(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 557 223 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
13.02.2013 Bulletin 2013/07

(21) Application number: **11762192.0**

(22) Date of filing: **23.03.2011**

(51) Int Cl.:
D06N 3/00 (2006.01) ***D04H 3/10*** (2012.01)
D04H 3/16 (2006.01) ***D06M 15/564*** (2006.01)

(86) International application number:
PCT/JP2011/001705

(87) International publication number:
WO 2011/121940 (06.10.2011 Gazette 2011/40)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **31.03.2010 JP 2010083508**

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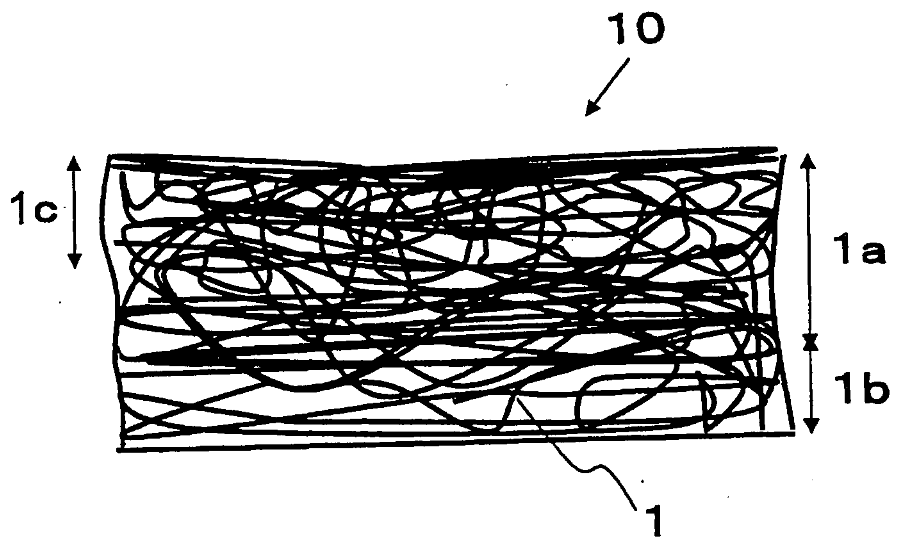
(54) LEATHER-LIKE SHEET

(57) Disclosed is a leather-like sheet including a fiber bundle entangled body which is an entangled body of a fiber bundle of ultrafine filaments. A fiber occupancy (A1) of a superficial layer that is a zone covering 2/3 of the thickness from a front surface of the fiber bundle entangled body, is 36 to 56 vol%. A fiber occupancy (A2) of a bottom layer thereof that is a zone covering 1/3 of the thickness from a back surface, is smaller than the fiber occupancy (A1). A ratio (A1/A2) of the fiber occupancy (A1) to the fiber occupancy (A2) is 1.08 to 1.8.

FIG. 1



Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a leather-like sheet containing a fiber-bundle entangled body of an ultrafine filament bundle, or a so-called ultrafine filament bundle entangled body. Specifically, the present invention relates to a leather-like sheet having a texture well-balanced in stiffness and flexibility.

Background Art

[0002] Leather-like sheets represented by artificial leather are superior to natural leather in, for example, lightness and handleability. Therefore, leather-like sheets have been widely used as surface materials for garments, general materials, sports items, and the like. Conventional artificial leather is produced, for example, as follows.

[0003] First, a sea-island (matrix-domain) type multi-component fiber composed of two polymers that have mutually different solvent solubilities is formed and then stapled (processed into short fibers). Then, the staple is formed into a web using a card, cross wrapper, random weaver, or the like. Then, fibers of the formed web are entangled with each other by needle punching to give a non-woven fabric. Next, the obtained non-woven fabric is impregnated with a polymer elastic body such as polyurethane. Then, the sea component polymer is removed by dissolution from the sea-island (matrix-domain) type multi-component fiber of the non-woven fabric, and only the ultrafine fiber composed of the island component polymer is retained. In this manner, artificial leather containing a non-woven fabric composed of ultrafine staple fibers and a polymer elastic body is obtained.

[0004] Artificial leather that contains the non-woven fabric composed of ultrafine staple fibers has the following problems. Namely, there is a problem in that since the fiber length of the ultrafine fibers is short, fiber detachment or fiber loss easily occurs. Accordingly, the napped surface of artificial napped leather in which such artificial leather is used as a substrate has poor abrasion resistance. Also, the grain resin layer of artificial grain leather in which such artificial leather is used as a substrate has poor adhesion. Also, there are problems in that during the production of such artificial leather, fibers on the surface of artificial leather become fluffy due to friction received in the production line, thus impairing stiffness or a surface texture, or fibers unevenly stretch when being wound up, thus resulting in inconsistent quality. Note that, the term "stiffness" refers to the texture having stiffness.

[0005] To solve such disadvantages of artificial leather, the following method is known. Specifically, for example, the extent of entanglement of a non-woven fabric is increased to raise the fiber density, and the proportion of the polymer elastic body is increased to intensify a restraint between fibers. However, when a restraint between fibers is intensified by increasing the extent of entangling or the proportion of the polymer elastic body, the appearance and texture of the obtained artificial leather are likely to be poor.

[0006] Also, as another type of artificial leather, artificial leather containing a non-woven fabric composed of ultrafine fibers of a filament (continuous fiber) is known. A non-woven fabric composed of ultrafine filaments has better strength and shape stability than a non-woven fabric composed of ultrafine staples. Also, since a series of large-scale items of equipment such as a raw-fiber feeder, fiber opener, and carding machine is not needed, the production process thereof can be simplified. However, a non-woven fabric composed of ultrafine filaments having a low fineness is likely to be bulky and have a texture similar to a fabric having poor stiffness. This is because filaments have less crimpability than staples.

[0007] Patent Document 1 below proposes, as a method for ameliorating the bulkiness of a non-woven fabric composed of ultrafine filaments, a method in which ultrafine filaments are partially cut to partially remove distortion for densification. However, this method is problematic in that the advantage of increased mechanical properties brought about by the long fiber length cannot be sufficiently demonstrated. Patent Document 2 below proposes a method for suppressing a change of the shape of a composite sheet by reinforcing a non-woven fabric with a knit/woven fabric. However, reinforcing a non-woven fabric with a knit/woven fabric is problematic in that creases are easily created. As a technique to solve these problems, Patent Document 3 below discloses an ultrafine filament entangled sheet containing a fiber entangled body of a fiber bundle of ultrafine filaments.

