trademark) series manufactured by Mitsui Chemicals, Inc.

[0058] Useful melamine based crosslinking agents include compounds containing two or more methylol groups or methoxy methylol groups in a molecule. Commercial products thereof include the Yuban (registered trademark) series manufactured by Mitsui Chemicals, Inc., the Cymel (registered trademark) series manufactured by Nihon Cytec, and the Sumimal (registered trademark) series manufactured by Sumitomo Chemical Co., Ltd.

[0059] Useful oxazoline based crosslinking agents include compounds containing two or more oxazoline groups (oxazoline backbone) in a molecule. Commercial products thereof include the Epocros (registered trademark) series manufactured by Nippon Shokubai Co., Ltd. Useful carbodiimide based crosslinking agents include compounds containing two or more carbodiimide groups in a molecule. Commercial products thereof include the Carbodilite (registered trademark) series manufactured by Nisshinbo Industries, Inc.

[0060] Useful epoxy based crosslinking agents include compounds containing two or more epoxy groups in a molecule. Commercial products thereof include the Denacol (registered trademark) series manufactured by Nagase ChemteX Corporation, diepoxy-polyepoxy based compounds manufactured by Sakamoto Yakuin Kogyo Co., Ltd., and the Epicron (registered trademark) series manufactured by DIC.

[0061] Useful aziridine based crosslinking agents include compounds containing two or more aziridinyl groups in a molecule. Useful hydrazine based crosslinking agents include hydrazine and compounds containing two or more hydrazine groups (hydrazine backbone) in a molecule.

[0062] Among others, preferable functional groups contained in polyurethane include hydroxyl group and/or carboxyl group and/or sulfonic group, and preferable crosslinking agents include polyisocyanate based crosslinking agents and carbodiimide compounds. Furthermore, the combined use of a carbodiimide compound and a polyisocyanate based crosslinking agent enhances the crosslinked structure of the polyurethane resin and in addition, enhances the moist

heat resistance improving effect while maintaining flexibility.

[0063] Water-dispersed polyurethane compounds generally contain a hydrophilic group in the molecular structure and accordingly, they are higher in affinity with water molecules and more liable to swelling and relaxation of the polyurethane's molecular structure in a wet environment than conventional organic solvent based polyurethanes. In a wet environment, therefore, they tend to fail to maintain good physical properties that they have in a dry environment. Compared to this, the use of the aforementioned crosslinking agents serves to enhance the moist heat resistance improving effect, making it possible to provide a sheet with high tensile strength in a wet environment. As a result, structural changes of the polyurethane molecule likely to be caused by water in the dyeing step can be depressed and the morphological stability of the sheet-like article and strong contact between polyurethane and fibrous base material can be maintained, thereby achieving high quality with good physical properties and a uniform feel.

[0064] Carbodiimide crosslinking agents show high crosslinking reactivity at low temperatures of 100°C or less and they are adopted favorably from the viewpoint of productivity. Besides reacting mainly with the hydroxyl group, the isocyanate compound and/or blocked isocyanate compound react actively with the urethane bond and/or urea bond in the hard segment (HS) part in polyurethane at high temperatures, particularly in the temperature range of 120°C or more and 200°C or less, preferably in the temperature range of 140°C or more and 200°C or less, to form an allophanate bond or burette bond, leading to the development of a stronger crosslinked structure and a distinct microphase separation structure of polyurethane.

[0065] It is preferable for the polyurethane film according to the present invention to have a storage elastic modulus E' of 1 to 100 MPa, more preferably 2 to 50 MPa, at a temperature of 20°C from the viewpoint of flexibility and impact resilience. The loss elastic modulus is preferably 0.1 MPa to 20 MPa, more preferably 0.5 MPa to 12 MPa. Furthermore, $\tan\delta$ is preferably 0.01 to 0.4, more preferably 0.02 to 0.35.

[0066] For the present invention, the storage elastic modulus E' and $\tan\delta$ are determined for a polyurethane film (film) with a film thickness of 200 μm using a storage elastic modulus measuring apparatus (DMA7100, manufactured by Hitachi High-Tech Science Corporation) at a frequency of 12 Hz. Here, $\tan\delta$ is calculated as E''/E' (E'' represents the loss elastic modulus).

[0067] E' indicates the elastic nature of polyurethane resin. The fold and crease recoverability of a sheet-like article decreases with a decreasing E' while the texture of the sheet-like article deteriorates with an increasing E' .

[0068] On the other hand, $\tan\delta$, which is calculated as E''/E' (where E'' is the loss elastic modulus and represents the viscosity), means the proportion of the viscosity relative to that of the polyurethane. As in the case of E' , the fold and crease recoverability of a sheet-like article decreases with a decreasing $\tan\delta$ while the texture of the sheet-like article becomes stiffer with an increasing E' .

[0069] It is preferable that the density of the sheet-like article according to the present invention is 0.2 to 0.7 g/cm^3 . The density is more preferably 0.2 g/cm^3 or more and still more preferably 0.25 g/cm^3 or more. A density of 0.2 g/cm^3 or more ensures a dense surface appearance and high quality. On the other hand, if a sheet-like article has a density of preferably 0.7 g/cm^3 or less, more preferably to 0.6 g/cm^3 or less, it serves to prevent the texture of the sheet-like article from becoming stiff.

[0070] It is preferable for the polyurethane in the sheet-like article according to the present invention to account for 10% to 80% by mass. If the content of the polyurethane is 10 mass% or more, more preferably 15 mass% or more, a sufficient sheet strength can be obtained and fibers can be prevented from falling off. Furthermore, if the content of the polyurethane is 80% by mass or less, more preferably 70% by mass or less, the texture can be prevented from becoming stiff and good raised hair quality can be obtained.

[0071] For the sheet-like article according to the present invention, a porous structure is produced from water-dispersed polyurethane (elastic polymer) and high fold and crease recoverability and flexibility closely equivalent to those of artificial leather products produced from solvent based polyurethane is realized by adopting an elastic polymer such as water-dispersed polyurethane, preparing a liquid by adding a viscosity improver to an aqueous dispersion of the water-dispersed polyurethane and other components, and coagulating it in hot water.

[0072] Thus, the present invention aims to provide a sheet-like article comprising a fibrous base material formed of ultrafine fibers and/or ultrafine fiber bundles provided with, as a binder, a polymer elastomer having a hydrophilic group, any thickness-directional cross section of the sheet-like article containing regions occupied by the polymer elastomer, the regions including independent regions each with a cross-sectional area of 50 μm^2 or more, the total area of the independent regions accounting for 0.1% or more and 5.0% or less of the cross-sectional area of the artificial leather in an observation view field.

[0073] In a preferred embodiment, the present invention provides a sheet-like article that includes a fibrous base material formed of ultrafine fibers and/or ultrafine fiber bundles and, as a binder, a polymer elastomer having a hydrophilic group, wherein 1 % or more and 35% or less of the circumferences of the cross sections of the ultrafine fibers and/or ultrafine fiber bundles observed in a cross section made by cutting the sheet-like article in the thickness direction is covered by film of the polymer elastomer.

[Method for producing sheet-like articles]

[0074] Described below are production methods for the sheet-like article according to the present invention.

[0075] As the fibrous base material for use in the invention, fabrics such as woven fabric, knitted fabric, and nonwoven fabric can be adopted favorably. Among others, the use of nonwoven fabric is preferable because the sheet-like article will have good surface quality after being subjected to surface hair raising treatment. The fibrous base material for use in the invention may be a laminate containing layers of these woven fabric, knitted fabric, and nonwoven fabric.

[0076] The nonwoven fabric for use in the invention may be either short-fiber nonwoven fabric or long-fiber nonwoven fabric, but short-fiber nonwoven fabric is preferred because good surface quality attributed to raised hairs with a uniform length is obtained.

[0077] The short fibers in the short-fiber nonwoven fabric preferably have a fiber length of 25 mm to 90 mm, more preferably 35 mm to 75 mm. A fiber length of 25 mm or more makes it possible to obtain a sheet-like article that has high abrasion resistance due to entanglement. Furthermore, controlling the fiber length at 90 mm or less makes it possible to obtain a sheet-like article with further improved quality.

[0078] As the fiber that constitutes the fibrous base material, it is possible to employ a fiber made up of a melt-spinnable thermoplastic resin such as polyesters such as polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, and polylactic acid; polyamides such as 6-nylon and 66-nylon; and others such as acryl, polyethylene, polypropylene, and thermoplastic cellulose. Particularly, it is preferable to use polyester fibers from the viewpoint of strength, dimensional stability, and light resistance. Furthermore, the fibrous base material may be composed of a mixture of fibers of difference materials.

[0079] The cross-sectional shape of fiber used for the present invention may be circular, and it also may be a deformed shape such as ellipse, flat, polygonal such as triangular, fan-shaped and cross.

[0080] The average fiber diameter of the fibers constituting a fibrous base material is preferably 0.1 to 7 μm , more preferably 0.3 to 5 μm . An average fiber diameter of the fibers of 7 μm allows the fibrous base material to have a more flexible feel. An average fiber diameter of the fibers of 0.1 μm or more, on the other hand, ensures improved color development after dyeing.

[0081] In the case where the fibrous base material used for the present invention is a nonwoven fabric, it is preferable to combine a woven fabric or a knitted fabric with the nonwoven fabric in order to improve strength and the like. The combination of the nonwoven fabric with a woven fabric or knitted fabric may be achieved by laminating the nonwoven fabric with a woven fabric or knitted fabric, or inserting a woven fabric or knitted fabric into the nonwoven fabric. Among others, it is preferable to use a woven fabric from the viewpoint of expected improvement in morphological stability and resistance.

[0082] Single yarns (warp and weft) that constitute the woven fabric or knitted fabric may be those of synthetic fiber such as polyester fiber and polyamide fiber, but they are preferably threads of the same fiber material as the ultrafine fibers that finally constitute the cloth such as nonwoven fabric.

