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(54) ARTIFICIAL LEATHER BASE MATERIAL AND GRAINED ARTIFICIAL LEATHER

(57) Disclosed is an artificial leather base material including: a fabric, and an elastic polymer, fine particles, and a plasticizer that have been applied to the fabric, wherein the elastic polymer includes a (meth)acrylic elastic polymer and a polyurethane, the fine particles have a Mohs hardness of 4 or less, and the product of a bending resistance, a durometer Shore C hardness, and a thickness of the artificial leather base material is 200 to 400 mm^2. Also disclosed is a grain-finished artificial leather obtained using the artificial leather base material.

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Description

[Technical Field]

[0001] The present invention relates to an artificial leather base material and a grain-finished artificial leather using the same.

[Background Art]

[0002] Conventionally, a grain-finished artificial leather is known in which a grain-like resin layer is stacked on an artificial leather base material obtained by impregnating an elastic polymer into voids inside a fabric. The grain-finished artificial leather has been used as an alternative to a natural leather for the skin materials of shoes, clothing, gloves, bags, balls, and the like, and the interior finishing materials for buildings and vehicles.

[0003] A natural leather includes dense collagenous fibers, and thus has both suppleness and fullness. When a natural leather is bent, its fullness allows the formation of fine fold creases with roundness and a quality appearance. A grain-finished leather has excellent surface flatness, and unevenness is less likely to be conspicuous even when a flat grain is formed thereon. However, it has been difficult to obtain a natural leather with a stable quality. Moreover, collagenous fibers have low heat resistance and low water resistance. Therefore, it has been difficult for a natural leather to be used in applications for which heat resistance and water resistance are required. To improve the heat resistance and the water resistance of a natural leather, a method is available in which the thickness of a grain-like resin layer (hereinafter also simply referred to as "grain layer"). However, when the thickness of the grain layer is increased, the suppleness, which is an advantage of a natural leather, is reduced.

[0004] On the other hand, a grain-finished artificial leather is superior in quality stability, heat resistance, water resistance, abrasion resistance, and ease of maintenance. However, it has the following problems. The grain-finished artificial leather includes, inside a fabric, voids that are not filled with an elastic polymer, and thus has low fullness. For this reason, when bent, the grain-finished artificial leather is not folded with roundness as in the case of a grain-finished leather, and instead, is folded so as to be buckled, thus forming coarse creases.

[0005] As a grain-finished artificial leather for which the above-described problems have been solved, for example, PTL 1 below discloses a grain-finished artificial leather with a high level of fullness that is obtained by stacking a grain-like resin layer on an artificial leather base material containing a filler, a liquid non-volatile oil, and an elastic polymer.

[Citation List]

[Patent Literature]

[0006] [PTL 1] WO 2014/132630

[Summary of Invention]

[Technical Problem]

[0007] As described above, a grain-finished artificial leather includes voids inside a fabric. Therefore, the grain-finished artificial leather has the problem that it has lower fullness than a grain-finished leather, and will not be folded with roundness as in the case of a natural grain-finished leather when bent, and instead, is folded so as to be buckled, thus forming coarse creases. In particular, in the case of a grain-finished artificial leather having a thin grain layer or a mirror surface-like flat grain layer, fold creases tend to be nonuniform, and coarse fold creases may be formed, resulting in a reduction in a quality appearance of the grain-finished artificial leather. When the content ratio of the elastic polymer applied to the fabric is increased in order to alleviate these problems of a lack of fullness, the nonuniformity of fold creases, and the formation of coarse fold creases, the grain-finished artificial leather will have a rubber-like rigid texture due to the resiliency of the elastic polymer. In addition, as another problem, the grain-finished artificial leather has a disadvantage of poor surface flatness.

[0008] It is an object of the present invention to provide a grain-finished artificial leather that has both suppleness and fullness, bends with roundness so as to form fine fold creases when bent, and also has excellent surface flatness.

[Solution to Problem]

[0009] An aspect of the present invention is directed to an artificial leather base material including: a fabric, and an elastic polymer, fine particles, and a plasticizer that have been applied to the fabric, wherein the elastic polymer includes a (meth)acrylic elastic polymer and a polyurethane, the fine particles have a Mohs hardness of 4 or less, and the product of a bending resistance, a durometer Shore C hardness, and a thickness of the artificial leather base material is 200 to 400 mm^2. By using such an artificial leather base material, it is possible to produce a grain-finished artificial leather that has both suppleness and fullness as those of a grain-finished leather, and bends with roundness so as to form fine fold creases when bent, and also has excellent surface flatness.

[0010] Another aspect of the present invention relates to a grain-finished artificial leather, including: the above-described artificial leather base material, and a grain-like resin layer formed on at least one surface of the artificial leather base material. Such a grain-finished artificial leather has both suppleness and fullness, and is likely to bend with roundness so as to form fine fold creases when bent.

[Advantageous Effects of Invention]

[0011] According to the present invention, it is possible to obtain a grain-finished artificial leather that has both suppleness and fullness, bends with roundness so as to form fine fold creases when bent, and also has excellent surface flatness.

[Description of Embodiment]

[0012] An artificial leather base material according to the present embodiment includes: a fabric, and an elastic polymer, fine particles, and a plasticizer that have been applied to the fabric, wherein the elastic polymer includes a (meth)acrylic elastic polymer and a polyurethane, the fine particles have a Mohs hardness of 4 or less, and the product of a bending resistance, a durometer Shore C hardness, and a thickness of the artificial leather base material is 200 to 400 mm^2. In the following, the artificial leather base material of the present embodiment will be described in detail.

[0013] Examples of the fabric include fiber structures, including, for example, a non-woven fabric, a woven fabric, and a knitted fabric. Among these, a non-woven fabric is particularly preferable because it has a reduced density unevenness of fibers, and thus can easily provide an artificial leather base material having suppleness, fullness, and surface flatness all together. In the following, a case where a non-woven fabric is used will be described in detail as a representative example.

[0014] The average fineness of the fibers is preferably 0.001 to 2.5 dtex, more preferably 0.001 to 0.9 dtex, particularly preferably 0.001 to 0.7 dtex, quite particularly preferably 0.001 to 0.5 dtex, further preferably 0.001 to 0.3 dtex. The fineness of the fibers can be measured by taking a photograph of a cross section of the artificial leather base material in the thickness direction using a scanning electron microscope (SEM) with a magnification of 2000X. More specifically, the cross-sectional area of the fibers is measured based on the photograph obtained with the SEM, and the fineness can be calculated from the cross-sectional area and the specific gravity of the resin that forms the fibers. The average fineness can be determined as an average value of the finenesses of average 100 single fibers, evenly obtained from the photograph.

[0015] The resin that forms the fibers is not particularly limited, and examples thereof include polyamides (nylon) such as polyamide 6, polyamide 66, polyamide 10, polyamide 11, polyamide 12, and polyamide 6-12; aromatic polyesters such as polyethylene terephthalate (PET), isophthalic acid-modified PET, sulfoisophthalic acid-modified PET, polybutylene terephthalate, and polyhexamethylene terephthalate; aliphatic polyesters such as polylactic acid, polyethylene succinate, polybutylene succinate, polybutylene succinate adipate, and a polyhydroxybutyrate-polyhydroxyvalerate resin; and polyolefins such as polypropylene, polyethylene, polybutene, polymethylpentene, and a chlorine-based polyolefin. These may be used alone or in a combination of two or more. Among these, PET or modified PET; polylactic acid; polyamide 6, polyamide 12, polyamide 6-12; and polypropylene are preferable.

[0016] Polyamide is particularly preferable from the viewpoint of forming an artificial leather base material having better suppleness and surface flatness. If necessary, additives such as a softening agent, a fiber ordering agent, an anti-fouling agent, a hydrophilizing agent, a lubricant, a degradation inhibitor, an ultraviolet absorber, and a flame retardant may be mixed in the fibers as long as the effects of the present invention are not impaired.

