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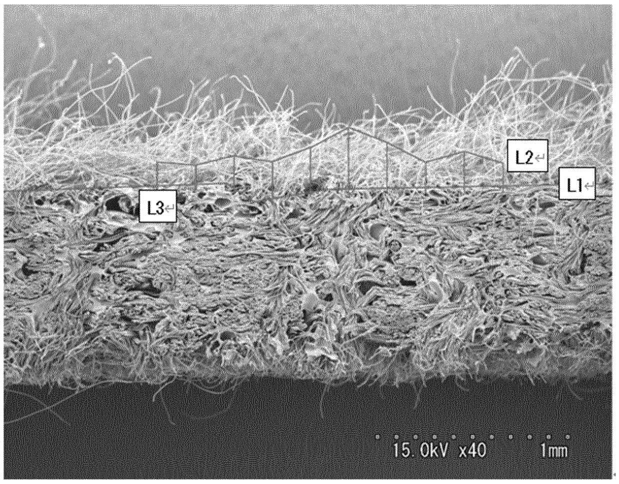
(54) NAPPED ARTIFICIAL LEATHER AND MANUFACTURING METHOD THEREFOR

(57) A napped artificial leather including: a nonwoven fabric containing microfine fibers and a high-molecular elastic body, the napped artificial leather having a napped surface, in which a content of the high-molecular elastic body is 15 to 35 mass%, an area ratio of the high-molecular elastic body present on the napped surface is 17% or less, and a napped fiber length is 250 μm or less.

[Fig. 3]



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Description

Technical Field

[0001] The present invention relates to a napped artificial leather and a method for manufacturing the same.

Background Art

[0002] Napped artificial leathers having a suede-like appearance which are used as surface materials of clothes, shoes, furniture, car seats, general merchandise, and the like have a napped surface which is formed by fluffing microfine fibers through a raising treatment. Such napped artificial leathers are generally colored for use. Heretofore, dyeing with dyestuffs of various colors ranging from a pale color to a dark color has been frequently performed.

[0003] A conventional napped artificial leather has a problem in that when the napped artificial leather including polyester fibers serving as microfine fibers and a polyurethane resin serving as a high-molecular elastic body is dyed with a disperse dyestuff and then reduced and cleaned, color unevenness occurs in the napped artificial leather, resulting in deterioration in appearance.

[0004] In order to deal with this problem, for example, PTL 1 has proposed an artificial leather in which within 200 μm in the thickness direction from the surface except for a napped portion of the artificial leather in a cross section obtained by cutting the artificial leather perpendicularly to the surface direction, the number of high-molecular elastic body blocks each having a size of 100 μm or more in the thickness direction per the cross-sectional length in the surface direction is 0.1 to 2.5 pcs/mm.

[0005] PTL 2 has proposed a substrate for an artificial leather in which the average value for the area of a high-molecular elastic body exposed to a sheet surface is 0.1 mm^2 or less.

[0006] The conventional napped artificial leather also has a problem in that the color tone and the color density are restricted and the artificial leather is difficult to color with various color tones at various color densities.

[0007] In order to deal with this problem, PTL 3 has proposed a suede-finished artificial leather including fibers colored with a pigment and a high-molecular elastic body colored with a pigment and having an average napped fiber length of 10 to 200 μm.

[0008] For napped artificial leathers, a texture close to that of natural leather, such as excellent denseness and softness and a good feeling are required.

[0009] In response to this requirement, for example, PTL 4 has proposed a nubuck-finished leather-like sheet-shaped product which includes a staple fiber nonwoven fabric having a single fiber fineness of 0.0001 to 0.5 dtex and an apparent density of 0.300 to 0.700 g/cm^3, has a napped fiber length of 5 to 500 μm, and does not include a film-shaped substance formed from an elastic polymer.

[0010] PTL 5 has proposed an artificial leather including a napped layer in which the average fiber length of microfine fibers is 250 μm or more and 500 μm or less and the surface coverage rate of the microfine fibers is 60% or more and 100% or less.

[0011] Further, PTL 6 has proposed a leather-like fabric in which a resin layer is intermittently formed on a napped surface, the area ratio of a resin portion in a fabric surface is 10 to 90%, and the resin layer is composed of two or more layers.

Citation List

Patent Literature

[0012]

PTL 1: JP 2016-69790 A
PTL 2: JP 2016-11477 A
PTL 3: JP 2004-143654 A
PTL 4: JP 2006-241620 A
PTL 5: WO2020/003866
PTL 6: WO2017/22387

Summary of Invention

Technical Problem

[0013] In the artificial leathers described in PTL 1 and PTL 2, the occurrence of color unevenness is suppressed, but mechanical strength such as frictional wear property and tensile strength is insufficient, and there remains a need for improvement.

[0014] The artificial leathers described in PTL 3, PTL 4, and PTL 6 do not sufficiently have mechanical strength such as tensile strength, and there remains a need for improvement.

[0015] The leather described in PTL 5 does not have a sufficiently satisfactory skin feeling, that is, have a rough skin feeling, and there remains a need for improvement.

[0016] On the other hand, as a method for suppressing dyeing unevenness unlike methods described in PTL 1 and PTL 2, a method in which color unevenness is concealed by increasing a napped fiber length has been also investigated. However, this method has a problem in that the skin feeling is deteriorated and the deneseness is reduced. Use application in which a person touches, such as furniture and a car seat, have caused problems such as excessive lighting and ununiform appearance.

[0017] Conventionally, the use of filaments in a napped artificial leather has been investigated to enhance the mechanical strength of the napped artificial leather. However, the use of filaments enhances the mechanical strength such as tensile strength, but results in a problem in that color unevenness more easily occurs than a napped artificial leather including staple fibers.

[0018] In view of the circumstances, the present invention is made, and an object of the present invention is to provide a napped artificial leather in which the occurrence of color unevenness is suppressed and which has a high mechanical strength and an excellent texture.

[0019] The term "excellent texture" as used herein means a texture close to that of natural leather, such as excellent denseness and softness and a good feeling.

Solution to Problem

[0020] The present invention is based on a finding that when the content of a high-molecular elastic body attached to a nonwoven fabric, the area ratio of the high-molecular elastic body present on a napped surface, and the napped fiber length are set to predetermined values, a napped artificial leather in which the occurrence of color unevenness is suppressed and which has a high mechanical strength and an excellent texture is obtained.

[0021] The present invention provides the following procedures.

[1] A napped artificial leather including: a nonwoven fabric containing microfine fibers and a high-molecular elastic body, the napped artificial leather having a napped surface, in which a content of the high-molecular elastic body is 15 to 35 mass%, an area ratio of the high-molecular elastic body present on the napped surface is 17% or less, and a napped fiber length is 250 μm or less.

[2] The napped artificial leather according to [1], in which the microfine fibers are polyester-based fibers.

[3] The napped artificial leather according to [1] or [2], in which the microfine fibers have an average fineness of 0.01 to 1.0 dtex.

[4] The napped artificial leather according to any one of [1] to [3], in which the nonwoven fabric is a spun-bond nonwoven fabric.

[5] A method for manufacturing the napped artificial leather according to any one of [1] to [4], the method including a step of removing a sea component from an entangled web containing the high-molecular elastic body, to obtain a nonwoven fabric containing the high-molecular elastic body.

[6] The method for manufacturing the napped artificial leather according to [5], the method including a step of melt-spinning a sea/island type composite fiber to obtain a web.

[7] The method for manufacturing the napped artificial leather according to [6], in which the step of obtaining a nonwoven fabric containing the high-molecular elastic body includes removing the sea component through dissolution in an organic solvent.

[8] The method for manufacturing the napped artificial leather according to any one of [5] to [7], the method including a step of forming the entangled web containing the high-molecular elastic body through use of a solvent-based polyurethane.

Advantageous Effects of Invention

[0022] The present invention provides a napped artificial leather in which the occurrence of color unevenness is suppressed and which has a high mechanical strength and an excellent texture, and a method for manufacturing the same.

Brief Description of Drawings

[0023]

Fig. 1 is an image obtained by photographing a napped surface of a napped artificial leather according to the present invention with a scanning electron microscope (SEM) at a magnification of 50 for measurement of the area ratio of a high-molecular elastic body present on the napped surface.

Fig. 2 is an image obtained by painting a portion of polyurethane which is the high-molecular elastic body on the image of Fig. 1 in black on an OHP sheet and transferring the polyurethane portion for measurement of the area ratio of the high-molecular elastic body present on the napped surface of the napped artificial leather according to the present invention.

Fig. 3 is a schematic view for illustrating a method for measuring the napped fiber length of the napped artificial leather according to the present invention.

Description of Embodiments

[0024] The following description is based on an example of embodiments of the present invention (hereinafter also referred to as "the present embodiment"). However, embodiments described below are examples for embodying the technical idea of the present invention, and the present invention is not limited to the following description.

[0025] The description shows preferred aspects of embodiments, but a combination of two or more of individual preferred aspects is also a preferred aspect. Regarding the matters indicated by the numerical ranges, in a case where there are several numerical ranges, it is possible to selectively combine the lower limit value and the upper limit value of the numerical ranges to obtain a preferred aspect.