[0083] With respect to the type of these single yarns, they may be filament yarns or spun yarns, and they are preferably in a hard twist form. In particular, the use of filament yarns is preferable because spun yarns are likely to suffer a loss of surface fuzzing.

[0084] When hard twist yarns are to be used, their twist count is preferably 1,000 T/m or more and 4,000 T/m or less, more preferably 1,500 T/m or more and 3,500 T/m or less. If the twist count is less than 1,000 T/m, the hard twist yarns will suffer more frequent breakage of constituent single fibers during the needle punching treatment, leading to products with deteriorated physical characteristics and exposure of many single fibers exposed from the product surface. If the twist count is more than 4,000 T/m, on the other hand, breakage of single fibers can be depressed, but the hard twist yarns that constitute the woven fabric or knitted fabric will become too stiff, tending to results in a hard texture.

[0085] For the invention, furthermore, the use of ultrafine fiber-developing type fibers as fibrous base material is preferable. The use of ultrafine fiber-developing type fibers in fibrous base material serves for stable formation of entangled bundles of the ultrafine fibers described above.

[0086] In the case where the fibrous base material is a nonwoven fabric, it is preferable for the nonwoven fabric to have a structure formed by the entanglement of bundles (fiber bundles) of ultrafine fibers. The entanglement of bundles of ultrafine fibers allows the sheet-like article to have improved strength. Such a nonwoven fabric can be produced by entangling ultrafine fiber-developing type fibers first and then converting them into ultrafine fibers.

[0087] Adoptable ultrafine fiber-developing type fibers include: island-in-sea type composite ones produced by using two thermoplastic resins different in solubility in a solvent as sea component and island component and dissolving and removing the sea component by using a solvent or the like to allow the island component to be left to form ultrafine fibers; and splittable type composite ones produced by alternately disposing two thermoplastic resins, radially or in layers, in the cross section thereof and splitting and separating the two components to form ultrafine fibers.

[0088] In particular, island-in-sea type composite fibers are preferred from the viewpoint of the flexibility and texture of the resulting sheet-like article because the removal of the sea regions will leave moderate gaps among island regions,

i.e., among ultrafine fibers.

[0089] Island-in-sea type composite fibers include island-in-sea type composite fibers produced by using a spinneret designed for island-in-sea type composite fibers to spin fibers in which two components, i.e. sea and island, are mutually arrayed, and blend-spun fibers produced by spinning a mixture of two components for sea and island, of which the island-in-sea type composite fibers have been used favorably because they can serve to produce ultrafine fibers with uniform fineness and also produce ultrafine fibers with an adequate length to ensure the production of a sheet-like article with increased strength.

[0090] Usable materials for the sea component of island-in-sea type composite fibers include polyethylene, polypropylene, polystyrene, polyester copolymers of sodium sulfoisophthalic acid, polyethylene glycol, or the like, polylactic acid, and polyvinyl alcohol. Particularly preferable are copolymerized polyester and polylactic acid produced from, for example, sodium sulfoisophthalic acid and polyethylene glycol, both of which are alkali resolvable and capable of being decomposed without using an organic solvent, and also preferable is polyvinyl alcohol that is soluble in hot water.

[0091] With respect to the ratio (proportion) between the sea component and the island component in island-in-sea type composite fiber, it is preferable for the island fiber to account for 0.2 to 0.9 by mass, more preferably 0.3 to 0.8, of the island-in-sea type composite fiber. If the mass ratio between the sea component and the island component is 0.2 or more, this ensures a small sea component removal ratio and leads to improved productivity. If the mass ratio is 0.9 or less, the fiber-opening capability of the island fiber will improve, and confluence of streams of the island component can be prevented. The number of island component streams can be controlled by appropriately adjusting the spinneret design.

[0092] The maximum diameter of each single fiber that constitutes the ultrafine fiber-developing type fiber, such as island-in-sea type composite fiber, is preferably 5 to 80 μm , more preferably 10 to 50 μm . If the maximum diameter of each single fiber is less than 5 μm , the fiber will be low in strength and tends to suffer single fiber breakage during treatment steps such as needle punching as described later. If the maximum diameter of each single fiber is less than 80 μm , on the other hand, treatment steps such as needle punching may fail to produce entanglement efficiently.

[0093] Usable methods for obtaining a nonwoven fabric to be used as fibrous base material for the present invention include the method of entangling a fiber web by needle punching or water jet punching, as well as the spun-bond method, melt-blow method, paper making method. In particular, methods containing a needle punching or water jet punching step are used favorably in order to obtain such ultrafine fiber bundles as described above.

[0094] To produce an integrated laminate of a woven fabric or knitted fabric and a nonwoven fabric to be used as fibrous base material, needle punching treatment, water jet punching treatment, etc., are used favorably from the viewpoint of efficient entanglement of fibers. In particular, needle punching treatment is used favorably from the viewpoint of orienting the fibers in the vertical direction of the fibrous base material regardless of the thickness of the sheet.

[0095] The needle used for needle punching treatment preferably has 1 to 9 barbs. The use of at least one needle barb allows fibers to be entangled efficiently. The use of 9 or less needle barbs, on the other hand, prevents fibers from being damaged significantly. The use of more than 9 needle barbs will lead to significant fiber damage and deterioration in product appearance due to needle marks left on the fibrous base material.

[0096] If a nonwoven fabric is to be integrated with a woven fabric or knitted fabric by entanglement, it is preferable for the nonwoven fabric to have preliminary entanglement, which serves to prevent significant crease generation when combining the nonwoven fabric with a woven fabric or knitted fabric by needle punching treatment. If such preliminary entanglement by needle punching treatment is adopted, it is effective when performed with a punching density of 20 punches/cm² or more. It is preferable for the preliminary entanglement to be performed with a punching density of 100 punches/cm² or more, and it is more preferable for the preliminary entanglement to be performed with a punching density of 300 punches/cm² to 1,300 punches/cm².

[0097] This is because if the punching density preliminary entanglement is less than 20 punches/cm², the width of the nonwoven fabric can be decreased during the steps of entanglement with a woven fabric or knitted fabric and subsequent needle punching treatment, possibly making it impossible to obtain a fibrous base material with a smooth surface due to creases in the woven fabric or knitted fabric attributable to changes in the width. If the punching density preliminary entanglement is more than 1,300 punches/cm², on the other hand, the entanglement in the nonwoven fabric itself proceeds to an excessive degree and the fibers will not be able to move easily to realize sufficient entanglement with the fibers in the woven fabric or knitted fabric, which is disadvantageous for achieving a perfectly integrated structure in which the nonwoven fabric and the woven fabric or knitted fabric are entangled strongly.

[0098] When fibers are entangled by needle punching treatment for the present invention, the punching density is preferably in the range of 300 punches/cm² to 6,000 punches/cm², more preferably 1,000 punches/cm² to 3,000 punches/cm², regardless of whether a woven fabric or knitted fabric exists or not.

[0099] To get a nonwoven fabric entangled with a woven fabric or knitted fabric, woven fabric or knitted fabric layers are laid over one or both sides of the nonwoven fabric, or woven fabric or knitted fabric layers are inserted between a plurality of nonwoven fabric layers, followed by needle punching to cause entanglement of fibers to provide a fibrous base material.

[0100] When performing water jet punching, it is preferable to use water in a columnar form. Specifically, water is preferably squirted through a nozzle with a diameter of 0.05 to 1.0 mm under a pressure of 1 to 60 MPa.

[0101] The nonwoven fabric formed of ultrafine fiber-generating type fibers processed by needle punching or water jet punching preferably has an apparent density of 0.13 to 0.45 g/cm³, more preferably 0.15 to 0.30 g/cm³. An apparent density of 0.13 g/cm³ or more makes it possible to produce artificial leather having sufficiently high morphological stability and dimensional stability. An apparent density of 0.45 g/cm³ or less, on the other hand, serves to maintain adequate spaces to accommodate a polymer elastomer.

[0102] The thickness of the fibrous base material is preferably 0.3 mm or more and 6.0 mm or less, more preferably 1.0 mm or more and 3.0 mm or less. If the thickness of the fibrous base material is less than 0.3 mm, the resulting sheet-like article may suffer from poor morphological stability. A thickness of more than 6.0 mm tends to lead to frequent occurrence of needle breakage in the needle punching step.

[0103] To ensure a denser surface, the nonwoven fabric formed of ultrafine fiber-generating type fibers obtained as described above may be shrunk by dry heat and/or wet heat to achieve a higher fiber density.

[0104] When using island-in-sea type composite fiber, the sea removal treatment intended to remove the sea component from the fiber may be performed either before or after adding a water-dispersed polyurethane dispersion liquid, which contains water-dispersed polyurethane, to the fibrous base material. If the sea removal treatment is carried out before the addition of the water-dispersed polyurethane dispersion liquid, the abrasion resistance of the sheet-like article increases because a structure in which the water-dispersed polyurethane adheres directly to the ultrafine fibers is easily formed so that the ultrafine fibers can be firmly held.

[0105] On the other hand, if inhibitory agents such as cellulose derivatives and polyvinyl alcohol (hereinafter occasionally abbreviated as PVA) are added together with ultrafine fibers before adding a water-dispersed polyurethane dispersion liquid, followed by adding a water-dispersed polyurethane dispersion liquid, the contact between the ultrafine fibers and polyurethane resin can be weakened to achieve a more flexible texture.

[0106] The aforementioned addition of inhibitory agents may be performed either before or after subjecting the sea-island structure fiber to sea removal treatment. The addition of inhibitory agents before sea removal treatment works to enhance the morphology retention capability of the fibrous base material even if the metsuke (weight per unit surface area) of the fiber decreases to cause a decline in the tensile strength of the sheet. Accordingly, this ensures not only stable processing of thin sheets, but also an increase in thickness retention capability of the fibrous base material during the sea removal treatment step, serving to prevent the density of the fibrous base material from increasing. On the other hand, adding inhibitory agents after sea removal treatment works to increase the density of the fibrous base material. Either of the procedures should be adopted to meet particular purposes.