[0017] The content ratio of the fabric in the artificial leather base material is not particularly limited, but is preferably 25 to 69.5 mass%, because an artificial leather base material that is well-balanced in shape stability, suppleness, and flatness can be obtained.

[0018] The elastic polymer includes at least a (meth)acrylic elastic polymer and a polyurethane. The elastic polymer imparts shape stability, suppleness, fullness, and the like to the artificial leather base material by restraining the fibers that form the fabric. A (meth)acrylic elastic polymer provides, in particular, suppleness, surface flatness, fine fold creases, and fullness. A polyurethane provides, in particular, shape stability, mechanical properties, and rigidity.

[0019] The (meth)acrylic elastic polymer can be obtained from a combination of ethylenically unsaturated monomers, specifically, for example, by appropriately combining and polymerizing various monomers of an ethylenically unsaturated monomer, and a cross-linkable monomer or the like used as needed. Note that the phrase "(meth)acrylic" means acrylic or methacrylic.

[0020] Specific examples of the ethylenically unsaturated monomer include 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, lauryl acrylate, lauryl methacrylate, stearyl (meth)acrylate, n-butyl acrylate, isobutyl acrylate, cyclohexyl acrylate, benzyl acrylate, ethyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, methyl methacrylate, ethyl methacrylate, diacetone acrylamide, isobutyl methacrylate, isopropyl methacrylate, acrylic acid, methacrylic acid, acrylamide, acrylonitrile, styrene, α-methyl styrene, p-methyl styrene, (meth)acryl amide, diacetone (meth)acrylamide, methyl methacrylate, maleic acid, itaconic acid, fumaric acid, cyclohexyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, vinyl chloride, acrylonitrile, vinyl ether, vinyl ketone, vinyl amide, ethylene, propylene, vinyl pyrrolidone, isopropyl acrylate, n-hexyl methacrylate, n-hexyl acrylate, methyl acrylate, n-butyl methacrylate, hydroxypropyl methacrylate, vinyl acetate, methyl acrylate, n-butyl methacrylate, hydroxypropyl methacrylate, dimethylaminoethyl methacrylate, and diethylaminoethyl methacrylate. These may be used alone, or in a combination of two or more.

[0021] The cross-linkable monomer is a monomer that causes a (meth)acrylic elastic polymer to form a cross-linked structure. Specific examples of the cross-linkable monomer include multifunctional ethylenically unsaturated monomers such as ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, and 1,6-hexanediol di(meth)acrylate; various monomers having a hydroxyl group, such as 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate; multifunctional ethylenically unsaturated monomers having a reactive group that can form a cross-linked structure, including, for example, a (meth)acrylic acid derivative having an epoxy group, such as glycidyl(meth)acrylate.

[0022] The (meth)acrylic elastic polymer has a glass transition temperature (Tg) of preferably -60 to 10°C, more preferably -50 to -5°C, from the viewpoint of easily providing a particularly supple artificial leather base material. Note that when the Tg of the (meth)acrylic elastic polymer is too low, the viscosity is increased, which may pose a problem during the production process or in practical use.

[0023] The (meth)acrylic elastic polymer has a 100% modulus of preferably 0.4 to 5 MPa, more preferably 0.7 to 4 MPa. With such a range, the (meth)acrylic elastic polymer sufficiently restrains the fibers of the fabric, so that a particularly supple artificial leather base material can be easily obtained.

[0024] As the polyurethane, any polyurethane that has been conventionally used for production of an artificial leather base material can be used without any particular limitation. Specific examples thereof include various polyurethanes such as a polycarbonate-based polyurethane and a polyether polyurethane that are obtained by reacting a polymer polyol having an average molecular weight of 200 to 6000, an organic polyisocyanate, and a chain extender at a predetermined molar ratio. In particular, a polyurethane including 60 mass% or more of a polycarbonate-based polyurethane is preferable because of its excellent durability.

[0025] The polyurethane has a 100% modulus of preferably 1 to 10 MPa, more preferably 2 to 8 MPa. With such a range, a supple artificial leather base material having excellent shape stability and excellent mechanical properties can be easily obtained.

[0026] The content ratio of the elastic polymer in the artificial leather base material is preferably 15 to 40 mass%. With such a range, an artificial leather base material that has excellent fullness and excellent surface flatness, and is likely to bend with roundness so as to form fine fold creases when bent can be easily obtained.

[0027] The content ratio of the (meth)acrylic elastic polymer to the total amount of the polyurethane and the (meth)acrylic elastic polymer is preferably 5 to 90 mass%, more preferably 5 to 70 mass%.

[0028] The artificial leather base material includes fine particles having a Mohs hardness of 4 or less, preferably a Mohs hardness of 0.5 to 4. Examples of the fine particles having a Mohs hardness of 4 or less include metals, metal oxides, inorganic compounds, organic compounds, and inorganic organic compounds that have a Mohs hardness of 4 or less. The fine particles having a Mohs hardness of 4 or less impart excellent fullness and excellent surface flatness to the artificial leather base material, and make the artificial leather base material likely to bend with roundness so as to form fine fold creases when bent.

[0029] The hardnesses of commonly known fine particles are approximately as follows: graphite (Mohs hardness of 0.5 to 1, the same applies to the following), talc (1), gypsum (1), lead (1.5), calcium sulfate (1.6 to 2), zinc (2), silver (2), amber (2 to 2.5), aluminum silicate (2 to 2.5), cerium oxide (2.5), magnesium hydroxide (2 to 3), mica (2.8), aluminum (2 to 2.9), aluminum hydroxide (3), calcium carbonate (3), magnesium carbonate (3 to 4), marble (3 to 4), copper (2.5 to 4), brass (3 to 4), magnesium oxide (4), zinc oxide (4 to 5), iron (4 to 5), glass (5), iron oxide (6), titanium oxide (5.5 to 7.5), silica (7), alumina (9), silicon carbide (9), and diamond (10). The artificial leather base material of the present embodiment includes fine particles having a Mohs hardness of 4 or less. When the Mohs hardness of the fine particles exceeds 4, the suppleness is reduced. The Mohs hardness can be measured by a known method. As the hardness, new Mohs hardness, Vickers hardness (HV), Shore hardness (HS), Knoop hardness and so forth are known, in addition to Mohs hardness. A Mohs hardness of 1 to 4 substantially corresponds to a Vickers hardness (HV) of 1 to 350, a Shore hardness (HS) of 1 to 40, and a Knoop hardness of 1 to 300. In the present embodiment, fine particles having a hardness that is measured by another hardness measurement method and corresponds to a Mohs hardness of 4 or less are also included.

[0030] Examples of the fine particles having a Mohs hardness of 4 or less (hereinafter also simply referred to as "fine particles") include graphite, talc, gypsum, calcium sulfate, amber, aluminum silicate, magnesium hydroxide, mica, aluminum hydroxide, calcium carbonate, magnesium carbonate, and magnesium oxide. Among these, talc, magnesium silicate, calcium sulfate, aluminum silicate, calcium carbonate, magnesium oxide, magnesium carbonate, magnesium hydroxide, aluminum hydroxide, and mica are particularly preferable, because they have excellent chemical stability and excellent thermal stability, and fine particles having a uniform particle size and a high purity are easily available. These may be used alone or in a combination of two or more.

[0031] Here, the chemical stability is a property of being less prone to be swollen or dissolved in water or hot water in a practical pH range, for example, a pH of 4 to 12. The thermal stability is a property of having a decomposition temperature and a melting point of 150°C or more, preferably 200°C or more. The solubility of the fine particles is preferably 1% or less. It is also possible to include fine particles having a Mohs hardness exceeding 4, together with the fine particles having a Mohs hardness of 4 or less, as long as the effects of the present invention are not impaired. It is also possible to use, for example, a softening agent, a fiber ordering agent, an anti-fouling agent, a hydrophilizing agent, a lubricant, a degradation inhibitor, an ultraviolet absorber, a flame retardant and so forth in combination.