[0008] It is known that natural leather has a structure with a density gradient in the thickness direction. Artificial leather having a density gradient in the fiber or polymer elastic body in the thickness direction so as to mimic the gradient structure of natural leather is also known (see, for example, Patent Documents 4, 5, and 6).

Prior Art Documents

Patent Documents

[0009]

Patent Document 1: Laid-Open Patent Publication No. JP2000-273769
Patent Document 2: Laid-Open Patent Publication No. JP S64-20368
Patent Document 3: WO 2005/124002
Patent Document 4: Laid-Open Patent Publication No. JP2007-46183
Patent Document 5: Laid-Open Patent Publication No. JP H6-280145
Patent Document 6: Laid-Open Patent Publication No. JP H11-012920

Disclosure of the Invention

Problem to be Solved by the Invention

[0010] An object of the present invention is to provide a leather-like sheet having a texture well-balanced in stiffness and flexibility similar to natural leather.

Means for Solving the Problem

[0011] One aspect of the present invention is a leather-like sheet containing a fiber bundle entangled body which is an entangled body of fiber bundles of ultrafine filaments, a fiber occupancy (A1) of a superficial layer that is a zone covering 2/3 of the thickness from a front surface of the fiber bundle entangled body being 36 to 56 vol%, a fiber occupancy (A2) of a bottom layer thereof that is a zone covering 1/3 of the thickness from a back surface being smaller than the fiber occupancy (A1), and a ratio (A1/A2) of the fiber occupancy (A1) to the fiber occupancy (A2) being 1.08 to 1.8.

Effect of the Invention

[0012] According to the present invention, a leather-like sheet having a texture well-balanced in stiffness and flexibility similar to natural leather is obtained.
Objects, features, aspects, and advantages of the present invention will become more apparent from the following detailed description and the accompanying drawings.

Brief Description of the Drawings

[0013]

FIG 1 is an explanatory schematic cross-sectional view showing a leather-like sheet 10 of one embodiment.
FIG 2 is a schematic cross-sectional view of a fiber bundle of ultrafine filaments f forming a fiber bundle entangled body 1.

Best Mode for Carrying Out the Invention

[0014] Conventional artificial leather is problematic in that, for example, the balance between stiffness and flexibility is poor. That is, as described above, when the fiber density of a non-woven fabric is increased, stiffness is enhanced but flexibility is deteriorated. Also, when the proportion of the polymer elastic body is increased, stiffness is enhanced, but this stiffness comes with a significant rubber-like feel. Accordingly, artificial leather having a texture well-balanced in stiffness and flexibility as in natural leather has not been obtained. The leather-like sheet of this embodiment can solve these problems. Hereinafter, the leather-like sheet of one embodiment of the present invention will now be described with reference to FIG 1.
[0015] The leather-like sheet 10 of this embodiment contains the fiber bundle entangled body 1 of ultrafine filaments as shown in FIG 1. FIG. 2 shows a schematic cross-sectional view of a fiber bundle of ultrafine filaments f forming the fiber bundle entangled body 1.
[0016] In the fiber bundle entangled body 1, the fiber occupancy (A1) in a superficial layer 1a that serves as a zone covering 2/3 of the thickness from the front surface thereof is 36 to 56 vol%. The fiber occupancy (A2) of a bottom layer 1 b that serves as a zone covering 1/3 of the thickness from the back surface is less than the fiber occupancy (A1) of the superficial layer 1a. The ratio (A1/A2) of the fiber occupancy (A1) to the fiber occupancy (A2) is 1.08 to 1.8. Note that in the case where the leather-like sheet is surface-treated, the fiber occupancy is calculated from the zone that does not include the surface-treated portion.
[0017] The fiber occupancy is a volume fraction of the fiber component relative to the space occupied by the superficial layer 1a or bottom layer 1b. Specifically, for example, it can be calculated, based on the apparent specific gravity of a fiber and the specific gravity of the polymer constituting the fiber that are obtained in accordance with JIS K 7112, using

the following formula:

$$\text{Fiber occupancy (\%)} = (\text{Apparent specific gravity of fiber} / \text{Specific gravity of polymer constituting fiber}) \times 100$$

[0018] Note that the fiber occupancy can also be estimated by observing a random cross-section that is in parallel with the thickness direction of an osmium oxide-stained leather-like sheet under a scanning electron microscope (100 to 200 magnification) at 100 to 200 magnification and performing image processing through binarization.

[0019] With the superficial layer 1a having an increased fiber density, the fiber bundle entangled body 1 has a configuration in which the fiber occupancy (A1) of the superficial layer 1a is significantly higher than the fiber occupancy (A2) of the bottom layer 1b. This configuration makes it possible to impart considerable stiffness to the superficial layer 1 a of the fiber bundle entangled body 1 and impart excellent lightweight properties and flexibility to the bottom layer 1b. Also, the bottom layer 1 b is sparser than the superficial layer 1 a, and therefore, for example, the bottom layer 1b easily deforms in accordance with the deformation of the superficial layer 1 a when the fiber bundle entangled body 1 is bent. Therefore, when the fiber bundle entangled body 1 is bent, a bent state similar to natural leather, i.e., the fiber bundle entangled body 1 is not likely to undergo loss of stiffness, can be reached. Moreover, the front surface thereof is dense, so the fiber bundle entangled body 1 has excellent surface abrasion resistance. Moreover, in the case where a grain layer is formed, the fiber bundle entangled body 1 demonstrates strong adhesion to the grain layer, and in the case where the fiber bundle entangled body 1 is napped, a dense fluffy texture is obtained. These properties are not obtainable from a method in which fiber bundle entangled bodies having different densities are merely adhesion-bonded to each other.

[0020] The fiber occupancy (A1) in the superficial layer 1a that serves as a zone covering 2/3 of the thickness from the front surface of the fiber bundle entangled body 1 is 36 to 56 vol%, preferably 40 to 56 vol%, and more preferably 40 to 50 vol%. When the fiber occupancy (A1) is less than 36 vol%, stiffness is insufficient. In this case, for example, the leather-like sheet easily undergoes loss of stiffness when bent. Note that, for example, with a leather-like sheet having a density gradient, which satisfies the aforementioned fiber occupancy solely by an outermost layer 1c that serves as a zone covering 1/3 of the thickness from the front surface of the fiber bundle entangled body 1, crude creases as those created when a cardboard is folded are likely to be created in the front surface when the leather-like sheet is folded. Also, when the fiber occupancy (A) exceeds 56 vol%, flexibility is insufficient, resulting in a paper-like hard texture. Of the superficial layer, the fiber occupancy (A3) of the outermost layer 1c that is a zone covering 1/3 of the thickness from the front surface is preferably 36 to 60 vol% and more preferably 45 to 60 vol%. When the fiber occupancy (A3) of the outermost layer 1c is 36 vol% or greater, stiffness is more similar to that of natural leather, and when it is 60 vol% or less, crude creases as found on cardboard are not likely to be created, and creases more similar to those of natural leather are obtained.

