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(54) ARTIFICIAL LEATHER

(57) Provided is artificial leather which has excellent clarity of emboss patterns, and which does not use organic solvents during the production process and thus has a low environmental impact. The artificial leather comprises a nonwoven fabric made of ultrafine fibers having a mean single fiber diameter of 0.3 μm to 7 μm, and water-dispersed polyurethane, wherein when the free induction decay (FID) signal in pulse NMR (solid echo method, proton observation, measuring temperature: 50°C) is fitted to two components: the S component (Gaussian component) and L component (Lorentz component), the spin-spin relaxation time Tl of the L component is 500 μsec to 800 μsec and the L component fraction Cl is 25% or greater and less than 55%.

Description

FIELD

[0001] The present invention relates to artificial leather which has excellent clarity of emboss patterns, and which does not use organic solvents during the production process and thus has a low environmental impact.

BACKGROUND

[0002] Artificial leather comprising a fiber sheet such as a nonwoven fabric (fibrous base material) and a polyurethane (PU) resin as primary materials exhibits excellent properties that are difficult to achieve with natural leather, including easy care, functionality and homogeneity, and it is therefore suitable for use in clothing, shoes and bags, as well as for upholstery materials and interior materials for seats in interiors, automobiles, aircraft and railway vehicles, or decorative materials such as ribbons or patch bases. Embossing of artificial leather surfaces can increase their design properties for use in such fields. However, thermal decomposition or heat shrinkage of the binder occurs due to heating during embossing, resulting in an indistinct emboss pattern.

[0003] In order to solve this problem, highly heat-resistant polycarbonate polyols have been used as polyurethane resin starting materials that are to be impregnated in fibrous base materials inside leather-like sheets.

[0004] One commonly employed method for producing artificial leather in the prior art is a method of impregnating a fiber sheet with an organic solvent solution of a PU resin, and then immersing it in a non-solvent for the PU resin (such as water or an organic solvent), for wet coagulation of the PU resin. In this case, the organic solvent used as the solvent for the polyurethane resin is a water-miscible organic solvent such as N,N-dimethylformamide, but because of the high toxicity of organic solvents for the human body and the environment, there is high demand for methods that do not employ organic solvents for production of artificial leather.

[0005] PTL 1 proposes different polycarbonate-based PU materials obtained by reaction between a diol having two hydroxyl groups at one end and polysiloxane on a side chain, two different copolymerized polycarbonate diols, an organic diisocyanate, and a chain extender, primarily for the purpose of improving the texture of synthetic leather. However, since the polycarbonate-based polyurethanes are dissolved in N,N-dimethylformamide, and an organic solvent is used during production of artificial leather, it is associated with the problems of high environmental impact and high toxicity for the human body.

[0006] PTL 2 proposes PU resins obtained by reaction between a polyol obtained by transesterification of a polycarbonate diol or polyester diol, a polyol having hydroxyl groups at both ends, an organic diisocyanate and a chain extender, for the purpose of preventing hardening of the sheet texture. However, due to the high proportion of cohesive groups such as urethane bonds and urea bonds in these PU resins, embossing onto artificial leather obtained by attachment to the fiber sheets causes heat shrinkage, making it difficult to produce distinct emboss patterns.

[0007] Urethane resin structures have conventionally been identified by local structural analysis of the urethane resins themselves by NMR (for the constituent isocyanate, chain extender and polyol monomer), but no technique (method) has been known in the technical field of artificial leather for non-destructive evaluation of the motility of a urethane resin in its solid state with the urethane resin adhering to a polyester fiber sheet. Consequently, the prior art has not known the relationship between the motility of urethane resins added to artificial leather as binders, and the clarity of emboss patterns in the artificial leather.

[0008] Artificial leather obtained by impregnating a PU resin into a nonwoven fabric using ultrafine fibers, and having a low environmental impact without usage of organic solvents during the production process, as well as excellent clarity of emboss patterns, has not yet been provided given the current state of the prior art.

[CITATION LIST]

[PATENT LITERATURE]

[0009]

[PTL 1] Japanese Patent Publication No. 4506754
[PTL 2] Japanese Patent Publication No. 6582992

SUMMARY

[TECHNICAL PROBLEM]

[0010] In light of the aforementioned situation of the prior art, the problem to be solved by the invention is to provide artificial leather having a low environmental impact, by not using organic solvents during the production process, and also exhibiting excellent clarity of emboss patterns.

[SOLUTION TO PROBLEM]

[0011] As a result of diligent experimentation with the aim of solving this problem, the present inventors have completed this invention upon finding, unexpectedly, that the problem can be solved by artificial leather having the following features.

[0012] Specifically, the present invention provides the following.

[1] Artificial leather comprising a nonwoven fabric made of ultrafine fibers having a mean single fiber diameter of 0.3 μm to 7 μm, and water-dispersed polyurethane, wherein when the free induction decay (FID) signal in pulse NMR (solid echo method, proton observation, measuring temperature: 50°C) is fitted to two components: the S component (Gaussian component) and L component (Lorentz component), the spin-spin relaxation time T1 of the L component is 500 μsec to 800 μsec and the L component fraction Cl is 25% or greater and less than 55%.
[2] The artificial leather according to [1] above, wherein the ultrafine fibers are polyester-based fibers.
[3] The artificial leather according to [1] or [2] above, wherein the nonwoven fabric is integrated by entangling with a scrim layer woven fabric.
[4] The artificial leather according to [3] above, wherein the scrim layer is a woven fabric of polyester-based fibers.
[5] The artificial leather according to any one of [1] to [4] above, wherein the water-dispersed polyurethane is obtained by reaction between a methyl methacrylate-based macromonomer having two hydroxyl groups at one end, a polymer polyol having hydroxyl groups at both ends, a short chain diol having hydroxyl groups at both ends, a hydrophilic agent, an organic diisocyanate, and a chain extender.
[6] The artificial leather according to [5] above, wherein the polymer polyol is a polycarbonate diol and/or a polyether diol.
[7] The artificial leather according to [6] above, wherein the polycarbonate diol is a copolymerized polycarbonate diol obtained by copolymerization of two or more polyhydric alcohols.
[8] The artificial leather according to any one of [5] to [7] above, wherein the proportion of the methyl methacrylate-based macromonomer having two hydroxyl groups at one end with respect to the organic diisocyanate is 0.1 mol% to 7.0 mol%.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0013] The artificial leather of the invention has a low environmental impact since it does not employ an organic solvent during the production process, while it also has excellent clarity of emboss patterns, and it can therefore be suitably used for upholstery or interior materials for seats in interiors, automobiles, aircraft and railway vehicles, or for clothing products.

BRIEF DESCRIPTION OF DRAWINGS

[0014]

Fig. 1 is a diagram showing a cross-sectional structure of artificial leather.
Fig. 2 is diagram illustrating how the mean diameter of a single fiber composing the fiber layer (A) is determined.
Fig. 3 is a diagram showing the structure of artificial leather.
Fig. 4 is an outline diagram for synthesis of a water-dispersed polyurethane resin.
Fig. 5 is a function diagram for a macromonomer.
Fig. 6 is an explanatory diagram for a methyl methacrylate-based macromonomer having two hydroxyl groups at one end.
Fig. 7 is a diagram of a polysiloxane-based macromonomer having two hydroxyl groups at one end.

DESCRIPTION OF EMBODIMENTS

[0015] Embodiments of the invention will now be explained in detail with the understanding that the invention is not limited to the embodiments. Unless otherwise specified, the values mentioned throughout the present disclosure are values obtained by the methods described herein under "Examples" or methods known to be equivalent to them by those skilled in the art.

<Artificial leather>

[0016] One embodiment of the invention is artificial leather comprising a nonwoven fabric made of ultrafine fibers having a mean single fiber diameter of 0.3 μm to 7 μm, and water-dispersed polyurethane, wherein when the free induction decay (FID) signal in pulse NMR (solid echo method, proton observation, measuring temperature: 50°C) is fitted to two components: the S component (Gaussian component) and L component (Lorentz component), the spin-spin relaxation time T1 of the L component is 500 μsec to 800 μsec and the L component fraction Cl is 25% or greater and less than 55%.

[0017] Throughout the present specification, "artificial leather" is that defined according to the Household Goods Quality Labeling Act as "leather comprising a special nonwoven fabric (mainly a fiber layer having a random three-dimensional spatial structure, impregnated with a PU resin or a polymer elastic solid of similar flexibility) as the base material". In the definition according to JIS-6601, artificial leather is classified as "smooth" having the grain side appearance of leather, or "napped" having a leather suede or velour outer appearance, and the artificial leather of this embodiment is classified as "napped" (that is, suede-like artificial leather having a brushed-style outer appearance). A suede-like outer appearance can be formed by buffing treatment (raising treatment) of the outer surface of the fiber layer (A) (the side that is to be the first outer surface of the artificial leather) using sandpaper or the like. For the purpose of the present specification, the outer surface of the artificial leather is the surface that is externally exposed when the artificial leather is used (the surface that contacts with the human body, in the case of a chair, for example) (see Fig. 1 and fiber layer (A), reference numeral 1). According to one aspect, for suede-like artificial leather the outer surface of the fiber layer (A) has raised or napped fibers produced by buffing, for example.

[0018] Unless otherwise specified, the term "fiber web" used herein refers to the state before tangling of staple fibers, the term "fiber sheet" refers to the state after tangling and before PU resin filling, the term "sheet" refers to the state after PU resin filling and before dye finishing, and the term "artificial leather" refers to the state of the product after dye finishing. The term "nonwoven fabric" encompasses "fiber web", "fiber sheet", "sheet" and "artificial leather", and the term "fibrous base material" encompasses woven or knitted fabrics in addition to "nonwoven fabric".

[0019] The fiber sheet (A) indicated by reference numeral 1 in Fig. 1 has a structure in which parts of the interlaced section of the fiber sheet comprising tangled polyester fibers are attached using a (poly)urethane resin as the binder, as shown in Fig. 3. Such a (poly)urethane resin is generally composed mainly of polyol amorphous components (soft segments held together by Van der Waals forces) that impart flexibility, softness, bendability, cold resistance, affinity and chemical resistance, while hard segments that are aggregated by hydrogen bonding of urethane (urea) bonds impart toughness, heat resistance, solvent resistance and elasticity.

[0020] As mentioned above, however, as of the current level of the prior art it has not been known to those skilled in the art what manner and extent of effect is exhibited by the use of which polyols and in what amounts, in the soft segments of urethane resins. This is even more true not only for the urethane resin itself, but also for artificial leather comprising the urethane resin adhering as a binder to a polyester fiber sheet.

[L component spin-spin relaxation time T1 and L component fraction Cl]

[0021] In the artificial leather of the embodiment, the free induction decay (FID) signal in pulse NMR (solid echo method, proton observation, measuring temperature: 50°C) is fitted to two components: the S component (Gaussian component) and L component (Lorentz component), the spin-spin relaxation time T1 of the L component is 500 μsec to 800 μsec and the L component fraction Cl is 25% or greater and less than 55%.

[0022] As described in detail below, information regarding both components with low and components with high molecular mobility could be obtained by pulse NMR (solid echo method) of the artificial leather.

[0023] In artificial leather comprising a polyester fiber sheet and a polyurethane resin, the component with low molecular mobility may be the polyester fiber, and the component with high molecular mobility may be the polyurethane resin.

[0024] In pulse NMR, the FID (free induction decay) decay curve is generally expressed by a function which is either Gaussian or Lorentzian, or Weibullian which is intermediate between them, depending on the active level of molecular motion in the sample. The relaxation time of nuclear spin has several classifications, with some relaxation taking place efficiently by molecular chain movement at Larmor frequency-level speed, but for evaluating transverse relaxation time (T_2) during measurement of artificial leather, slow molecular motion is more sensitive to low frequencies, and the nuclear spin relaxes more efficiently with slower molecular motion and a longer correlation time, shortening the relaxation time. In other words, a component with longer relaxation time can be judged to be a component with high molecular mobility. For a component with low molecular mobility such as a crystal phase (polyester fiber, for example), the decay curve of magnetization exhibits Gaussian decay, while the amorphous phase with high molecular mobility (a urethane resin soft segment, for example) exhibits Lorentzian decay for the decay curve.