[0032] The average particle size of the fine particles is preferably 0.5 to 10 μm, more preferably 1 to 7 μm, because the fine particles can be easily applied uniformly in the voids inside the fabric. When the average particle size is too small, the artificial leather base material tends to be hard.

[0033] The absolute specific gravity of the fine particles is preferably 1.2 to 4.5 g/cm^3, because the fine particles can be easily applied uniformly in the voids inside the fabric, and an artificial leather base material having particularly excellent fullness can be easily obtained.

[0034] The content ratio of the fine particles in the artificial leather base material is preferably 15 to 40 mass%, from the viewpoint of easily providing an artificial leather base material that has excellent fullness and excellent surface flatness, and is likely to bend with roundness so as to form fine fold creases when bent. When the content ratio of the fine particles is too high, the surface flatness tends to be reduced.

[0035] The ratio of the (meth)acrylic elastic polymer to the total amount of the fine particles and the (meth)acrylic elastic polymer is preferably 5 to 50 mass%, more preferably 5 to 40 mass%, from the viewpoint of easily providing an artificial leather base material in which the product of the bending resistance, the durometer Shore C hardness, and the thickness is 200 to 400 mm^2 can be easily obtained.

[0036] The artificial leather base material of the present embodiment includes a plasticizer. The plasticizer is mixed in order to improve the plastic deformability by softening the fabric, the elastic polymer, and the fine particles. Examples of the plasticizer include a liquid, viscous, wax-like, or solid oil or fatty acid ester. Specific examples thereof include fatty acid esters, hydrocarbon-based oils such as paraffin oil, hydrocarbon-based waxes, carnauba waxes, phthalic acid esters, phosphoric acid esters, and hydroxy carboxylic acid esters. These may be used alone or in a combination of two or more. Among these, a plasticizer that has a melting point of 60°C or less and preferably that is liquid at 23°C, in particular, a fatty acid ester is preferable, because an artificial leather base material having a texture with both suppleness and fullness can be obtained.

[0037] A fatty acid ester is a compound obtained by esterification of an alcohol and an acid. Specific examples thereof include monohydric alcohol esters, monohydric alcohol esters of polybasic acids, fatty acid esters of polyhydric alcohols and derivatives thereof, and fatty acid esters of glycerin. Examples of the alcohol include methyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, n-octyl alcohol, 2-ethylhexyl alcohol, n-decyl alcohol, isodecyl alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, octyldodecyl alcohol, glycerin, sorbitan, polyoxyethylene sorbitan, polyoxyethylene sorbitol, ethylene glycol, polyethylene glycol, propylene glycol, pentaerythritol, and polyoxyethylene bisphenol A. Examples of the acid include caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, behenic acid, cocconut fatty acid, methacrylic acid, 2-ethylhexanoic acid, phthalic acid, adipic acid, azelaic acid, maleic acid, sebacic acid, and trimellitic acid.

[0038] Specific examples of the fatty acid ester include cetyl 2-ethylhexanoate, cocconut fatty acid methyl, methyl laurate, isopropyl myristate, isopropyl palmitate, 2-ethylhexyl palmitate, octyldodecyl myristate, methyl stearate, butyl stearate, 2-ethylhexyl stearate, isotridecyl stearate, methyl oleate, myristyl myristate, stearyl stearate, isobutyl oleate, dinormalalkyl phthalate, di-2-ethylhexyl phthalate, diisononyl phthalate, didecyl phthalate, ditridecyl phthalate, trinormalalkyl trimellitate, tri-2-ethylhexyl trimellitate, triisodecyl trimellitate, diisobutyl adipate, diisodecyl adipate, sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan tristearate, sorbitan monooleate, sorbitan trioleate, sorbitan monostearate, sorbitan sesquioleate, sorbitan monolaurate, sorbitan monopalmitate, polyoxyethylene sorbitan monolaurate, polyoxyethylene monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan monooleate, polyoxyethylene trioleate, polyoxyethylene sorbitol tetraoleate, sorbitan monolaurate, polyoxyethylene monolaurate, polyoxyethylene monolaurate, polyethylene glycol monostearate, polyethylene glycol monooleate, polyethylene glycol distearate, polyethylene glycol bisphenol A lauric acid ester, pentaerythritol monooleate, pentaerythritol monostearate, pentaerythritol tetrapalmitate, monoglyceride stearate, monoglyceride stearate, monoglyceride palmitate, monoglyceride oleate, mono-diglyceride stearate, triglyceride 2-ethylhexanoate, monoglyceride behenate, mono-diglyceride caprate, triglyceride caprate, and lauryl methacrylate.

[0039] Among the fatty acid esters, it is preferable to use a fatty acid ester that has a melting point of 60°C or less and preferably that is liquid at 23°C, in particular, a fatty acid ester of a fatty acid having 12 to 18 carbon atoms and a polyhydric alcohol, from the viewpoint of easily providing an artificial leather base material having a texture with both suppleness and fullness.

[0040] The content ratio of the plasticizer in the artificial leather base material is not particularly limited, but is preferably 0.5 to 5 mass%, more preferably 1 to 5 mass%, particularly preferably 2 to 4 mass%, because the effect of improving suppleness is fully exerted. When the content ratio of the plasticizer is too high, the plasticizer tends to reduce the flame retardancy, and to bleed out, thus causing stickiness.

[0041] In the artificial leather base material of the present embodiment, the product of the bending resistance, the durometer Shore C hardness, and the thickness is 200 to 400 mm^2. For the conventional artificial leather base materials, there is a trade-off relationship between the surface hardness and the suppleness. As a result of the product of the bending resistance, the durometer Shore C hardness, and the thickness being adjusted to 200 to 400 mm^2, the artificial leather base material of the present embodiment has both high surface hardness and high suppleness. The product of the bending resistance, the durometer Shore C hardness, and the thickness is 200 to 400 mm^2, preferably 210 to 350 mm. When the product of the bending resistance, the durometer Shore C hardness, and the thickness is less than 200 mm^2, one of the surface hardness or the suppleness becomes insufficient, so that coarse fold creases are likely to be formed. On the other hand, when the product of the bending resistance, the durometer Shore C hardness, and the thickness exceeds 400 mm^2, the resulting artificial leather base material lacks elasticity or has poor fullness, or is likely to bend sharply because of the excessively hard surface.

[0042] The bending resistance indicates a degree of suppleness of an artificial leather base material. The bending resistance of the artificial leather base material is measured using a softness tester. The bending resistance of the artificial leather base material is preferably 1.8 to 6 mm, more preferably 2 to 5 mm, because an artificial leather base material that is well-balanced in suppleness and fullness can be obtained. Here, it is preferable that the bending resistance is measured from the surface on which a grain layer is formed in the case of producing a grain-finished artificial leather.

[0043] The durometer Shore C hardness indicates a surface hardness. The durometer Shore C hardness of the artificial leather base material is preferably 48 to 80, more preferably 52 to 76, because an artificial leather base material that has a particularly high surface flatness, and is likely to realize fine fold creases in particular can be obtained. Here, it is preferable to measure the durometer Shore C on the same side as the side on which the bending resistance is measured, and to carry out measurement on the side on which a grain layer is to be formed in the case of producing a grain-finished artificial leather.

[0044] The thickness of the artificial leather base material is not particularly limited, but is preferably about 100 to 3000 μm, more preferably about 300 to 2000 μm, from the viewpoint of easily providing an artificial leather base material in which the product of the bending resistance, the durometer Shore C hardness, and the thickness is 200 to 400 mm^2.