[0021] Regarding the fiber bundle entangled body 1, the fiber occupancy (A2) of the bottom layer 1 b is smaller than the fiber occupancy (A1) of the superficial layer 1 a, and the ratio (A1/A2) of the fiber occupancy (A1) to the fiber occupancy (A2) is in the range of 1.08 to 1.8, and preferably in the range of 1.1 to 1.5. When the fiber occupancy ratio (A1/A2) is in such a range, a leather-like sheet well-balanced in stiffness and flexibility is obtained. When the fiber occupancy ratio (A1/A2) is less than 1.08, flexibility is excessively small or large, and stiffness and flexibility as found in natural leather cannot be provided. When the ratio exceeds 1.8, the difference between the fiber density of the superficial layer 1 a and the fiber density of the bottom layer 1 b is excessive, and the superficial layer 1 a is excessively unstretchable and the bottom layer 1b is excessively stretchable. Therefore, the sheet easily undergoes loss of stiffness when bent, and the textural balance perceived when the sheet is held or touched is also deteriorated.

[0022] Also, regarding the fiber bundle entangled body 1, the ratio (A3/A1) of the fiber occupancy (A3) of the outermost layer 1 c to the fiber occupancy (A1) of the superficial layer 1 a is preferably in the range of 0.95 to 1.2, and is more preferably in the range of 1.0 to 1.1. When the fiber occupancy ratio (A3/A1) is 0.95 or greater, excellent stiffness and creases are obtained, and when 1.2 or less, crude creases as found on cardboard are not likely to be generated.

[0023] It is preferable that the average fineness of the ultrafine filaments f constituting the fiber bundle of the fiber bundle entangled body 1 is in the range of 0.001 to 0.5 dtex, particularly 0.01 to 0.4 dtex, and especially 0.02 to 0.3 dtex. When the average fineness of the ultrafine filaments f is excessively small, fibers do not mutually loosen and are tied together, and as a result, it is likely that the rigidity of the fiber bundle entangled body 1 is increased, and the flexibility is impaired. When the average fineness of the ultrafine filaments f is excessively large, surface denseness and voluminousness as found in natural leather are not likely to be obtained. Note that adjusting the average fineness of the ultrafine filaments f makes it possible to further control the balance between stiffness and flexibility of the fiber bundle entangled body 1. For example, it is more preferable that when the average fineness is 0.001 to 0.05 dtex, the fiber occupancy (A) is 40 to 56%, when the average fineness is 0.05 to 0.2 dtex, the fiber occupancy (A) is 40 to 50%, and when the average fineness is 0.2 to 0.5 dtex, the fiber occupancy (A) is 36 to 50%.

[0024] The resin that forms the ultrafine filaments is not particularly limited as long as it is a thermoplastic resin capable of forming the ultrafine filaments. Specific examples indude aromatic polyesters such as polyethylene terephthalate (PET), isophthalic acid-modified polyethylene terephthalate, dimethylisophthalic acid-modified polyethylene terephthalate, sulfoisophtharic acid-modified polyethylene terephthalate, polytrimethylene terphthalate, polybutylene terephthalate, and polyhexamethylene terephthalate; aliphatic polyesters such as polylactic acid, polyethylene succinate, polybutylene succinate, polybutylene succinate adipate, and polyhydroxybutyrate-polyhydroxy valerate copolymers; polyamides such as polyamide 6, polyamide 66, polyamide 10, polyamide 11, polyamide 12, and polyamide 6-12; polyolefins such as polyethylene, polypropylene (PP), polybutene, polymethylpentene, and chlorinated polyolefins; polyvinyl alcohols containing an ethylene unit in a proportion of 25 to 70 mol%; and thermoplastic elastomers such as polyurethane-based elastomers, polyamide-based elastomers, and polyester-based elastomers.

[0025] Among the aforementioned resins, PET, modified PET such as isophthalic acid-modified PET, polylactic acid, polyamide 6, polyamide 12, polyamide 6-12, polypropylene, and the like are preferable. In particular, PET and modified resins such as isophthalic acid-modified PET demonstrate favorable shrinkage characteristics when subjected to a heat-moisture shrinking treatment, which will be described below, and thus are particularly preferable.

It is preferable that the extent of modification in modified PET is in the range of, for example, 0.1 to 30 mol%, particularly 0.5 to 15 mol%, and especially 1 to 10 mol%.

[0026] Depending on the resin, the modulus of elasticity of a fiber varies, and therefore it is also preferable to control the balance between stiffness and flexibility of the fiber bundle entangled body 1 by more suitably adjusting the fiber occupancy (A) according to the resin. Specifically, for example, when an aromatic polyester such as PET or modified PET or a polyolefin such as PP having a large modulus of elasticity is used, the fiber occupancy (A) is preferably in the range of 36 to 50%. When an aliphatic polyamide having a small modulus of elasticity is used, the fiber occupancy (A) is preferably in the range of 40 to 56%.

[0027] Note that it is preferable that the fiber bundle entangled body 1 is composed of a fiber bundle that is continuously spun and that has a substantially uniform fineness, and has little variation in fineness. In this case, the superficial layer and the bottom layer has excellent uniformity, and therefore the fiber bundle entangled body 1 demonstrates tension, firmness, and stiffness when bent and demonstrates large peeling strength, thus being preferable. Note that the fiber bundle entangled body that is continuously produced and has a substantially uniform fineness means that it is not created by bonding different non-woven fabrics to each other. When a leather-like sheet is formed from a fiber bundle entangled body obtained by entangling a web composed of different fiber components that are different in, for example, resin composition of a fiber, ultrafine fiber fineness, fiber bundle fineness, and fiber cross-sectional structure, the peeling strength is likely to be insufficient. Meanwhile, conventionally, a method for locally densifying, by thermal pressing or the like, only the zone covering a thickness of about 0.1 mm, which ranges about 1/3 or less of the thickness of the entire layers, from the superficial layer is also known. However, when a part of the superficial layer is locally densified by this method, it is likely that only the surface is hardened, the leather-like sheet undergoes loss of stiffness when bent, the texture lacks flexibility, or the textural balance perceived when the sheet is held or touched is deteriorated.