[0025] For pulse NMR measurement (solid echo method) in the Examples described below, assuming two curves deriving from two components: the low motility Gaussian component (S component) and the high motility Lorentz component (L component), the obtained free induction decay curve of spin-spin relaxation of ^1H was fitted by the following formula 1:

$$M(t) = Cs*\exp((-1/2)*(t/Ts)^2) + Cl*\exp(-t/Tl) \quad \text{Formula 1}$$

{where M(t) is the signal strength at a given time t, Cs is the low motility component fraction, Cl is the high motility component fraction, Ts is the low motility component T_2 relaxation time, and Tl is the high motility component T_2 relaxation time}.

[0026] Based on such measurement, the present inventors have found for the first time, that if the spin-spin relaxation time Tl of the L component is 500 μsec to 800 μsec and the L component fraction Cl is 25% to 54%, then heat shrinkage of the polyurethane resin during embossing is inhibited and emboss patterns in the resulting artificial leather are sufficiently distinct, and the present invention has been completed based on this finding.

[0027] The present inventors have confirmed that the high motility component fraction Cl and the proportion of PU resin with respect to the total mass of the sheet are in a strongly correlated relationship, and further that no artificial leather currently exists wherein the spin-spin relaxation time Tl of the L component is 500 μsec to 800 μsec.

[Adhesion rate of PU resin with respect to total mass of sheet fibers]

[0028] In the artificial leather of this embodiment, the adhesion rate of the PU resin with respect to the total mass of the sheet fibers is preferably 15 mass% to 50 mass%, more preferably 22 mass% to 45 mass% and even more preferably 26 mass% to 40 mass%. The proportion of PU resin with respect to the total mass of the sheet fibers affects the heat shrinking property of the polyurethane resin, and the consequent clarity of emboss patterns. A PU resin proportion of 15 mass% or greater with respect to the total mass of the sheet fibers will allow the fibers to be satisfactorily held by the PU resin, so that mechanical strength including abrasion resistance on a level satisfying commercial demand can be more easily obtained. A PU resin proportion of 50 mass% or lower with respect to the total mass of the sheet fibers, on the other hand, can result in artificial leather having a very soft hand quality and luxuriant feel.

[Polyurethane (PU) resin]

[0029] The PU resin is preferably obtained by reacting a polymer polyol, an organic diisocyanate and a chain extender.

[Polymer polyol]

[0030] Examples of polymer diols to be used include polycarbonate-based, polyester-based, polyether-based, silicone-based and fluorine-based diols, as well as copolymers of any two or more of these. In the PU resin in the artificial leather of the embodiment, however, the spin-spin relaxation time Tl of the L component is 500 μsec to 800 μsec, due to addition of an appropriately selected macromonomer component (having a side chain) as part of the short chain diol component, as a high molecular prepolymer component or chain extender, as described below.

[0031] From the viewpoint of hydrolysis resistance, it is preferred to use a polycarbonate-based or polyether-based diol, or a combination thereof. From the viewpoint of light fastness and heat resistance, polycarbonate-based or polyester-based diols, or their combinations, are preferred. From the viewpoint of cost competitiveness, a polyether-based or polyester-based diol, or a combination thereof, is preferred.

[0032] A polycarbonate-based diol can be produced by transesterification reaction of an alkylene glycol and a carbonic acid ester, or by reaction between phosgene or a chlorformic acid ester and an alkylene glycol. Examples of alkylene glycols include straight-chain alkylene glycols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 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 diols such as bisphenol A; used either alone, or in any combinations of two or more.

[0033] Polyester-based diols include polyester diols obtained by condensation between any of various low molecular weight polyols and polybasic acids. Examples of low molecular weight polyols include one or more selected from among ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,8-octanediol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, cyclohexane-1,4-diol and cyclohexane-1,4-dimethanol. An addition product of an alkylene oxide with bisphenol A may also be used. Examples of polybasic acids include one or more selected from the group consisting of succinic acid, maleic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid and hexahydroisophthalic acid.

[0034] Examples of polyether-based diols include polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and copolymer diols comprising their combinations.

[0035] The number-average molecular weight of the polymer diol is preferably 500 to 7000. The number-average molecular weight is 500 or higher and more preferably 1500 or higher to help prevent hardening of the texture. The number-average molecular weight is 7000 or lower to help maintain satisfactory strength of the PU resin.

[Macromonomer]

[0036] Figs. 5 to 7 show examples of macromonomers.

[0037] As shown by the example in Fig. 5, a macromonomer is generally a monomer having an optional side chain introduced on the polymer main chain, the introduction of the side chain being able to prevent association between main chains. The right hand side of Fig. 5 shows a state in which the side chains form a microphase-separated structure, helping to avoid association between the main chains. It should be noted, however, that in Fig. 5 the main chains are copolymerized with methyl methacrylate and are not macromonomers with two hydroxyl groups at one end, as used in the Examples and Comparative Examples.

[0038] Fig. 6 shows an example of a methyl methacrylate-based macromonomer as a polymer having two hydroxyl groups (a dihydroxyl group) at one end, and methyl methacrylate as the side chain. The methyl methacrylate-based macromonomer may be "AA-6" by Toagosei Co., Ltd., having a Mn of 6,000.

[0039] Fig. 7 shows an example of a polydimethylsiloxane-based macromonomer, having two hydroxyl groups (a dihydroxyl group) at one end, and polydimethylsiloxane as the side chain. The polydimethylsiloxane-based macromonomer may be "X-22-176DX" by Shin-Etsu Chemical Co., Ltd., having a molecular weight of 3000, or "X-22-177GX-A" by Shin-Etsu Chemical Co., Ltd., having a molecular weight of 14,000.

[0040] Without being constrained by any particular theory, it is conjectured that the desired effect exhibited when using PMMA compared to a siloxane was due to the fact that the resin solubility parameter (SP value) is 7.3 to 7.6 for polydimethylsiloxane and 9.3 for polymethylmethacrylate with respect to 10.0 for polyurethane, and therefore polymethyl methacrylate has higher affinity with polyurethane.

[Organic diisocyanate]

[0041] Examples of organic diisocyanates include aliphatic diisocyanates such as hexamethylene diisocyanate, dicyclohexylmethane diisocyanate, isophorone diisocyanate and xylylene diisocyanate; and aromatic diisocyanates such as diphenylmethane diisocyanate and tolylene diisocyanate, and their combinations may also be used. Preferred among these from the viewpoint of light fastness are aliphatic diisocyanates such as hexamethylene diisocyanate, dicyclohexylmethane diisocyanate and isophorone diisocyanate.

[Hydrophilic agent]

[0042] Examples of hydrophilic agents include dialkylolalkanoic acids such as 2,2-dimethylolpropionic acid, 2,2-dimethylolbutanoic acid, 2,2-dimethylolheptanoic acid and 2,2-dimethyloloctanoic acid; amino acids such as glycine, alanine and valine; compounds with carboxyl groups such as tartaric acid; compounds with sulfo groups such as 3-(2,3-dihydroxypropoxy)-1-propanesulfonic acid and di(ethyleneglycol) sulfoisophthalate ester; and compounds with sulfamic acid groups such as N,N-bis(2-hydroxylethyl)sulfamic acid; or these same compounds as salts neutralized with a neutralizing agent as described below. Preferred for use among these are 2,2-dimethylolpropionic acid and 2,2-dimethylolbutanoic acid.

[Neutralizing agent]

[0043] Examples of neutralizing agents include primary amines such as monomethylamine, monoethylamine, monobutylamine, monoethanolamine and 2-amino-2-methyl-1-propanol; secondary amines such as dimethylamine, diethylamine, dibutylamine, diethanolamine and N-methyldiethanolamine; and tertiary amines such as trimethylamine, triethylamine, dimethylethylamine and triethanolamine. Of these, triethylamine, monoethanolamine, diethanolamine and N-methyldiethanolamine are preferably used from the viewpoint of odor of the aqueous dispersion.

[Chain extender]

[0044] Chain extenders to be used include amine-based chain extenders such as ethylenediamine and methylenebisaniline, or diol-based chain extenders such as ethylene glycol. A polyamine obtained by reacting a polyisocyanate and water may also be used as a chain extender.

[Water-dispersed PU resin]

[0045] For production of artificial leather according to the embodiment, it is preferred to use a water-dispersed PU resin as the PU resin to be added, from the viewpoint of eliminating the need for organic solvents to reduce the environmental impact.

[0046] Fig. 4 shows an example of a method for producing a water-dispersible polyurethane resin.

[0047] In Fig. 4, a water-dispersed polyurethane is produced by reacting a polymer polyol, a short chain diol, a hydrophilic agent and an isocyanate in a ketone-based solvent to synthesize a prepolymer in the first step, emulsifying the obtained prepolymer in water using a neutralizing agent in the second step, and reacting the prepolymer with a diamine as the chain extender and removing the ketone-based solvent, in the third step.

[0048] For production of artificial leather according to the embodiment, an appropriately selected macromonomer component (with a side chain) is used for synthesis of the prepolymer in first step, as mentioned above.

[0049] However, the method for producing the water-dispersed PU resin is not limited to the one illustrated in Fig. 4.

[0050] The water-dispersed PU resin used may be a self-emulsifying PU resin containing hydrophilic groups within the PU molecules, or a forced-emulsifying PU resin in which the PU resin has been emulsified with an external emulsifying agent.

[0051] A crosslinking agent may also be used with the water-dispersed PU resin in order to improve the durability, including resistance to moist heat, abrasion resistance and hydrolysis resistance. A crosslinking agent is also preferably added to improve the durability during jet dyeing, reduce loss of the fibers and obtain excellent surface quality. The crosslinking agent may be an external crosslinking agent added as an addition component to the PU resin, or it may be a reactive group-introducing internal crosslinking agent that can produce a crosslinked structure beforehand within the PU resin structure.

[0052] Since the water-dispersed PU resin used in the artificial leather will generally have a crosslinked structure to provide dyeing resistance, it tends to be poorly soluble in organic solvents such as N,N-dimethylformamide. Therefore when observing a cross-section with an electron microscope, for example, if a resinous substance remains which lacks the form of the fibers after immersion of the artificial leather in N,N-dimethylformamide at room temperature for 12 hours to dissolve the PU resin, the resinous substance may be judged to be the water-dispersed PU resin.

[0053] The mean primary particle size of the polyurethane resin is the value obtained by measurement of the PU resin dispersion using a laser diffraction particle size distribution analyzer ("LA-920" by Horiba, Ltd.). If the mean primary particle size of the PU resin is 0.1 μm or greater, then the force with which the PU resin holds the fibers together in the fiber sheet (binding force) will be satisfactory, allowing artificial leather with excellent mechanical strength to be obtained. Limiting the mean primary particle size of the PU resin to 0.8 μm or smaller will inhibit aggregation and coarsening of the PU resin, which is advantageous for controlling the standard deviation of the surface PU resin area ratio to 20% or lower. If the mean primary particle size of the PU resin in the PU resin dispersion is 0.1 μm to 0.8 μm, then the fibers composing the artificial leather (surface layer) will be held together at more points, making it possible to obtain a soft hand quality (stiffness) and excellent mechanical strength (such as abrasion resistance), for example.

[Solid concentration of PU resin dispersion]

[0054] According to a typical aspect, as explained below, the PU resin is impregnated as an impregnating liquid in the form of a solution (dissolved in a solvent) or dispersion (water-dispersed). The solid concentration of the water-dispersed PU resin dispersion may be 10 wt% to 35 wt%, for example, and is preferably 15 to 30 mass% and more preferably 15 to 25 mass%. According to one aspect, the impregnating liquid is prepared and impregnated into the fiber sheet so that the adhesion rate of the PU resin with respect to 100 mass% of the fiber sheet is 15 mass% to 50 mass%.

[0055] The impregnating liquid containing the PU resin (such as the water-dispersed PU resin) may also contain additives such as stabilizers (ultraviolet absorbers and antioxidants), flame retardants, antistatic agents and pigments (such as carbon black), as necessary. The total amount of additives in the artificial leather may be 0.1 to 10.0 parts by mass, 0.2 to 8.0 parts by mass or 0.3 to 6.0 parts by mass, for example, with respect to 100 parts by mass of the PU resin. Such additives become distributed in the PU resin of the artificial leather. The values of the size of the PU resin and the mass ratio with respect to the fiber sheet mentioned herein are assumed to be the values including the additives (when used).