[0107] PVA is used favorably as an inhibitory agent because it serves effectively to reinforce the fibrous base material and will not be dissolved easily in water. Of the various types of PVA, particularly preferable is the use of a highly saponified, water-insoluble PVA because the inhibitory agent will not be dissolved easily in water when a water-dispersed polyurethane dispersion liquid is added and also because the contact between ultrafine fibers and polyurethane can be impeded effectively.

[0108] For the highly saponified PVA, the degree of saponification is preferably 95% or more and 100% or less, more preferably 98% or more and 100% or less. If the degree of saponification is 95% or more, the dissolution of the water-dispersed polyurethane dispersion liquid during its addition is depressed.

[0109] The PVA preferably has a degree of polymerization of 500 or more and 3,500 or less, more preferably 500 or more and 2,000 or less. If the degree of polymerization of the PVA is 500 or more, the highly saponified PVA will not undergo significant dissolution during the addition of the polyurethane dispersion liquid. If the degree of polymerization of the PVA is less than 3,500, on the other hand, the solution of highly saponified PVA will not become too high in viscosity and the addition of the highly saponified PVA to the fibrous base material can be performed stably.

[0110] The quantity of the PVA to be added is preferably 0.1 mass% to 80 mass%, more preferably 5 mass% or more 60 mass% or less, relative to the quantity of the fibrous base material that will remain in the final product. If the quantity of the highly saponified PVA added is 0.1 mass% or more, the morphological stability is maintained high during the sea removal treatment step and poor contact between ultrafine fibers and polyurethane can be prevented. If the quantity of the highly saponified PVA added is 80 mass% or less, the contact between ultrafine fibers and polyurethane will not become too poor and uniform raised hairs will be formed, serving to provide a product with uniform surface quality.

[0111] To add an inhibitory agent as described above to the fibrous base material, the process of dissolving the inhibitory agent in water, impregnating the fibrous base material with it, and heat-drying it is used favorably because this allows the inhibitory agent to be added uniformly. With respect to the drying temperature, a long drying time will be necessary if the temperature is too low whereas the inhibitory agent will be completely insolubilized and its removal by dissolution will become impossible if the temperature is too high. Accordingly, it is preferable for the drying temperature to be 80°C or more and 180°C or less, more preferably 110°C or more and 160°C or less. The drying time is preferably one minute or more and 30 minutes or less from the viewpoint of processability.

[0112] According to a preferred embodiment, dissolution and removal of the inhibitory agent is carried out by leaving

the fibrous base material containing the inhibitory agent in steam at a temperature of 100°C or more and in hot water at a temperature of 60°C or more and 100°C or less, followed by squeezing the liquid using a mangle or the like as required, to achieve dissolution and removal.

[0113] The sea removal treatment can be carried out by immersing the fibrous base material containing the island-in-sea composite fiber in a solvent and then squeezing the liquid. Solvents usable for dissolving the sea component include organic solvents such as toluene and trichloroethylene for a sea component of polyethylene, polypropylene, or polystyrene; alkaline solutions such as aqueous sodium hydroxide solution for a sea component of copolymerized polyester or polylactic acid; and hot water for a sea component of polyvinyl alcohol.

[0114] Described next is the polyurethane to be used as a polymer elastomer for the present invention.

[0115] If polyurethane is used in the form of particles to be dispersed in an aqueous medium, the hydrophilic group-containing active hydrogen component is preferably adopted as a component of the polyurethane from the viewpoint of dispersion stability of the polyurethane, and according to a more preferred embodiment, a neutralized salt should be used.

[0116] The neutralization agents that are usable for the neutralized salt of a compound containing a hydrophilic group and an active hydrogen include amine based compounds such as trimethylamine, triethylamine, and triethanolamine, and hydroxides such as sodium hydroxide and potassium hydroxide.

[0117] There are no specific limitations on the timing of adding a neutralization agent to be used for a hydrophilic group-containing active hydrogen component, and it may be added before or after the polyurethane polymerization step, before or after the aqueous medium dispersion step, etc., but from the viewpoint of the stability of the polyurethane in the aqueous dispersion liquid, it is preferable to add it before the step of dispersion in an aqueous medium or during the step of dispersion in an aqueous medium.

[0118] From the viewpoint of dispersion stability and water resistance of the polyurethane, the content of the hydrophilic group-containing active hydrogen component and/or salts thereof is preferably 0.005 to 30 mass%, more preferably 0.01 to 15 mass%, relative to the mass of the polyurethane.

[0119] If polyurethane is used in the form of particles to be dispersed in an aqueous medium, a surface active agent, in addition to the aforementioned hydrophilic group-containing active hydrogen component, may be used as an external emulsifier for the polyurethane to allow the polyurethane to be dispersed in an aqueous medium.

[0120] Such surface active agents include nonionic surface active agents, anionic surface active agents, cationic surface active agents, and amphoteric surface active agents. These surface active agents may be used singly or as a combination of two or more thereof.

[0121] Useful nonionic surface active agents include alkylene oxide addition type ones such as polyoxyethylene nonylphenyl ether, polyoxyethylene dinonylphenyl ether, polyoxyethylene lauryl ether, and polyoxyethylene stearyl ether, and polyhydric alcohol type ones such as glycerin monostearate.

[0122] Useful anionic surface active agents include carboxylates, sulfate ester salts, sulfonates, and phosphate ester salts such as sodium laurate, sodium lauryl sulfate, lauryl ammonium sulfate, sodium dodecylbenzene sulfonate, and fatty alcohol sodium phosphate diester.

[0123] Useful cationic surface active agents include quaternary ammonium salts such as distearyl dimethylammonium chloride. Useful amphoteric surface active agents include methyl laurylaminopropionate, lauryl dimethylbetaine, and coconut fatty acid amidopropyldimethylamino acetic acid betaine.

[0124] A conventional polyurethane dispersion liquid production method may be applied to prepare a dispersion liquid of polyurethane to be used for the present invention. Available ones include, for example, a method in which a liquid polymer prepared by reacting a polyisocyanate, polyol, chain extender, and/or hydrophilic group-containing polyol as described above is emulsified in water in the presence of an emulsifier, a method in which a prepolymer having an isocyanate group at an molecular end is prepared by reacting a polyisocyanate, polyol, and/or chain extender, and/or hydrophilic group-containing polyol as described above and the prepolymer is then emulsified in water in the presence of an emulsifier, while or followed by completing the chain elongation reaction using a chain extender, and a method in which a polyisocyanate, polyol, and/or chain extender, and/or hydrophilic group-containing polyol as described above are reacted together and directly emulsified in water without using an emulsifier. When polymerization is performed without forming such a prepolymer or when polymerization of such a prepolymer is performed, it may be carried out in the absence of a solvent or may be carried out in the presence of an organic solvent such as methyl ethyl ketone, toluene, and acetone.

[0125] For example, a fibrous base material may be immersed in a water-dispersed polyurethane dispersion liquid containing the water-dispersed polyurethane synthesized above to add the polyurethane to the fibrous base material, followed by performing heat-drying to achieve coagulation and solidification.

[0126] For the present invention, a water-dispersed polyurethane dispersion liquid containing a viscosity improver as described above is added to a fibrous base material, and the water-dispersed polyurethane is coagulated in hot water preferably at a temperature of 50°C to 100°C, more preferably at a temperature of 60°C to 97°C, to produce a porous structure of polyurethane.

[0127] The immersion time in hot water is preferably 10 seconds or more and 5 minutes or less, more preferably 30

seconds or more and 3 minutes or less. Adjusting the immersion time in this range allows the polyurethane to be sufficiently coagulated.

[0128] If the hot water coagulation technique is used to coagulate the polyurethane as described above, the quantity of heat per unit time required for heating the polyurethane increases and accordingly the coagulation speed becomes faster. Then, the shift of the water-dispersed polyurethane dispersion liquid toward the fibrous base material decreases and accordingly, the adhesion between the fiber and polyurethane declines, leading to a flexible texture.

[0129] If a viscosity improver is combined with the water-dispersed polyurethane dispersion liquid, the polyurethane emulsion in the water-dispersed polyurethane dispersion liquid used to impregnate the fibrous base material suffers suppression of the Brownian movement under the influence of the viscosity of the liquid. Accordingly, the frequency of contact among emulsion particles decreases, making it possible to decrease the size of polyurethane masses in the coagulation step, thereby achieving a flexible texture. In addition, the dispersion liquid will not diffuse significantly in the hot water and the separation of polyurethane during the coagulation step can be depressed, serving to realize a coagulation process with a very high productivity.

[0130] If a dispersion liquid prepared by combining a viscosity improver with an aqueous dispersion liquid such as water-dispersed polyurethane is coagulated in hot water, the film coats of the water-dispersed polyurethane (elastic polymer) will become smaller to achieve a flexible texture. Furthermore, the polyurethane film coats that cover the fibrous base material become smaller in quantity to achieve a flexible texture.

[0131] Useful viscosity improvers to be added to the water-dispersed polyurethane dispersion liquid include nonionic, anionic, cationic, and amphoteric ones. Of these, the use of a nonionic viscosity improver is preferred.

[0132] Available viscosity improvers are divided into two groups: association type viscosity improvers and water-soluble polymer type viscosity improvers. Association type viscosity improvers include urethane modified compounds, acrylic modified compounds, and copolymer compounds thereof, and generally known association type viscosity improvers can be applied. Examples include urethane based association type viscosity improvers as disclosed in Japanese Unexamined Patent Publication (Kokai) No. 2003-292937, Japanese Unexamined Patent Publication (Kokai) No. 2001-254068, Japanese Unexamined Patent Publication (Kokai) No. SHO-60-49022, Japanese Unexamined Patent Publication (Kokai) No. 2008-231421, Japanese Unexamined Patent Publication (Kokai) No. 2002-069430, and Japanese Unexamined Patent Publication (Kokai) No. HEI-9-71766, and the association type viscosity improvers produced by copolymerization of urethane monomers and other acrylic monomers as disclosed in Japanese Unexamined Patent Publication (Kokai) No. SHO-62-292879 and Japanese Unexamined Patent Publication (Kokai) No. HEI-10-121030.