[0028] The leather-like sheet may contain, if necessary, a polymer elastic body to impart shape stability by putting a restraint on the fiber bundle entangled body, to impart rigidity by putting a restraint on the ultrafine filaments constituting the fiber bundle, or to improve or adjust the texture.

[0029] When the leather-like sheet contains a polymer elastic body, the proportion thereof relative to the mass of the fiber bundle entangled body is preferably 15 mass% or less, more preferably 0.1 to 15 mass%, even more preferably 0.2 to 10 mass%, and especially preferably 0.5 to 5 mass%. When the proportion of the polymer elastic body is excessive, a rubber-like feel is considerable, and the texture is likely to be impaired.

[0030] When the leather-like sheet contains a polymer elastic body, the inside of the fiber bundle may be impregnated with the polymer elastic body, or the polymer elastic body is adhered to the outside of the fiber bundle. When the inside of the fiber bundle is impregnated with the polymer elastic body, the polymer elastic body puts a restraint on the ultrafine filaments f that constitute the fiber bundle, and thus the rigidity is adjusted. When the proportion of the polymer elastic body with which the inside of the fiber bundle of the ultrafine filaments is impregnated is 5 mass% or less relative to the total mass of the entire polymer elastic body, which is the sum of the polymer elastic body present outside the fiber bundle of the fiber bundle entangled body and the polymer elastic body with which the inside of the fiber bundle is impregnated, the ultrafine filaments are excessively tied together, and thus excellent flexibility is obtained. Also, when the proportion of the polymer elastic body present inside the fiber bundle of the ultrafine filaments exceeds 5 mass%, excellent stiffness is obtained. Accordingly, adjusting the proportion of the polymer elastic body with which the inside of the fiber bundle is impregnated makes it possible to adjust the balance between flexibility and stiffness.

[0031] Rubbers, elastomers, and the like are used without particular limitations as the polymer elastic body. Specific examples thereof indude diene-based rubbers such as butadiene rubber, isoprene rubber, chloroprene rubber, and styrene-butadiene rubber, nitrile-based rubbers such as nitrile rubber and hydrogenated nitrile rubber, acryl-based rubbers such as acrylic rubber, urethane-based rubbers such as polyether urethane rubber and polyester urethane rubber, silicone-based rubbers; olefin-based rubbers such as ethylene-propylene rubber, fluorine-based rubbers; polystyrenebased elastomers such as styrene-butadiene block copolymers, styrene-isoprene block copolymers, styrene-butadiene-styrene block copolymers, styrene-isoprene-styrene block copolymers, acrylonitrile-butadiene-styrene copolymers, acrylonitrile-styrene copolymers, or hydrogenated or epoxidized products thereof; polyolefin-based elastomers such as propylene-ethylene/propylene rubber copolymers and like copolymers of olefins and rubber components, or hydrogenated products thereof; polyurethane-based elastomers such as polyether urethane elastomers, polyester urethane elastomers, polyether ester urethane elastomers, polycarbonate urethane elastomers, polyether carbonate urethane elastomers, and polyester carbonate urethane elastomers; polyester-based elastomers such as polyether ester elastomers and polyester ester elastomers; polyamide-based elastomers such as polyester amide elastomers and polyether ester amide elastomers; halogen-based elastomers such as vinyl chloride-based elastomers; and the like. These may be used alone or in a combination of two or more.

[0032] Among the aforementioned polymer elastic bodies, polyurethane-based, polyester-based, and polyamide-based, and like elastomers, and in particular, polyurethane-based elastomers are preferable.

[0033] It is preferable that the leather-like sheet of this embodiment has a peeling strength of 3.0 kg/1.0 cm or greater on the superficial layer side and a ratio of the peeling strength on the superficial layer side to the peeling strength on the bottom layer side (the peeling strength on the superficial layer side / the peeling strength on the bottom layer side) of 1.08 to 2.0 and particularly 1.15 to 1.8 because an excellent leather-like sheet is obtained due to the balance between flexibility and stiffness. Note that it can be said that the greater the peeling strength in each layer, the higher the extent of entangling of the fibers.

[0034] It is preferable that the leather-like sheet of this embodiment has a logarithmic value of a tensile storage elastic modulus at 20°C of 6.0 to 7.8 Pa and particularly 6.5 to 7.5 Pa. The tensile storage elastic modulus represents properties correlating to the sheet hardness during minor deformation of the leather-like sheet and the extent of entangling or restraint of fibers. When the logarithmic value of the tensile storage elastic modulus is excessively small, entangling of fibers is poor, and thus shape retainability is likely to be insufficient. When the logarithmic value of the tensile storage elastic modulus is excessively large, fibers are strongly restrained in an excessive manner, and it is thus likely that flexibility is impaired and sewing processability is impaired. The tensile storage elastic modulus at 20°C can be adjusted by adjusting the extent of entangling of fibers or using the polymer elastic body.

[0035] It is preferable that when a cross-section of the superficial layer (A1) of the fiber bundle entangled body is viewed under an electron microscope of 20 to 50 magnification, the vertical cross-section of the fiber bundle is in the range of 50 bundles/width of 1 mm to 1000 bundles/width of 1 mm and particularly 200 bundles/mm^2 to 4000 bundle s/mm^2, and especially 100 bundles/width of 1 mm to 1000 bundles/width of 1 mm and 400 bundles/mm^2 to 4000 bundles/mm^2 because shape retainability becomes favorable and little fiber loss occurs on the superficial layer side.

[0036] Regarding the leather-like sheet of this embodiment, usually, a desired finishing treatment may be performed on the surface of the superficial layer, e.g., a grain resin layer may be further formed or a napping treatment may be performed as described below.

[Method for producing leather-like sheet]

[0037] Next, an example of a method for producing the leather-like sheet of this embodiment will now be described in detail.

[0038] A method for producing the leather-like sheet of this embodiment includes the steps of, for example, (1) producing a spunbond sheet composed of a sea-island (matrix-domain) type multi-component fiber obtained by melt-spinning a water-soluble thermoplastic resin and a water-insoluble thermoplastic resin, (2) forming an entangled sheet by entangling multiple pieces of the spunbond sheet stacked one on top of the other, (3) creating a shrunk web by subjecting the entangled sheet to heat-moisture shrinking or hot water shrinking, and (4) forming a fiber entangled body of a fiber bundle of ultrafine filaments by dissolving the water-soluble thermoplastic resin of the sea-island (matrix-domain) type multi-component fiber in hot water. If necessary, the method includes steps of (5) impregnating the fiber bundle entangled body with an aqueous liquid of a polymer elastic body and drying and solidifying the impregnated product, and (6) performing a surface treatment. Hereinbelow, each step will now be described in detail.