[Hot water-soluble resin]

[0056] When the water-dispersed PU resin dispersion is to be impregnated into the fiber sheet and the PU resin subsequently coagulated by heating to obtain the sheet filled with the PU resin, a step of adhering the hot water-soluble resin to the fiber sheet may be carried out before the water-dispersed PU resin dispersion is impregnated into the fiber sheet. The method of adhering the hot water-soluble resin (such as a PVA resin) may be preparation of an aqueous solution of the hot water-soluble resin followed by impregnation of the fiber sheet with the water-soluble solution and drying. Removing the hot water-soluble resin from the fiber sheet using hot water in the finishing-process steps or dyeing step can inhibit adhesion between the fibers and PU resin or can divide part of the continuous layer of the PU resin and form pores to micronize the state of adhesion of the PU resin, thus tending to improve the texture of the artificial leather.

[0057] The hot water-soluble resin may be a partially saponified PVA resin or completely saponified PVA resin. Since a completely saponified PVA resin tends to be less elutable into water at ordinary temperature (20°C) compared to a partially saponified PVA resin, a completely saponified PVA resin is preferably used as the hot water-soluble resin. From the viewpoint of inhibiting elution into water at ordinary temperature (20°C), the saponification degree of the completely saponified PVA resin is preferably 95 mol% or greater and more preferably 98 mol% or greater. In order to increase the permeability of the aqueous hot water-soluble resin solution during impregnation, the polymerization degree is preferably 1000 or lower and more preferably 700 or lower.

[Fiber sheet]

[0058] As shown in Fig. 1, the fiber sheet 1 includes at least the fiber layer (A) 12, with the scrim 11 and fiber layer (B) 13 being optional and not essential elements. The artificial leather of this embodiment may therefore be a single layer of the fiber layer (A), or two layers consisting of the fiber layer (A) and the scrim or fiber layer (B), or three layers consisting of the fiber layer (A), the scrim and the fiber layer (B).

[0059] When a scrim 11 and/or fiber layer (B) 13 are not included, the fiber layer (A) may be a single-layer fiber sheet which is sliced in half horizontally and then filled with the PU resin, as explained below. According to one aspect, the fiber sheet has a monolayer structure with no scrim. This will allow productivity to be increased by slicing in half horizontally.

[0060] According to another aspect, the fiber sheet has a three-layer structure with a scrim as the intermediate layer. For example, a woven or knitted fabric scrim 11 may be inserted in a sandwich manner between the fiber layer (A) 12 constituting the first outer surface of the artificial leather and the fiber layer (B) 13 constituting the second outer surface of the artificial leather, thus forming a three-layer structure with the fibers tangled between the layers, this structure being preferred for dimensional stability, tensile strength and tear strength. A three-layer structure of the fiber layer (A), fiber layer (B) and a scrim inserted between them also allows the fiber layer (A) and fiber layer (B) to have separate designs, and is therefore preferred from the viewpoint of free customization of the diameters and types of fibers composing each layer to match the functions and usages required for artificial leather. For example, using ultrafine fibers for fiber layer (A) and flame-retardant fibers for fiber layer (B) allows both excellent surface quality and high flame retardance to be obtained.

[0061] When the fiber sheet includes a scrim, it may be a woven or knitted fabric scrim which is preferably made of a polymer of the same type as the fibers composing the fiber layer (A), from the viewpoint of obtaining the same color by dyeing. If the fibers of the fiber layer (A) are polyester-based, for example, the fibers of the scrim are also preferably polyester-based, and when the fibers of the fiber layer (A) are polyamide-based, the fibers of the scrim are also preferably polyamide-based. For a knitted fabric scrim, it is preferably a single knit of 22-gauge to 28-gauge. A woven fabric scrim can exhibit higher dimensional stability and strength than a knitted fabric. The woven fabric texture may be a plain weave, twill weave or satin weave, but is preferably a plain weave from the viewpoint of cost and tangling properties.

[0062] The yarn composing the woven fabric may be monofilament or multifilament yarn. The single fiber fineness of the yarn is preferably 5.5 dtex or smaller to more easily obtain flexible artificial leather. The form of the yarn composing the woven fabric may be fully drawn yarn of polyester or polyamide, or false twisted yarn with added twisting of 0 to 3000 T/m. When multifilaments are used they may be common ones, and are preferably 33 dtex/6f, 55 dtex/24f, 83 dtex/36f, 83 dtex/72f, 110 dtex/36f, 110 dtex/48f, 167 dtex/36f or 166 dtex/48f polyester or polyamide, for example. The yarn composing a woven fabric may consist of multifilament long fibers. The woven density of the yarn in a woven fabric is preferably 30 to 150/inch and more preferably 40 to 100/inch from the viewpoint of obtaining artificial leather that is flexible with excellent mechanical strength. In order to obtain satisfactory mechanical strength and suitable texture, the basis weight of the woven fabric is preferably 20 to 150 g/m^2. The presence or absence of false twisting, the number of twists, the multifilament single fiber fineness and woven density for a woven fabric also contribute to the tangling properties between the fibers composing the fiber layer (A) and the optional fiber layer (B), and to the mechanical properties including flexibility, seam strength, tearing strength, tensile strength and elongation and stretchability of the artificial leather, and they may be selected as appropriate for the desired physical properties and intended use.

[0063] From the viewpoint of obtaining artificial leather with even higher levels of abrasion resistance, dye affinity and surface quality, the fiber layer (A) in the artificial leather of this embodiment is preferably composed of ultrafine fibers with mean diameters of 0.3 μm to 7 μm, more preferably 2 μm to 6 μm and even more preferably 2 μm to 5 μm. If the mean diameter of the fibers is 1 μm or greater, the abrasion resistance, dye coloring properties and light fastness will be satisfactory. If the mean diameter of the fibers is 8 μm or smaller, on the other hand, the large number density of the fibers will result in a high luxuriant feel and smooth surface tactile sensation, to obtain artificial leather with more satisfactory surface quality.

[0064] The fibers composing the fiber layers of the artificial leather (the fiber layer (A) and the optional fiber layer (B) and additional layers) may be synthetic fibers, which includes polyester-based fibers such as polyethylene terephthalate, polybutylene terephthalate and polytrimethylene terephthalate; and polyamide-based fibers such as nylon 6, nylon 66 and nylon 12. Considering the durability required for use in the field of car seats, for example, polyethylene terephthalate is preferred among these from the viewpoint of excellent color fastness without yellowing of the fibers themselves when exposed to direct sunlight for long periods. From the viewpoint of reducing environmental impact, the fibers composing the fiber layer of the artificial leather are more preferably made of chemical-recycled or material-recycled polyethylene terephthalate, or polyethylene terephthalate obtained using a plant-derived starting material.

[0065] If the artificial leather is composed of the fiber layer (A) alone, the basis weight of the fibers of the fiber layer (A) is preferably 40 g/m^2 to 500 g/m^2, more preferably 50 g/m^2 to 370 g/m^2 and even more preferably 60 g/m^2 to 320 g/m^2, from the viewpoint of mechanical strength including abrasion resistance.

[0066] When the artificial leather has a three-layer structure of the fiber layer (A), a scrim and the fiber layer (B), the basis weight of the fibers of the fiber layer (A) is preferably 10 g/m^2 to 200 g/m^2, more preferably 30 g/m^2 to 170 g/m^2 and even more preferably 60 g/m^2 to 170 g/m^2, from the viewpoint of mechanical strength including abrasion resistance. The basis weight of the fibers of the fiber layer (B) is preferably 10 g/m^2 to 200 g/m^2 and more preferably 20 g/m^2 to 170 g/m^2, from the viewpoint of cost and facilitated production. The basis weight of the scrim is preferably 20 g/m^2 to 150 g/m^2, more preferably 20 g/m^2 to 130 g/m^2 and even more preferably 30 g/m^2 to 110 g/m^2 from the viewpoint of mechanical strength and tangling between the fiber layers and scrim.

[0067] The basis weight of the artificial leather filled with the PU resin is preferably 50 g/m^2 to 550 g/m^2, more preferably 60 g/m^2 to 400 g/m^2 and even more preferably 70 g/m^2 to 350 g/m.^{2}

<Method for production of artificial leather>

[0068] An example of a method for producing artificial leather of this embodiment will now be described.

[0069] One example of the method for producing artificial leather of this embodiment may include the following steps:

a step of forming a fiber web of sea-island staple fibers, and then needle punching the web and subjecting the obtained fiber sheet to removal of the sea component to obtain a fiber sheet with the island component single filaments exposed; and
optionally, a step of adding a hot water-soluble resin to the obtained fiber sheet; and may further include the following steps:

a step of impregnating the single filament-dispersed fiber sheet with a water-dispersed PU resin dispersion, and then coagulating the PU resin by heating to obtain a sheet filled with the PU resin; and
a step of using hot water to remove the hot water-soluble resin from the obtained sheet. Each step will now be explained in order.

[Step of forming fiber web of sea-island staple fibers, needle punching the web and removal of the sea component of the fiber sheet to obtain fiber sheet with the island component single filaments exposed]

[0070] The method for producing each fiber layer forming the fiber sheet of the artificial leather (the fiber layer (A), and the optional fiber layer (B) and other layers) may be a direct spinning method (such as a spunbond method or meltblown method), or a method of forming a fiber sheet with staple fibers (such as a carding method, airlaid method or other dry method, or a wet method such as a papermaking method), which are all suitable, but for this embodiment sea-island fibers (SIF) are used as the starting material. A fiber sheet produced using staple fibers is preferred because it has low basis weight variation and excellent homogeneity, and tends to form uniform piles and thus improve the surface quality for artificial leather.

[0071] Fibers capable of ultrafine fiber generating may be used as the means for forming the ultrafine fibers of the fiber sheet. Using fibers capable of ultrafine fiber generating can stabilize the entangling forms of the ultrafine fiber bundles.

[0072] The fibers capable of ultrafine fiber generating used may be sea-island fibers having two thermoplastic resin components with different solvent solubilities as the sea component and island component, with the island component as the ultrafine fibers by dissolving removal of the sea component with a solvent, or peelable composite fibers having two thermoplastic resin components situated alternately in a radial or multilayer manner in the fiber cross-sections and being split into ultrafine fibers by peeled splitting of the components. Sea-island fibers can provide suitable voids between the island component (ultrafine fibers) by removal of the sea component, and are therefore preferred for use from the viewpoint of flexibility and texture of the sheet.

[0073] Sea-island fibers include sea-island composite fibers obtained by spinning the sea component and island component in mutual alignment using a sea-island compositing nozzle, and sea-island mixed fibers obtained by spinning a mixture of the sea component and island component. Sea-island composite fibers are preferably used from the viewpoint of obtaining ultrafine fibers of uniform fineness and of obtaining ultrafine fibers of adequate length to contribute to the sheet strength.

[0074] The sea component for sea-island fibers may be a copolymerized polyester obtained by copolymerizing polyethylene, polypropylene, polystyrene, sodium sulfoisophthalic acid or polyethylene glycol, or polylactic acid. For environmental considerations it is preferred to use an alkali-decomposable copolymerized polyester obtained by copolymerizing sodium sulfoisophthalic acid or polyethylene glycol, or polylactic acid, which can be decomposed without using organic solvents.

[0075] When sea-island fibers are used, the sea component is preferably removed before the PU resin is applied to the fiber sheet. Removal of the sea component before application of the PU resin allows the ultrafine fibers to be firmly held since the structure has the PU resin directly adhering to the ultrafine fibers, and therefore results in satisfactory abrasion resistance of the sheet.

[0076] The method of tangling the fibers or fiber bundles of the fiber web may be by cutting the sea-island fibers to predetermined fiber lengths to form staple fibers, passing them through a carding machine and cross lapper to form a fiber web, and tangling them by hydroentangling treatment by means of needle punching or any desired spunlace method.

[0077] For a needle punching method, the number of needle barbs used is preferably 1 to 9. If the number of barbs is 1 or greater a tangling effect will be obtained and damage to the fibers can be minimized. If the number of barbs is 9 or less, damage to the fibers can be reduced in size and fewer needle marks will be left in the artificial leather, allowing the outer appearance of the product to be improved.