[0026] In the description, when there is a description of a numerical range of "XX to YY", it means "XX or more and YY or less".

[Napped Artificial Leather]

[0027] A napped artificial leather of an embodiment is a napped artificial leather including: a nonwoven fabric containing microfine fibers and a high-molecular elastic body, the napped artificial leather having a napped surface, in which the content of the high-molecular elastic body is 15 to 35 mass%, the area ratio of the high-molecular elastic body present on the napped surface is 17% or less, and the napped fiber length is 250 μm or less.

[0028] In the napped artificial leather of the embodiment, the occurrence of color unevenness is suppressed, and a high mechanical strength and an excellent texture are achieved.

[0029] The term "napped fiber length" as used herein means the length of napped fibers present on a napped surface of a napped artificial leather, and the term "color unevenness" means color unevenness caused during colorization of the napped artificial leather.

[0030] Although the reason that the aforementioned effects can be produced by the aforementioned configuration of the napped artificial leather of the embodiment is not clear, it is considered that the reason is as follows.

[0031] In general, different components are used for the fibers and the high-molecular elastic body constituting the nonwoven fabric of the napped artificial leather. For example, polyester-based fibers may be used as the fibers, and a polyurethane-based resin may be used as the high-molecular elastic body. When such a napped artificial leather is colored with a colorant such as a disperse dyestuff, there may be differences in the color tone and the color density between the fibers and the high-molecular elastic body due to a difference in colorability between the fibers and the high-molecular elastic body. In particular, when there are differences in the color tone and the color density between the high-molecular elastic body exposed to the napped surface and the fibers present on the napped surface, the differences are considered to be recognized as color unevenness.

[0032] In the napped artificial leather of the present invention, the content of the high-molecular elastic body is 15 to 35 mass% and the area ratio of the high-molecular elastic body present on the napped surface is 17% or less, and therefore it is considered that exposure of the high-molecular elastic body to the napped surface is suppressed, resulting in suppression of color unevenness.

[0033] In the napped artificial leather of the embodiment, the content of the high-molecular elastic body is 15 to 35 mass%, and therefore the color unevenness is suppressed, and excellent denseness and softness, a good feeling, and a texture similar to that of natural leather are further achieved. That is, the napped artificial leather has a good texture.

[0034] From the viewpoint of obtaining a napped artificial leather having a better texture, the content of the high-molecular elastic body is preferably 16 to 34 mass%, more preferably 16.5 to 33.5 mass%, further preferably 17 to 33 mass%.

[0035] In the napped artificial leather of the embodiment, the area ratio of the high-molecular elastic body present on the napped surface is 17% or less. When the area ratio of the high-molecular elastic body is 17% or less, exposure of the high-molecular elastic body to the napped surface is suppressed, and the high-molecular elastic body cannot be completely viewed or can be extremely slightly viewed, resulting in suppression of color unevenness. From the viewpoint of further suppressing color unevenness, the area ratio of the high-molecular elastic body is preferably 15% or less, more preferably 14% or less, and further preferably 13% or less. From the viewpoint of obtaining a napped artificial leather having more excellent softness and elasticity, the area ratio of the high-molecular elastic body is preferably 5% or more, more preferably 6% or more, and further preferably 7% or more.

[0036] The "area ratio of the high-molecular elastic body present on the napped surface" as used herein is measured and calculated by the following method.

[0037] Three different portions of the napped surface of the napped artificial leather are photographed with a scanning electron microscope (SEM) at a magnification of 50. From each of the resultant images, the total area of a region where the high-molecular elastic body is present is determined with an image processing apparatus and the like, and from the determined total area and the total area of the entire region of each of the images, the area ratio of the high-molecular elastic body is calculated by the following expression.

Area ratio of high-molecular elastic body = total area of region where high-molecular elastic body is present/total area of entire region of image × 100 (%)

[0038] Specifically, the measurement and the calculation follow methods described in Examples below.

[0039] In the napped artificial leather of the embodiment, the napped fiber length is 250 μm or less. When the napped fiber length is 250 μm or less, napped fibers are finely dispersed and have a uniform length, and therefore a napped surface having excellent softness and a smooth feeling can be formed. From the viewpoint of forming a napped surface having more excellent softness and a smooth feeling, the napped fiber length is preferably 150 μm or less, more preferably 120 μm or less, and further preferably 100 μm or less. From the viewpoint of preventing the exposure of the high-molecular elastic body at the lower portion of the napped fibers, which results in a deterioration in appearance, and keeping a soft feeling of the microfine fibers, the napped fiber length is preferably 40 μm or more, more preferably 50 μm or more, and further preferably 60 μm or more.

[0040] The thickness of the napped artificial leather of the embodiment is not particularly limited, but from the viewpoint of obtaining a napped artificial leather having a high mechanical strength and an excellent texture, it is preferably 0.1 to 1.5 mm, and more preferably 0.3 to 1.0 mm.

[0041] The basis weight of the napped artificial leather is not particularly limited, but from the viewpoint of obtaining a napped artificial leather having a high mechanical strength and an excellent texture, it is preferably 100 to 1,000 g/m^2, and further preferably 150 to 800 /m^2.

[0042] The apparent density of the napped artificial leather of the embodiment is preferably 0.35 g/cm^3 or more, more preferably 0.37 g/cm^3 or more, and further preferably 0.38 g/cm^3 or more, and preferably 0.70 g/cm^3 or less, more preferably 0.50 g/cm^3 or less, and further preferably 0.48 g/cm^3 or less. When the apparent density is 0.35 g/cm^3 or more, the napped artificial leaser has excellent elasticity, the fibers are prevented from dragging and protruding during rubbing of the napped surface, and elegant appearance of the napped fibers is easily achieved. When the apparent density is 0.70 g/cm^3 or less, the napped artificial leaser has excellent softness.

<Nonwoven Fabric>

[0043] The nonwoven fabric of the embodiment contains the microfine fibers and the high-molecular elastic body. From the viewpoint of imparting a texture close to that of natural leather and achieving a high mechanical strength, the nonwoven fabric preferably has a structure (three-dimensional entangled body) in which a plurality of microfine fibers form fiber bundles and the fiber bundles are entangled.

[0044] From the viewpoint of easily achieving a high mechanical strength and simplifying a production process, the nonwoven fabric is preferably a spun-bond nonwoven fabric, and more preferably a spun-bond nonwoven fabric containing microfine fibers of filaments.

[0045] The "filament" means a continuous fiber, which is not a staple fiber prepared by intentional cutting after spinning. Specifically, the filament means a filament or a continuous fiber which is not a staple fiber prepared by intentional cutting at a fiber length of about 3 to 80 mm.

[0046] The nonwoven fabric is preferably obtained by spinning a sea/island (matrix-domain) type composite fiber to obtain a web and performing an entangling treatment for the web, followed by a microfine fiber-forming treatment.

(Microfine Fibers)

[0047] The microfine fibers of the present invention are fibers obtained by making multicomponent-based fibers (composite fibers) formed from at least two or more kinds of fiber-forming polymers having different chemical or physical properties microfine by extracting and removing at least one kind of polymer at an appropriate stage before or after impregnation with the high-molecular elastic body. The multicomponent-based fibers which form the microfine fibers are microfine fibers-generating fibers. Typical examples thereof include a sea/island type composite fiber, a multi-layered composite fiber, and a radial layered composite fiber, which are obtained by methods such as a chip blending (blend spinning) method and a composite spinning method. Among these, a sea/island type composite fiber is preferred in terms of little fiber damage when an entangling treatment is performed with needle punch or the like, and uniform average fineness of the microfine fibers.

[0048] Examples of a resin constituting the microfine fibers contained in the nonwoven fabric of the embodiment include a polyethylene terephthalate (hereinafter also referred to as "PET"), a modified PET such as isophthalic acid-modified PET, sulfoisophthalic acid-modified PET, or cationic dyestuff-dyeable PET, an aromatic polyester such as polybutylene terephthalate or polyhexamethylene terephthalate; an aliphatic polyester such as polylactic acid, polyethylene succinate, polybutylene succinate, polybutylene succinate adipate, or a polyhydroxy butyrate-polyhydroxy valerate resin; nylon such as nylon 6, nylon 66, nylon 10, nylon 11, nylon 12, or nylon 6-12; and fibers of polypropylene, polyethylene, polybutene, polymethylpentene, or chlorine-containing polyolefin. Further, the modified PET is a PET in which at least part of a dicarboxylic acid-based monomer unit or a diol-based monomer unit of an unmodified PET, which has an ester-forming property, is replaced by a replaceable monomer unit. Specific examples of a modification monomer unit for replacing the dicarboxylic acid-based monomer unit include a unit derived from isophthalic acid, sodium sulfo-isophthalic acid, sodium sulfo-naphthalene dicarboxylic acid, or adipic acid, which is to replace a terephthalic acid unit. Further, specific examples of a modification monomer unit for replacing the diol-based monomer unit include a unit derived from diol such as butane diol or hexane diol, which is to replace an ethylene glycol unit.