[0133] Useful water-soluble polymer compounds include natural polymer compounds, semisynthetic polymer compounds, and synthetic polymer compounds.

[0134] Useful natural polymer compounds include nonionic compounds such as tamarind gum, guar gum, roast bean gum, tragacanth gum, starch, dextrin, gelatin, agarose, casein, and curdian; anionic compounds such as xanthan gum, carrageenan, acacia gum, pectin, collagen, sodium chondroitin sulfate, sodium hyaluronate, carboxymethyl starch, and starch phosphate; and cationic compounds such as cation starch and chitosan.

[0135] Useful semisynthetic polymer compounds include nonionic compounds such as methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, ethyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose, soluble starch, and methyl starch, and anionic compounds such as carboxymethyl cellulose, carboxymethyl starch, and alginates.

[0136] Useful synthetic polymer compounds include nonionic compounds such as polyvinyl alcohol, polyacrylamide, polyvinyl pyrrolidone, polymethyl vinyl ether, polyethylene glycol, and polyisopropyl acrylamide; anionic compounds such as carboxyvinyl polymer, sodium polyacrylate, and sodium polystyrene sulfonate; and cationic compounds such as dimethylaminoethyl (meth)acrylate quaternary salts, dimethyldiallylammonium chloride, polyamidine, polyvinyl imidazoline, and polyethylene imine.

[0137] Preferable viscosity improvers for the present invention include nonionic viscosity improvers that do not have significant influence on the stability of the water-dispersed polyurethane dispersion liquid.

[0138] The water-dispersed polyurethane dispersion liquid that contains a viscosity improver preferably show non-Newtonian properties. If the water-dispersed polyurethane dispersion liquid is one that, in addition to being non-Newtonian, has a tendency to decrease in viscosity when receiving a force, its viscosity will decrease when a force is applied by, for example, stirring and accordingly, the fibrous base material will be able to be impregnated uniformly with the dispersion liquid. If it is left to stand after the impregnation, the original viscosity will be restored and the dispersion liquid infiltrated in the fibrous base material will not come off easily from the fibrous base material.

[0139] It is more preferable for the water-dispersed polyurethane dispersion liquid that contains a viscosity improver to show thixotropy. If the water-dispersed polyurethane dispersion liquid is thixotropic, its viscosity will decrease when a force is applied by, for example, stirring and accordingly, the fibrous base material will be able to be impregnated uniformly with the dispersion liquid. If it is left to stand after the application of a force, the original viscosity will be restored and the dispersion liquid infiltrated in the fibrous base material will not come off easily from the fibrous base material.

[0140] Useful viscosity improvers that have thixotropy include some selected appropriately from those listed above, but natural polymer compounds (polysaccharides) are used favorably because they are likely to have large viscosity

improving effect even when added in small amounts. More preferable viscosity improvers include guar gum, which is high in solubility in water, high in compatibility with water-dispersed polyurethane liquids, and high in thixotropy even when low in concentration.

[0141] An aqueous resin dispersion liquid containing a viscosity improver preferably has a viscosity of 200 mPa·s to 100,000 mPa·s, more preferably 200 mPa·s to 10,000 mPa·s, and still more preferably 200 mPa·s to 5,000 mPa·s. If the viscosity of the aqueous resin dispersion liquid is maintained at 200 mPa·s or more, the polyurethane can be prevented from falling off during the hot water coagulation step, while maintaining the viscosity at 100,000 mPa·s or less allows the water-dispersed polyurethane dispersion liquid to infiltrate uniformly in the fibrous base material.

[0142] The water-dispersed polyurethane dispersion liquid to be added to a fibrous base material preferably contain a thermosensitive coagulant from the viewpoint of depressing the migration of the polyurethane during the polyurethane coagulation step to allow the polyurethane to infiltrate uniformly in the fibrous base material.

[0143] Useful thermosensitive coagulants include inorganic salts such as sodium sulfate, magnesium sulfate, calcium sulfate, calcium chloride, magnesium chloride, and calcium chloride; and ammonium salts such as sodium persulfate, potassium persulfate, ammonium persulfate, and ammonium sulfate. They may be used singly or as a combination of two or more thereof in an appropriately adjusted amount. The water-dispersed polyurethane coagulation temperature is adjusted and then the water-dispersed polyurethane dispersion liquid is destabilized by heating so that it will be coagulated.

[0144] The aforementioned thermosensitive coagulation temperature of a water-dispersed polyurethane dispersion liquid is preferably 40°C to 90°C, more preferably 50°C to 80°C, from the viewpoint of storage stability and texture of the processed fiber product.

[0145] In addition to the crosslinking agents and thermosensitive coagulants described above, the polyurethane dispersion liquid may further contain other various additives as mentioned below.

[0146] Examples of these additives include pigments such as carbon black; weathering stabilization agents such as antioxidants (hindered phenolic based, sulfur based, and phosphorous based antioxidants), ultraviolet absorbers (benzotriazole based, triazine based, benzophenone based, and benzoate based ultraviolet absorbers), and hindered amine based photostabilizers; and others including flexible water repellent agents (polysiloxane, modified silicone oil, other silicone compounds, polymer based on fluoroalkyl esters of acrylic acids, and other fluorine compound based flexible water repellent agents), wetting agents (ethylene glycol, diethylene glycol, propylene glycol, glycerin, and other similar wetting agents), antifoam agents (octyl alcohol, sorbitan monooleate, polydimethyl siloxane, polyether modified silicone, and fluorine modified silicone, and other similar antifoam agents), fillers (fine particles of calcium carbonate, titanium oxide, silica, talc, ceramics, or resin, hollow beads, and other similar fillers), flame retardants (halogen based, phosphorus based, antimony based, melamine based, guanidine based, guanylurea based, silicone based, and other inorganic flame retardants), microballoons (such as Matsumoto Microsphere (registered trademark) manufactured by Matsumoto Yushi-Seiyaku Co., Ltd.), foaming agents [examples include dinitrosopentamethylene tetramine (such as Celmike A (registered trademark) manufactured by Sankyo Kasei Co., Ltd.), azodicarbonamide (such as Celmike CAP (registered trademark) manufactured by Sankyo Kasei Co., Ltd.), p,p'-oxy bisbenzenesulfonyl hydrazide (such as Celmike S (registered trademark) manufactured by Sankyo Kasei Co., Ltd.), N,N'-dinitrosopentamethylene tetramine (such as Cellular GX (registered trademark) manufactured by Eiwa Chemical Ind. Co., Ltd.), other organic foaming agents, sodium hydrogen carbonates (such as Celmike 266 (registered trademark) manufactured by Sankyo Kasei Co., Ltd.), and other inorganic foaming agents], 2,2'-azobis[2-methyl-N-(2-hydroxyethyl) propione amide] (such as VA-086 manufactured by Wako Pure Chemical Industries, Ltd.), viscosity adjustors, plasticizers (phthalic esters, adipic esters, etc.), and mold releasing agents (wax based, metal soap based, and their mixture based mold releasing agents).

[0147] According to a preferred embodiment, additional heating (for curing) is performed after the infiltration and coagulation of the water-dispersed polyurethane dispersion liquid in a fibrous base material, in order to promote the fusion bonding of the water-dispersed polyurethane emulsion and allow the polyurethane to form a proper molecular structure, thereby improving the moist heat resistance. Curing may be carried out by continuous coagulation and curing steps after infiltrating the water-dispersed polyurethane dispersion liquid in a fibrous base material, or by a separate curing step performed after infiltrating and coagulating the water-dispersed polyurethane dispersion liquid in a fibrous base material.

[0148] In regard to the drying temperature, a long drying time is required at low drying temperatures while heat decomposition of the polyurethane is accelerated at high temperatures, and therefore, the drying is performed preferably at a temperature of 80°C or more and 200°C or less, more preferably at 120°C or more and 190°C or less, still more preferably 150°C or more and 180°C or less.

[0149] From the viewpoint of processability, the drying time is preferably 1 minute or more and 60 minutes or less, more preferably 1 minute or more and 30 minutes or less. For the present invention, completing the curing step quickly at a high temperature ensures an increase in the flowability of the polyurethane molecules, an increase in the coagulation rate of the hard segment (HS) parts and the formation of a distinct microphase separation structure between the hard segment (HS) parts and the soft segment (SS) parts in the molecular structure which consists of hard segment (HS)

parts formed mainly of urethane groups and urea groups and soft segment (SS) parts formed mainly of polyol, which will lead to an improved moist heat resistance.

[0150] According to a preferred embodiment, after the addition of polyurethane, the resulting polyurethane-impregnated sheet-like article is divided into halves or a few parts in the sheet thickness direction, which ensures a high production efficiency.

[0151] Prior to the hair raising step described later, a lubricant such as silicone emulsion may be added to the polyurethane-impregnated sheet-like article. According to another preferred embodiment, an antistatic agent is added prior to the hair raising step so that the ground powder produced from the grinding of the sheet-like article is hindered from depositing on the sandpaper.

[0152] A hair raising step may be performed in order to raise hairs on the surface of the sheet-like article. The hair raising treatment can be performed by grinding with sandpaper, roll sander, or the like.

[0153] The thickness of the sheet-like article is preferably 0.1 to 5 mm because if the thickness is too small, physical characteristics such as tensile strength and tear strength of the sheet-like article will deteriorate whereas if the thickness is too large, the texture of the sheet-like article will become stiff.

[0154] The sheet-like article may be dyed. A preferable dyeing method is the use of a jet dyeing machine which has a kneading effect to soften the sheet-like article while drying the sheet-like article. The polyurethane may degrade if the dyeing temperature is too high whereas dyeing may not be achieved completely if it is too low, and therefore, it may be set appropriately depending on the type of the fiber. In general, the dyeing temperature is preferably 80°C or more and 150°C or less, more preferably 110°C or more and 130°C or less.