[0078] Considering the effect on fiber tangling and product appearance, the total barb depth (length from the tip to the base of the barb) is preferably 0.05 mm to 0.10 mm. If the total barb depth is 0.05 mm or greater, the barbs will be able to satisfactorily hook the fibers, allowing efficient fiber tangling to be achieved. If the total barb depth is 0.10 mm or less, fewer needle marks will be left on the artificial leather, resulting in improved quality. Considering the balance between barb strength and fiber tangling, the total barb depth is more preferably 0.06 mm to 0.08 mm.

[0079] When the fibers are to be tangled by needle punching, the punch density range is preferably 300/cm^2 to 6000/cm^2 and more preferably 1000/cm^2 to 6000/cm^2.

[0080] The fiber sheet obtained by needle punching may be immersed for 2 minutes in 98°C water for shrinkage, and dried at a temperature of 100°C for 5 minutes to form the fiber sheet prior to sea removal.

[0081] Removal of the sea component may be carried out by immersing the sea-island fibers in a solvent to cause shrinkage. The solvent used to dissolve the sea component may be an aqueous alkali solution of sodium hydroxide or the like when the sea component is a copolymerized polyester or polylactic acid. For environmental considerations in this step, the removal of the sea component is preferably carried out with an aqueous alkali solution of sodium hydroxide.

[0082] When a method using staple fibers is selected, the staple fiber lengths are preferably 13 mm to 102 mm, more preferably 25 mm to 76 mm and even more preferably 38 mm to 76 mm for a dry method (carding method or airlaid method), and preferably 1 mm to 30 mm, more preferably 2 mm to 25 mm and even more preferably 3 mm to 20 mm for a wet method (papermaking method). For staple fibers used in a wet method (papermaking method), for example, the aspect ratio (L/D), as the ratio of the length (L) and diameter (D), is preferably 500 to 2000 and more preferably 700 to 1500. This aspect ratio range is preferred because the dispersibility and dispersibility of the staple fibers in the slurry of the staple fibers dispersed in water will be satisfactory during preparation of the slurry, the fiber layer strength will be satisfactory, and fiber balls known as "pilling" caused by abrasion will be less likely to be outwardly apparent since the fiber lengths are shorter than by a dry method, allowing the single filaments to more easily disperse. The fiber lengths of staple fibers with diameters of 4 μm, for example, are preferably 2 mm to 8 mm and more preferably 3 mm to 6 mm.

[Step of adding hot water-soluble resin to obtained fiber sheet]

[0083] By adhering the aforementioned hot water-soluble resin before impregnating the obtained fiber sheet with the water-dispersed PU resin dispersion, and removing the hot water-soluble resin from the obtained fiber sheet using hot water either in the finishing-process steps or dyeing step, it is possible to inhibit adhesion between the fibers and PU resin or to divide part of the continuous layer of the PU resin and form pores to micronize the state of adhesion of the PU resin, thus tending to improve the texture of the artificial leather.

[Step of impregnating single filament-dispersed fiber sheet with water-dispersed PU resin dispersion, and then coagulating PU resin by heating to obtain sheet filled with the PU resin]

[0084] In this step, the fiber sheet is impregnated with a water-dispersed PU resin dispersion, and then the PU resin is coagulated by heating to fill the sheet with the PU resin. As a typical aspect, the PU resin is impregnated as an impregnating liquid in the form of a dispersion (water-dispersed form). The concentration of the PU resin in the impregnating liquid may be 10 to 35 mass%, for example. As another aspect, the impregnating liquid is prepared and impregnated into the fiber sheet so that the PU resin proportion is 15 to 50 mass% with respect to 100 mass% of the fiber sheet.

[0085] Water-dispersed PU resins are classified as forced-emulsifying PU resins that are forcibly dispersed and stabilized using a surfactant, and self-emulsifying PU resins that have a hydrophilic structure in the PU molecular structure and disperse and stabilize in water without the presence of a surfactant. Either type may be used for this embodiment.

[0086] The water-dispersed PU resin dispersion may be impregnated and coated onto the fiber sheet, and subjected to dry heat coagulation, moist heat coagulation, hot water coagulation or a combination of these, to coagulate the PU resin. The temperature for moist heat coagulation is preferably 40 to 200°C, and above the heat-sensitive coagulation temperature of the PU resin. If the moist heat coagulation temperature is 40°C or higher and more preferably 80°C or higher, then it will be possible to shorten the time until coagulation of the PU resin and better inhibit its migration. If the moist heat coagulation temperature is 200°C or lower and more preferably 160°C or lower, heat degradation of the PU resin or PVA resin can be prevented. The temperature for hot water coagulation is preferably 40 to 100°C, and above the heat-sensitive coagulation temperature of the PU resin. If the hot water coagulation temperature in hot water is 40°C or higher and more preferably 80°C or higher, then it will be possible to shorten the time until coagulation of the PU resin and better inhibit its migration. The dry coagulation temperature and drying temperature are preferably 80 to 180°C. A dry coagulation temperature and drying temperature of 80°C or higher and more preferably 90°C or higher will result in excellent productivity. If the dry coagulation temperature and drying temperature are 180°C or lower and more preferably 160°C or lower, heat degradation of the PU resin or PVA resin can be prevented.

[Step of using hot water to remove hot water-soluble resin from obtained sheet]

[0087] The means for removing the hot water-soluble resin from the sheet may be, for example, a method of immersion in hot water at 60°C or higher and preferably 80°C or higher, or a method of removing the hot water-soluble resin while circulating hot water at 80°C or higher in a jet dyeing machine before dyeing. A method of removing the hot water-soluble resin in a jet dyeing machine is especially preferred because it can eliminate the steps of drying and winding of the sheet after removal of the hot water-soluble resin, and thus increase production efficiency. According to this embodiment, removal of the hot water-soluble resin from the sheet after application of the PU resin yields a flexible sheet. While the method of removing the hot water-soluble resin is not particularly restricted, a preferred aspect is dissolving removal by immersion of the sheet in hot water at 60 to 100°C, with squeezing using a mangle if necessary.

[Finishing-process steps]

[0088] After the fiber sheet has been filled with the PU resin and the hot water-soluble resin has been removed, the sheet filled with the PU resin may be sliced in half horizontally, if it does not include a scrim. This can increase production efficiency.

[0089] Before the buffing treatment described below, the PU resin-filled sheet may be coated with a lubricant, such as a silicone dispersion. Application of an antistatic agent before buffing treatment is also preferred so that grinding powder generated from the sheet by grinding will be less likely to accumulate on sandpaper.

[0090] Buffing treatment may be carried out to form naps on the surface of the sheet. The buffing treatment may be by a method of grinding using sandpaper or a roll sander. Applying silicone as a lubricant before buffing treatment allows naps to be easily formed by surface grinding, resulting in very satisfactory surface quality.

[0091] The artificial leather is preferably subjected to dyeing treatment to increase the value for sensibility (i.e. the visual effect). Dyestuff may be selected according to the type of fibers composing the fiber sheet, and for example, a disperse dyestuff may be employed for polyester-based fibers, an acid dyestuff or metal complexed dyestuff may be employed for polyamide-based fibers, or any combination of such dyestuffs may be used. When a disperse dyestuff has been used for dyeing, the dyeing may be followed by reduction cleaning. The dyeing method used may be any one commonly known in the dyeing industry. The dyeing method preferably employs a jet dyeing machine to simultaneously provide a rubbing effect while the sheet is dyed, in order to soften the sheet. The dyeing temperature will depend on the type of fiber but is preferably 80 to 150°C. If the dyeing temperature is 80°C or higher and more preferably 110°C or higher it will be possible to efficiently dye the fibers. If the dyeing temperature is 150°C or lower and more preferably 130°C or lower it will be possible to prevent degradation of the PU resin.

[0092] The artificial leather dyed in this manner is preferably subjected to soaping and if necessary reduction cleaning

(cleaning in the presence of a chemical reducing agent) to remove the excess dyestuff. It is also preferred to use a dyeing aid during dyeing. Using a dyeing aid can increase the dyeing uniformity and reproducibility. Whether in the same bath as dyeing or after dyeing, finishing-process may be carried out using a flexibilizer such as silicone, or an antistatic agent, water-repellent agent, flame retardant, light fastness agent or antimicrobial agent.

[0093] The artificial leather of this embodiment can be suitably used as an interior finishing material with a very delicate outer appearance when used as an upholstery for furniture, chairs or wall materials, or for seats, ceilings or interior finishings for vehicle interiors of automobiles, electric railcars or aircraft, or as clothing materials used in parts of shirts, jackets, uppers or trims for shoes including casual shoes, sports shoes, men's shoes or women's shoes, or bags, belts and wallets, or even as industrial materials such as wiping cloths, abrasive cloths or CD curtains.

EXAMPLES

[0094] The present invention will now be described in greater detail by Examples and Comparative Examples, with the understanding that the invention is not limited by the Examples. The physical properties and quality of the artificial leather samples used in the Examples and Comparative Examples were evaluated by the following protocols and methods.

(1) T_2 relaxation time Tl (μsec) of L component (Lorentz component), and L component fraction Cl (%)

· Preprocessing

[0095] An artificial leather sample cut with scissors was packed into a 1 cm-diameter pulse NMR glass tube to a height of about 1.0 cm to 1.5 cm, and provided for measurement.

· Measurement

[0096] Observation was with a pulse NMR device ("Minispec MQ20" by Bruker Corp. Japan). The observation conditions were as follows.

Measurement nucleus: ^1H
Measurement method: Solid echo
Number of scans: 256
Repetition time: 3 s
Measuring temperature: 50°C

· Analysis

[0097] Assuming two curves deriving from two components: the low motility Gaussian component (S component) and the high motility Lorentz component (L component), the obtained free induction decay curve of spin-spin relaxation of ^1H was fitted by the following formula 1:

$$M(t) = Cs*\exp((-1/2)*(t/Ts)^2) + Cl*\exp(-t/Tl) \quad \text{Formula 1}$$

{where M(t) is the signal strength at a given time t, Cs is the low motility component fraction, Cl is the high motility component fraction, Ts is the low motility component T_2 relaxation time, and Tl is the high motility component T_2 relaxation time}. All of the variables (Cs, Cl, Ts, Tl) were used as variable parameters for fitting. The fitting range was 0 ms to 0.6 ms.

(2) Embossing ratio (%)

[0098] The embossing ratio was calculated by the following formula:

$$\text{Embossing ratio (\%)} = S1/S0 \times 100,$$

based on the area (S 1) of heights in the embossing roll area (S0).

(3) Clarity of embossing (grade)

· Preprocessing

[0099] After inserting a sample between an embossing roll with an embossing ratio of 40%, and a presser roll, which had raised section heights of 300 μm and were heated to 200°C, at a speed of 2.0 m/min, embossing was carried out with a linear pressure of 60 kg/cm to obtain a sample having a concave design.

· Evaluation

[0100] The embossing clarity was calculated by the following formula:

$$\text{Embossing clarity A (\%)} = \text{d/D} \times 100$$

using the average value (d) for the depths of the recesses in a cross-section of the obtained sample measured at a total of 20 points using a caliper, and the height (D) of the raised sections of the presser roll.

[0101] The calculated embossing clarity was judged based on the following grade scale:

Grade 5: 30% ≤ A, distinct concave design shape;
Grade 4: 25% ≤ A < 30%, partially indistinct concave design shape;
Grade 3: 20% ≤ A < 25%, halfway indistinct concave design shape;
Grade 2: 15% ≤ A < 20%, mostly indistinct concave design shape;
Grade 1: 15% > A, indistinct concave design shape.

(4) PU resin proportion with respect to total mass of sheet fibers, and PU resin proportion with respect to fiber sheet filled with PU resin

[0102] The PU resin proportion with respect to the total mass of the sheet fibers was measured by the following method.