[0049] Among these, from the viewpoint of obtaining a napped artificial leather having colorability and both a high mechanical strength and an excellent texture, polyester-based resins such as an aromatic polyester and an aliphatic polyester are preferred. From the viewpoint of productivity, mechanical strength, and the like during spinning, polyethylene terephthalate (PET), modified PETs such as isophthalic acid-modified PET, sulfoisophthalic acid-modified PET, and cationic dyestuff-dyeable PET; aromatic polyesters such as polybutylene terephthalate and polyhexamethylene terephthalate; aliphatic polyesters such as polylactic acid, polyethylene succinate, polybutylene succinate, polybutylene succinate adipate, and a polyhydroxy butyrate-polyhydroxy valerate resin; nylons such as nylon 6, nylon 66, nylon 10, nylon 11, nylon 12, and nylon 6-12; polyolefins such as polypropylene, polyethylene, polybutene, polymethylpentene, and chlorine-containing polyolefin are preferred.

[0050] From the viewpoint of obtaining a napped artificial leather having excellent denseness of a napped surface and excellent softness and elasticity, the average fineness (average fiber diameter) of the microfine fibers is preferably 0.01 to 1.0 dtex, more preferably 0.05 to 0.7 dtex, and further preferably 0.1 to 0.5 dtex.

[0051] The resin constituting the microfine fibers of the embodiment may include various additives as long as the effects of the present invention are not impaired. Examples of the additives include a catalyst, a colorant, a heat-resistant agent, a flame retarder, a lubricant, a stain-proofing agent, a fluorescent brightener, a flatting agent, a luster improver, an anti-static agent, a fragrance, a deodorant, an anti-microbial agent, an anti-mite agent, and inorganic fine particles.

<High-Molecular Elastic Body>

[0052] Examples of the high-molecular elastic body contained in the nonwoven fabric of the embodiment include a polyurethane-based resin, an acrylonitrile-based elastomer, an olefinic elastomer, a polyester-based elastomer, a polyamide-based elastomer, an acrylic elastomer, and a modified product, a copolymer, and a mixture thereof. Among these, from the viewpoint of obtaining a napped artificial leather having excellent softness and elasticity, a polyurethane-based resin is preferred.

[0053] Examples of the polyurethane-based resin include various polyurethane-based resins obtained by a reaction of a high-molecular-weight polyol having a weight average molecular weight of 200 to 6,000 with an organic polyisocyanate, and if necessary, a chain extender at a predetermined molar ratio.

[0054] Specific examples of the high-molecular-weight polyol include a polyether-based polyol such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, or poly(methyltetramethylene glycol), and a copolymer thereof; a polyester-based polyol such as polybutylene adipate diol, polybutylene sebacate diol, polyhexamethylene adipate diol, poly(3-methyl-1,5-pentylene adipate) diol, poly(3-methyl-1,5-pentylene cebacate) diol, or polycaprolactone diol, and a copolymer thereof; a polycarbonate-based polyol such as polyhexamethylene carbonate diol, poly(3-methyl-1,5-pentylene carbonate) diol, polypentamethylene carbonate diol, or polytetramethylene carbonate diol, and a copolymer thereof; and polyester carbonate polyol. A multifunctional alcohol such as trifunctional alcohol or a tetrafunctional alcohol, or a short-chain alcohol such as ethylene glycol may be used in combination, if necessary. These compounds may be used alone, or two or more kinds thereof may be used in combination.

[0055] Specific examples of the organic polyisocyanate include a non-yellowing diisocyanate including an aliphatic or alicyclic diisocyanate such as hexamethylene diisocyanate, isophorone diisocyanate, norbornene diisocyanate, or 4,4'-dicyclohexylmethane diisocyanate; and an aromatic diisocyanate such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and xylylene diisocyanate polyurethane. A multifunctional isocyanate such as a trifunctional isocyanate or a tetrafunctional isocyanate may be used in combination, if necessary. These compounds may be used alone, or two or more kinds thereof may be used in combination.

[0056] Specific examples of the chain extender include a diamine such as hydrazine, ethylenediamine, propylenediamine, hexamethylenediamine, nonamethylenediamine, xylylenediamine, isophoronediamine, piperazine or a derivative thereof, adipic acid dihydrazide, or isophthalic acid dihydrazide; a triamine such as diethylenetriamine; a tetramine such as triethylenetetramine; a diol such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-bis(β-hydroxyethoxy)benzene, or 1,4-cyclohexanediol; a triol such as trimethylolpropane; a pentaol such as pentaerythritol; and an amino alcohol such as aminoethyl alcohol, or aminopropyl alcohol. These compounds may be used alone, or two or more kinds thereof may be used in combination. During a chain extension reaction, a monoamine such as ethylamine, propylamine, or butyl amine; a carboxy group-containing monoamine compound such as 4-aminobutanoic acid or 6-aminohexanoic acid; or a monool such as methanol, ethanol, propanol, or butanol may be used with the extender.

[0057] Specific examples of the polyurethane-based resin include polycarbonate urethane, polyether urethane, polyester urethane, polyether ester urethane, polyether carbonate urethane, and polyester carbonate urethane. Among these, from the viewpoint of obtaining a napped artificial leather having excellent softness and elasticity, polycarbonate urethane is preferred.

[0058] The high-molecular elastic body may contain an additive, for example, a colorant such as a pigment including carbon black or a dyestuff, a solidification adjusting agent, an antioxidant, an ultraviolet absorber, a fluorescer, a mildewproofing agent, a penetrant, an antifoaming agent, a lubricant, a water repellent, an oil repellent, a thickener, an extender, a curing accelerator, a foaming agent, a water-soluble high-molecular-weight compound such as polyvinyl alcohol or carboxymethylcellulose, inorganic fine particles, or a conducting agent as long as the effects of the present invention are not impaired. When small-scale production of a large number of bland kinds of napped artificial leathers is required, it is preferable that the high-molecular elastic body do not contain a colorant such as a pigment or a dyestuff from the viewpoint of suppressing pollution in a process due to contamination of the pigment or the dyestuff contained in the high-molecular elastic body and improving productivity.

[Method for Manufacturing Napped Artificial Leather]

[0059] From the viewpoint of obtaining a napped artificial leather in which the occurrence of color unevenness is suppressed and which has a high mechanical strength and an excellent texture, a method for manufacturing the napped artificial leather of the embodiment preferably includes Steps 1 to 5 below:

Step 1: a step of obtaining a web;
Step 2: a step of performing an entangling treatment for the web, to obtain an entangled web;
Step 3: a step of obtaining the entangled web containing a high-molecular elastic body;
Step 4: a step of removing a sea component from the entangled web containing a high-molecular elastic body; and
Step 5: a step of performing a buffing treatment.

<Step 1>

[0060] Step 1 is a step of obtaining a web.

[0061] In the embodiment, from the viewpoint of obtaining a napped artificial leather in which the occurrence of color unevenness is suppressed and which has a high mechanical strength and an excellent texture, the step of obtaining a web is preferably melt-spinning a sea/island type composite fiber to obtain a web.

[0062] Examples of a method for melt-spinning a sea/island type composite fiber to obtain a web include a method in which a sea/island type composite fiber spined according to a spun bonding method is collected on a net without cutting, to obtain a web of filaments; and a method in which staple fibers of sea/island type composite fiber obtained by crimping and cutting a melt-spined sea/island type composite fiber are carded to obtain a web of the staple fibers. Among these, from the viewpoint of mechanical strength, easiness of adjustment of an entangled state, softness, elasticity, and the like, the method in which a sea/island type composite fiber spined according to a spun-bond method is collected on a net without cutting, to form a web of filaments (hereinafter also referred to as "method for forming a web of filaments") is preferred.

[0063] The "spun-bond method" as used herein refers to a method which includes: continuously extruding melt-strands for a sea/island composite fiber at a prescribed ejection rate through spinning nozzles by means of a spinneret for composite spinning where plural nozzle holes are disposed in a prescribed pattern, stretching the melt-strands while cooling with a fast gas stream, and then depositing the resultant on a moving net like a conveyer belt.

[0064] A web of filaments formed by the spun-bond method may be subjected to a fusion treatment to impart a shape stability thereto. Hereinafter, the details of the method for forming a web of filament will be described.

[0065] In order to form a web of filaments, the fiber length of a sea/island composite fiber before melt-spinning and before formation of microfine fibers is preferably 100 mm or more, and may be several meters, several hundred meters, or several kilometers or more as long as it is technically producible and is not subjected to an inevitable cutting in the production step. In needle-punching during an entangling treatment or a step of a buffing treatment, which is a subsequent step, part of the filaments may be inevitably cut to become staple fibers.

[0066] Examples of a resin for an island component which is contained in the sea/island type composite fiber and becomes microfine fibers later include the same resins as the resin constituting microfine fibers in the aforementioned "microfine fibers".

[0067] As a resin for a sea component which is contained in the sea/island type composite fiber and is removed by extraction, dissolution, or the like, a resin which has different solubility or resolvability from the resin for the island component and low compatibility is preferably used. It is preferable that such a resin be appropriately selected depending on the kind of the resin for the island component or a production method therefor.