[0045] The apparent density of the artificial leather base material is preferably 0.45 to 0.85 g/cm^3, more preferably 0.55 to 0.80 g/cm^3, from the viewpoint of easily providing an artificial leather base material in which the product of the bending resistance, the durometer Shore C hardness, and the thickness is 200 to 400 mm^2. In particular, when a non-woven fabric of ultrafine fibers of polyamide-based fibers is used as the fabric, the apparent density is preferably 0.55 to 0.80 g/cm^3, more preferably 0.60 to 0.75 g/cm^3.

[0046] The total of the apparent density of the fine particles having a Mohs hardness of 4 or less and the apparent density of the (meth)acrylic elastic polymer including the apparent density of the artificial leather base material is preferably 0.15 to 0.40 g/cm^3, from the viewpoint of easily providing an artificial leather base material in which the product of the bending resistance, the durometer Shore C hardness, and the thickness is 200 to 400 mm^2.

[0047] Next, a method for producing the above-described artificial leather base material will be described. In the present embodiment, a case where a non-woven fabric of ultrafine fibers is used as the fabric will be described in detail as a representative example.

[0048] The non-woven fabric of ultrafine fibers is obtained, for example, by subjecting ultrafine fiber-generating fibers such as island-in-the-sea (matrix-domain) composite fibers to entangling treatment, and then to ultrafine fiber-generating treatment. Although the present embodiment describes in detail a case where the island-in-the-sea composite fibers are used, it is also possible to use ultrafine fiber-generating fibers other than the island-in-the-sea composite fibers. Alternatively, it is also possible to directly spin ultrafine fibers without using ultrafine fiber-generating fibers. Note that specific examples of the ultrafine fiber-generating fibers other than the island-in-the-sea composite fibers include strip/division-type fibers and petal-shaped fibers.

[0049] Examples of the protuction method of the non-woven fabric of ultrafine fibers include a method in which island-in-the-sea composite fibers are melt spun using a thermoplastic resin serving as a sea component and a thermoplastic resin serving as an island component, to produce a web, and the web is subjected to entangling treatment, and, thereafter, the sea component is selectively removed from the island-in-the-sea composite fibers, to form ultrafine fibers including the thermoplastic resin serving as the island component.

[0050] As the thermoplastic resin serving as the sea component, a thermoplastic resin that differs from the thermoplastic resin serving as the island component in solubility in a solvent or in decomposability in a decomposition agent is selected. Specific examples of the thermoplastic resin constituting the sea component include water-soluble polyvinyl alcohol-based resins, polyethylene, polypropylene, polystyrene, ethylene-propylene resins, ethylene-vinyl acetate resins, styrene-ethylene resins, and styrene-acrylic resins.

[0051] Examples of the production method of the web include a method in which filaments of the island-in-the-sea composite fibers that have been spun by spunbonding or the like are collected on a net, without being cut, to form a filament web, and a method in which filaments are cut into staples to form a staple web. Among these, a filament web is particularly preferable because of excellent denseness and excellent fullness. Note that a filament means a continuous fiber, rather than a staple that has been intentionally cut after being spun. More specifically, a filament means a fiber other than a staple that has been intentionally cut so as to have a fiber length of about 3 to 80 mm, for example. The fiber length of the island-in-the-sea composite fibers before being subjected to ultrafine fiber generation is preferably 100 mm or more, and may have a fiber length of several meters, several hundred meters, several kilometers, or more, as long as the fibers are technically producible and are not inevitably cut during the production process. Note that some of filaments may be inevitably cut into short fibers during the production process by needle punching during entanglement or surface buffing. The formed web may be subjected to fusion bonding treatment in order to impart shape stability thereto.

[0052] Examples of the entangling treatment include a method in which about 5 to 100 layers of the web are placed on top of each other, and subjected to needle punching or high-pressure water jetting treatment.

[0053] In production of a non-woven fabric of ultrafine fibers, first, a thermoplastic resin for forming a selectively-removable sea component (matrix component) of island-in-the-sea composite fibers, and a thermoplastic resin for forming an island component (domain component), i.e., resin components for forming ultrafine fibers, of the island-in-the-sea composite fibers are melt spun and then stretched, thereby obtaining island-in-the-sea composite fibers.

[0054] In any of the processes until the sea component of the island-in-the-sea composite fibers is removed to form ultrafine fibers, fiber shrinking treatment such as heat-moisture shrinking treatment using water vapor may be performed, thus densifying the island-in-the-sea composite fibers to enhance the fullness.

[0055] The sea component of the island-in-the-sea composite fibers is removed by dissolution or decomposition at an appropriate stage after the web has been formed. Through such removal by decomposition or through dissolution and extraction, the island-in-the-sea composite fibers are subjected to ultrafine fiber generation, and ultrafine fibers in the form of fiber bundles are formed.

[0056] The method for applying the elastic polymer including the (meth)acrylic elastic polymer and the polyurethane to the fabric is not particularly limited. An example is a method in which the fabric is impregnated with a dispersion in which an emulsion or aqueous dispersion of the (meth)acrylic elastic polymer and an emulsion or aqueous dispersion of the polyurethane are mixed, followed by drying. As another example, only one of the polyurethane-based elastic polymer and the (meth)acrylic elastic polymer is applied to the fabric in advance, and, thereafter, only the other is further applied thereto. In the case of using a non-woven fabric of ultrafine fibers produced from island-in-the-sea composite fibers, these elastic polymers may be applied to a non-woven fabric of island-in-the-sea composite fibers before being subjected to ultrafine fiber generation, or may be applied to the non-woven fabric of ultrafine fibers.

[0057] When the ultrafine fibers form fiber bundles derived from ultrafine fiber-generating fibers, the elastic polymer may be impregnated inside the fiber bundles, may be attached to the outside of the fiber bundles, or may be attached to the inside and the outside of the fiber bundles. When the elastic polymer is impregnated inside the fiber bundles, the texture can be adjusted by adjusting the restraint of the ultrafine fibers forming the fiber bundles. For example, when island-in-the-sea composite fibers are subjected to ultrafine fiber-generating treatment, the water-soluble thermoplastic resin is removed from the island-in-the-sea composite fibers, to form voids inside the ultrafine fiber bundles. A dispersion of the elastic polymer can easily enter the thus formed voids by capillary action. Accordingly, when the elastic polymer is applied inside the fiber bundles, the shape stability of the non-woven fabric is increased.

[0058] The method for applying the (meth)acrylic elastic polymer, the polyurethane, the fine particles, and the plasticizer to the voids of the fabric is not particularly limited. Specific examples thereof include a method in which the fabric is impregnated with a dispersion including the polyurethane, the (meth)acrylic elastic polymer, the fine particles, and the plasticizer, and dried.

[0059] When the fabric is a non-woven fabric of ultrafine fibers produced from island-in-the-sea composite fibers, it is preferable, in terms of the production process, that the polyurethane is applied before the island-in-the-sea composite fibers are subjected to ultrafine fiber generation, and a dispersion including the (meth)acrylic elastic polymer, the fine particles, and the plasticizer is applied after ultrafine fiber generation, and dried. The use of such a process is preferable because the (meth)acrylic elastic polymer, the fine particles, and the plasticizer are also applied inside the fiber bundles of the ultrafine fibers. Here, when the (meth)acrylic elastic polymer and the plasticizer are applied before island-in-the-sea composite fibers are subjected to ultrafine fiber generation, the deterioration or deformation of the (meth)acrylic elastic polymer and the detachment of the plasticizer tend to be caused by the treatment during the process of performing ultrafine fiber generation.

[0060] When the fabric is a non-woven fabric of ultrafine fibers produced from island-in-the-sea composite fibers, the polyurethane and the fine particles may be applied before the island-in-the-sea composite fibers are subjected to ultrafine fiber generation, and a dispersion including the (meth)acrylic elastic polymer and the plasticizer may be applied after ultrafine fiber generation, and be dried.