Step (1) for producing spunbond sheet

[0039] In this step, a spunbond sheet composed of a sea-island (matrix-domain) type multi-component fiber is produced by melt-spinning a water-soluble thermoplastic resin and a water-insoluble thermoplastic resin.

[0040] The sea-island (matrix-domain) type multi-component fiber is obtained by separately melt-spinning a water-soluble thermoplastic resin and a water-insoluble thermoplastic resin that is poorly compatible with the water-soluble thermoplastic resin and then integrating the resins. From the industrial-point of view, the fineness of the sea-island (matrix-domain) type multi-component fiber is preferably in the range of 0.5 to 3 dtex.

[0041] As the water-soluble thermoplastic resin, a thermoplastic resin that is removable by dissolution in water, an aqueous alkaline solution, an aqueous acidic solution, or the like and on which melt-spinning can be performed is preferably used. Specific examples of such water-soluble thermoplastic resins include polyvinyl alcohol-based resins (PVA-based resins); modified polyesters containing polyethylene glycol and/or alkali metal sulfonate as a copolymer component; polyethylene oxide; and the like. Among these, in particular, PVA-based resins are preferably used for the following reasons.

[0042] When a PVA-based resin is used as the water-soluble thermoplastic resin component of the sea-island (matrix-domain) type multi-component fiber, the formed ultrafine filament is greatly crimped. Accordingly, a fiber bundle entangled body having a large fiber density is obtained.

[0043] As specific examples of the water-insoluble thermoplastic resin, the aforementioned polyethylene terephthalate (PET), modified PET, isophthalic acid-modified PET, polylactic acid, polyamide 6, polyamide 12, polyamide 6-12, polypropylene, or like various thermoplastic resins that can form ultrafine filaments are usable.

[0044] The water-insoluble thermoplastic resin may contain various additives. Specific examples of additives indude catalysts, anti-coloring agents, heat-resisting agents, flame retardants, lubricants, stain-proofing agents, fluorescent whitening agents, delustering agents, coloring agents, gloss improving agents, anti-static agents, fragrances, deodorizers, bactericidal agents, miticidal agents, inorganic fine particles, and the like.

[0045] Next, the method in which the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin are melt-spun to form a sea-island (matrix-domain) type multi-component fiber, and a spunbond sheet is formed from the obtained sea-island (matrix-domain) type multi-component fiber will now be described in detail.

[0046] According to spunbonding, after the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin are integrated by being melt-spun, performing stretching and stacking yields a spunbond sheet composed of a sea-island (matrix-domain) type multi-component fiber of a filament. Note that the "filament" is a fiber produced without a cutting process unlike in staple production.

[0047] First, the water-soluble thermoplastic resin and the water-insoluble thermoplastic resin are each melt-kneaded with separate extruders, and strands of molten resins are simultaneously discharged from different spinnerets, thus forming a sea-island (matrix-domain) type multi-component fiber. It is preferable that the mass ratio of the water-soluble thermoplastic resin to the water-insoluble thermoplastic resin is in the range of 5/95 to 50/50 and particularly 10/90 to 40/60 because a high-density fiber entangled body is obtained, and ultrafine filament formability is excellent.

[0048] In melt-spinning of a multi-component fiber, it is preferable that the number of islands in the sea-island (matrix-domain) type multi-component fiber is 4 to 4000 islands/fiber and particularly 10 to 1000 islands/fiber because an ultrafine fiber bundle having a small single fiber fineness and a high fiber density is obtained.

[0049] The sea-island (matrix-domain) type multi-component fiber is cooled with a cooling device and then stretched by a high-speed airflow at a rate corresponding to the withdrawal rate of 1000 to 6000 m/min using a suction device such as an air jet nozzle so as to attain the intended fineness. Then, the stretched sea-island (matrix-domain) type multi-component fiber is deposited on a moving collection surface, thus forming a spunbond sheet. At this time, the spunbond sheet may be partially pressure-bonded if necessary. It is preferable that the weight per unit area of the spunbond sheet is in the range of 20 to 500 g/m^2 because a homogeneous fiber bundle entangled body is obtained and excellent productivity is achieved.

Step (2) for entangling multiple pieces of spunbond sheet stacked one on top of the other

[0050] Next, an example of the step of forming an entangled sheet by entangling multiple pieces of the obtained spunbond sheet stacked one on top of the other will now be described.

[0051] An entangled sheet is formed by performing an entangling treatment on multiple pieces of the spunbond sheet stacked one on top of the other using a known non-woven fabric production method such as needle punching or a high-pressure water flow treatment.

[0052] First, a silicone-based oil or a mineral oil-based oil such as a needle break preventing oil, an antistatic oil, or an entangling enhancing oil is applied to the spunbond sheet. To reduce non-uniformity in weight per unit area, an oil may be applied after two or more pieces of the spunbond sheet are stacked one on top of the other by a cross wrapper.

[0053] To make the extent of entangling on the superficial layer side greater than the extent of entangling on the bottom layer side, the amounts or types of oils applied to the front surface side and the back surface side may be changed so as to adjust the coefficient of friction of the fiber on the front surface side that is located on the superficial layer side and the coefficient of friction of the fiber on the back surface side that is located on the bottom layer side.

[0054] After an application of an oil, for example, an entangling treatment for three-dimensionally entangling the spunbond sheet is performed by needle punching. Needle punching is preferably performed under needle conditions such that the extent of entangling on the superficial layer side is large and the extent of entangling on the bottom layer side is small. Adjusting the needle conditions on the superficial layer side and on the bottom layer side in this way enables the fiber occupancy (A1) of the superficial layer and the fiber occupancy (A3) of the outermost layer of the obtained leather-like sheet to be higher than the fiber occupancy (A2) of the bottom layer.