[0103] The mass of the fiber sheet before PU resin impregnation is recorded as A (g). The fiber sheet is impregnated with the PU resin dispersion, and then a pin tenter dryer is used for heated air drying at 130°C, after which it is immersed in hot water heated to 90°C for softening and dried, to obtain a fiber sheet filled with the PU resin (hereunder also referred to as "resin-filled fiber sheet"). The mass of the resin-filled fiber sheet (sheet) is designated as B1 (g). The PU resin proportion (C 1) with respect to the total mass of the sheet fibers and the PU resin proportion (D1) with respect to the resin-filled fiber sheet were calculated by the following formulas:

$$\text{C1} = (\text{B1 - A})/\text{A} \times 100 \text{ (wt\%)}$$

$$\text{D1} = (\text{B1 - A})/\text{B1} \times 100 \text{ (wt\%)}.$$

(5) Single fiber mean diameter (μm) in fiber sheet

[0104] The mean diameter of fibers composing the fiber sheet is determined by photographing the first outer surface of the artificial leather using a scanning electron microscope (SEM, "JSM-5610" by JEOL Corp.), at a magnification of 1500x, randomly selecting 100 fibers on the first outer surface of the artificial leather, measuring the diameters of the single filament cross-sections, and determining the arithmetic mean value for the 100 fibers.

[0105] When the observed shape of the cross-section of a single fiber is not circular, the distance between the outer circumferences on a straight line perpendicular to the middle point of the longest diameter of the single fiber cross section was taken as the fiber diameter.

[0106] Fig. 2 is a conceptual drawing illustrating how a fiber diameter is determined. When the cross-section A of the fiber is elliptical as in Fig. 2, for example, the fiber diameter is considered to be the outer circumferential distance c on a straight line b perpendicular to the midpoint p of the maximum diameter "a" of the cross-section A in the observed image.

(6) Mean primary particle size of PU resin in PU resin dispersion

[0107] Measurement was performed using a laser diffraction particle size distribution analyzer ("LA-920" by Horiba, Ltd.) according to the manufacturer's instruction manual, and the median diameter was recorded as the mean primary particle size.

(7) Saponification degree of hot water-soluble resin

[0108] This was measured according to JIS K 6726(1994)3.5.

(8) Polymerization degree of hot water-soluble resin (PVA)

[0109] This was measured according to JIS K 6726(1994)3.7.

[Method for preparing water-dispersed polyurethane resin]

[Synthesis Example 1: Preparation of water-dispersed polyurethane resin A]

[0110] After charging 154.0 parts by mass of 1,6-hexanediol polycarbonate polyol (0.0770 mol) with a Mn of 2,000 ("DURANOL T6002" by Asahi Kasei Corp., hereunder "PC-1") as a polymer polyol, 23.1 part by mass of a polymethyl methacrylate-based macromonomer (0.00385 mol) with a Mn of 6,000 as a macromonomer ("AA-6" by Toagosei Co., Ltd., hereunder "M-1"), 1.2 parts by mass of 1,4-butanediol (molecular weight: 30.12, 0.014 mol) as a short chain diol, 5.2 parts by mass of 2,2-dimethylolpropionic acid (molecular weight: 134.13, 0.039 mol) as a hydrophilic agent and 96.3 parts by mass of methyl ethyl ketone (molecular weight: 72.11, 1.34 mol) as a solvent into a pressure-resistant reactor equipped with a stirrer, thermometer and heating apparatus, under a nitrogen stream, and uniformly mixing the components, 40.4 parts by mass of dicyclohexylmethane diisocyanate (molecular weight: 262.35, 0.154 mol) as an isocyanate was added, and then 0.01 parts by mass of dibutyltin dilaurate as a catalyst was added and reaction was carried out for 400 minutes at 75°C under a dry nitrogen atmosphere, to obtain a methyl ethyl ketone solution of a urethane prepolymer having isocyanate groups at the molecular ends and a free isocyanate group content of 2.4 mass% with respect to the solid content. After cooling the solution to 30°C or lower, 3.9 parts by mass of triethylamine (molecular weight: 101.19, 0.039 mol) as a neutralizing agent was added to neutralize the carboxyl groups in the urethane prepolymer, and then 360.7 parts by mass of water (molecular weight: 18.015, 20.0 mol) was added, 2.1 part by mass of ethylenediamine (EDA) (molecular weight: 60.1, 0.035 mol) was further added as a chain extender, and reaction was conducted. Upon completion of the reaction, the methyl ethyl ketone was distilled off under reduced pressure to obtain an aqueous urethane resin composition (hereunder referred to as "resin A") (nonvolatile content: 40 mass%, mean primary particle size: 0.34 μm).

[Synthesis Example 2: Preparation of water-dispersed polyurethane resin B]

[0111] After charging 77.0 parts by mass of polycarbonate diol PC-1 (molecular weight: 2000, 0.0385 mol) and 77.0 parts by mass of a polycarbonate diol with a Mn of 2,000 (0.0385 mol) ("DURANOL T5652" by Asahi Kasei Corp., hereunder "PC-2") as polymer polyols, 4.6 parts by mass of polymethyl methacrylate-based macromonomer M-1 (molecular weight: 6000, 0.00077 mol) as a macromonomer, 1.0 parts by mass of ethylene glycol (molecular weight: 62.07, 0.015 mol) as a short chain diol, 5.2 parts by mass of 2,2-dimethylolpropionic acid (molecular weight: 134.13, 0.039 mol) as a hydrophilic agent and 94.4 parts by mass of methyl ethyl ketone (molecular weight: 72.11, 1.31 mol) as a solvent into a pressure-resistant reactor equipped with a stirrer, thermometer and heating apparatus, under a nitrogen stream, and uniformly mixing the components, 40.4 parts by mass of dicyclohexylmethane diisocyanate (molecular weight: 262.35, 0.154 mol) as an isocyanate was added, and then 0.01 parts by mass of dibutyltin dilaurate as a catalyst was added and reaction was carried out for 400 minutes at 75°C under a dry nitrogen atmosphere, to obtain a methyl ethyl ketone solution of a urethane prepolymer having isocyanate groups at the molecular ends and a free isocyanate group content of 2.8 mass% with respect to the solid content. After cooling the solution to 30°C or lower, 3.9 parts by mass of triethylamine (molecular weight: 101.19, 0.039 mol) as a neutralizing agent was added to neutralize the carboxyl groups in the urethane prepolymer, and then 346.8 parts by mass of water (molecular weight: 18.015, 19.3 mol) was added, 3.6 parts by mass of piperazine (molecular weight: 86.14, 0.042 mol) was further added as a chain extender, and reaction was conducted. Upon completion of the reaction, the methyl ethyl ketone was distilled off under reduced pressure to obtain an aqueous urethane resin composition (hereunder referred to as "resin B") (nonvolatile content: 40 mass%, mean primary particle size: 0.53 μm).

[Synthesis Example 3: Preparation of water-dispersed polyurethane resin C]

[0112] After charging 101.6 parts by mass of polycarbonate diol PC-2 (molecular weight: 20,000, 0.0508 mol) and

78.5 parts by mass of a polyether diol with a Mn of 3,000 (0.0262 mol) ("PTMG3000" by Mitsubishi Chemical Holdings Corp., hereunder "PTMG") as polymer polyols, 13.9 parts by mass of polymethyl methacrylate-based macromonomer M-1 (molecular weight: 6000, 0.00231 mol) as a macromonomer, 1.1 part by mass of 1,4-butanediol (molecular weight: 90.12, 0.012 mol) as a short chain diol, 5.2 parts by mass of 2,2-dimethylolpropionic acid (molecular weight: 134.13, 0.039 mol) as a hydrophilic agent and 103.3 parts by mass of methyl ethyl ketone (molecular weight: 72.11, 1.43 mol) as a solvent into a pressure-resistant reactor equipped with a stirrer, thermometer and heating apparatus, under a nitrogen stream, and uniformly mixing the components, 34.2 parts by mass of isophorone diisocyanate (molecular weight: 222.3, 0.154 mol) as an isocyanate was added, and then 0.01 parts by mass of dibutyltin dilaurate as a catalyst was added and reaction was carried out for 400 minutes at 75°C under a dry nitrogen atmosphere, to obtain a methyl ethyl ketone solution of a urethane prepolymer having isocyanate groups at the molecular ends and a free isocyanate group content of 2.2 mass% with respect to the solid content. After cooling the solution to 30°C or lower, 3.9 parts by mass of triethylamine (molecular weight: 101.19, 0.039 mol) as a neutralizing agent was added to neutralize the carboxyl groups in the urethane prepolymer, and then 327.1 parts by mass of water (molecular weight: 18.015, 18.2 mol) was added, 2.1 parts by mass of EDA (molecular weight: 60.1, 0.035 mol) was further added as a chain extender, and reaction was conducted. Upon completion of the reaction, the methyl ethyl ketone was distilled off under reduced pressure to obtain an aqueous urethane resin composition (hereunder referred to as "resin C") (nonvolatile content: 40 mass%, mean primary particle size: 0.19 μm).

[Synthesis Example 4: Preparation of water-dispersed polyurethane resin D]

[0113] After charging 61.6 parts by mass of polycarbonate diol PC-2 (molecular weight: 2000, 0.0308 mol) and 138.6 parts by mass of a polyether diol PTMG (molecular weight: 3000, 0.0462 mol) as polymer polyols, 32.3 parts by mass of polymethyl methacrylate-based macromonomer M-1 (molecular weight: 6000, 0.00539 mol) as a macromonomer, 1.0 part by mass of ethylene glycol (molecular weight: 62.07, 0.015 mol) as a short chain diol, 5.2 parts by mass of 2,2-dimethylolpropionic acid (molecular weight: 134.13, 0.039 mol) as a hydrophilic agent and 97.7 parts by mass of methyl ethyl ketone (molecular weight: 72.11, 1.36 mol) as a solvent into a pressure-resistant reactor equipped with a stirrer, thermometer and heating apparatus, under a nitrogen stream, and uniformly mixing the components, 40.4 parts by mass of dicyclohexylmethane diisocyanate (molecular weight: 262.35, 0.154 mol) as an isocyanate was added, and then 0.01 parts by mass of dibutyltin dilaurate as a catalyst was added and reaction was carried out for 400 minutes at 75°C under a dry nitrogen atmosphere, to obtain a methyl ethyl ketone solution of a urethane prepolymer having isocyanate groups at the molecular ends and a free isocyanate group content of 1.6 mass% with respect to the solid content. After cooling the solution to 30°C or lower, 3.9 parts by mass of triethylamine (molecular weight: 101.19, 0.039 mol) as a neutralizing agent was added to neutralize the carboxyl groups in the urethane prepolymer, and then 342.8 parts by mass of water (molecular weight: 18.015, 19.0 mol) was added, 3.8 parts by mass of piperazine (molecular weight: 86.14, 0.045 mol) was further added as a chain extender, and reaction was conducted. Upon completion of the reaction, the methyl ethyl ketone was distilled off under reduced pressure to obtain an aqueous urethane resin composition (hereunder referred to as "resin D") (nonvolatile content: 40 mass%, mean primary particle size: 0.28 μm).

[Synthesis Example 5: Preparation of water-dispersed polyurethane resin E]

[0114] After charging 154.0 parts by mass of polycarbonate diol PC-2 (molecular weight: 2000, 0.0770 mol) as a polymer polyol, 69.3 parts by mass of polymethyl methacrylate-based macromonomer M-1 (molecular weight: 6000, 0.00770 mol) as a macromonomer, 1.2 parts by mass of 1,4-butanediol (molecular weight: 90.12, 0.01386 mol) as a short chain diol, 5.2 parts by mass of 2,2-dimethylolpropionic acid (molecular weight: 134.13, 0.039 mol) as a hydrophilic agent and 88.0 parts by mass of methyl ethyl ketone (molecular weight: 72.11, 1.22 mol) as a solvent into a pressure-resistant reactor equipped with a stirrer, thermometer and heating apparatus, under a nitrogen stream, and uniformly mixing the components, 34.2 parts by mass of isophorone diisocyanate (molecular weight: 222.3, 0.154 mol) as an isocyanate was added, and then 0.01 parts by mass of dibutyltin dilaurate as a catalyst was added and reaction was carried out for 400 minutes at 75°C under a dry nitrogen atmosphere, to obtain a methyl ethyl ketone solution of a urethane prepolymer having isocyanate groups at the molecular ends and a free isocyanate group content of 1.5 mass% with respect to the solid content. After cooling the solution to 30°C or lower, 3.9 parts by mass of triethylamine (molecular weight: 101.19, 0.039 mol) as a neutralizing agent was added to neutralize the carboxyl groups in the urethane prepolymer, and then 389.1 parts by mass of water (molecular weight: 18.015, 21.6 mol) was added, 3.3 parts by mass of diethylenetriamine (molecular weight: 103.17, 0.032 mol) was further added as a chain extender, and reaction was conducted. Upon completion of the reaction, the methyl ethyl ketone was distilled off under reduced pressure to obtain an aqueous urethane resin composition (hereunder referred to as "resin E") (nonvolatile content: 40 mass%, mean primary particle size: 0.39 μm).