[0061] When the fabric is a non-woven fabric of ultrafine fibers produced from island-in-the-sea composite fibers, the fine particles, the polyurethane, and the (meth)acrylic elastic polymer may be applied before the island-in-the-sea composite fibers are subjected to ultrafine fiber generation, and an aqueous dispersion including the plasticizer may be applied after ultrafine fiber generation, and be dried. With such a process, the fine particles and the elastic polymer are mixed and integrated with each other, and can be easily uniformly applied.

[0062] Here, it is preferable that the fine particles are present inside the elastic polymer because the effects of the present invention can be achieved particularly prominently.

[0063] In this manner, the artificial leather base material of the present embodiment is obtained. The artificial leather base material may be optionally subjected to: thickness adjustment and planarization treatment by slicing treatment and buffing treatment; or finishing treatment such as flexibilizing treatment by crumpling, softening treatment by milling, reverse seal brushing treatment, antifouling treatment, hydrophilization treatment, lubricant treatment, softener treatment, antioxidant treatment, ultraviolet absorber treatment, fluorescent agent treatment, and flame retardant treatment.

[0064] For the purpose of adjusting the fullness and the suppleness of the artificial leather base material, it is also preferable to perform softening processing on the artificial leather base material. The method for softening processing is not particularly limited. Specifically, it is preferable to use a method in which the artificial leather base material is brought into close contact with an elastic sheet, and mechanically shrunk in a longitudinal direction (MD on production line), and then subjected to heat treatment in the shrunk state for heat setting. With such a method, it is possible to soften the artificial leather base material, while improving the flatness thereof.

[0065] If necessary, the artificial leather base material may be subjected to thickness adjustment and planarization treatment by slicing treatment and buffing treatment.

[0066] The artificial leather base material of the present embodiment can be suitably used for production of a grain-finished artificial leather obtained by forming a grain layer on an artificial leather base material. The grain layer may be a monolayer of a resin layer, or may have a stacked structure composed of a plurality of layers including, for example, a resin layer serving as a skin layer and an adhesive layer.

[0067] The method for forming the grain layer on the artificial leather base material is not particularly limited. Specifically, for example, a grain-like resin layer including an elastic polymer such as a polyurethane or a (meth)acrylic elastic polymer is formed by dry forming or direct coating. The dry forming is a method in which a coating liquid including a colored resin for forming a grain-like skin layer is applied to a release sheet, followed by drying to form a film, and then the film is attached to the surface of an artificial leather base material via an adhesive layer, followed by releasing the release sheet. The direct coating is a method in which a resin solution forming a grain layer is directly applied to the surface of an artificial leather base material using a roll coater or a spray coater, followed by drying, to form a grain layer. With the direct coating, it is possible to form a thin grain-like coating film as the grain layer. The thickness of such a grain-like coating film is preferably 10 to 1000 μm, more preferably 30 to 300 μm.

[0068] In this manner, the grain-finished artificial leather of the present embodiment is obtained. The apparent density of the grain-finished artificial leather of the present embodiment is preferably 0.60 to 0.85 g/cm^3, more preferably 0.65 to 0.80 g/cm^3, because a high level of fullness can be achieved. The grain-finished artificial leather of the present embodiment has both suppleness and a high level of fullness that resemble those of natural leather. Specifically, for example, the bending resistance as measured using a softness tester is preferably 3.5 mm or more, more preferably 4.0 mm or more when the thickness of the grain-finished artificial leather is 0.5 mm, preferably 3.0 mm or more when the aforementioned thickness is 0.7 mm, preferably 2.5 mm or more when the aforementioned thickness is 1 mm, preferably 3.0 mm or more when the aforementioned thickness is 1.0 mm, and preferably 2.0 mm or more when the aforementioned thickness is 1.5 mm.

[0069] By using the artificial leather base material of the present embodiment, it is possible to obtain a grain-finished artificial leather that has both suppleness and fullness, that bends with roundness so as to form fine fold creases when bent, and that has an excellent surface flatness. Such a grain-finished artificial leather can be used in various applications for which a quality appearance is required, such as shoes, bags, interior goods, wall coverings, and general merchandise.

[Examples]

[0070] Hereinafter, the present invention will be described more specifically by way of examples. It should be appreciated that the scope of the present invention is by no means limited by the examples.

[Example 1]

<Production of Artificial Leather Base Material>

[0071] Water-soluble thermoplastic polyvinyl alcohol (PVA) as a sea component and isophthalic acid-modified polyethylene terephthalate (IPA6-PET) having a degree of modification of 6 mol% as an island component were used. Each of PVA and IPA6-PET was supplied to a multicomponent fiber spinning spinneret set at a spinneret temperature of 260°C and having nozzle holes disposed in parallel so as to form a cross section on which 200 island component portions with a uniform cross-sectional area were distributed in the sea component, and the molten strand was discharged from the nozzle holes. At this time, the sea component and the island component were supplied while adjusting the pressure such that the mass ratio therebetween satisfied Island component/Sea component =70/30.

[0072] Then, the molten strand was stretched by suction using a suction apparatus such that average spinning speed was 3700 m/min, and thereby to spin filaments of the island-in-the-sea composite fibers having an average fineness of 3.3 dtex. The spun filaments of the island-in-the-sea composite fibers were continuously piled on a movable net, and thereafter lightly pressed with a metal roll at 42°C in order to suppress the fuzzing on the surface. Then, the piled filaments of the island-in-the-sea composite fibers that had been removed from the net were allowed to pass between a grid-patterned metal roll having a surface temperature of 55°C and a back roll, to hot press the filaments with a linear load of 200 N/mm. In this manner, a web having a basis weight of 31 g/m^2 was obtained.

[0073] Twelve layers of the obtained web were stacked using a cross lapper apparatus so as to have a total basis weight of 330 g/m^2, and an oil solution for preventing the needle from breaking was sprayed thereto, and, thereafter, the web was needle-punched alternately from both sides under a condition of a density of 3500 punch/cm^2 at a punching depth of 10 mm, using a 1-barb needle with a distance of 3.2 mm from the needle tip to the first barb. The area shrinkage of the web due to the needle punching was 68%. In this manner, an entangled web having a basis weight of 600 g/m^2 was obtained.

[0074] Then, the web was allowed to pass under 70°C and a humidity of 50% RH or less for 30 seconds at a take-up line speed of 10 m/min, to cause heat-moisture shrinking. The area shrinkage of the entangled web due to the heat-moisture shrinking treatment was 47%. Then, a water-dispersible polyurethane (emulsion) was impregnated into the entangled web, and thereafter dried at 150°C, to solidify the polyurethane as a first elastic polymer. Here, the polyurethane emulsion was an emulsion including 21 mass%, as a solid content, of a water-dispersible amorphous polycarbonate/ether polyurethane having a 100% modulus of 2.5 MPa and a glass transition temperature of -25°C, and 1.5 mass% of sodium sulfate. Then, to remove PVA as the sea component by dissolution, the entangled web that had been impregnated with the polyurethane was repeatedly subjected to dip-nipping treatment in hot water at 95°C. Then, the web was dried at 120°C, to produce a first intermediate sheet including a non-woven fabric in which fiber bundles each including 200 ultrafine filaments with an average fineness of 0.015 dtex were three-dimensionally entangled.

[0075] Then, the first intermediate sheet was finished into a second intermediate sheet by buffing the surface thereof. The second intermediate sheet was a sheet including 85 mass% of the ultrafine filaments and 15 mass% of the polyurethane, and having a basis weight of 680 g/m^2 and an apparent density of 0.60 g/cm^3.