[0055] Specific examples of needle conditions are as follows.
For example, needle punching from the front surface side is performed with a needle having a large number of barbs, and needle punching from the back surface side is performed with a needle having a small number of barbs. The larger the number of barbs, the more preferable, as long as the needles do not break, and specifically, needles having, for example, 1 to 9 barbs are selected for the respective needles.
[0056] It is also preferable, for example, to perform needle punching from the front surface side with a needle having a large barb depth or a large kick-up depth and needle punching from the back surface side with a needle having a small barb depth or a small kick-up depth.
[0057] Also, the number of times needle punching is performed from the front surface side is made greater than the number of times needle punching is performed from the back surface side. Although the number of times needle punching is performed is adjusted according to the needle shape, the type and amount of oil used, and the like, specifically, 500 to 5000 punches/cm^2 are preferable.
[0058] For example, it is also preferable to perform needle punching from the front surface side to reach a large needle depth and perform needle punching from the back surface side to reach a small needle depth.
[0059] These conditions may be used alone or in a combination.
[0060] Such a method makes it easy to adjust the fiber occupancy (A1) of the superficial layer that serves as a zone covering 2/3 of the thickness from the front surface of the fiber bundle entangled body constituting the leather-like sheet so as to be 36 to 56 vol% and the ratio (A1/A2) of the fiber occupancy (A1) to the fiber occupancy (A2) so as to be 1.08 to 1.8.
[0061] It is preferable that the entangled sheet obtained in the above-described manner is a sheet that has undergone an entangling treatment so as to have a mass ratio of 1.2 or greater and particularly 1.5 or greater relative to the weight per unit area of the spunbond sheet before the entangling treatment. The upper limit is not particularly set, and it is preferable that the mass ratio is 4 or less in order to avoid an increase of production costs caused by a lowered treatment rate. Also, the weight per unit area of the entangled sheet is suitably selected according to the intended thickness of the fiber bundle entangled body and like features, and specifically, it is preferable that the weight per unit area is in the range of 100 to 1500 g/m^2 because excellent handleability is obtained.
[0062] The resistance to interlayer separation of the entangled sheet is preferably 7 kg/2.5 cm or greater and particularly 9 kg/2.5 cm or greater because a fiber bundle entangled body that has a favorable shape retainability, undergoes little fiber loss, and has a high fiber density can be obtained. Note that the resistance to interlayer separation serves as a measure of the extent of three-dimensional entangling. When the resistance to interlayer separation is excessively small, the fiber density of the fiber bundle entangled body is not sufficiency increased, and thus the fiber bundle entangled body is not preferable. The upper limit of the resistance to interlayer separation of the entangled sheet is not particularly set, and 30 kg/2.5 cm or less is preferable for an efficient entangling treatment.

Step (3) for performing heat-moisture shrinking treatment

[0063] Next, the shrinking treatment step for forming a shrunk web by subjecting the obtained entangled sheet to heat-moisture shrinking or hot water shrinking will now be described. The shrinking treatment step is a step of producing a shrunk web in which the extent of entangling of a filament-containing entangled sheet is further raised to increase the fiber density of the fiber bundle entangled body.
[0064] It is preferable to perform the heat-moisture shrinking treatment under water absorbing conditions such as steam heating or a hot water treatment.
As for steam heating conditions, it is preferable to perform a heating treatment at an atmosphere temperature in the range of 60 to 130°C, at a relative humidity of 75% or greater, particularly a relative humidity of 90% or greater, for 60 to 600 seconds. These heating conditions are preferable because it is possible to shrink the entangled sheet with a large degree of shrinkage. Note that when the relative humidity is excessively low, moisture that has come into contact with the fiber dries promptly, and shrinking is likely to be insufficient.
[0065] As for the hot water treatment conditions, the temperature is preferably in the range of 50 to 130°C and particularly 60 to 95°C because shrinking can be attained with a large degree of shrinkage. Note that when the temperature is excessively low, shrinking is likely to be insufficient, and when the temperature is excessively high, shrinking is likely to be non-uniform.
[0066] In the shrinking treatment, it is preferable to shrink the entangled sheet such that the degree of area shrinkage is 35% or greater and particularly 40% or greater. Allowing the entangled sheet to shrink with such a high degree of shrinkage yields the shrunk web having a high fiber density and a further increased extent of fiber entangling. The upper limit of the degree of area shrinkage is not particularly set, and it is about 80% for an efficient treatment. Note that it is also possible to adjust the degrees of shrinkage on the front surface side and on the back surface side by performing the treatment on the front surface side and the back surface side under different temperature, humidity, and like conditions.
[0067] Note that the degree of area shrinkage (%) is calculated according to formula (1) below:

(Area of sheet surface before shrinking treatment - Area of sheet surface after shrinking treatment) / Area of sheet surface before shrinking treatment × 100 ... (1)

The area refers to the average area of the area of the front surface and the area of the back surface of the sheet

[0068] Also, the fiber density may be increased by further subjecting the shrunk web obtained by the heat-moisture shrinking treatment to a heating roller or a heating press at a temperature equal to or higher than the heat deflection temperature of at least one component of the sea-island (matrix-domain) type multi-component fiber. It is also possible to adjust the fiber densities on the front surface side and on the back surface side by subjecting the front surface side and the back surface side to a heating roller or a heating press under different conditions.

[0069] As for the change of weight per unit area before and after the heat-moisture shrinking treatment, it is preferable that the weight per unit area of the shrunk web is 1.2 times or greater and particularly 1.5 times or greater and 4 times or less and particularly 3 times or less than the weight per unit area of the entangled sheet before the shrinking treatment.

Step (4) for forming ultrafine fiber

[0070] Next, the step of forming a fiber bundle entangled body of a fiber bundle of ultrafine filaments by dissolving the water-soluble thermoplastic resin present in the sea-island (matrix-domain) type multi-component fiber in hot water will now be described.

[0071] The ultrafine fiber forming treatment is a treatment for removing by dissolution or removing by decomposition the water-soluble thermoplastic resin by subjecting the shrunk web to a hot water heating treatment with water, an aqueous alkaline solution, an aqueous acidic solution, or the like.

[0072] As for a specific example of conditions of the hot water heating treatment, it is preferable that immersion in hot water at 65 to 90°C for 5 to 300 seconds is performed as a first stage, and then a treatment in hot water at 85 to 100°C for 100 to 600 seconds is performed as a second stage. In order to increase dissolution efficiency, a nipping treatment with a roll, a high-pressure water flow treatment, ultrasonication, a shower treatment, a stirring treatment, a rubbing treatment, or a like treatment may be performed if necessary.

[0073] In this step, when the water-soluble thermoplastic resin is dissolved from the sea-island (matrix-domain) type multi-component fiber, the formed ultrafine filament is greatly crimped. Since this crimping increases the fiber density, the fiber bundle entangled body having high fiber density is obtained.