[0068] Examples of the resin for the sea component include an olefinic resin such as polyethylene, polypropylene, an ethylene propylene copolymer, or an ethylene vinyl acetate copolymer; a resin which has a solubility in an organic solvent and is removable through dissolution in the organic solvent, such as polystyrene, a styrene acrylate copolymer, or a styrene ethylene copolymer, and a water-soluble resin such as a water-soluble polyvinyl alcohol. Among these, from the viewpoint of melt-spinning the resin for the island component having a high intrinsic viscosity, the resin which is removable through dissolution in an organic solvent is preferred, and polyethylene is more preferred.

[0069] From the viewpoint of mechanical strength, the mass ratio (sea component/island component) of the sea component to the island component contained in the sea/island type composite fiber is preferably 10/90 to 60/40, more preferably 20/80 to 50/50.

[0070] From the viewpoint of forming a fiber bundle of microfine fibers having appropriate voids, the number of the island component which becomes the microfine fibers later in the cross section of each of the sea/island type composite fibers during melt-spinning is preferably 5 to 200, more preferably 10 to 50, and further preferably 10 to 30.

[0071] The sea/island type composite fiber may contain a dark color pigment such as carbon black, a white pigment such as zinc oxide, lead white, lithopone, titanium dioxide, sedimentary barium sulfate, or baryta powder, an anti-weathering agent, an anti-mold agent, a hydrolysis-preventing agent, a lubricant, fine particles, a frictional resistance-adjusting agent, or the like, if necessary, as long as the effects of the present invention are not impaired.

[0072] The web obtained by melt-spinning the sea/island type composite fiber may be subjected to a shrinking treatment of immersing the web in a hot water at a temperature of about 60 to 150°C, to form a dense entangled state of the web in advance.

<Step 2>

[0073] Step 2 is a step of performing an entangling treatment for the web, to obtain an entangled web.

[0074] Step 2 is a step in which the web obtained in Step 1 is stacked into multiple layers, and the multiple layers are subjected to an entangling treatment such as needle punching or a hydroentangling treatment, to obtain an entangled web in which filaments are entangled in the thickness direction. The number of layers in the stacked web is not particularly limited. From the viewpoint of mechanical strength, it is preferably 4 or more, and more preferably 8 or more, and from the viewpoint of production easiness, it is preferably 20 or less, more preferably 16 or less.

[0075] When needle punching is used as the entangling treatment, the kind of used felt needle is not particularly limited. From the viewpoint of sufficiently enhancing tangling of fibers in the thickness direction and obtaining an artificial leather having an excellent mechanical strength, a fine felt needle or a felt needle having a small number of barbs, such as a needle with a barb, is preferably used. From the viewpoint of suppressing cutting of fibers, the number of barb of a felt needle is preferably 3 or more, more preferably 5 or more, and further preferably 6.

[0076] The number of felt needles used for needle punching per unit area is not particularly limited, but is preferably 200 to 5,500 needles/cm^2. In particular, it is preferably 1,500 to 5,000 needles/cm^2 from the viewpoint of enhancing mechanical strength, orienting the arrangement of fibers present on the surface in a longitudinal direction, and reducing the area ratio of a high-molecular elastic body on the surface within a predetermined range of the present invention.

[0077] At any step of from the step of spinning a sea/island type composite fiber to the entangling treatment, an oily agent or an anti-static agent may be attached to the web or the entangled web.

[0078] From the viewpoint of obtaining a napped artificial leather having a high mechanical strength and an excellent texture, the basis weight of the entangled web is preferably 100 to 2,000 g/m^2.

[0079] From the viewpoint of further enhancing the fiber density and the entanglement degree of the entangled web, the entangled web may be subjected to a heat shrinking treatment.

[0080] For the purposes such as the purpose of setting the shape of the entangled web and the purpose of flattening the surface, in addition to the purpose of further making the dense entangled web denser by a heat shrinking treatment, for example, the entangled web may be pressed with a heat roller having a surface temperature of 100 to 150°C, or may be heated at a temperature equal to or higher than the softening point of the resin constituting the fibers (island component) in the entangled web and may be pressed with a cooling roller having a surface temperature which is equal to or lower than the softening point of the resin. In particular, from the viewpoint of flattening the surface, the surface temperature of the cooling roller is preferably lower than the softening point of the resin by 30°C or higher.

<Step 3>

[0081] Step 3 is a step of impregnating the entangled web with a high-molecular elastic body and attaching the high-molecular elastic body to the entangled web to obtain the entangled web containing the high-molecular elastic body.

[0082] From the viewpoint of obtaining a napped artificial leather having excellent shape stability, softness, and elasticity, in the method for manufacturing the napped artificial leather of the embodiment, it is preferable to impregnate the entangled web with the high-molecular elastic body and attach the high-molecular elastic body before removing the sea component.

[0083] When the entangled web is thus impregnated with the high-molecular elastic body and the high-molecular elastic body is attached before removing the sea component, voids which are formed by removing the sea component are formed among microfine fibers which form a fiber bundle after removing the sea component. As a result, the microfine fibers inside the fiber bundle are hardly confined by the high-molecular elastic body, that is, the microfine fibers are hardly affected by the high-molecular elastic body, and a napped artificial leather having excellent softness is obtained.

[0084] In Step 3, the entangled web is impregnated with the high-molecular elastic body by using an emulsion or a solution containing the high-molecular elastic body, and the high-molecular elastic body is then solidified to obtain the entangled web containing the high-molecular elastic body. When the high-molecular elastic body is solidified, the high-molecular elastic body may attached to the voids of the fibers in the entangled web.

[0085] A method for impregnating the entangled web with the high-molecular elastic body by using an emulsion or a solution containing the high-molecular elastic body is not particularly limited, but an impregnation method through a dip-nip method is preferred.

[0086] Examples of the high-molecular elastic body include those described in <High-Molecular Elastic Body> above, and a polyurethane-based resin is preferred.

[0087] The entangled web containing the high-molecular elastic body is obtained preferably by using a solution containing the high-molecular elastic body, more preferably by using a solvent-based polyurethane in which a polyurethane-based resin is dissolved in a solvent such as N,N-dimethylformamide (DMF) during impregnation with the high-molecular elastic body and attachment of the high-molecular elastic body. When the solution containing the high-molecular elastic body, particularly the solvent-based polyurethane is thus used, polyurethane serving as the high-molecular elastic body and the microfine fibers are appropriately released from each other to easily obtain a napped artificial leather having a soft texture.

[0088] In order to set the area ratio of the high-molecular elastic body present on the napped surface to 17% or less, the entangled web may be pre-treated before the impregnation with and the attachment of the high-molecular elastic body, or the high-molecular elastic body may be selectively removed from the entangled web after the impregnation with the high-molecular elastic body and attachment of the high-molecular elastic body.

[0089] Examples of a pre-treatment of the entangled web include a method for applying a thermoplastic resin such as polyvinyl alcohol to the entangled web or impregnating the entangled web with the thermoplastic resin, and a method for disposing the thermoplastic resin on the surface of the entangled web or incorporating the thermoplastic resin into the entangled web by a gravure coater method, a knife coater method, a pipe coater method, a comma coater method, or the like.

[0090] Examples of a method for selectively removing the high-molecular elastic body include a method in which the high-molecular elastic body is removed by applying a contact pressure to the surface of the entangled web with a nip roll, a squeeze bar, a doctor knife, or the like.

[0091] In the embodiment, it is preferable that the entangled web be impregnated with the high-molecular elastic body and the high-molecular elastic body is attached to the entangled web so that the content of the high-molecular elastic body in the napped artificial leather is 15 to 35 mass%, to obtain the entangled web containing the high-molecular elastic body, and the high-molecular elastic body be then selectively removed from the entangled web so that the area ratio of the high-molecular elastic body present on the napped surface is 17% or less.

[0092] Examples of a method for solidifying the high-molecular elastic body include a solidifying method by drying and removing water contained in the emulsion or the solution, and a wet-solidifying method.

[0093] Examples of the solidifying method by drying and removing include a method in which a heat treatment is performed in a dryer at 50 to 200°C, a method in which a heat treatment is performed in a dryer after heating by infrared radiation, a method in which a heat treatment is performed in a dryer after a steam treatment, or a method in which a heat treatment is performed in a dryer after heating by ultrasonic wave, and a combination thereof.

[0094] In the wet-solidifying method, the entangled web containing the high-molecular elastic body is immersed in a poor solvent for the high-molecular elastic body contained in a treatment bath, to solidify the high-molecular elastic body in a porous form. As the poor solvent for the high-molecular elastic body, water is preferably used. For example, when a polyurethane-based resin is used as the high-molecular elastic body, a treatment bath of a mixture of water and a good solvent for the high-molecular elastic body, such as dimethylformamide (DMF), is preferably used. This is because the solidification state, that is, the size, the number, and the shape of many voids formed, and the like can be controlled by appropriately setting the mixing ratio thereof.

[0095] When the high-molecular elastic body is attached using an emulsion containing the high-molecular elastic body, addition of a heat-sensitive gellant in advance and a dry method or a combination of a dry method with a method such as steaming or far-infrared heating allow for uniform solidification in the thickness direction.