[0076] Next, an acrylic elastic polymer as a second elastic polymer, calcium carbonate having a Mohs hardness of 3, and a plasticizer were applied to the second intermediate sheet. Specifically, an aqueous dispersion including 30 mass% of the calcium carbonate (Mohs hardness of 3), 10 mass% of the acrylic elastic polymer, and 4 mass% of a fatty acid ester that had 20 to 50 carbon atoms as the main component and was liquid at 23°C was prepared. Here, the calcium carbonate had an average particle size of 2.5 μm. The acrylic elastic polymer had a 100% modulus of 0.8 MPa and a glass transition temperature of -17°C.

[0077] Then, the second intermediate sheet was impregnated with the aqueous dispersion at a pick-up rate of 100%, and the moisture was further dried at 120°C, to obtain an artificial leather base material. The artificial leather base material included 59 mass% of the non-woven fabric, 10.5 mass% of the polyurethane, 7 mass% of the acrylic elastic polymer, 21 mass% of the calcium carbonate, and 2.5 mass% of the fatty acid ester.

[0078] Then, the artificial leather base material was subjected to shrinkage processing treatment for shrinking the artificial leather base material in the longitudinal direction (length direction) by 5.0%. The shrinkage processing treatment was performed using a shrinkage processing apparatus (sanforizing machine manufactured by Komatsubara Tekko K.K.) set to have a drum temperature of 120°C in the shrinking portion, a drum temperature of 120°C in the heat setting portion, and a transport speed of 10 m/min. The shrunk artificial leather base material had a thickness of 1.4 mm, a basis weight of 1035 g/m^2, and an apparent density of 0.74 g/cm^3. The apparent densities of the components of the shrunk artificial leather base material were as follows: 0.44 g/cm^3 for the non-woven fabric of ultrafine filaments serving as the fabric, 0.08 g/cm^3 for the polyurethane, 0.05 g/cm^3 for the acrylic elastic polymer, 0.16 g/cm^3 for the calcium carbonate, and 0.019 g/cm^3 for the fatty acid ester. The total of the apparent densities of the acrylic elastic polymer and the calcium carbonate was 0.21 g/cm^3. The ratio of the (meth)acrylic elastic polymer to the total of the calcium carbonate and the (meth)acrylic elastic polymer was 25 mass%.

[0079] Then, the durometer (Shore) C hardness, the bending resistance, and the thickness were determined by the method described below. The durometer (Shore) C hardness was 63, the bending resistance was 2.8 mm, the thickness was 1.4 mm. Also, the product of the bending resistance, the durometer Shore C hardness, and the thickness was 247 mm^2.

(Durometer (Shore) C hardness)

[0080] The measurement was performed in accordance with JIS K 7312. Specifically, the durometer (Shore) C hardness of the artificial leather base material on the side on which the grain layer was to be formed was measured using a durometer Asker rubber C hardness meter (manufactured by KOBUNSHI KEIKI CO., LTD.).

(Bending Resistance)

[0081] The bending resistance was measured using a softness tester (leather softness measuring instrument ST 300, manufactured by MSA Engineering Systems Limited of the United Kingdom). Specifically, a predetermined ring with a diameter of 25 mm was set on a lower holder of the instrument, and, thereafter, the artificial leather base material was set on the lower holder. Then, a metal pin having a diameter of 5 mm fixed to an upper lever was pressed down toward the artificial leather base material. Then, the upper lever was pressed down, and the value at the time when the upper lever was locked was read. Note that the value indicated the penetration depth, and the larger the value, the suppler the leather was.

(Thickness)

[0082] The thickness of the artificial leather base material was measured in accordance with the JIS L 1096A method.

<Production of Grain-finished Artificial Leather>

[0083] A grain-like coating film was formed on the surface of the shrunk artificial leather base material by direct coating, to obtain a grain-finished artificial leather. Specifically, a polyurethane solution was applied to the surface of the shrunk artificial leather base material using a reverse coater, and dried, to form an undercoat layer. The thickness of the undercoat layer was adjusted to a thickness of about 10 μm, which is a thickness with which the water absorption time when 3 mL of water droplets were dripped was 3 minutes or more. Next, a skin intermediate layer-forming resin solution including a pigment, a polyurethane, and an acrylic elastic polymer was applied to the surface of the undercoat layer, to form a skin intermediate layer having a thickness of 30 μm. Then, a skin topcoat layer having a thickness of 30 μm was formed on the surface of the skin intermediate layer, to obtain a grain-finished artificial leather. The skin topcoat layer was formed by spray coating a lacquer that had been adjusted to 30 cp using the Iwata Cup (IWATA NK-2 12s). In this manner, a grain-finished artificial leather having a thickness of 1.45 mm, a basis weight of 1075 g/m^2, and an apparent density of 0.74 g/m^2 was obtained.

<Evaluation of Grain-finished Artificial Leather>

[0084] The properties of the obtained grain-finished artificial leather were evaluated in the following manner.

(Fold creases · Texture)

[0085] The grain-finished artificial leather was cut to have a size of 20 × 20 cm, to prepare a sample. Then, the appearance of the artificial leather when bent inward at the center thereof, and the appearance thereof when held, as observed when the surface was visually checked, were evaluated according to the following criteria.

A: When bent, the artificial leather bent with roundness, and formed dense and fine fold grain.
B: The artificial leather had a rubber-like texture with strong resiliency, or had a texture with a significantly low degree of fullness, and formed coarse grain when bent.
C: The artificial leather had a hard texture, and caused sharp bending when bent.

(Flatness)

[0086] The grain-finished artificial leather was cut to have a size of 20 × 20 cm, to prepare a sample. Then, the grain-finished surface was observed, and the extent of the surface unevenness was evaluated according to the following criteria.

A: The surface exhibited excellent flatness with little unevenness, and had a quality appearance with a gloss.
B: The surface had conspicuous unevenness, and was inferior in terms of the quality appearance.

(Apparent Density)

[0087] The thickness (mm) and the basis weight (g/cm^2) were measured in accordance with JIS L 1913, and the apparent density (g/cm^2) was calculated from these values.

[0088] The results of the above evaluation are shown Table 1 below.

[Table 1]

Example No.			Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Island component	Polymer type		IPA6-PET	6Ny	IPA6-PET	6Ny	6Ny	IPA6-PET	IPA6-PET
	Fineness	dtex	0.015	0.01	0.015	0.01	0.01	0.015	0. 015
Sea component	Polymer type		PVA	Polyethylene	PVA	Polyethylene	Polyethylene	PVA	PVA
Island component/Sea component	Mass ratio	-	70/30	50/50	70/30	50/50	50/50	70/30	70/30
Polyurethane	Type		Aqueous dispersion	DMF solution	Aqueous dispersion	DMF solution	DMF solution	Aqueous dispersion	Aqueous dispersion
	100% modulus	MPa	2.5	8	2.5	8	8	2.5	2.5
	Tg	°C	-25	-22	-25	-22	-22	-25	-25
Acrylic	100% modulus	MPa	0.8	0.8	0.8	1.5	0.8	1.5	0.8
	Tg	°C	-17	-17	-17	-17	-17	-17	-12
Fine particles	Type		Calcium carbonate	Calcium carbonate	Aluminum hydroxide	Aluminum hydroxide	Talc	Talc	Calcium carbonate
	Mohs hardness		3	3	3	3	1	1	3
	Average particle size	μm	2.5	2.5	1.5	1.5	1	1	2.5
	Mixed elastic polymer		Acrylic	Polyurethane	Polyurethane	Polyurethane	Acrylic	Acrylic	Acrylic
Plasticizer	Type		Fatty acid ester	Fatty acid ester	Fatty acid ester	Fatty acid ester	Fatty acid ester	Fatty acid ester	Paraffin oil

(continued)