[0155] The dye to be used should be selected to meet the type of the fiber that constitutes the fibrous base material. For example, a dispersed dye may be used for a polyester-based fiber, and an acidic dye or a metal-containing dye may be used for a polyamide based fiber. Moreover, combinations of these dyes may also be employed. In the case where the sheet-like article is dyed with a dispersed dye, reduction cleaning may be performed after the dyeing.

[0156] According to another preferred embodiment, a dyeing assistant may be used in the dyeing step. The use of a dyeing assistant can serve to improve the dyeing uniformity and reproducibility. Furthermore, finishing with a softening agent, such as silicone, an antistatic agent, a water repellent, a flame retardant, a light resistance agent, an antimicrobial agent, etc. may be performed simultaneously with dyeing in the same bath or sequentially by adding them after the dyeing step.

[0157] The sheet-like article obtained according to the present invention can be suitably used mainly as artificial leather components of, for example, the following: furniture, chairs and wall materials; interior materials with highly graceful external appearance for surface decoration of seats, ceilings, interiors, etc. of vehicles including motor vehicles, trains, and aircraft; shirts, jackets, and uppers, trims, etc. of casual shoes, sports shoes, men's shoes, women's shoes, etc.; bags, belts, wallets, etc., and clothing materials used as parts thereof; and industrial use materials such as wiping clothes, grinding clothes, and CD curtains.

[Examples]

[0158] Hereinafter, the sheet-like materials according to the present invention and the method for production therefor are described in more detail with reference to Examples, although the present invention is not limited only to these Examples.

[Evaluation methods]

(1) Falling-off rate of polyurethane during coagulation:

[0159] The mass of the fibrous base material alone and the mass of the fibrous base material impregnated with a water-dispersed polyurethane dispersion liquid were measured, and the mass of solid polyurethane contained in the material that corresponds to the difference between the measurements was defined as polyurethane content A. Then, the aforementioned fibrous base material impregnated with a water-dispersed polyurethane dispersion liquid was subjected to a coagulation step using hot water or steam and a subsequent drying step, followed by measuring the mass difference from the fibrous base material to give polyurethane content B. The falling-off rate of polyurethane during coagulation is expressed by the following equation and the average of ten calculations made for different measuring points was used for evaluation.

$$\cdot \text{Falling-off rate of polyurethane (\%)} = \text{polyurethane content B} / \text{polyurethane content A} \times 100$$

(2) Measurement of viscosity of water-dispersed polyurethane dispersion liquid:

[0160] A water-dispersed polyurethane dispersion liquid was prepared and its viscosity was measured using a rotation viscometer (Brookfield type viscometer manufactured by Tokyo Keiki Inc.) under the conditions of an ambient temperature of 25°C and rotating speeds of 0.5 rpm and 10 rpm.

(3) External appearance quality of sheet-like article

[0161] The external appearance quality of a sheet-like article was rated on a scale of 1 to 5 based on visual inspection and sensory evaluation by a total of 20 raters made up of 10 males and 10 females who were both healthy adults. The rating given by the greatest number of raters was taken to represent the external appearance quality. For the external appearance quality, specimens rated as grade 4 or grade 5 were assumed to be acceptable.

Grade 5: Uniformly raised hairs were found and the dispersed state of fiber is good, resulting in a good external appearance.

Grade 4: This grade is between grade 5 and grade 4.

Grade 3: The dispersed state of fiber is partially not very good, but raised hairs were found, resulting in a fairly good external appearance.

Grade 2: This grade is between grade 3 and grade 1.

Grade 1: The dispersed state of fiber is very poor as a whole, and the external appearance is at rejectable level.

(4) Texture of sheet-like article

[0162] The texture of a sheet-like article was rated on a scale of 1 to 3 based on haptic sensory evaluation by a total of 20 raters made up of 10 males and 10 females who were both healthy adults. The rating given by the greatest number of raters was taken to represent the texture. Specimens having good texture (high in rubber elastic) were given the mark "◎".

◎: Higher in flexibility and crease recoverability than artificial leather products produced from an organic solvent based polyurethane and having the same level of metsuke.

○: Comparable in flexibility and crease recoverability to artificial leather products produced from an organic solvent based polyurethane and having the same level of metsuke.

×: The sheet is stiff and has a paper-like feel.

(5) Method for calculating the proportion accounted for by nonporous polymer elastomer masses each with a size of 50 μm^2 or more (parameter A)

[0163] A specimen of artificial leather was cut either in the length direction or in the width direction and the thickness-directional cross section of the artificial leather was observed by scanning electron microscopy (SEM) at a magnification of x500 to provide ten SEM images. An image analysis software program, namely, ImageJ (version 1.44p), developed by the National Institutes of Health in the U.S. was used to calculate the proportion of those nonporous polymer elastomer masses each with a size of 50 μm^2 or more among all the polyurethane masses observed in the cross section to the total cross section of the artificial leather contained in the field of view ($4.3 \times 10^4 \mu\text{m}^2$) in each SEM image, followed by calculating the average over the ten images, which was used for evaluation. Fig. 3 is a schematic diagram showing the calculation method for parameter A. Fig. 3 is a schematic diagram showing a polyurethane mass, referred to as mass 1, for parameter A. Mass 1 of polyurethane represents a cross-sectional polyurethane region (those parts behind the cross section are not included) observed in the cross section of the artificial leather specimen.

(6) Method for calculating the polymer elastomer coverage on the cross section of ultrafine fibers (parameter B):

[0164] A specimen of artificial leather was cut in the length direction or in the width direction and the thickness-directional cross section of the artificial leather obtained was observed by scanning electron microscopy (SEM) at a magnification of x500 to provide ten SEM images. An image analysis software program, namely, ImageJ (version 1.44p), developed by the National Institutes of Health in the U.S. was used to select five ultrafine fiber bundles that were observed to have been cut perpendicularly to the length direction of the fibers and calculate the proportion of the circumference of each ultrafine fiber bundle where it is in contact with resin film with a thickness of 1 μm or more. For the total of 50 observed ultrafine fibers (5×10 images), the average of the polymer elastomer coverage on the cross section was calculated for evaluation. Fig. 4 is a schematic diagram showing the calculation method for parameter B. For parameter B, Fig. 4 gives

a schematic diagram that shows the circumference (circumference 2) of an ultrafine fiber and/or ultrafine fiber bundle and the circumference (circumference 3) that is covered by the polymer elastomer film. The solid line part illustrates circumference 2 of an ultrafine fiber bundle and the dotted line part shows circumference 3 that is covered by the polymer elastomer film.

[Preparation of polyurethane liquid A]

[0165] A polycarbonate diol with a Mn of 2,000 [Duranol (registered trademark) T5652, manufactured by Asahi Kasei Chemicals Corporation] used as polyol, MDI as isocyanate, and 2,2-dimethylol propionic acid as the intramolecular hydrophilic group were reacted in a toluene solvent to prepare a prepolymer. Then, ethylene glycol and ethylene diamine used as chain extenders, polyoxyethylene nonylphenyl ether as external emulsifier, and water were added and stirred, followed by removal of toluene under reduced pressure to provide water-dispersed polyurethane dispersion liquid A.

[Preparation of polyurethane liquid B]

[0166] A polycarbonate diol with a Mn of 2,000 [Duranol (registered trademark) T6002, manufactured by Asahi Kasei Chemicals Corporation] used as polyol, IPDI as isocyanate, and a diol compound with a polyethylene glycol-containing side chain and 2,2-dimethylol propionic acid as the intramolecular hydrophilic groups were reacted in an acetone solvent to prepare a prepolymer. Then, ethylene glycol and ethylene diamine used as chain extenders, and water were added and stirred, followed by removal of acetone under reduced pressure to provide water-dispersed polyurethane dispersion liquid B.

[Preparation of polyurethane C]

[0167] A polycarbonate diol with a Mn of 2,000 [Duranol (registered trademark) T5652, manufactured by Asahi Kasei Chemicals Corporation] used as polyol, IPDI as isocyanate, and trimethylolpropane as the intramolecular hydrophilic group were reacted in a methyl ethyl ketone solvent to prepare a prepolymer. Then, ethylene glycol and ethylene diamine used as chain extenders, polyoxyethylene nonylphenyl ether as external emulsifier, and water were added and stirred, followed by removal of methyl ethyl ketone under reduced pressure to provide water-dispersed polyurethane dispersion liquid D.

[Example 1]

[0168] Polyethylene terephthalate copolymerized with 8 mol% sodium 5-sulfoisophthalate was used as sea component and polyethylene terephthalate was used as island component to produce an island-in-sea type composite fiber in which the composition ratio was 20 mas% sea component and 80 mas% island component, the number of islands was 16 islands/filament, and the average filament diameter was 20 μm . The island-in-sea type composite fiber obtained was cut into pieces with a fiber length of 51 mm to provide staple. It was then passed through a card and a cross lapper to form a fiber web, which was subjected to needle punching to produce a non-woven fabric.

[0169] The non-woven fabric obtained in this manner was shrunk by immersing it in hot water at a temperature of 97°C for 2 minutes, and then dried at a temperature of 100°C for 5 minutes. Subsequently, the resulting nonwoven fabric was impregnated with a dispersion liquid prepared by adjusting water-dispersed polyurethane dispersion liquid A to a polyurethane solid content of 20%, adding an association type viscosity improver [Thickner 627N, manufactured by San Nopco Limited] to an effective component content of 4 mass% relative to the polyurethane solid content, and also adding magnesium sulfate to 1.2 mass% relative to the polyurethane solid content. The fabric was then treated in hot water at a temperature of 95°C for 1 minute and air-dried in hot air at a drying temperature of 100°C for 15 minutes, and the resulting sheet was heated additionally at a temperature of 160°C for 20 minutes.