[0096] When the high-molecular elastic body is attached using a solution containing an organic solvent and the high-molecular elastic body, use of a solidification adjusting agent allows for formation of more uniform voids. Examples of the organic solvent include dimethylformamide, dimethylacetamide, and dimethylsulfoxide. When the high-molecular elastic body contained in the entangled web is solidified in a porous form, a texture similar to that of natural leather can be obtained.

[0097] In particular, the wet-solidifying method is preferred, and a method in which the entangled web is immersed in a treatment liquid in which dimethylformamide as the organic solvent is mixed with water, and then solidified is more preferred.

<Step 4>

[0098] Step 4 is a step of removing a sea component from the entangled web containing the high-molecular elastic body. When the sea component is removed, fibers that can form microfine fibers are converted to a bundle of microfine fibers. That is, from the fibers in the entangled web, microfine fibers are formed, and a nonwoven fabric containing the microfine fibers and the high-molecular elastic body (hereinafter also referred to as nonwoven fabric containing the high-molecular elastic body) is obtained.

[0099] Examples of a method for removing a resin of the sea component include a method in which a resin is removed using a solvent or a decomposer that can selectively remove only the resin of the sea component.

[0100] In the embodiment, from the viewpoint of melt-spinning a resin having a high intrinsic viscosity of the island component, polyethylene is preferably used, and from this viewpoint, the sea component is preferably removed through dissolution in the organic solvent.

[0101] When the resin of the island component is a polyamide resin or a polyester-based resin and the resin of the sea component is polyethylene, examples of the organic solvent for removing the sea component through dissolution include toluene, trichloroethylene, and tetrachloroethylene.

[0102] When the sea component is removed, a dip-nip treatment is preferably performed at the same time.

[0103] While the sea/island type composite fiber is melt-spined to obtain the web and the sea component is then removed, the fibers may be made dense by a heat shrinking treatment (fiber shrinking treatment) with water vapor, hot water, dry heat, or the like.

[0104] The nonwoven fabric containing the high-molecular elastic body is preferably dried after the resin of the sea component is removed. Examples of a method include a method in which a heat treatment is performed in a dryer at 50 to 200°C, a method in which a heat treatment is performed in a dryer after heating by infrared radiation, a method in which a heat treatment is performed in a dryer after a steam treatment, or a method in which a heat treatment is performed in a dryer after heating by ultrasonic wave, and a combination thereof.

[0105] The nonwoven fabric containing the high-molecular elastic body may be cut into a predetermined thickness, if necessary.

[0106] From the viewpoint of mechanical strength, the basis weight of the nonwoven fabric containing the high-molecular elastic body is preferably 140 to 3,000 g/m^2, more preferably 200 to 2,000 g/m^2.

<Step 5>

[0107] Step 5 is a step of performing a buffing treatment for the nonwoven fabric containing the high-molecular elastic body obtained in Step 4.

[0108] When a surface or both surfaces of the nonwoven fabric containing the high-molecular elastic body is subjected to a buffing treatment, the fibers present on the surface of the nonwoven fabric are napped, to obtain a napped artificial leather having a napped surface. The buffing treatment is performed preferably using a 120 to 600 grit, more preferably 320 to 600 grit sandpaper or emery paper. Thus, a napped artificial leather having a napped surface or napped surfaces is obtained. The napped fiber length can be adjusted by appropriately adjusting the grain size of sandpaper, the grain size of emery paper, the rotation speed, the contact length, or the contact pressure of the paper, or the like. The napped fiber length can be shortened by increasing the rotation speed, the contact length, and the contact pressure of the paper.

[0109] In order to further improve a texture, the napped artificial leather may be subjected to a finishing treatment such as a shrinkage processing treatment for imparting softness, a crumpling-softening treatment, a brushing treatment to a reverse seal, an antifouling treatment, a hydrophilic treatment, a lubricant treatment, a softener treatment, an antioxidant treatment, a ultraviolet absorber treatment, a fluorescent treatment, or a flame-retardant treatment.

[0110] The napped artificial leather of the embodiment can be colored, and is preferably colored with a dyestuff or a pigment. In contrast with a pigment in which a combination of a resin or the like is required for fixing and a texture is likely to become hard, dyeing with the dyestuff is preferred from the viewpoint that a combination of a resin is not required since the resin is incorporated into the fibers, there is a small concern about a deteriorated texture and coloring in various color is simple and easy according to the kind or the density adjustment of a dyestuff.

[0111] For example, when the microfine fibers are formed from a polyester-based resin, dyeing with a disperse dyestuff or a cationic dyestuff as dyestuff is preferred. Specific examples of the disperse dyestuff include a benzeneazo-based dyestuff (monoazo, disazo, etc.), a heterocyclic azo-based dyestuff (thiazole azo, benzothiazole azo, quinolineazo, pyridineazo, imidazoleazo, thiopheneazo, etc.), an anthraquinone-based dyestuff, and a condensed dyestuff (quinophthaline, styryl, coumarin, etc.). These are put on a market as the dyestuffs having the prefix "Disperse". These may be used alone, or two or more kinds thereof may be used in combination. As the dyeing method, a dyeing method such as a high-pressure fluid dyeing method, a jigger dyeing method, a thermosol continuous dyeing machine method, or a sublimation printing system can be used.

Examples

[0112] Hereinafter, the present invention will be described more specifically using Examples and Comparative Examples, but the present invention is not limited to the following examples.

[Evaluation]

<Average Fineness>

[0113] A napped artificial leather was cut in the thickness direction thereof, and a cross section thereof was photographed with a scanning electron microscope (SEM) (S-3000N manufactured by Hitachi, Ltd.) at a magnification of 3,000. From the resultant image, 15 microfine fibers were randomly selected, and each cross-sectional area thereof was measured. Subsequently, the average value of the cross-sectional areas (average value for the 15 microfine fibers) was calculated, and from the average value of the cross-sectional area and the density of a resin constituting the microfine fibers, the average fineness was determined.

<Napped Fiber Length>

[0114] A napped artificial leather was cut in the thickness direction thereof, and napped fibers present on the napped surface of the napped artificial leather were arranged in a reverese direction with a brush for arrangement or the like. After that, the cross section of the napped artificial leather was photographed with a scanning electron microscope (SEM) at a magnification of 40. In the resultant image, a line L1 was drawn on the bottom of microfine fibers in a nonwoven fabric, or if a high-molecular elastic body film was formed, on the upper limit of a high-molecular elastic body film, and a line L2 was drawn on the upper limit when a fiber closest to an observation side was raised. A plurality of lines L3's were drawn at intervals of 200 μm in a direction perpendicular to the surface of the napped artificial leather.

[0115] The lengths of 10 lines of the lines L3's between the line L1 and the line L2 were measured, and the arithmetic average value thereof was determined.

[0116] The aforementioned operation was performed at 10 optionally selected portions of the napped artificial leather. The obtained arithmetic average values at the 10 portions were arithmetically averaged, and rounded off to the closest whole number to obtain the napped fiber length (μm).

[0117] Fig. 3 shows a schematic view for illustrating a method of measuring the napped fiber length of the napped artificial leather.

<Content of High-Molecular Elastic Body>

[0118] A piece was cut from a napped artificial leather, and the weight (W1) thereof was measured. The piece was immersed in dimethylformamide for 12 hours, then subjected to a pressing treatment, immersed in dimethylformamide for 5 minutes, and then subjected to a pressing treatment. This operation was repeated five times in total, and a high-molecular elastic body was extracted. After the extraction of the high-molecular elastic body, a nonwoven fabric was dried, and the weight (W2) of the dried nonwoven fabric was measured. The content (B) of the high-molecular elastic body was calculated by the following expression.

$$(B)=(W1-W2)/W1\times 100\ (\text{mass}\%)$$

<Area Ratio of High-Molecular Elastic Body>

[0119] Three different portions of a napped surface of a napped artificial leather were photographed with a scanning electron microscope (SEM) at a magnification of 50, and each of the resultant images was printed on an A4-size sheet. The printed sheet was stacked on an overhead projector (OHP) sheet, and a portion of the high-molecular elastic body was painted in black on and transferred to the OHP sheet. A pattern of the black-painted portion of the high-molecular elastic body on the OHP sheet was scanned with a scanner, to form an image.

[0120] Subsequently, the total area of a region where the high-molecular elastic body was present on the formed image was determined using an image processing soft Image-Pro Premier 9.2 (image-pro plus, manufactured by Media Cybernetics). From the determined total area and the total area of the entire region of the image, the area ratio of the high-molecular elastic body was calculated by the following expression.

[0121] Area ratio of high-molecular elastic body = total area of region where high-molecular elastic body is present/total area of entire region of image ×100 (%)

[0122] Fig. 1 shows an image obtained by photographing the napped surface with a scanning electron microscope (SEM) at a magnification of 50, and Fig. 2 shows an image obtaining by painting a portion of polyurethane which is the high-molecular elastic body of the image of Fig. 1 in black on an OHP sheet and transferring the polyurethane portion.

<Apparent Density>

[0123] The thickness (mm) and the basis weight (g/cm^2) were measured in accordance with JIS L 1096:2010, and from these values, the apparent density (g/cm^3) was determined.