Example No.			Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Mass ratio	Fiber fabric	mass%	59	38	63	38	26	44	59
	Polyurethane		10.5	30	12	30	22	7	10.5
	Acrylic		7	2	5	2	10	15	7
	Fine particles		21	28	16	28	38	30	21
	Plasticizer		2.5	2	4	2	4	4	2.5
	Polyurethane + Acrylic		17.5	32	17	32	32	22	17.5
	Acrylic to total of fine particles and acrylic		25	7	24	7	21	33	25
Apparent density	Fiber fabric	g/cm^3	0.44	0.25	0.48	0.25	0.20	0.35	0.37
	Polyurethane		0.08	0.20	0.09	0.20	0.17	0.06	7.00
	Acrylic		0.05	0.01	0.04	0.01	0.08	0.12	0.04
	Fine particles		0.16	0.18	0.12	0.18	0.29	0.24	0.13
	Plasticizer		0.019	0.013	0.030	0.013	0.030	0.032	0.016
	Total		0.74	0.65	0.76	0.65	0.75	0.8	0.62
	Fine particles + Acrylic		0.21	0.20	0.16	0.20	0.36	0.36	0.17
Bending resistance		mm	2.8	4.8	3.8	4.4	2.6	2	3.8
Thickness		mm	1.4	1.4	1.4	1.4	1.4	1.4	0.9
Durometer C hardness			63	55	60	56	62	76	60
Bending resistance × C hardness × Thickness		mm^2	247	370	319	345	226	213	205
Quality evaluation	Fold creases · Texture		A	A	A	A	A	A	A
	Surface flatness		A	A	A	A	A	A	A

[Example 2]

[0089] Polyethylene (PE) was used as the sea component, and 6-nylon (6Ny) was used as the island component. Each of PE and 6Ny was supplied to a multicomponent fiber spinning spinneret set at a spinneret temperature of 260°C and having nozzle holes disposed in parallel so as to form a cross section on which 200 island component portions having uniform cross-sectional areas were distributed in the sea component, and then discharged from the nozzle holes. At this time, the sea component and the island component were supplied while adjusting the pressure such that the mass ratio therebetween satisfied Island component/sea component = 50/50.

[0090] Then, the discharged molten fibers were stretched by suction using a suction apparatus so as to provide an average spinning speed of 3700 m/min, and thereby to spin filaments of the island-in-the-sea composite fibers with a fineness of 2.5 dtex. The spun filaments of the island-in-the-sea composite fibers were continuously piled on a movable net, and then lightly pressed with a metal roll at 42°C, to suppress the fuzzing on the surface. Then, the filaments of the island-in-the-sea composite fibers were removed from the net, and allowed to pass between a grid-patterned metal roll having a surface temperature of 55°C and a back roll. In this manner, the filaments were hot-pressed with a linear load of 200 N/mm, to obtain a filament web having a basis weight of 34 g/m^2.

[0091] Next, 12 layers of the obtained web were stacked using a cross lapper apparatus so as to have a total basis weight of 400 g/m^2, and an oil solution for preventing the needle from breaking was further sprayed thereto. Then, the web was needle-punched alternately from both sides at a density of 2500 punch/cm^2 at a punching depth of 10 mm, using a 1-barb needle with a distance of 3.2 mm from the needle tip to the first barb. The area shrinkage due to the needle punching was 75%, and the basis weight of the needle-punched entangled web was 540 g/m^2. The entangled web was heat-treated at 140°C, and thereafter pressed to smooth the surface such that the entangled non-woven fabric had a specific gravity of 0.33 g/cm^3.

[0092] Then, 15 mass%, as a solid content, of a polyether/ester-based polyurethane as a first elastic polymer having a 100% modulus of 8.0 MPa and a glass transition temperature of -22°C and dissolved in N-dimethylformamide (DMF), and calcium carbonate having a Mohs hardness of 3 and an average particle size of 2.5 μm were mixed at a solid content ratio of 57/43. The mixture was impregnated into the entangled non-woven fabric, and thereafter solidified in a liquid mixture of DMF and water, followed by washing with hot water. Then, PE as the sea component in the island-in-the-sea composite fibers was removed by dissolution in hot toluene, and dried at 140°C, to produce a first intermediate sheet including a non-woven fabric in which fiber bundles each including 200 ultrafine filaments with a fineness of 0.01 dtex were three-dimensionally entangled.

[0093] Then, the first intermediate sheet was finished into a second intermediate sheet by buffing the surface thereof. Then, the second intermediate sheet was impregnated with an aqueous dispersion including the acrylic elastic polymer and the plasticizer that were the same as those used in Example 1, at a pick-up rate of 100%, and the moisture was further dried at 120°C, followed by shrinkage processing treatment, to obtain an artificial leather base material having the composition as shown in Table 2.

[0094] Then, a grain-finished artificial leather was obtained and evaluated in the same manner as in Example 1, except that the above-described artificial leather base material was used in place of the artificial leather base material obtained in Example 1. The results are shown in Table 1.

[Examples 3 to 7]

[0095] Grain-finished artificial leathers were obtained and evaluated in the same manner as in Example 1 or 2, except that the compositions of the components in Example 1 were changed as shown in Table 1. The results are shown in Table 1.

[Comparative Example 1]

[0096] An artificial leather base material was obtained and evaluated in the same manner as in Example 1, except that the calcium carbonate was not added. Also, a grain-finished artificial leather was obtained and evaluated in the same manner as in Example 1. The results are shown in Table 2.

[Table 2]

Comparative Example No.			Com Ex. 1	Com Ex. 2	Com Ex. 3	Com Ex. 4	Com Ex. 5	Com Ex. 6
Island component	Polymer type		IPA6-PET	IPA6-PET	IPA6-PET	IPA6-PET	6Ny	IPA6-PET
	Fineness	dtex	0.015	0.015	0.015	0.015	0.01	0.015
Sea component	Polymer type		PVA	PVA	PVA	PVA	Polyethylene	PVA
Island component/Sea component	Mass ratio	-	70/30	70/30	70/30	70/30	50/50	70/30
Polyurethane	Type		Aqueous dispersion	Aqueous dispersion	Aqueous dispersion	Aqueous dispersion	DMF solution	Aqueous dispersion
	100% modulus	MPa	2.5	2.5	2.5	2.5	8	2.5
	Tg	°C	-25	-25	-25	-25	-22	-25
Acrylic	100% modulus	MPa	0.8	-	1.5	0.8	-	0.8
	Tg	°C	-17	-	-16	-17	-	-17
Fine particles	Type		-	Calcium carbonate	Silica	Alumina	Calcium carbonate	Calcium carbonate
	Mohs hardness		-	3	7	9	3	3
	Average particle size	µm	-	2.5	0.1	12	2.5	2.5
	Mixed elastic polymer		-	-	Acrylic	Acrylic	Polyurethane	Acrylic
Plasticizer	Type		Fatty acid ester	Fatty acid ester	-	Fatty acid ester	Fatty acid ester	Fatty acid ester

(continued)

Comparative Example No.			Com Ex. 1	Com Ex. 2	Com Ex. 3	Com Ex. 4	Com Ex. 5	Com Ex. 6
Mass ratio	Fiber fabric	mass%	76	59	37	40	50	40
	Polyurethane		14	10.5	5	6	40	6
	Acrylic		7.5	0	30	7	0	7
	Fine particles		0	28	28	44	8	44
	Plasticizer		2.5	2.5	0	3	2	3
	Polyurethane + Acrylic		21.5	10.5	35	13	40	13
	Acrylic to total of fine particles and acrylic		100	-	52	14	-	14
Apparent density	Fiber fabric	g/cm^3	0.49	0.43	0.26	0.33	0.21	0.33
	Polyurethane		0.09	0.08	0.04	0.05	0.17	0.05
	Acrylic		0.05	0.00	0.21	0.06	0.00	0.06
	Fine particles		0.00	0.20	0.20	0.36	0.03	0.36
	Plasticizer		0.016	0.018	-	0.025	0.008	0.025
	Total		0.65	0.73	0.7	0.82	0.42	0.82
	Fine particles + Acrylic		0.05	0.20	0.41	0.42	0.03	0.42
Bending resistance		mm	2.3	2.4	1.4	1.8	3.4	2
Thickness		mm	1.4	1.4	1.4	1.4	1.4	1.4
Durometer C hardness			59	56	84	70	46	68
Bending resistance × C hardness × Thickness		mm^2	190	188	165	176	219	190
Quality evaluation	Fold creases · Texture		B	B	C	C	B	C
	Surface flatness		B	A	A	B	B	B

[Comparative Example 2]

[0097] An artificial leather base material was obtained and evaluated in the same manner as in Example 1, except that the acrylic elastic polymer was not added. Also, a grain-finished artificial leather was obtained and evaluated in the same manner as in Example 1. The results are shown in Table 2.