Step (5) for impregnation with polymer elastic body

[0074] Before performing the ultrafine fiber forming treatment on the shrunk web or after performing the ultrafine fiber forming treatment on the shrunk web, the shrunk web or the entangled sheet before the shrinking treatment may be impregnated, if necessary, with a polymer elastic body to increase the shape stability of the fiber bundle entangled body or to adjust the mechanical properties, texture, or the like of the fiber bundle entangled body

[0075] Hereinbelow, as for the method for impregnation with a polymer elastic body, a case where an aqueous liquid of an aqueous polyurethane-based resin is used will now be described as a representative example. Examples of the aqueous liquid of an aqueous polyurethane-based resin indude an aqueous solution in which a resin component forming an aqueous polyurethane-based resin is dissolved in an aqueous medium and an aqueous dispersion in which a resin component forming an aqueous polyurethane-based resin is dispersed in an aqueous medium. The aqueous dispersion includes a suspended dispersion and an emulsified dispersion. In particular, it is more preferable to use the aqueous dispersion because it has excellent water resistance.

[0076] Examples of the polyurethane-based resin indude various polyurethane-based resins obtained by reacting a polymeric polyol having an average molecular weight of 200 to 6000, an organic polyisocyanate, and a chain extender in a specific molar ratio.

[0077] Specific examples of the polymeric polyol indude polyether-based polyols such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and poly(methyltetramethylene glycol), as well as copolymers thereof; polyester-based polyols 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 sebacate) diol, and polycaprolactone diol, as well as copolymers thereof; polycarbonate-based polyols such as polyhexamethylene carbonate diol, poly(3-methyl-1,5-pentylene carbonate) diol, polypentamethylene carbonate diol, and polytetramethylene carbonate diol, as well as copolymers thereof; polyester carbonate polyols; and the like. If necessary, short-chain alcohols such as trifunctional alcohols or tetrafunctional alcohols or ethylene glycol may be used in combination. These may be used alone or may be used in a combination of two or more. In particular, amorphous polycarbonate-based polyols, alicyclic polycarbonate-based polyols, linear polycarbonate-based polyol copolymers, polyether-based polyols, and the like are preferable because an excellent leather-like sheet is obtained due to the balance between flexibility and stiffness.

[0078] Specific examples of the organic polyisocyanate indude non-yellowing diisocyanates such as hexamethylene diisocyanate, isophorone diisocyanate, norbomane diisocyanate, 4,4'-dicydohexylmethane diisocyanate, and like aliphatic or alicyclic diisocyanates; aromatic diisocyanates such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and xylylene diisocyanate polyurethane; and the like. If necessary, a polyfunctional isocyanate such as a trifunctional isocyanate or a tetrafunctional isocyanate may be used in combination. These may be used alone or may be used in a combination of two or more. Among these, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and xylylene diisocyanate have excellent mechanical properties and are thus preferable.

[0079] Specific examples of the chain extender indude diamines such as hydrazine, ethylenediamine, propylenediamine, hexamethylenediamine, nonamethylenediamine, xylylenediamine, isophoronediamine, piperazine and derivatives thereof, adipic acid dihydrazide, and isophthalic acid dihydrazide; triamines such as diethylenetriamine; tetramines such as triethylenetetramine; diols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-bis(β-hydroxyethoxy)benzene, and 1,4-cydohexanediol; triols such as trimethylolpropane; pentaols such as pentaerythritol; amino alcohols such as aminoethyl alcohol and aminopropyl alcohol; and the like. These may be used alone or may be used in a combination of two or more. Among these, it is preferable to use two or more members in combination selected from hydrazine, piperazine, hexamethylenediamine, isophoronediamine and derivatives thereof, and triamines such as ethylenetriamine for mechanical properties. Also, a monoamine such as ethylamine, propylamine, or butylamine; a carboxyl group-containing monoamine compound such as 4-aminobutanoic acid or 6-aminohexanoic acid; a monool such as methanol, ethanol, propanol, or butanol may be used in combination with the chain extender during the chain extending reaction.

[0080] Also, use of a carboxyl group-containing diol such as 2,2-bis(hydroxymethyl)propionic acid, 2,2-bis(hydroxymethyl)butanoic acid, or 2,2-bis(hydroxymethyl)valeric acid in combination in order to introduce a carboxyl group or a like ionic group into the backbone of the polyurethane-based elastic body makes it possible to adjust producibility and various properties.

[0081] To control the water absorption, adhesion to a fiber, and hardness of the polymer elastic body, a crosslinked structure may be formed by adding a crosslinking agent that contains within the molecule two or more functional groups that can react with a functional group contained in the monomeric unit that forms polyurethane or by adding a self-crosslinkable compound such as a polyisocyanate-based compound or a polyfunctional blocked isocyanate-based compound.

[0082] It is preferable that the dispersion average particle diameter of the aqueous dispersion of the polyurethane-based resin is 0.01 to 1 μm and particularly 0.03 to 0.5 μm.

[0083] Examples of the method to impregnate the shrunk web or the entangled sheet before the shrinking treatment with the polymer elastic body indude a method in which a knife coater, a bar coater, or a roll coater is used, a method in which dipping is performed, and a like method.

[0084] Then, drying the shrunk web or the entangled sheet impregnated with an aqueous liquid or an aqueous dispersion of the polymer elastic body by heating makes it possible to solidify the polymer elastic body. Examples of a drying method indude a method in which a heat treatment is performed in a drier at 50 to 200°C, a method in which a heat treatment is performed in a drier after infrared heating, a method in which a heat treatment is performed in a drier after a steam treatment, a method in which a heat treatment is performed in a drier after ultrasonic heating, a method in which these procedures are used in combination, and the like. A method may be employed in which a heat-sensitive gelating agent is added and a heat treatment is performed to achieve solidification by gelation prior to removal of water or the like.

[0085] In step (5) for impregnation with the polymer elastic body, performing the ultrafine fiber forming treatment on the sea-island (matrix-domain) type multi-component fiber removes the water-soluble thermoplastic resin and creates voids inside the ultrafine fiber bundle. When ultrafine filaments form the fiber bundle, impregnation with an aqueous liquid of the polymeric elastic body easily occurs due to capillarity. Accordingly, when the polymer elastic body is applied after performing the ultrafine fiber forming treatment, so far as the inside of the ultrafine fiber bundle is impregnated with the polymer elastic body, and thus the ultrafine filaments in the ultrafine fiber bundle duster together. In this case, the shape retainability of the fiber bundle entangled body is further enhanced. In contrast, when the polymer elastic body is applied before performing the ultrafine fiber forming treatment, the inside of the ultrafine fiber bundle is barely impregnated with the polymer elastic body, and the polymer elastic body is mainly present on the outer portion of the ultrafine fibers, and the looseness of the ultrafine fiber bundle is increased, and thus the leather-like sheet is likely to have a more flexible texture.