<Tensile Strength>

[0124] Using a test piece of 2.5 cm × 16 cm cut from a napped artificial leather, a stress-strain curve was obtained in accordance with JIS L 1096:2010 8.14.1 "tensile strength test".

[0125] As test pieces, three test pieces cut so that the long side was in the longitudinal direction of the napped artificial leather and three test pieces cut so that the long side was in the transverse direction thereof were used.

[0126] From a stress-strain curve obtained using each of the test pieces, a stress at break was read, the average value of the stress of the three test pieces cut so that the long side was in the longitudinal direction and the average value of the stress of the three test pieces cut so that the long side was in the transverse direction were calculated, and the lower value (the average value) was considered as tensile strength.

<Appearance>

[0127] The appearance of a napped artificial leather was evaluated in accordance with the following criteria.

A: A high-molecular elastic body present on a napped surface is not completely viewed or is extremely slightly viewed, color unevenness is suppressed, and excellent color developability is achieved.
B: A high-molecular elastic body present on a napped surface is viewed in an uneven state, and color unevenness occurs.

<Denseness>

[0128] The denseness of a napped artificial leather was evaluated by visual check and a feeling in accordance with the following criteria.

A: Napped fibers are finely dispersed and have a uniform length, and a feeling is smooth.
B: Napped fibers are coarsely dispersed and have a non-uniform length, a feeling is rough, and lighting is not provided.

<Texture>

[0129] The texture of a napped artificial leather during bending was evaluated by visual check and a feeling in accordance with the following criteria.

A: Excellent softness, elasticity, and the like are exhibited.
B: At least one of softness and elasticity is low.

(Example 1)

[0130] Polyethylene terephthalate (PET) was prepared as an island component, and polyethylene was prepared as a sea component, the PET and the polyethylene were extruded through a melt-composition spinneret in which the number of islands was set to 12 at a spinneret temperature of 280°C and a single hole extrusion rate of 1.2 g/ min under a pressure adjusted so that the mass ratio of the sea component to the island component was 35/65, to spin a sea/island type composite fiber having a fineness of 3 dtex at a spinning rate of 4,000 m/min.

[0131] The obtained sea/island type composite fiber was continuously accumulated on a movable net, and slightly pressed by a metal roll heated to reduce fluff of the surface. The sea/island type composite fiber was peeled from the net, and passed between the heated metal roll and a back roll under pressing, to produce a web of filaments having a basis weight of 40 g/m^2.

[0132] Twelve sheets of the obtained web were laminated to form a laminate web. The laminate web was subjected to a needle punch treatment using 6-barb needles at a punching density of 2,050 needles/cm^2 to form an entangled web having a basis weight of 600 g/m^2. The obtained entangled web was subjected to a shrinking treatment in hot water at 90°C, dried, and then hot-pressed to obtain a hot-shrunk entangled web having a basis weight of 800 g/m^2.

[0133] Subsequently, the hot-shrunk entangled web was impregnated with a DMF solution (solid content: 15 mass%) of a polycarbonate-based polyurethane having a 100% modulus of 4.5 MPa, which was a high-molecular elastic body, so that the content of the high-molecular elastic body in a napped artificial leather was 18 mass%. After the impregnation, the polycarbonate-based polyurethane present on the surface of the entangled web was selectively removed by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on a napped surface was 5%, and the residual polycarbonate-based polyurethane was impregnated with a DMF aqueous solution having a mass ratio of water to DMF of 70 to 30 to solidify the polycarbonate-based polyurethane. Thus, the polycarbonate-based polyurethane (polyurethane-based resin) was attached to the entangled web.

[0134] Next, the entangled web to which the polyurethane-based resin was attached was immersed in toluene at 85°C with nipping, to remove the polyethylene as the sea component through dissolution, and then dried, to obtain a nonwoven fabric containing polyester microfine fibers and the polyurethane-based resin attached as the high-molecular elastic body. The basis weight of the obtained nonwoven fabric was 600 g/m^2.

[0135] The obtained nonwoven fabric was half-cut in the thickness direction to form an artificial leather gray fabric, one surface was subjected to a buffing treatment in which a half-cut surface was buffed by sandpapers #180 and #240 and a non-half-cut surface was then ground by sandpapers #320 and #600. Thus, a napped artificial leather having a napped surface was obtained.

[0136] Next, the dyestuff concentration of a disperse dyestuff was adjusted to 6% o.w.f., the obtained napped artificial leather was subjected to high-pressure dyeing at 130°C with a circular dyeing machine, reduced and cleaned, followed by an oxidation treatment and water-washing, to obtain a colored napped artificial leather. The evaluation results of the colored napped artificial leather are shown in Table 1.

(Example 2)

[0137] A colored napped artificial leather was obtained in the same manner as in Example 1 except that selective removal was performed by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on the napped surface was 9.3% instead of the selective removal by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on the napped surface was 5%. The evaluation results are shown in Table 1.

(Example 3)

[0138] A colored napped artificial leather was obtained in the same manner as in Example 1 except that a 0.4 mm napped artificial leather was obtained by a buffing treatment. The evaluation results are shown in Table 1.

(Example 4)

[0139] A colored napped artificial leather was obtained in the same manner as in Example 1 except that the hot-shrunk entangled web was impregnated with a DMF solution (solid content: 18.5 mass%) of a polycarbonate-based polyurethane having a 100% modulus of 4.5 MPa, which was a high-molecular elastic body, so that the content of the high-molecular elastic body in the napped artificial leather was 32 mass% instead of impregnation of the hot-shrunk entangled web with a DMF solution (solid content: 15%) of a polycarbonate-based polyurethane having a 100% modulus of 4.5 MPa, which was a high-molecular elastic body, so that the content of the high-molecular elastic body in the napped artificial leather was 18 mass%. The evaluation results are shown in Table 1.

(Example 5)

[0140] A colored napped artificial leather was obtained in the same manner as in Example 1 except that a napped artificial leather having a thickness of 1.0 mm and having a napped surface was obtained by a buffing treatment for one surface in which one surface of the obtained nonwoven fabric was buffed by sandpapers #180 and #240 to form an artificial leather gray fabric and an untreated surface was then ground by sandpapers #320 and #600. The evaluation results are shown in Table 1.

(Example 6)

[0141] Polyethylene terephthalate (PET) was prepared as an island component, and polyethylene was prepared as a sea component, the PET and the polyethylene were extruded through a melt-composition spinneret in which the number of islands was set to 16 at a spinneret temperature of 280°C and a single hole extrusion rate of 1.2 g/ min under a pressure adjusted so that the mass ratio of the sea component to the island component was 35/65, to spin fibers at a spinning rate of 820 m/min, and the fibers were stretched and subjected to a crimping treatment, to obtain a sea/island type composite fiber which was a staple fiber having a fineness of 4.0 dtex.

[0142] Next, the sea/island type composite fiber was carded to produce a web of staple fibers.

[0143] A plurality of sheets of the obtained web were laminated to form a laminate web. The laminate web was subjected to a needle punch treatment using 1-barb needles at a punching density of 2,050 needles/cm^2 to form an entangled web having a basis weight of 600 g/m^2. The obtained entangled web was subjected to a shrinking treatment in hot water at 90°C, dried, and then hot-pressed to obtain a hot-shrunk entangled web having a basis weight of 800 g/m^2.

[0144] Subsequently, the hot-shrunk entangled web was impregnated with a DMF solution (solid content: 15 mass%) of a polycarbonate-based polyurethane having a 100% modulus of 4.5 MPa, which was a high-molecular elastic body, so that the content of the high-molecular elastic body in a napped artificial leather was 18 mass%. After the impregnation, the polycarbonate-based polyurethane present on the surface of the entangled web was selectively removed by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on a napped surface was 5%, and the residual polycarbonate-based polyurethane was impregnated with a DMF aqueous solution having a mass ratio of water to DMF of 70 to 30 to solidify the polycarbonate-based polyurethane. Thus, the polycarbonate-based polyurethane (polyurethane-based resin) was attached to the entangled web.

[0145] Next, the entangled web to which the polyurethane-based resin was attached was immersed in toluene at 85°C with nipping, to remove the polyethylene as the sea component through dissolution, and then dried, to obtain a nonwoven fabric containing polyester microfine fibers and the polyurethane-based resin attached as the high-molecular elastic body. The basis weight of the obtained nonwoven fabric was 820 g/m^2.

(Comparative Example 1)

[0146] A colored napped artificial leather was obtained in the same manner as in Example 1 except that selective removal was performed by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on the napped surface was 17.6% instead of the selective removal by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on the napped surface was 5%. The evaluation results are shown in Table 1.

(Comparative Example 2)

[0147] A colored napped artificial leather was obtained in the same manner as in Example 1 except that selective removal was performed by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on the napped surface was 14.8% instead of the selective removal by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on the napped surface was 5% and the napped fiber length was adjusted to 250 μm during the buffing treatment. The evaluation results are shown in Table 1.