Thus, the resulting sheet consisted of a nonwoven fabric to which water-dispersed polyurethane was added so that polyurethane accounted for 35 mass% relative to the mass of the island component. The falling-off rate of polyurethane during the polyurethane coagulation step in hot water was as small as 0.1 %, suggesting scarce occurrence.

[0170] Subsequently, the sheet thus obtained was immersed in an aqueous sodium hydroxide solution with a concentration of 10 g/L heated at 95°C and treated for 25 minutes to remove the sea component from the island-in-sea type composite fiber, thus providing a sea-free sheet. The single fibers on the surface of the resulting sea-free sheet had an average single fiber diameter of 4.2 μm . Subsequently, the sea-free sheet was cut in half perpendicularly to the thickness direction using a cutting-in-half machine with an endless band knife and the non-cut surface was polished with 120-mesh and 240-mesh sandpapers to raise hairs. Then, it was dyed with a disperse dye using a circular dyeing machine, followed by reduction cleaning to provide artificial leather with a metsuke of 221 g/m². The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 4.0% and parameter B was 27.1%.

[Example 2]

[0171] Except that the same nonwoven fabric as in Example 1 was impregnated with a dispersion liquid prepared by adjusting water-dispersed polyurethane dispersion liquid A to a solid content of 20%, adding an epoxy based crosslinking agent [CR-5L, manufactured by DIC] to an effective component content of 5 mass% relative to the polyurethane solid content, adding an association type viscosity improver [Thickner 627N, manufactured by San Nopco Limited] to an effective component content of 4 mass% relative to the polyurethane solid content, and adding magnesium sulfate to 1.2 mass% relative to the polyurethane solid content, the same procedure as in Example 1 was carried out to provide artificial leather with a metsuke of 223 g/m². The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.1%, suggesting scarce occurrence. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 4.1% and parameter B was 25.4%.

[Example 3]

[0172] Polyethylene terephthalate copolymerized with 8 mol% sodium 5-sulfoisophthalate was used as sea component and polyethylene terephthalate was used as island component to produce an island-in-sea type composite fiber in which the composition ratio was 20 mas% sea component and 80 mas% island component, the number of islands was 16 islands/filament, and the average filament diameter was 20 μm. The island-in-sea type composite fiber obtained was cut into pieces with a fiber length of 51 mm to provide staple. It was then passed through a card and a cross lapper to form a fiber web, which was subjected to needle punching to produce a non-woven fabric.

[0173] The non-woven fabric obtained in this manner was shrunk by immersing it in hot water at a temperature of 97°C for 5 minutes, and then dried at a temperature of 100°C for 10 minutes. Subsequently, an aqueous solution containing 10 mass% (solid content) of PVA with a degree of saponification of 99% and a degree of polymerization of 1,400 [NM-14, manufactured by Nippon Synthetic Chemical Industry Co., Ltd.] was added to the resulting nonwoven fabric, followed by drying at a temperature of 100°C for 10 minutes and additional heating at a temperature of 150°C for 20 minutes to provide a sheet. Then, an aqueous sodium hydroxide solution with a concentration of 100 g/L was heated at 50°C and the sheet obtained above was immersed in it for 20 minutes to remove the sea component from the island-in-sea type composite fiber, thereby providing a sea-free sheet. The single fibers on the surface of the resulting sea-free sheet had an average fiber diameter of 4.2 μm. Following this, the sea-free sheet was impregnated with water-dispersed polyurethane dispersion liquid A prepared as in Example 2, treated in hot water at a temperature of 95°C for 1 minute, and air-dried in hot air at a drying temperature of 100°C for 15 minutes to provide a sheet containing water-dispersed polyurethane in such a manner that polyurethane accounted for 35 mass% relative to the mass of the island component in the nonwoven fabric. The aforementioned sheet containing water-dispersed polyurethane was immersed in hot water at a temperature of 98°C for 10 minutes to remove the PVA added before, followed by drying at a temperature of 100°C for 10 minutes. Subsequently, the resulting sheet was further subjected to additional heating at a temperature of 160°C for 20 minutes.

[0174] Then, the sea-free sheet was cut in half perpendicularly to the thickness direction using a cutting-in-half machine with an endless band knife, and the non-cut surface was polished with 120-mesh and 240-mesh sandpapers to raise hairs and dyed with a disperse dye using a circular dyeing machine, followed by reduction cleaning to provide artificial leather with a metsuke of 230 g/m². The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.2%, suggesting scarce occurrence. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 3.8% and parameter B was 20.3%.

[Example 4]

[0175] Except that the same nonwoven fabric as in Example 1 was impregnated with a dispersion liquid prepared by adjusting water-dispersed polyurethane dispersion liquid B to a solid content of 20% and adding an association type viscosity improver [Thickner 623N, manufactured by San Nopco Limited] to an effective component content of 3 mass% relative to the polyurethane solid content, the same procedure as in Example 1 was carried out to provide artificial leather with a metsuke of 218 g/m².

[0176] The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.1%, suggesting scarce occurrence. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 4.0% and parameter B was 26.8%.

[Example 5]

[0177] Except that the same nonwoven fabric as in Example 1 was impregnated with a dispersion liquid prepared by adjusting water-dispersed polyurethane dispersion liquid B to a solid content of 20%, adding aqueous isocyanate [Desmo-

dur (registered trademark) N3900, manufactured by Bayer Material Science] to an effective component content of 3 mass% relative to the polyurethane solid content, adding carbodiimide based crosslinking agent [Carbodilite (registered trademark) V-02-L2, manufactured by Nisshinbo Chemical Inc.] to an effective component content of 3 mass% relative to the polyurethane solid content, and adding an association type viscosity improver [Thickner 623N, manufactured by San Nopco Limited] to an effective component content of 3 mass% relative to the polyurethane solid content, the same procedure as in Example 1 was carried out to provide artificial leather with a metsuke of 220 g/m².

[0178] The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.2%, suggesting scarce occurrence. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 4.3% and parameter B was 30.3%.

[Example 6]

[0179] Except that the same nonwoven fabric as in Example 3 was impregnated with a dispersion liquid prepared by adjusting water-dispersed polyurethane dispersion liquid B to a solid content of 20%, adding aqueous isocyanate [Desmodur (registered trademark) N3900, manufactured by Bayer Material Science] to an effective component content of 3 mass% relative to the polyurethane solid content, adding carbodiimide based crosslinking agent [Carbodilite (registered trademark) V-02-L2, manufactured by Nisshinbo Chemical Inc.] to an effective component content of 3 mass% relative to the polyurethane solid content, and adding an association type viscosity improver [Thickner 623N, manufactured by San Nopco Limited] to an effective component content of 3 mass% relative to the polyurethane solid content, the same procedure as in Example 3 was carried out to provide artificial leather with a metsuke of 220 g/m².

[0180] The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.2%, suggesting scarce occurrence. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 4.2% and parameter B was 20.4%.

[Example 7]

[0181] Except that the same island-in-sea composite fiber as in Example 1 was passed through a card and a cross lapper to form fiber webs and the resulting webs were stacked, followed by sandwiching the stack of fiber webs between two pieces of woven fabric with a weaving density of 96 ends and 76 picks formed of 84-dtex, 72-filament twisted yarns used as both warp and weft and processing the stack by needle punching to provide complex nonwoven fabric; that water-dispersed polyurethane was added in such a manner that the mass of the polyurethane accounted for 28 mass% relative to the mass of the island component of the nonwoven fabric; that the sea-free sheet was cut perpendicularly to the thickness direction using a cutting-in-half machine with an endless band knife; and that the exposed face was polished with 120-mesh and 240-mesh sandpapers to raise hairs; the same procedure as in Example 6 was carried out to produce artificial leather with a metsuke of 393 g/m². The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.2%, suggesting scarce occurrence. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 3.6% and parameter B was 20.1%.

[Example 8]

[0182] Except that the same nonwoven fabric as in Example 3 was impregnated with a dispersion liquid prepared by adjusting water-dispersed polyurethane dispersion liquid A to a solid content of 20%, adding aqueous isocyanate [Desmodur (registered trademark) N3900, manufactured by Bayer Material Science] to an effective component content of 3 mass% relative to the polyurethane solid content, adding a carbodiimide based crosslinking agent [Carbodilite (registered trademark) V-02-L2, manufactured by Nisshinbo Chemical Inc.] to an effective component content of 3 mass% relative to the polyurethane solid content, adding a polysaccharide viscosity improver, namely, guar gum [Neosoft G, manufactured by Taiyo Kagaku Co., Ltd.], to an effective component content of 2 mass% relative to the polyurethane solid content, and adding magnesium sulfate to 1.2 mass% relative to the polyurethane solid content, and that hot water treatment was performed at a temperature of 95°C for 3 minutes after the impregnation with a polyurethane dispersion liquid, the same procedure as in Example 3 was carried out to provide artificial leather with a metsuke of 221 g/m².

[0183] The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.1 %, suggesting scarce occurrence. It was also found that the face exposed by the cutting with a cutting-in-half machine had little unevenness in polyurethane distribution and the fibrous base material was impregnated uniformly with polyurethane. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 3.3% and parameter B was 18.9%.

[Example 9]

[0184] Except that the same island-in-sea composite fiber as in Example 1 was passed through a card and a cross lapper to form fiber webs and the resulting webs were stacked, followed by sandwiching the stack of fiber webs between two pieces of woven fabric with a weaving density of 96 ends and 76 picks formed of 84-dtex, 72-filament twisted yarns used as both warp and weft and processing the stack by needle punching to provide complex nonwoven fabric; that water-dispersed polyurethane was added in such a manner that the mass of the polyurethane accounted for 28 mass% relative to the mass of the island component of the nonwoven fabric; that the sea-free sheet was cut perpendicularly to the thickness direction using a cutting-in-half machine with an endless band knife; and that the exposed face was polished with 120-mesh and 240-mesh sandpapers to raise hairs; the same procedure as in Example 8 was carried out to produce artificial leather with a metsuke of 390 g/m². The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.1%, suggesting scarce occurrence. It was also found that the face exposed by the cutting with a cutting-in-half machine had little unevenness in polyurethane distribution and the fibrous base material was impregnated uniformly with polyurethane. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 2.9% and parameter B was 19.2%.