[Comparative Example 3]

[0098] An artificial leather base material was obtained and evaluated in the same manner as in Example 1, except that silica was used in place of the calcium carbonate, and the plasticizer was not added. Also, a grain-finished artificial leather was obtained and evaluated in the same manner as in Example 1. The results are shown in Table 2.

[Comparative Example 4]

[0099] An artificial leather base material was obtained and evaluated in the same manner as in Example 1, except that the alumina shown in Table 2 was used in place of the calcium carbonate, and the mass ratio was changed to that shown in Table 2. Also, a grain-finished artificial leather was obtained and evaluated in the same manner as in Example 1. The results are shown in Table 2.

[Comparative Example 5]

[0100] An artificial leather base material was obtained and evaluated in the same manner as in Example 2, except that the acrylic elastic polymer was not used, and the mass ratio of the calcium carbonate was changed to that shown in Table 2. Also, a grain-finished artificial leather was obtained and evaluated in the same manner as in Example 1. The results are shown in Table 2.

[Comparative Example 6]

[0101] Grain-finished artificial leathers were obtained and evaluated in the same manner as in Example 1, except that the compositions of the components of Example 1 were changed as shown in Table 2. The results are shown in Table 1.

[0102] The grain-finished artificial leathers obtained in Examples 1 to 7, in which the product of the bending resistance, the durometer Shore C hardness, and the thickness was 200 to 400 mm^2, had a supple texture and excellent fullness, formed fine fold creases, exhibited excellent flatness with little surface unevenness, and had a quality appearance with a gloss. On the other hand, in Comparative Examples 1 to 4, the product of the bending resistance, the durometer Shore C hardness, and the thickness was less than 200 mm^2. The grain-finished artificial leather obtained in Comparative Example 1, in which the fine particles having a Mohs hardness of 4 or less were not added, lacked fullness, and was also inferior in terms of the fold creases and the surface flatness. The grain-finished artificial leather obtained in Comparative Example 2, in which the acrylic elastic polymer was not added, was inferior in terms of the fullness and the fold creases. Comparative Example 3, in which silica having a Mohs hardness exceeding 4 was used for the fine particles, and the plasticizer was not added, had a hard texture, and formed sharply bent, coarse fold creases. Comparative Example 4, in which large fine particles having a Mohs hardness exceeding 4 were used, had a hard texture, formed sharply bent, coarse fold creases, and had a poor surface flatness. Comparative Example 5, in which the product of the bending resistance, the durometer Shore C hardness, and the thickness was 200 to 400 mm^2, but the acrylic elastic polymer was not contained, and the amount of fine particles was small, lacked fullness, and was also inferior in terms of the fold creases and the surface flatness.

[Industrial Applicability]

[0103] The artificial leather base material according to the present invention can be used for production of a grain-finished artificial leather that has suppleness and surface flatness that resemble those of a natural leather, forms fine fold creases, and also has a texture with fullness. Such a grain-finished artificial leather can be suitably used in applications such as shoes, bags, clothing, gloves, interior goods, vehicle interior finishing, transport interior finishing, and building interior finishing.

Claims

1. An artificial leather base material comprising:

a fabric, and an elastic polymer, fine particles, and a plasticizer that have been applied to the fabric,
wherein the elastic polymer includes a (meth)acrylic elastic polymer and a polyurethane,
the fine particles have a Mohs hardness of 4 or less, and
the product of a bending resistance, a durometer Shore C hardness, and a thickness of the artificial leather base material is 200 to 400 mm^2.

2. The artificial leather base material according to claim 1,
wherein the fine particles are included in an amount of 15 to 40 mass%.

3. The artificial leather base material according to claim 1 or 2,
wherein the elastic polymer is included in an amount of 15 to 40 mass%.

4. The artificial leather base material according to any one of claims 1 to 3,
wherein the plasticizer is included in an amount of 0.5 to 5 mass%.

5. The artificial leather base material according to any one of claims 1 to 4,
wherein the fabric is included in an amount of 25 to 69.5 mass%.

6. The artificial leather base material according to claim 1,
wherein the elastic polymer is included in an amount of 15 to 40 mass%, the fine particles are included in an amount of 15 to 40 mass%, and the plasticizer is included in an amount of 0.5 to 5 mass%.

7. The artificial leather base material according to any one of claims 1 to 6,
wherein a ratio of the (meth)acrylic elastic polymer to a total of the fine particles and the (meth)acrylic elastic polymer is 5 to 50 mass%.

8. The artificial leather base material according to any one of claims 1 to 7,
wherein a total of an apparent density of the fine particles and an apparent density of the (meth)acrylic elastic polymer is 0.15 to 0.4 g/cm^3.

9. The artificial leather base material according to any one of claims 1 to 8,
wherein the fine particles include at least one selected from the group consisting of calcium carbonate, aluminum hydroxide, and talc.

10. The artificial leather base material according to any one of claims 1 to 9,
wherein the fabric includes a non-woven fabric of fibers having an average fineness of 0.7 dtex or less.

11. The artificial leather base material according to claim 10,
wherein the fibers are polyamide-based fibers.

12. A grain-finished artificial leather, comprising:
the artificial leather base material according to any one of claims 1 to 11, and a grain-like resin layer formed on at least one surface of the artificial leather base material.

13. The grain-finished artificial leather according to claim 12,
wherein the grain-like resin layer has a thickness of 30 to 300 μm.

14. The grain-finished artificial leather according to claim 12 or 13,
wherein the grain-like resin layer is a coating film.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/016625

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. D06N3/04(2006.01)i, D06N3/14(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. D06N1/00-D06N7/06

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2015-124444 A (KURARAY CO., LTD.) 06 July 2015, claims, paragraphs [0001], [0014], [0018], [0021], [0025], [0029], [0031]-[0032], [0036]-[0037], [0042]-[0047], [0050]-[0054], [0056], [0059]-[0062], [0067], [0072]-[0089], [0092]-[0094], [0097], table 1 (Family: none)	1-14

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
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"&" document member of the same patent family

Date of the actual completion of the international search 10 July 2018 (10.07.2018)	Date of mailing of the international search report 17 July 2018 (17.07.2018)
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/016625

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2015-55023 A (TORAY INDUSTRIES, INC.) 23 March 2015, entire text (Family: none)	1-14
A	JP 55-128078 A (SUZUTORA SEISEN KOJO K.K.) 03 October 1980, entire text (Family: none)	1-14
A	JP 2017-2419 A (KURARAY CO., LTD.) 05 January 2017, entire text (Family: none)	1-14
A	JP 2012-117154 A (KURARAY CO., LTD.) 21 June 2012, entire text (Family: none)	1-14
A	JP 50-16401 A (TEIJIN LTD.) 12 June 1975, entire text (Family: none)	1-14
A	JP 60-181370 A (KANEBO KABUSHIKI KAISHA) 17 September 1985, entire text (Family: none)	1-14

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