(Comparative Example 3)

[0148] A colored napped artificial leather was obtained in the same manner as in Example 1 except that a DMF solution (solid content: 15%) of a polycarbonate-based polyurethane having a 100% modulus of 4.5 MPa in which carbon black was added resulting in coloring so that the content was 1.0 mass% was used instead of a DMF solution (solid content: 15%) of a polycarbonate-based polyurethane having a 100% modulus of 4.5 MPa, and selective removal of the polycarbonate-based polyurethane present on the entangled web was performed by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on the napped surface was 18.4% instead of the selective removal of the polycarbonate-based polyurethane present on the surface of the nonwoven fabric by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on the napped surface was 5%. The evaluation results are shown in Table 1.

(Comparative Example 4)

[0149] A colored napped artificial leather was obtained in the same manner as in Example 1 except that a polyvinyl alcohol was used instead of the polyethylene as the sea component, the entangled web was immersed in hot water to remove the polyethylene as the sea component through dissolution instead of immersion in toluene to remove the polyethylene through dissolution, and the hot-shrunk entangled web was impregnated with a self-emulsifying type amorphous polycarbonate-based polyurethane emulsion solution (solid content: 15 mass%) having a 100% modulus of 3.0 MPa so that the content of the high-molecular elastic body in the napped artificial leather was 10 mass% instead of impregnation of the hot-shrunk nonwoven fabric with a DMF solution (solid content: 15%) of a polycarbonate-based polyurethane having a 100% modulus of 4.5 MPa so that the content of the high-molecular elastic body in the napped artificial leather was 18 mass%. The evaluation results are shown in Table 1.

(Comparative Example 5)

[0150] Polyethylene terephthalate (PET) was prepared as an island component, and polyethylene was prepared as a sea component, the PET and the polyethylene were extruded through a melt-composition spinneret in which the number of islands was set to 16 at a spinneret temperature of 280°C and a single hole extrusion rate of 1.2 g/ min under a pressure adjusted so that the mass ratio of the sea component to the island component was 35/65, to spin fibers at a spinning rate of 820 m/min, and the fibers were stretched and subjected to a crimping treatment, to obtain sea/island type composite fibers which was a staple fiber having a fineness of 3.6 dtex.

[0151] The obtained sea/island type composite fiber was carded to produce a web of staple fibers.

[0152] A plurality of sheets of the obtained web were laminated to form a laminate web. The laminate web was subjected to a needle punch treatment using 1-barb needles at a punching density of 2,050 needles/cm^2 to form an entangled web having a basis weight of 600 g/m^2. The obtained entangled web was subjected to a shrinking treatment in hot water at 90°C, dried, and then hot-pressed to obtain a hot-shrunk entangled web having a basis weight of 800 g/m^2.

[0153] Subsequently, the hot-shrunk entangled web was impregnated with a DMF solution (solid content: 15 mass%) of a polycarbonate-based polyurethane having a 100% modulus of 4.5 MPa, which was a high-molecular elastic body, so that the content of the high-molecular elastic body in a napped artificial leather was 40 mass%. After the impregnation, the polycarbonate-based polyurethane present on the surface of the entangled web was selectively removed by applying a contact pressure so that the area ratio of the polycarbonate-based polyurethane present on a napped surface was 5%, and the residual polycarbonate-based polyurethane was impregnated with a DMF aqueous solution having a mass ratio of water to DMF of 70 to 30 to solidify the polycarbonate-based polyurethane. Thus, the polycarbonate-based polyurethane (polyurethane-based resin) was attached to the entangled web.

[0154] Next, the entangled web to which the polyurethane-based resin was attached was immersed in toluene at 85°C with nipping, to remove the polyethylene as the sea component through dissolution, and then dried, to obtain a nonwoven fabric containing polyester microfine fibers and the polyurethane-based resin attached as the high-molecular elastic body. The basis weight of the obtained nonwoven fabric was 654 g/m^2.

[0155] The obtained nonwoven fabric was half-cut in the thickness direction to form an artificial leather gray fabric, one surface was subjected to a buffing treatment in which a half-cut surface was buffed by sandpapers #180 and #240 and a non-half-cut surface was then ground by sandpapers #320 and #600. Thus, a napped artificial leather having a napped surface was obtained.

[0156] Next, the dyestuff concentration of a disperse dyestuff was adjusted to 6% o.w.f., the obtained napped artificial leather was subjected to high-pressure dyeing at 130°C with a circular dyeing machine, reduced and cleaned, followed by an oxidation treatment and water-washing, to obtain a colored napped artificial leather. The evaluation results of the colored napped artificial leather are shown in Table 1.

Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Fiber content	mass%	82	82	82	68	82	82
High-molecular elastic body content	mass%	18	18	18	32	18	18
Fiber kind	-	Filament	Filament	Filament	Filament	Filament	Staple fiber
Average fineness	dtex	0.2	0.2	0.2	0.2	0.2	0.2
Napped fiber length	µm	71	68	83	231	78	221
Kind of high-molecular elastic body	-	Solvent-based	Solvent-based	Solvent-based	Solvent-based	Solvent-based	Solvent-based
Spin-dyeing of high-molecular elastic body*1		None	None	None	None	None	None
Area ratio of high-molecular elastic body	%	11.5	9.3	10.7	16.7	11.2	13.6
Thickness of napped artificial leather	mm	0.5	0.5	0.4	0.5	1.0	0.8
Apparent density	g/cm^3	0.40	0.39	0.39	0.43	0.41	0.40
Tensile strength	kg/2.5 cm	18.7	18.2	12.2	16.2	59.8	30.4
Appearance	-	A	A	A	A	A	A
Denseness	-	A	A	A	A	A	A
Texture	-	A	A	A	A	A	A
*1: this represents whether a high-molecular elastic body is colored before the high-molecular elastic body is attached to an entangled web.							

Table 1 (continued)

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Fiber content	mass%	82	82	82	90	60
High-molecular elastic body content	mass%	18	18	18	10	40
Fiber kind	-	Filament	Filament	Filament	Filament	Staple fiber
Average fineness	dtex	0.2	0.2	0.2	0.1	0.1
Napped fiber length	µm	75	268	98	192	63
Kind of high-molecular elastic body	-	Solvent-based	Solvent-based	Solvent-based	Aqueous	Solvent-based
Spin-dyeing of high-molecular elastic body*1		None	None	Spin-dyeing	None	None

(continued)

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Area ratio of high-molecular elastic body	%	17.6	14.8	18.4	6.8	25.5
Thickness of napped artificial leather	mm	0.5	0.5	0.5	0.5	0.4
Apparent density	g/cm^3	0.40	0.40	0.41	0.52	0.30
Tensile strength	kg/2.5 cm	19.5	19.9	19.1	21.1	9.1
Appearance	-	B	A	B	A	B
Denseness	-	A	B	A	A	A
Texture	-	A	A	A	B	A
*1: this represents whether a high-molecular elastic body is colored before the high-molecular elastic body is attached to an entangled web.						

[0157] In the napped artificial leathers obtained in Examples 1 to 6, the high-molecular elastic body present on each napped surface was not completely viewed or was extremely slightly viewed, dyeing unevenness was suppressed, and excellent color developability was achieved. Further, the napped fibers were finely dispersed and had a uniform length, and a feeling was smooth.

[0158] On the other hand, in the napped artificial leather obtained in Comparative Example 1, the content of the high-molecular elastic body was within the range of 15 to 35 mass%, the napped fiber length was 250 μm or less, but the area ratio of the high-molecular elastic body present on the napped surface was more than 17%. The high-molecular elastic body (polyurethane-based resin) present on the napped surface was viewed in an uneven state, and dyeing unevenness occurred.

[0159] In the napped artificial leather obtained in Comparative Example 2, the content of the high-molecular elastic body was within the range of 15 to 35 mass%, the area ratio of the high-molecular elastic body present on the napped surface was 17% or less, but the napped fiber length was more than 250 μm. The napped fibers were coarsely dispersed and had a non-uniform length, a feeling was rough, and lighting was not provided.

[0160] In the napped artificial leather obtained in Comparative Example 3, the content of the high-molecular elastic body was within the range of 15 to 35 mass%, the napped fiber length was 250 μm or less, but the area ratio of the high-molecular elastic body present on the napped surface was more than 17%. Since the high-molecular elastic body contains carbon black, dyeing unevenness was suppressed to some extent, but the dyeing unevenness occurred to a visually recognizable extent.

[0161] In the napped artificial leather obtained in Comparative Example 4, the area ratio of the high-molecular elastic body present on the napped surface was 17% or less, the napped fiber length was more than 250 μm, but the content of high-molecular elastic body attached to the nonwoven fabric was not equal to or less than the lower limit of the range of 15 to 35 mass%. This napped artificial leather was a napped artificial leather having low softness and elasticity and a hard texture.

[0162] The napped artificial leather obtained in Comparative Example 5 was a napped artificial leather having a thickness of 0.4 mm using staple fibers. In the napped artificial leather, the napped fiber length was 250 μm or less, but the content of the high-molecular elastic body attached to the nonwoven fabric was more than the upper limit of the range of 15 to 35 mass%, and the area ratio of the high-molecular elastic body present on the napped surface was more than 17%. The high-molecular elastic body (polyurethane-based resin) present on the napped surface was viewed in an uneven state, dyeing unevenness was generated, and the mechanical strength was not sufficient.