[Synthesis Example 6: Preparation of water-dispersed polyurethane resin F]

[0115] After charging 154.0 parts by mass of polycarbonate diol PC-2 (molecular weight: 2000, 0.0770 mol) as a polymer polyol, 69.3 parts by mass of polymethyl methacrylate-based macromonomer M-1 (molecular weight: 6000, 0.0116 mol) as a macromonomer, 0.80 parts by mass of ethylene glycol (molecular weight: 62.07, 0.012 mol) as a short chain diol, 5.2 parts by mass of 2,2-dimethylolpropionic acid (molecular weight: 134.13, 0.039 mol) as a hydrophilic agent and 81.0 parts by mass of methyl ethyl ketone (molecular weight: 72.11, 1.12 mol) as a solvent into a pressure-resistant reactor equipped with a stirrer, thermometer and heating apparatus, under a nitrogen stream, and uniformly mixing the components, 34.2 parts by mass of isophorone diisocyanate (molecular weight: 222.3, 0.154 mol) as an isocyanate was added, and then 0.01 parts by mass of dibutyltin dilaurate as a catalyst was added and reaction was carried out for 400 minutes at 75°C under a dry nitrogen atmosphere, to obtain a methyl ethyl ketone solution of a urethane prepolymer having isocyanate groups at the molecular ends and a free isocyanate group content of 2.3 mass% with respect to the solid content. After cooling the solution to 30°C or lower, 3.9 parts by mass of triethylamine (molecular weight: 101.19, 0.039 mol) as a neutralizing agent was added to neutralize the carboxyl groups in the urethane prepolymer, and then 433.6 parts by mass of water (molecular weight: 18.015, 24.1 mol) was added, 6.3 parts by mass of isophoronediamine (molecular weight: 170.3, 0.037 mol) was further added as a chain extender, and reaction was conducted. Upon completion of the reaction, the methyl ethyl ketone was distilled off under reduced pressure to obtain an aqueous urethane resin composition (hereunder referred to as "resin F") (nonvolatile content: 40 mass%, mean primary particle size: 0.52 μm).

[Synthesis Example 7: Preparation of water-dispersed polyurethane resin G]

[0116] After charging 154.0 parts by mass of polycarbonate diol PC-2 (molecular weight: 2000, 0.0770 mol) as a polymer polyol, 0.80 parts by mass of ethylene glycol (molecular weight: 62.07, 0.012 mol) as a short chain diol, 5.2 parts by mass of 2,2-dimethylolpropionic acid (molecular weight: 134.13, 0.039 mol) as a hydrophilic agent and 97.2 parts by mass of methyl ethyl ketone (molecular weight: 72.11, 1.35 mol) as a solvent into a pressure-resistant reactor equipped with a stirrer, thermometer and heating apparatus, under a nitrogen stream, and uniformly mixing the components, 25.9 parts by mass of hexamethylene diisocyanate (molecular weight: 168.2, 0.154 mol) as an isocyanate was added, and then 0.01 parts by mass of dibutyltin dilaurate as a catalyst was added and reaction was carried out for 400 minutes at 75°C under a dry nitrogen atmosphere, to obtain a methyl ethyl ketone solution of a urethane prepolymer having isocyanate groups at the molecular ends and a free isocyanate group content of 2.3 mass% with respect to the solid content. After cooling the solution to 30°C or lower, 3.9 parts by mass of triethylamine (molecular weight: 101.19, 0.039 mol) as a neutralizing agent was added to neutralize the carboxyl groups in the urethane prepolymer, and then 485.2 parts by mass of water (molecular weight: 18.015, 26.9 mol) was added, 2.6 parts by mass of ethylenediamine (molecular weight: 60.1, 0.034 mol) was further added as a chain extender, and reaction was conducted. Upon completion of the reaction, the methyl ethyl ketone was distilled off under reduced pressure to obtain an aqueous urethane resin composition (hereunder referred to as "resin G") (nonvolatile content: 40 mass%, mean primary particle size: 0.40 μm).

[Synthesis Example 8: Preparation of water-dispersed polyurethane resin H]

[0117] After charging 154.0 parts by mass of polycarbonate diol PC-2 (molecular weight: 2000, 0.0770 mol) as a polymer polyol, 4.6 parts by mass of a polydimethylsiloxane-based macromonomer ("X-22-176DX" by Shin-Etsu Chemical Co., Ltd., hereunder "M-2") (molecular weight: 3000, 0.015 mol) as a macromonomer, 1.2 parts by mass of 1,4-butanediol (molecular weight: 90.12, 0.014 mol) as a short chain diol, 5.2 parts by mass of 2,2-dimethylolpropionic acid (molecular weight: 134.13, 0.039 mol) as a hydrophilic agent and 98.6 parts by mass of methyl ethyl ketone (molecular weight: 72.11, 1.37 mol) as a solvent into a pressure-resistant reactor equipped with a stirrer, thermometer and heating apparatus, under a nitrogen stream, and uniformly mixing the components, 40.4 parts by mass of dicyclohexylmethane diisocyanate (molecular weight: 262.35, 0.154 mol) as an isocyanate was added, and then 0.01 parts by mass of dibutyltin dilaurate as a catalyst was added and reaction was carried out for 400 minutes at 75°C under a dry nitrogen atmosphere, to obtain a methyl ethyl ketone solution of a urethane prepolymer having isocyanate groups at the molecular ends and a free isocyanate group content of 2.9 mass% with respect to the solid content. After cooling the solution to 30°C or lower, 3.9 parts by mass of triethylamine (molecular weight: 101.19, 0.039 mol) as a neutralizing agent was added to neutralize the carboxyl groups in the urethane prepolymer, and then 411.5 parts by mass of water (molecular weight: 18.015, 22.8 mol) was added, 2.6 parts by mass of ethylenediamine (molecular weight: 60.1, 0.043 mol) was further added as a chain extender, and reaction was conducted. Upon completion of the reaction, the methyl ethyl ketone was distilled off under reduced pressure to obtain an aqueous urethane resin composition (hereunder referred to as "resin H") (nonvolatile content: 40 mass%, mean primary particle size: 0.38 μm).

[Synthesis Example 9: Preparation of water-dispersed polyurethane resin I]

[0118] After charging 154.0 parts by mass of polycarbonate diol PC-2 (molecular weight: 2000, 0.077 mol) as a polymer polyol, 21.6 parts by mass of a polydimethylsiloxane-based macromonomer ("X-22-177GX-A" by Shin-Etsu Chemical Co., Ltd., hereunder "M-3") (molecular weight: 14,000, 0.00154 mol) as a macromonomer, 1.4 parts by mass of 1,4-butanediol (molecular weight: 90.12, 0.015 mol) as a short chain diol, 5.2 parts by mass of 2,2-dimethylolpropionic acid (molecular weight: 134.13, 0.039 mol) as a hydrophilic agent and 87.7 parts by mass of methyl ethyl ketone (molecular weight: 72.11, 1.22 mol) as a solvent into a pressure-resistant reactor equipped with a stirrer, thermometer and heating apparatus, under a nitrogen stream, and uniformly mixing the components, 34.2 parts by mass of isophorone diisocyanate (molecular weight: 222.3, 0.154 mol) as an isocyanate was added, and then 0.01 parts by mass of dibutyltin dilaurate as a catalyst was added and reaction was carried out for 400 minutes at 75°C under a dry nitrogen atmosphere, to obtain a methyl ethyl ketone solution of a urethane prepolymer having isocyanate groups at the molecular ends and a free isocyanate group content of 2.2 mass% with respect to the solid content. After cooling the solution to 30°C or lower, 3.9 parts by mass of triethylamine (molecular weight: 101.19, 0.039 mol) as a neutralizing agent was added to neutralize the carboxyl groups in the urethane prepolymer, and then 458.9 parts by mass of water (molecular weight: 18.015, 25.5 mol) was added, 2.3 parts by mass of ethylenediamine (molecular weight: 60.1, 0.039 mol) was further added as a chain extender, and reaction was conducted. Upon completion of the reaction, the methyl ethyl ketone was distilled off under reduced pressure to obtain an aqueous urethane resin composition (hereunder referred to as "resin I") (nonvolatile content: 40 mass%, mean primary particle size: 0.20 μm).

[Production of artificial leather]

[Example 1]

[0119] Using polyethylene terephthalate copolymerized with 8 mol% sodium 5-sulfoisophthalate as the sea component and polyethylene terephthalate as the island component, a sea-island composite fiber with a mean fiber fineness of 18 μm was obtained with a composite ratio of 20 mass% sea component and 80 mass% island component, and 16 islands/1f. The obtained sea-island composite fiber was cut to fiber lengths of 51 mm as staple fibers and passed through a carding machine and cross lapper to form a fiber web, and after layering the obtained fiber web, it was needled-punched to obtain a fiber sheet. The obtained fiber sheet was immersed in 95°C hot water for contraction and a pin tenter dryer was used for drying at 100°C for 5 minutes, to obtain a single-layer fiber sheet with a basis weight of 600 g/m^2.

[0120] The obtained fiber sheet was immersed in a 10 g/L sodium hydroxide aqueous solution that had been heated to 95°C for 25 minutes of treatment, for removal of the sea component of the sea-island composite fibers. The single fiber mean diameter of the fibers composing the fiber sheet after sea component removal was 4 μm.

[0121] Next, PVA with a saponification degree of 98 to 99% and a polymerization degree of 1200 (N-300 by Nippon Synthetic Chemical Industry Co., Ltd.) was added to water at a temperature of 25°C, and the mixture was heated to a temperature of 90°C, keeping the temperature at 90°C while stirring for 2 hours, to prepare an aqueous solution with a 10 mass% solid content as a PVA aqueous solution. The fiber sheet from which the sea component had been removed was impregnated with the PVA aqueous solution and heat dried for 10 minutes at a temperature of 140°C, to obtain a PVA-added sheet having a PVA adhesion amount of 15 mass% with respect to the fiber mass of the fiber sheet.

[0122] An impregnating liquid containing the water-dispersed polyurethane resin A obtained in Synthesis Example 1 at 25.0% (solid mass%) in the impregnating liquid and anhydrous sodium sulfate as an impregnation aid at 3.0 wt% (solid mass%) in the impregnating liquid was then used for impregnation into the PVA-added sheet, after which moist heat coagulation was carried out for 5 minutes at 100°C and a hot air drier was used for hot air drying at 130°C for 5 minutes.

[0123] It was then immersed in hot water that had been heated to 95°C for removal of the impregnated anhydrous sodium sulfate, to obtain a sheet filled with the water-dispersed PU resin. The proportion of water-dispersed PU resin with respect to the total mass of the sheet fibers was 29 mass%.

[0124] A half-cut machine with an endless band knife was then used for half-cutting of the sheet perpendicular to the thickness direction, and the non-half-cut side was subjected to buffing treatment using #400 emery paper, after which a jet dyeing machine was used for dyeing at 130°C for 15 minutes with a blue disperse dyestuff ("BlueFBL" by Sumitomo Chemical Co., Ltd.) at a 5.0% owf dyeing density, and reduction cleaning was carried out. A hot air drier was then used for drying at 100°C for 5 minutes to obtain single-layer artificial leather.

[Example 2]

[0125] Artificial leather was obtained in the same manner as Example 1, except that the fiber sheet was impregnated with the water-dispersed polyurethane resin B obtained in Synthesis Example 2, and the PU resin proportion was 27 mass% with respect to the fiber sheet.