[Example 10]

[0185] Except for omitting the step of adding, to non-woven fabric, PVA with a degree of saponification of 99% and a degree of polymerization of 1,400 [NM-14, manufactured by Nippon Synthetic Chemical Industry Co., Ltd.] and the step of drying, the same procedure as in Example 9 was carried out to produce artificial leather with a metsuke of 388 g/m². The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.1%, suggesting scarce occurrence. It was also found that the face exposed by the cutting with a cutting-in-half machine had little unevenness in polyurethane distribution and the fibrous base material was impregnated uniformly with polyurethane. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 1.1% and parameter B was 4.9%.

[Example 11]

[0186] Except that nonwoven fabric was impregnated with a dispersion liquid prepared by adjusting water-dispersed polyurethane dispersion liquid B to a solid content of 20%, adding aqueous isocyanate [Desmodur (registered trademark) N3900, manufactured by Bayer Material Science] to an effective component content of 4 mass% relative to the polyurethane solid content, and adding a polysaccharide viscosity improver, namely, guar gum [Neosoft G, manufactured by Taiyo Kagaku Co., Ltd.], to an effective component content of 2.5 mass% relative to the polyurethane solid content, the same procedure as in Example 9 was carried out to provide artificial leather with a metsuke of 388 g/m².

[0187] The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.1 %, suggesting scarce occurrence. It was also found that the face exposed by the cutting with a cutting-in-half machine had little unevenness in polyurethane distribution and the fibrous base material was impregnated uniformly with polyurethane. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 2.5% and parameter B was 14.3%.

[Example 12]

[0188] Except that nonwoven fabric was impregnated with a dispersion liquid prepared by adjusting water-dispersed polyurethane dispersion liquid C to a solid content of 20%, adding a carbodiimide based crosslinking agent [Carbodilite (registered trademark) V-02-L2, manufactured by Nisshinbo Chemical Inc.] to an effective component content of 4 mass% relative to the polyurethane solid content, adding a polysaccharide viscosity improver, namely, guar gum [Neosoft G, manufactured by Taiyo Kagaku Co., Ltd.], to an effective component content of 2 mass% relative to the polyurethane solid content, and adding magnesium sulfate to 3.0 mass% relative to the polyurethane solid content, the same procedure as in Example 9 was carried out to provide artificial leather with a metsuke of 386 g/m².

[0189] The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.1 %, suggesting scarce occurrence. It was also found that the face exposed by the cutting with a cutting-in-half machine had little unevenness in polyurethane distribution and the fibrous base material was impregnated uniformly with polyurethane. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 1.2% and parameter B was 5.2%.

[Example 13]

[0190] Except for omitting the step of adding PVA with a degree of saponification of 99% and a degree of polymerization of 1,400 [NM-14, manufactured by Nippon Synthetic Chemical Industry Co., Ltd.] and the step of drying, the same procedure as in Example 12 was carried out to produce artificial leather with a metsuke of 388 g/m². The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was as small as 0.1%, suggesting scarce occurrence. It was also found that the face exposed by the cutting with a cutting-in-half machine had little unevenness in polyurethane distribution and the fibrous base material was impregnated uniformly with polyurethane. The resulting artificial leather had good appearance quality and good texture free of a paper-like feel. Parameter A was 0.7% and parameter B was 4.0%.

[0191] Fig. 1 is a cross section of the artificial leather sample prepared in Example 13. The observation of polyurethane masses and ultrafine fiber bundles given in Fig. 1 shows that the cross-sectional sizes of the polyurethane masses are small (polyurethane masses are small) and also that the contact area between the ultrafine fiber bundles and the polyurethane masses is small.

[Comparative example 1]

[0192] Except that the same nonwoven fabric as in Example 1 was impregnated with a dispersion liquid prepared by adjusting water-dispersed polyurethane dispersion liquid A to a solid content of 20% and adding magnesium sulfate to 1.2 mass% relative to the polyurethane solid content, the same procedure as in Example 1 was carried out to provide artificial leather with a metsuke of 223 g/m². The falling-off rate of polyurethane during the water-dispersed polyurethane coagulation step in hot water was 22.1%, suggesting the occurrence of uneven distribution of polyurethane added to the fibrous base material.

[Comparative example 2]

[0193] Except that the same nonwoven fabric as in Example 1 was impregnated with water-dispersed polyurethane dispersion liquid B adjusted to a solid content of 20%, the same procedure as in Example 1 was carried out to provide artificial leather with a metsuke of 223 g/m². The falling-off rate of the polyurethane during the polyurethane coagulation step in hot water was 15.1%, suggesting the occurrence of uneven distribution of polyurethane added to the fibrous base material.

[Comparative example 3]

[0194] Except that the same nonwoven fabric as in Example 1 was impregnated with water-dispersed polyurethane dispersion liquid B adjusted to a solid content of 20%, treated for 5 minutes in a wet hot atmosphere at a temperature of 97°C and a humidity of 100%, and dried for 15 minutes at a temperature of 110°C in order for the addition of water-dispersed polyurethane resin to lead the polyurethane to account for 35 mas% relative to the mass of the island component of the nonwoven fabric, the same procedure as in Example 1 was carried out to provide artificial leather with a metsuke of 223 g/m². The falling-off rate of the polyurethane during the water-dispersed polyurethane coagulation step in hot water was 0.0%, but the resulting artificial leather had a texture with a significantly paper-like feel. Parameter A was 7.9% and parameter B was 42.2%.

[Comparative example 4]

[0195] Except that the same nonwoven fabric as in Example 13 was impregnated with water-dispersed polyurethane dispersion liquid B adjusted to a solid content of 20%, treated for 5 minutes in a wet hot atmosphere at a temperature of 97°C and a humidity of 100%, and dried for 15 minutes at a temperature of 110°C in order for the addition of water-dispersed polyurethane resin to lead the polyurethane to account for 28 mas% relative to the mass of the island component of the nonwoven fabric, the same procedure as in Example 13 was carried out to provide artificial leather with a metsuke of 389 g/m². The falling-off rate of the polyurethane during the water-dispersed polyurethane coagulation step in hot water was 0.0%, but the resulting artificial leather had a texture with a significantly paper-like feel. Parameter A was 8.1% and parameter B was 43.1%.

[0196] Fig. 2 is a cross section of the artificial leather sample prepared in Comparative example 4. The observation of polyurethane masses and ultrafine fiber bundles given in Fig. 2 shows that the cross-sectional sizes of the polyurethane masses are large (polyurethane masses are large) and also that the contact area between the ultrafine fiber bundles and the polyurethane masses is large.

[0197] Results obtained in Examples 1 to 7 and Comparative examples 1 to 4 are summarized in Tables 1 and 2.

[Table 1]

	Polyurethane liquid	Water-dispersed polyurethane dispersion liquid		Processability			
		viscosity improver					
		type	content (mass%)	coagulation method	viscosity of prepared PU liquid (mPa·s) 0.5 rpm	viscosity of prepared PU liquid (mPa·s) 10 rpm	resin falling-off rate (%)
Example 1	A	Thickener 627N	4.0	hot water	650	653	0.1
Example 2	A	Thickener 627N	4.0	hot water	700	710	0.1
Example 3	A	Thickener 627N	4.0	hot water	700	710	0.2
Example 4	B	Thickener 623N	3.0	hot water	800	803	0.2
Example 5	B	Thickener 623N	3.0	hot water	830	828	0.1
Example 6	B	Thickener 623N	3.0	hot water	830	828	0.2
Example 7	B	Thickener 623N	3.0	hot water	830	828	0.2
Example 8	A	Neosoft G	2.0	hot water	2500	690	0.1
Example 9	A	Neosoft G	2.0	hot water	2500	690	0.1
Example 10	A	Neosoft G	2.0	hot water	2500	690	0.1
Example 11	B	Neosoft G	2.5	hot water	2620	540	0.1
Example 12	C	Neosoft G	2.0	hot water	2300	682	0.1
Example 13	C	Neosoft G	2.0	hot water	2300	682	0.1
Comparative example 1	A	-	-	hot water	4.3	4.1	22.1
Comparative example 2	B	-	-	hot water	5.1	5.2	15.1
Comparative example 3	B	-	-	moist heat	5.1	5.2	0.0
Comparative example 4	B	-	-	moist heat	5.1	5.2	0.0

[Table 2]

	Polyurethane liquid	Artificial leather			
		parameter A	parameter B	texture	appearance quality
Example 1	A	4.0	27.1	○	3
Example 2	A	4.1	25.4	○	4

(continued)

		Polyurethane liquid	Artificial leather			
			parameter A	parameter B	texture	appearance quality
5	Example 3	A	3.8	20.3	⊙	5
	Example 4	B	4.0	26.8	○	3
	Example 5	B	4.3	30.3	○	4
10	Example 6	B	4.2	20.4	⊙	5
	Example 7	B	3.6	20.1	⊙	5
	Example 8	A	3.3	18.9	⊙	5
15	Example 9	A	2.9	19.2	⊙	5
	Example 10	A	1.1	4.9	⊙	5
	Example 11	B	2.5	14.3	⊙	5
20	Example 12	C	1.2	5.2	⊙	5
	Example 13	C	0.7	4.0	⊙	5
	Comparative example 1	A	-	-	-	-
25	Comparative example 2	B	-	-	-	-
	Comparative example 3	B	7.9	42.2	×	3
	Comparative example 4	B	8.1	43.1	×	3

[0198] The values of parameter A in Examples are smaller than those in Comparative examples, suggesting that the polyurethane masses are smaller and polyurethane is dispersed uniformly in the artificial leather to give a soft texture. The values of parameter B in Examples are also smaller than those in Comparative examples, suggesting that the contact area between the ultrafine fiber bundles and polyurethane masses is smaller to give a soft texture.