Claims

1. A napped artificial leather comprising: a nonwoven fabric containing microfine fibers and a high-molecular elastic body, the napped artificial leather having a napped surface, wherein

a content of the high-molecular elastic body is 15 to 35 mass%,
an area ratio of the high-molecular elastic body present on the napped surface is 17% or less, and
a napped fiber length is 250 μm or less.

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

3. The napped artificial leather according to claim 1 or 2, wherein the microfine fibers have an average fineness of 0.01 to 1.0 dtex.

4. The napped artificial leather according to any one of claims 1 to 3, wherein the nonwoven fabric is a spun-bond nonwoven fabric.

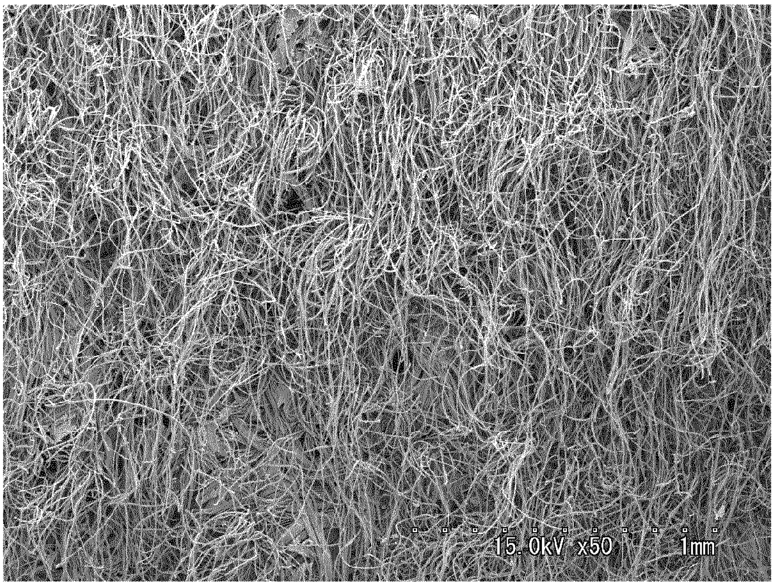
5. A method for manufacturing the napped artificial leather according to any one of claims 1 to 4, the method comprising a step of removing a sea component from an entangled web containing the high-molecular elastic body, to obtain a nonwoven fabric containing the high-molecular elastic body.

6. The method for manufacturing the napped artificial leather according to claim 5, the method comprising a step of melt-spinning sea/island type composite fibers to obtain a web.

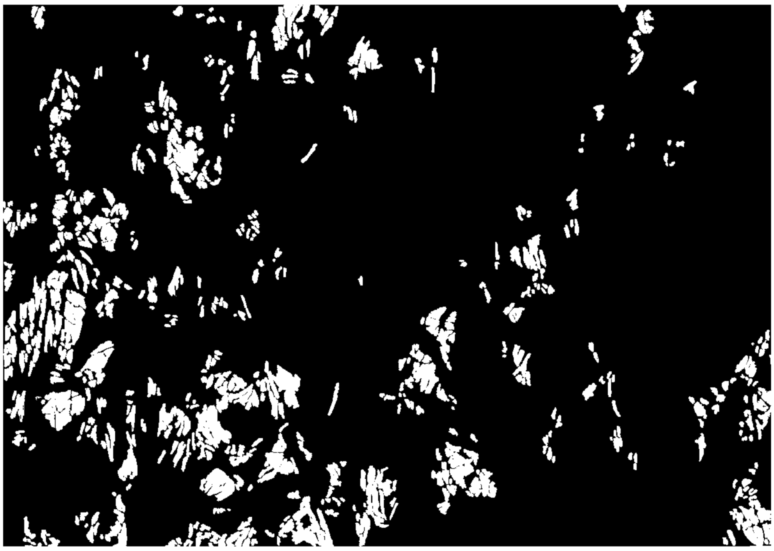
7. The method for manufacturing the napped artificial leather according to claim 6, wherein the step of obtaining a nonwoven fabric containing the high-molecular elastic body includes removing the sea component through dissolution in an organic solvent.

8. The method for manufacturing the napped artificial leather according to any one of claims 5 to 7, the method comprising a step of forming the entangled web containing the high-molecular elastic body through use of a solvent-based polyurethane.

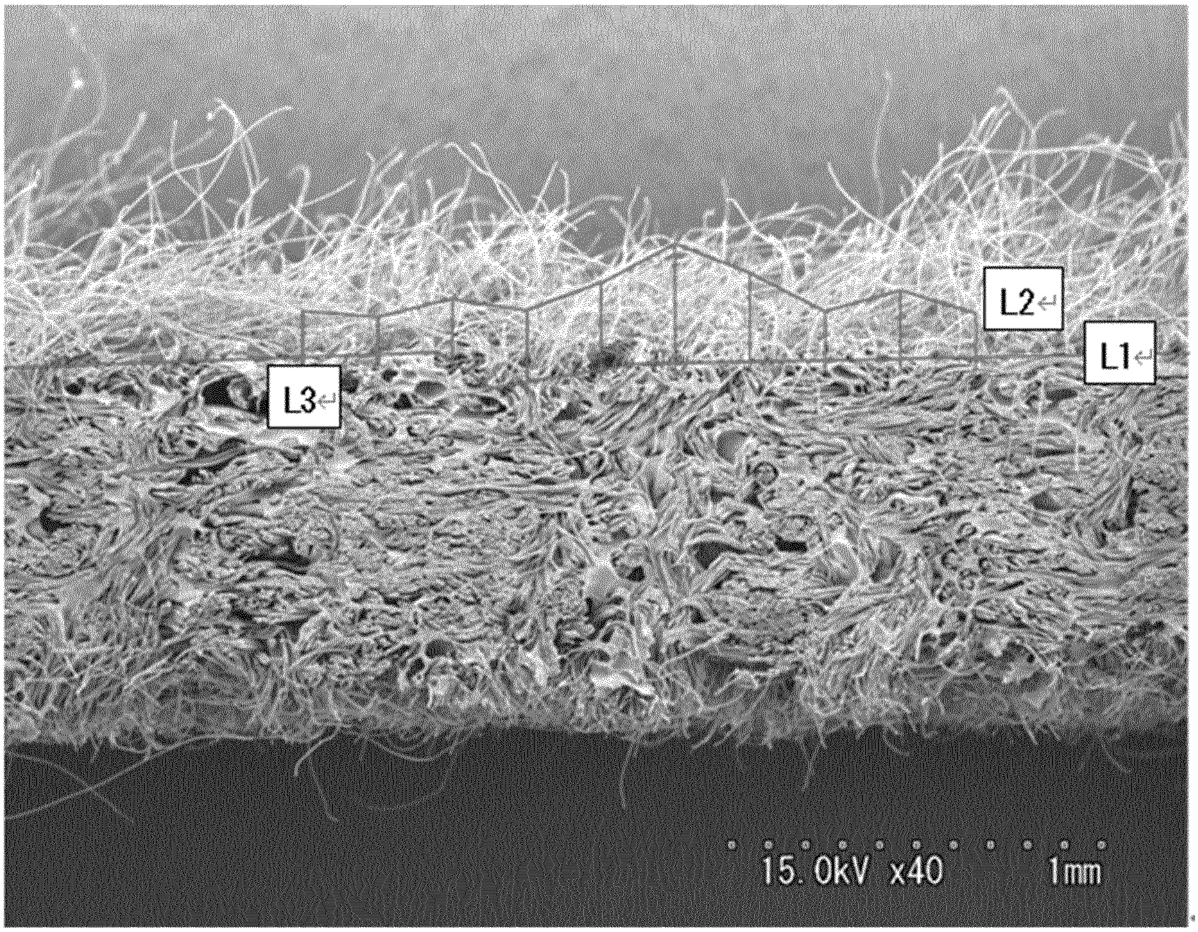
[Fig. 1]



[Fig. 2]



[Fig. 3]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/024418

A. CLASSIFICATION OF SUBJECT MATTER

D06N 3/14(2006.01)i
FI: D06N3/14

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)

D06N3/14

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 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	claims, example 2	7, 8
X	WO 2020/189592 A1 (TORAY INDUSTRIES, INC.) 24 September 2020 (2020-09-24) claims, paragraphs [0045], [0063], [0081], [0083], [0108], [0113], examples	1-8
A	WO 2020/003866 A1 (TORAY INDUSTRIES, INC.) 02 January 2020 (2020-01-02) entire text, all drawings	1-8
A	JP 2004-143654 A (KURARAY CO., LTD.) 20 May 2004 (2004-05-20) entire text	1-8
A	WO 2021/049413 A1 (KURARAY CO., LTD.) 18 March 2021 (2021-03-18) entire text, all drawings	1-8
A	JP 2015-509149 A (ALCANTARA S. P. A.) 26 March 2015 (2015-03-26) entire text, all drawings	1-8

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

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search **13 September 2023**	Date of mailing of the international search report **26 September 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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