[Example 3]

[0126] Artificial leather was obtained in the same manner as Example 1, except that the fiber sheet was impregnated with the water-dispersed polyurethane resin C obtained in Synthesis Example 3, and the PU resin proportion was 28 mass% with respect to the fiber sheet.

[Example 4]

[0127] Artificial leather was obtained in the same manner as Example 1, except that the fiber sheet was impregnated with the water-dispersed polyurethane resin D obtained in Synthesis Example 4, and the PU resin proportion was 27 mass% with respect to the fiber sheet.

[Example 5]

[0128] The staple fibers of Example 1 were processed with a carding machine and cross lapper to produce a fiber web with a basis weight of 128 g/m^2, which was used as fiber layer (A). A fiber web with a basis weight of 60 g/m^2 was also produced by the same method for use as fiber layer (B).

[0129] A scrim (plain weave fabric) with a basis weight of 95 g/m^2 composed of 166 dtex/48f polyethylene terephthalate fibers was inserted between fiber layer (A) and fiber layer (B), forming a 3-layer body, which was then processed by needle punching to form a fiber sheet having a three-layer structure.

[0130] The sheet was immersed in a bath at a temperature of 97°C for shrinkage and dried using a pin tenter dryer at 100°C for 5 minutes, after which it was immersed for 25 minutes in a 10 g/L-concentration aqueous sodium hydroxide solution which had been heated to a temperature of 95°C, and then treated for removal of the sea component of the sea-island composite fibers. The single fiber mean diameter of the fibers composing the fiber sheet after sea component removal was 4 μm.

[0131] Next, PVA with a saponification degree of 98 to 99% and a polymerization degree of 1200 (N-300 by Nippon Synthetic Chemical Industry Co., Ltd.) was added to water at a temperature of 25°C, and the mixture was heated to a temperature of 90°C, keeping the temperature at 90°C while stirring for 2 hours, to prepare an aqueous solution with a 10 mass% solid content as a PVA aqueous solution. The fiber sheet from which the sea component had been removed was impregnated with the PVA aqueous solution and heat dried for 10 minutes at a temperature of 140°C, to obtain a PVA-added sheet having a PVA adhesion amount of 15 mass% with respect to the fiber mass of the fiber sheet.

[0132] An impregnating liquid containing the water-dispersed polyurethane resin E obtained in Synthesis Example 5 at 25.0% (solid mass%) in the impregnating liquid and anhydrous sodium sulfate as an impregnation aid at 3.0 wt% (solid mass%) in the impregnating liquid was then used for impregnation into the PVA-added sheet, after which moist heat coagulation was carried out for 5 minutes at 100°C and a hot air drier was used for hot air drying at 130°C for 5 minutes.

[0133] It was then immersed in hot water that had been heated to 95°C for removal of the impregnated anhydrous sodium sulfate, to obtain a sheet filled with the water-dispersed PU resin. The proportion of water-dispersed PU resin with respect to the total mass of the sheet fibers was 28 mass%.

[0134] The outer surface of the fiber layer (A) of the sheet was subjected to buffing treatment using #400 emery paper, after which a jet dyeing machine was used for 15 minutes of dyeing at 130°C with a blue disperse dyestuff ("BlueFBL" by Sumitomo Chemical Co., Ltd.) to a dyeing density of 5.0% owf, and reduction cleaning was carried out. A hot air drier was then used for drying at 100°C for 5 minutes to obtain artificial leather with a three-layer structure.

[Example 6]

[0135] Artificial leather was obtained in the same manner as Example 3, except that the PU resin proportion was 37 mass% with respect to the fiber sheet.

[Example 7]

[0136] Artificial leather was obtained in the same manner as Example 3, except that the PU resin proportion was 18 mass% with respect to the fiber sheet.

[Example 8]

[0137] Artificial leather was obtained in the same manner as Example 4, except that the PU resin proportion was 37 mass% with respect to the fiber sheet.

[Example 9]

[0138] Artificial leather was obtained in the same manner as Example 4, except that the PU resin proportion was 18 mass% with respect to the fiber sheet.

[Example 10]

[0139] Artificial leather was obtained in the same manner as Example 5, except that the PU resin proportion was 37 mass% with respect to the fiber sheet.

[Example 11]

[0140] Artificial leather was obtained in the same manner as Example 5, except that the PU resin proportion was 18 mass% with respect to the fiber sheet.

[Comparative Example 1]

[0141] Artificial leather was obtained in the same manner as Example 4, except that the PU resin proportion was 12 mass% with respect to the fiber sheet.

[Comparative Example 2]

[0142] Artificial leather was obtained in the same manner as Example 4, except that the PU resin proportion was 51 mass% with respect to the fiber sheet.

[Comparative Example 3]

[0143] Artificial leather was obtained in the same manner as Example 1, except that the fiber sheet was impregnated with the water-dispersed polyurethane resin F obtained in Synthesis Example 6, and the PU resin proportion was 12 mass% with respect to the fiber sheet.

[Comparative Example 4]

[0144] Artificial leather was obtained in the same manner as Example 1, except that the fiber sheet was impregnated with the water-dispersed polyurethane resin G obtained in Synthesis Example 7, and the PU resin proportion was 12 mass% with respect to the fiber sheet.

[Comparative Example 5]

[0145] Artificial leather was obtained in the same manner as Example 1, except that the fiber sheet was impregnated with the water-dispersed polyurethane resin H obtained in Synthesis Example 8, and the PU resin proportion was 30 mass% with respect to the fiber sheet.

[Comparative Example 6]

[0146] Artificial leather was obtained in the same manner as Example 1, except that the fiber sheet was impregnated with the water-dispersed polyurethane resin I obtained in Synthesis Example 9, and the PU resin proportion was 30 mass% with respect to the fiber sheet.

[Comparative Example 7]

[0147] Artificial leather was obtained in the same manner as Example 1, except that the fiber sheet was impregnated with the water-dispersed polyurethane resin H obtained in Synthesis Example 8, and the PU resin proportion was 47 mass% with respect to the fiber sheet.

[Comparative Example 8]

[0148] Artificial leather was obtained in the same manner as Example 1, except that the fiber sheet was impregnated with the water-dispersed polyurethane resin I obtained in Synthesis Example 9, and the PU resin proportion was 50 mass% with respect to the fiber sheet.

[0149] The artificial leather samples obtained in Examples 1 to 11 and Comparative Examples 1 to 8 were measured by pulse NMR (solid echo method) to determine the L component spin-spin relaxation time Tl and the L component fraction Cl, and the embossing clarity was also evaluated. The results are shown in Table 1 below.

[Table 1]

Water-dispersed polyurethane resin composition (resin)			Measurement results for pulse NMR (solid echo method) and properties of artificial leather			Adhesion rate of water-dispersed polyurethane resin	
	Resin	Ratio of macromonomer to isocyanate	L component spin-spin relaxation time Tl	L component fraction Cl	Embossing clarity	Proportion of water-dispersed polyurethane resin with respect to (fiber sheet + water-dispersed polyurethane resin)	Proportion of water-dispersed polyurethane resin with respect to fiber sheet (total mass of the sheet fibers) (adhesion rate)
Units		mol%	μsec	%	Grade	wt%	wt%
Example 1	Resin A	2.5	612	41	5	22%	29%
Example 2	Resin B	0.5	512	39	5	21%	27%
Example 3	Resin C	1.5	543	40	5	22%	28%
Example 4	Resin D	3.5	694	39	5	21%	27%
Example 5	Resin E	5	789	40	4	22%	28%
Example 6	Resin C	1.5	548	50	5	27%	37%
Example 7	Resin C	1.5	547	28	4	15%	18%
Example 8	Resin D	3.5	650	50	5	27%	37%
Example 9	Resin D	3.5	652	28	5	15%	18%
Example 10	Resin E	5	789	50	5	27%	37%
Example 11	Resin E	5	789	28	5	15%	18%

(continued)

Water-dispersed polyurethane resin composition (resin)			Measurement results for pulse NMR (solid echo method) and properties of artificial leather			Adhesion rate of water-dispersed polyurethane resin	
	Resin	Ratio of macromonomer to isocyanate	L component spin-spin relaxation time Tl	L component fraction Cl	Embossing clarity	Proportion of water-dispersed polyurethane resin with respect to (fiber sheet + water-dispersed polyurethane resin)	Proportion of water-dispersed polyurethane resin with respect to fiber sheet (total mass of the sheet fibers) (adhesion rate)
Units		mol%	μsec	%	Grade	wt%	wt%
Comp. Example 1	Resin D	3.5	650	20	2	11%	12%
Comp. Example 2	Resin D	3.5	650	60	2	34%	51%
Comp. Example 3	Resin F	7.5	850	20	2	11%	12%
Comp. Example 4	Resin G	0	412	20	2	11%	12%
Comp. Example 5	Resin H	1	450	43	2	23%	30%
Comp. Example 6	Resin I	1	925	42	2	23%	30%
Comp. Example 7	Resin H	1	452	59	1	32%	47%
Comp. Example 8	Resin I	1	920	61	1	33%	50%

[0150] Based on the results, the embossing clarity was more satisfactory in Examples 1 to 11, where the L component spin-spin relaxation time Tl was 500 μsec to 800 μsec and the L component fraction Cl was 25% or greater and less than 55% with fitting of the free induction decay (FID) signal in pulse NMR (solid echo method, proton observation, measuring temperature: 50°C) to two components: the S component (Gaussian component) and L component (Lorentz component), compared to Comparative Examples 1 to 8 in which the values were outside of these ranges.

INDUSTRIAL APPLICABILITY

[0151] The artificial leather of the invention has a low environmental impact while also having excellent embossing clarity, and it can therefore be suitably used for upholstery or interior materials for seats in interiors, automobiles, aircraft and railway vehicles, or for clothing products. More specifically, the artificial leather of the invention can be suitably used as an interior finishing material with a very delicate outer appearance when used as an upholstery for furniture, chairs or wall materials, or for seats, ceilings or interior finishings for vehicle interiors of automobiles, electric railcars or aircraft, or as clothing materials used in parts of shirts, jackets, uppers or trims for shoes including casual shoes, sports shoes, men's shoes or women's shoes, or bags, belts and wallets, or even as industrial materials such as wiping cloths, abrasive cloths or CD curtains.

REFERENCE SIGNS LIST

[0152]

1 Fiber sheet
11 Scrim (optional)
12 Fiber layer (A)
13 Fiber layer (B)
A Cross-section of fiber with elliptical cross-section
a Maximum diameter of cross-section A
b Straight line perpendicular to maximum diameter "a" passing through midpoint p of maximum diameter "a"
c Outer circumferential distance on straight line b
p Midpoint of maximum diameter "a"

Claims

1. Artificial leather comprising a nonwoven fabric made of ultrafine fibers having a mean single fiber diameter of 0.3 μm to 7 μm, and water-dispersed polyurethane, wherein when the free induction decay (FID) signal in pulse NMR (solid echo method, proton observation, measuring temperature: 50°C) is fitted to two components: the S component (Gaussian component) and L component (Lorentz component), the spin-spin relaxation time T1 of the L component is 500 μsec to 800 μsec and the L component fraction Cl is 25% or greater and less than 55%.

2. The artificial leather according to claim 1, wherein the ultrafine fibers are polyester-based fibers.

3. The artificial leather according to claim 1 or 2, wherein the nonwoven fabric is integrated by entangling with a scrim layer woven fabric.

4. The artificial leather according to claim 3, wherein the scrim layer is a woven fabric of polyester-based fibers.

5. The artificial leather according to claim 1 or 2, wherein the water-dispersed polyurethane is obtained by reaction between a methyl methacrylate-based macromonomer having two hydroxyl groups at one end, a polymer polyol having hydroxyl groups at both ends, a short chain diol having hydroxyl groups at both ends, a hydrophilic agent, an organic diisocyanate, and a chain extender.

6. The artificial leather according to claim 5, wherein the polymer polyol is a polycarbonate diol and/or a polyether diol.

7. The artificial leather according to claim 6, wherein the polycarbonate diol is a copolymerized polycarbonate diol obtained by copolymerization of two or more polyhydric alcohols.

8. The artificial leather according to claim 5, wherein the proportion of the methyl methacrylate-based macromonomer

having two hydroxyl groups at one end with respect to the organic diisocyanate is 0.1 mol% to 7.0 mol%.