[Explanation of numerals]

[0199]

- 1: mass of polyurethane
- 2: circumference of an ultrafine fiber bundle
- 3: circumference covered by polymer elastomer film

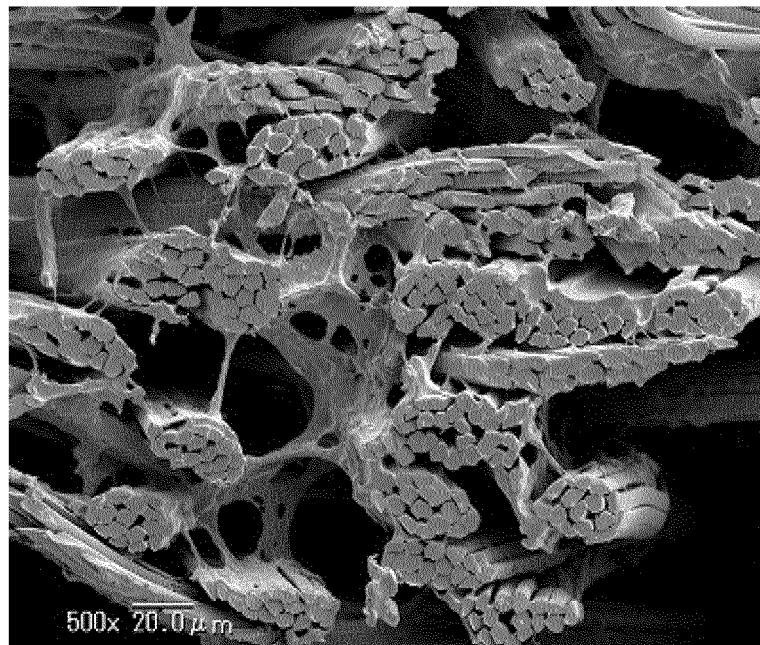
Claims

1. A sheet-like article comprising a fibrous base material formed of ultrafine fibers and/or ultrafine fiber bundles provided with, as a binder, a polymer elastomer having a hydrophilic group, any thickness-directional cross section of the sheet-like article containing regions occupied by the polymer elastomer, the regions including independent regions each with a cross-sectional area of 50 μm^2 or more, the total area of the independent regions accounting for 0.1% or more and 5.0% or less of the cross-sectional area of the artificial leather in an observation view field.
2. A sheet-like article as claimed in claim 1, wherein 1% or more and 35% or less of the circumferences of the cross sections of the ultrafine fibers and/or ultrafine fiber bundles observed in a cross section made by cutting the sheet-like article in the thickness direction is covered by film of the polymer elastomer.
3. A sheet-like article as claimed in either claim 1 or 2, wherein the polymer elastomer has a crosslinked structure produced by using a crosslinking agent.
4. A production method for a sheet-like article including a fibrous base material formed of ultrafine fibers and, as a

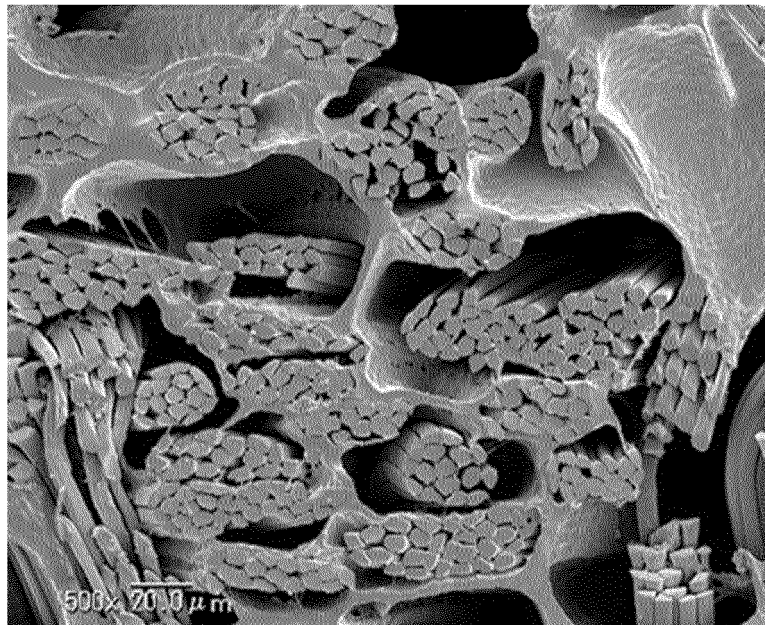
binder, a polymer elastomer having a hydrophilic group, comprising a step for adding an aqueous resin dispersion liquid containing a water-dispersed polymer elastomer and a viscosity improver to a fibrous base material and a step for coagulating the polymer elastomer in hot water at a temperature of 50°C to 100°C.

- 5 **5.** A production method for a sheet-like article as claimed in claim 4, wherein the aqueous resin dispersion liquid has non-Newtonian properties.
6. A production method for a sheet-like article as claimed in either claim 4 or 5, wherein the viscosity improver is a nonionic viscosity improver.
- 10 **7.** A production method for a sheet-like article as claimed in any one of claims 4 to 6, wherein the aqueous resin dispersion liquid has thixotropic properties.
8. A production method for a sheet-like article as claimed in any one of claims 4 to 7, wherein the viscosity improver is a polysaccharide viscosity improver.
- 15 **9.** A production method for a sheet-like article as claimed in any one of claims 4 to 8, wherein the viscosity improver is guar gum.
- 20 **10.** A production method for a sheet-like article as claimed in any one of claims 4 to 9, wherein the aqueous resin dispersion liquid contains a thermosensitive coagulant.
11. A production method for a sheet-like article as claimed in any one of claims 4 to 10, wherein the aqueous resin dispersion liquid contains a crosslinking agent.
- 25 **12.** A production method for a sheet-like article as claimed in any one of claims 4 to 11, wherein the polymer elastomer is water-dispersed polyurethane.

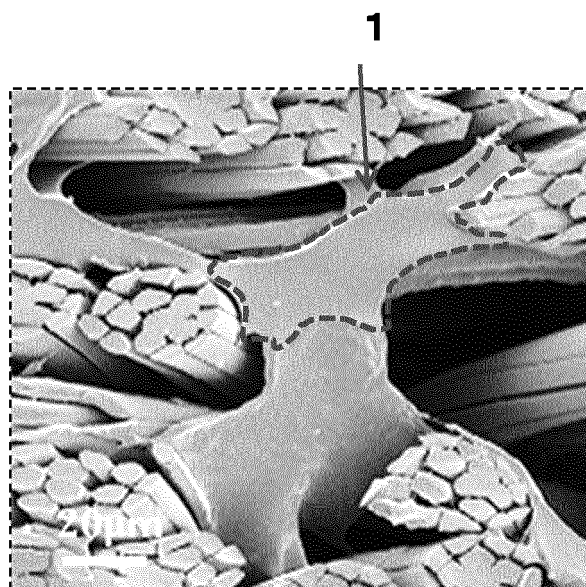
【F i g. 1】



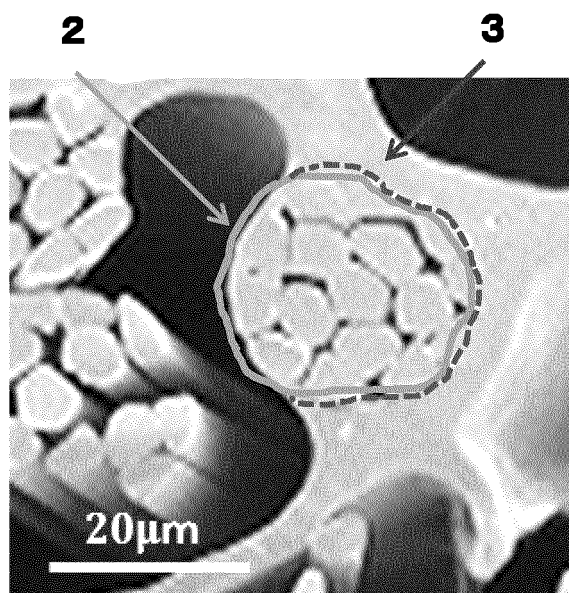
【F i g. 2】



【F i g. 3】



【 F i g . 4 】



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/054941

A. CLASSIFICATION OF SUBJECT MATTER

D06N3/14(2006.01)i, D06M15/564(2006.01)i, D06N3/00(2006.01)i

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, D06M13/00-15/715

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2015

Kokai Jitsuyo Shinan Koho 1971-2015 Toroku Jitsuyo Shinan Koho 1994-2015

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 55-051076 B2 (Kuraray Co., Ltd.), 22 December 1980 (22.12.1980), claims; page 2, right column, line 29 to page 3, right column, line 19; page 4, right column, line 36 to page 5, left column, line 29; page 6, left column, line 30 to right column, line 14 (Family: none)	1, 2, 4-10, 12 1-12
Y	JP 2013-234409 A (Toray Industries, Inc.), 21 November 2013 (21.11.2013), claims; paragraphs [0035], [0036] (Family: none)	1-12

☒ Further documents are listed in the continuation of Box C.
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Date of the actual completion of the international search
14 May 2015 (14.05.15)Date of mailing of the international search report
26 May 2015 (26.05.15)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/054941

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y A	JP 62-033884 A (Toray Industries, Inc.), 13 February 1987 (13.02.1987), claims; page 2, upper right column, line 12 to lower left column, line 5; page 2, lower right column, line 8 to page 3, upper left column, line 9; page 3, lower left column, line 12 to page 4, upper left column, line 13; page 4, upper right column, line 17 to lower right column, line 20 (Family: none)	1-3 4-12
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A	JP 2011-162908 A (Asahi Kasei Chemicals Corp.), 25 August 2011 (25.08.2011), entire text (Family: none)	1-12

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REFERENCES CITED IN THE DESCRIPTION

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