FIG. 1

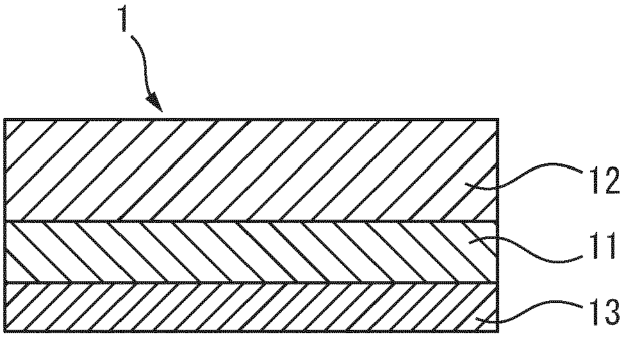


FIG. 2

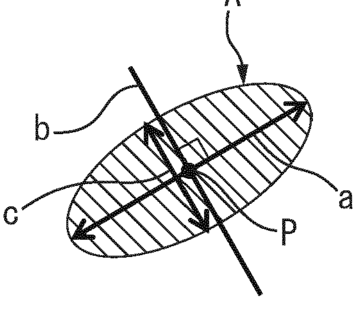


FIG. 3

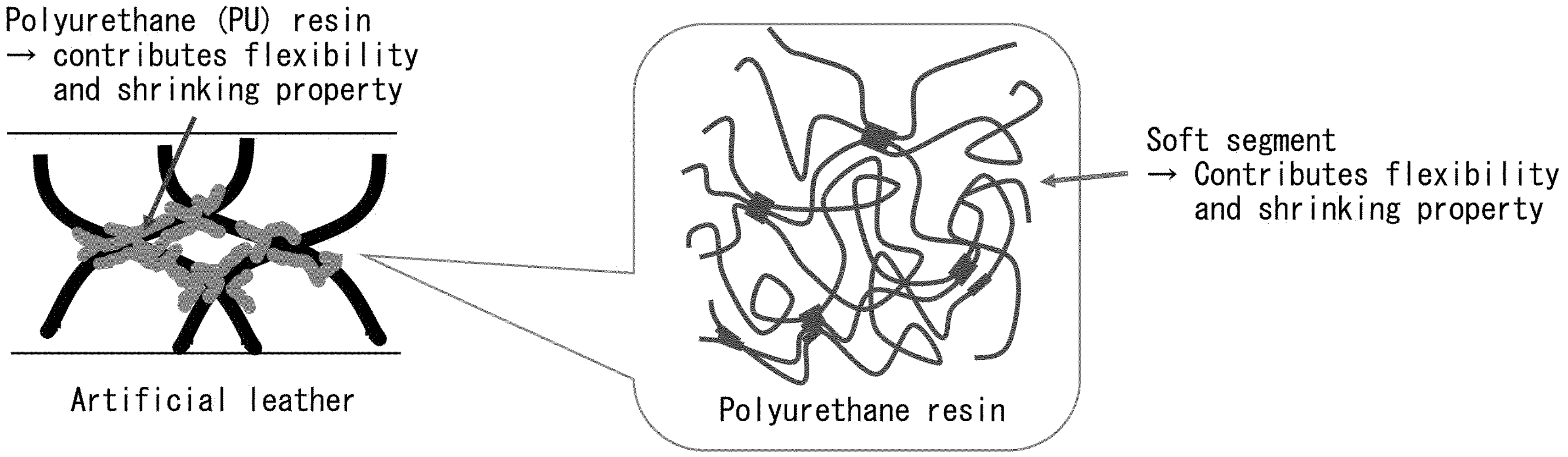

Polyurethane (PU) resin
→ contributes flexibility
and shrinking property
Artificial leather
Polyurethane resin
Soft segment
→ Contributes flexibility
and shrinking property

FIG. 4

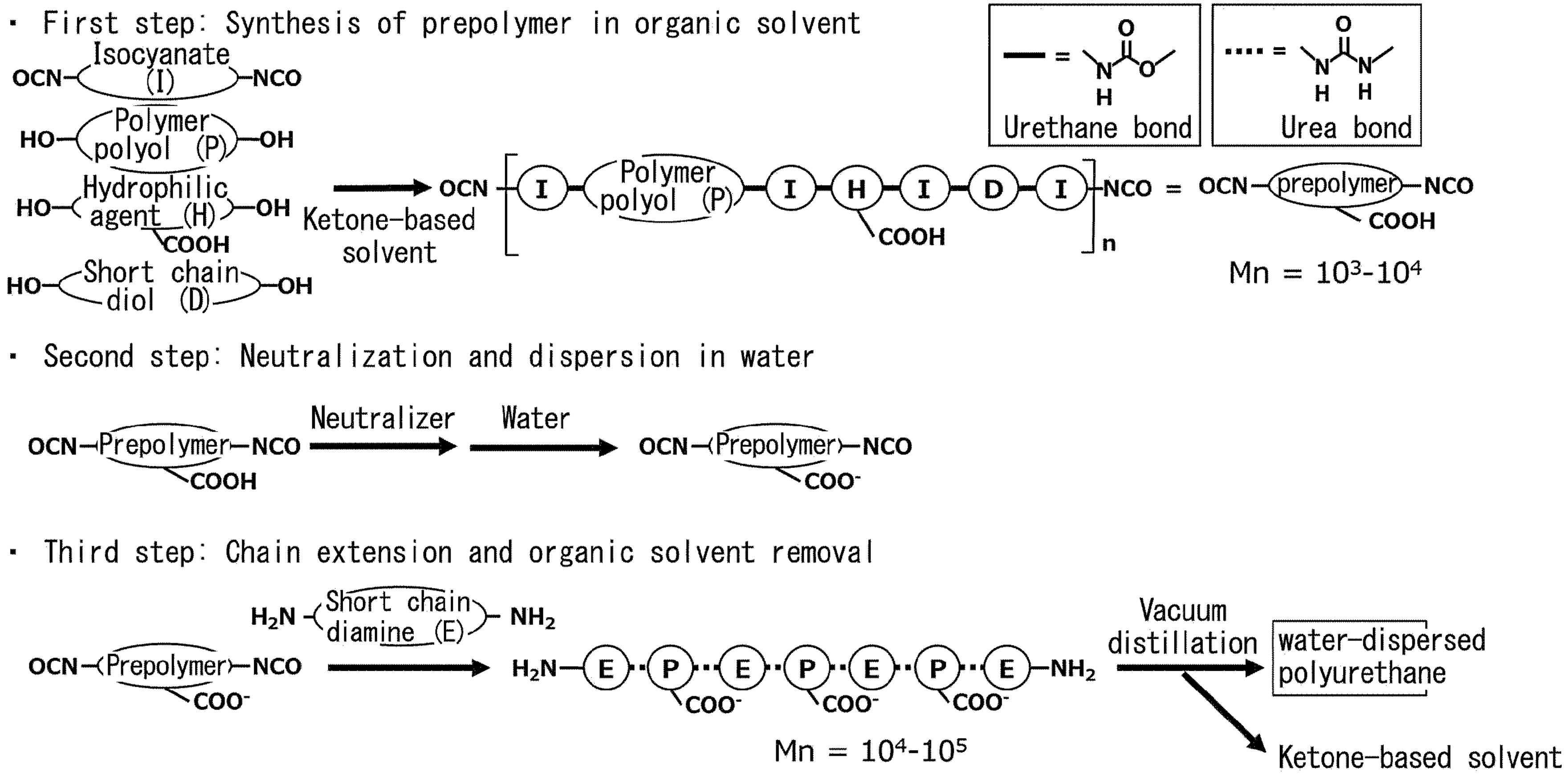
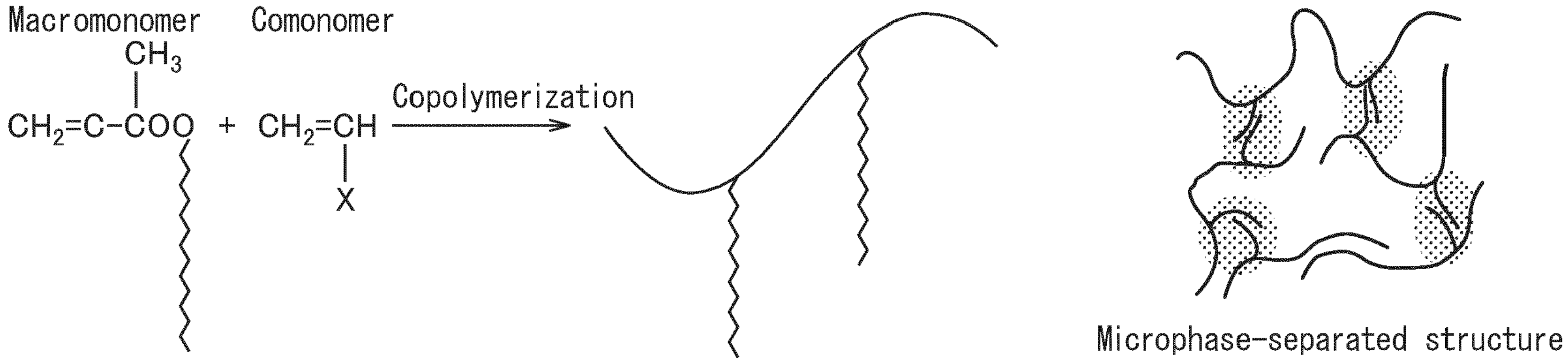

· First step: Synthesis of prepolymer in organic solvent
OCN–Isocyanate (I)–NCO
HO–Polymer polyol (P)–OH
HO–Hydrophilic agent (H)–OH
COOH
HO–Short chain diol (D)–OH
Ketone-based solvent
OCN
I
Polymer polyol (P)
I
H
I
D
I
NCO
COOH
n
= OCN–prepolymer–NCO
COOH
Mn = 10³-10⁴
= Urethane bond
O
N
H
O
···· = Urea bond
O
N
H
N
H
· Second step: Neutralization and dispersion in water
OCN–Prepolymer–NCO
COOH
Neutralizer
Water
OCN–Prepolymer–NCO
COO⁻
· Third step: Chain extension and organic solvent removal
OCN–Prepolymer–NCO
COO⁻
H₂N–Short chain diamine (E)–NH₂
H₂N–E·P··E·P··E·P··E–NH₂
COO⁻
COO⁻
COO⁻
Mn = 10⁴-10⁵
Vacuum distillation
water-dispersed polyurethane
Ketone-based solvent

FIG. 5



→Monomer introducing optional side chain into main chain

Association between main chains inhibited by introduced side chains

FIG. 6

Dihydroxyl group (HOCH$_2$-CH(OH)-□-□-□-□........)

□ □ □ □=Methyl methacrylate

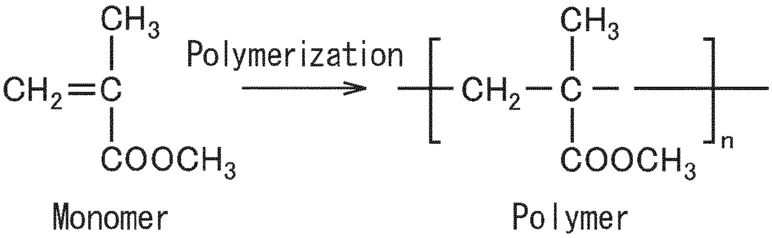
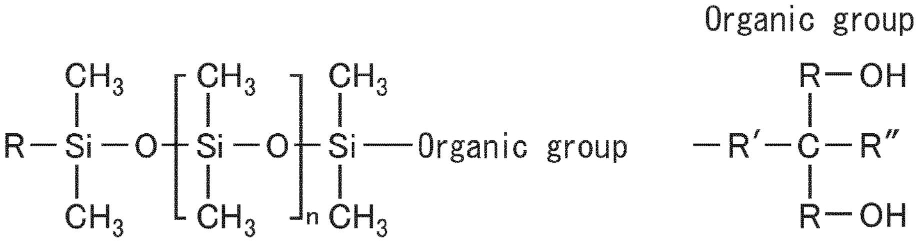


FIG. 7



REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 4506754 B **[0009]**
- JP 6582992 B **[0009]**