[Post-processing of leather-like sheet]

[0086] The fiber bundle entangled body obtained in the above-described manner is usually subjected to post-processing such as a nap-raising treatment, a grain treatment, a softening treatment, a two-segment treatment, a molding treatment, and a coloring treatment according to applications.

[0087] Note that the fiber bundle entangled body of this embodiment has favorable shape retainability and falls out fibers little even without an application of the polymer elastic body. Therefore, even without a treatment to enhance shape stability by applying the polymer elastic body to the fiber bundle entangled body as performed in conventional artificial leather production, post-processing can be performed.

[0088] When a grain leather-like sheet is produced by surface-finishing the leather-like sheet, a grain resin layer composed of a polymer elastic body is formed on the front surface of the fiber bundle entangled body as a surface layer. As a method for forming a surface layer composed of a polymer elastic body, a method in which a surface layer is formed by directly applying a dispersion or a solution of a polymer elastic body to the front surface of the fiber bundle entangled body, a method in which a grain resin layer formed by applying a polymer elastic body to a release paper having a design pattern is bonded to the front surface of the fiber bundle entangled body, or a like method is used. As the polymer elastic body used for formation of the surface layer, a polymer elastic body that has been conventionally used for production of a grain leather-like sheet is used without particular limitations. The thickness of the grain resin layer is not particularly limited, and specifically, it is preferable that the thickness is in the range of, for example, 2 to 300 μm, particularly 3 to 100 μm or less, especially 3 to 80 μm, and notably 3 to 50 μm.

[0089] Also, when a napped leather-like sheet is produced by surface-finishing the fiber bundle entangled body, a method that is conventionally used for production of a napped leather-like sheet in which the front surface of the fiber bundle entangled body is made fluffy by a buffing treatment using sandpaper, card clothing, or the like is used.

[0090] Also, the grain leather-like sheet and the napped leather-like sheet may be colored during the step of forming the ultrafine fiber. If necessary, a machine kneading treatment in a dry state; a relaxing treatment in a wet state using a coloring machine, a washing machine, or the like; a softening agent treatment; a functionality imparting treatment with a fireproofing agent, a bactericidal agent, a deodorizer, a water/oil repelling agent, or the like; a tactile feel modifier imparting treatment with a silicone-based resin, a silk protein-containing treatment agent, a grippability imparting resin, or the like; or a finishing treatment with a coloring agent, a coating resin for an enamel tone, or the like may be performed. Since the superficial layer of the fiber bundle entangled body of this embodiment has a very high fiber density, a relaxing treatment in a wet state and a softening agent treatment in which a treatment is performed in water at a temperature in the range of about 60 to 140°C are particularly preferable treatments to significantly improve the texture so as to be similar to natural leather.

[0091] It is also preferable that the ultrafine fiber entangled body to which the polymer elastic body has not been applied is dyed and then the polymer elastic body is applied after dyeing. In this case, the polymer elastic body does not become colored, and thus color spots and surface non-uniformity resulting from the difference between the dye absorption properties of the fiber and the polymer elastic body can be avoided, thus improving quality stability. Also, when it is used for artificial suede-like leather, various fastness properties such as fastness against wet rubbing are improved. Therefore, it is preferable that the ultrafine fiber that constitutes the leather-like sheet of this embodiment is dyed, and the polymer elastic body is not substantially dyed or is not dyed at all.

[0092] The apparent density of the leather-like sheet obtained in the above-described manner is not particularly limited, and it is preferably in the range of 0.5 to 0.85 g/cm^3 because the leather-like sheet attains a superior balance in stiffness and flexibility as well as superior mechanical properties and shape retainability. Also, the thickness of the leather-like sheet is not particularly limited, and it is preferably in the range of about 0.3 to 4 mm because a texture well-balanced in stiffness and flexibility is obtained.

Examples

[0093] The present invention will now be described in more detail below by way of examples, but the scope of the present invention is not limited to the examples. Note that in the examples, part and % are based on mass unless specified otherwise.

[0094] First, the evaluation methods used in the examples are described all together.

<Fiber occupancy of leather-like sheet>

[0095] A leather-like sheet was sliced so as to be divided into 3 segments or 2 segments in the thickness direction. Specifically, when divided into 3 segments, the sheet was sliced such that each layer had the same thickness, and when divided into 2 segments, the sheet was sliced at a portion corresponding to 2/3 of the thickness from the front surface. Then, the apparent specific gravity of each divided layer was obtained in accordance with JIS K 7112. Then, the fiber occupancy was calculated according to the following formula based on the apparent specific gravity of the fiber of each layer, i.e., superficial layer, outermost layer, and bottom layer, and the specific gravity of the polymer that constitutes the fiber:

$$\text{Fiber occupancy (\%)} = (\text{Apparent specific gravity of fiber} / \text{Specific gravity of polymer constituting fiber}) \times 100$$

<Resistance to interlayer separation of entangled sheet>

[0096] From the obtained entangled sheet, a test piece having a length in the sheet length direction of 23 cm and a width of 2.5 cm was cut out. Next, an incision was made with a razor in a substantially central part, relative to the superficial layer side or the bottom layer side in the thickness direction, of an edge face in the longitudinal direction of the test piece. Thereafter, through separation by hand into 2 parts in the thickness direction from the central portion toward the superficial layer portion and from the central portion toward the bottom portion, the test piece was separated by being pulled from the edge to the middle such that the divided length of the edge of the superficial layer portion and the edge of the bottom layer portion after separation was about 10 cm. Then, the respective edges of the separated superficial layer portion and bottom layer portion were fixed to the upper and lower chucks of a tensile tester, and the peeling strength was measured at a tensile rate of 100 mm/min. Then, a stress-strain curve (SS curve) was obtained, and the stress at the flat portion thereof was regarded as resistance to interlayer separation. Note that the result is an average of N = 3.

<Peeling strength of leather-like sheet>

[0097] A test piece having a length of 23 cm and a width of 2.5 cm was cut out from the obtained leather-like sheet. Then, one surface (on the superficial layer side or the bottom layer side) of the obtained test piece was adhered to a rubber plate using a polyurethane-based adhesive, and the test piece was pressed at ordinary temperatures and dried and then left to stand at 25°C for 24 hours. Then, the test piece and the rubber plate were grasped by the upper and lower chucks of a tensile tester, respectively, and a tensile test was performed at a tensile rate of 100 mm/min. The result is an average of N = 3. Then, a stress-strain curve (SS curve) was obtained, and the stress at the flat portion thereof was converted so as to correspond to the test piece width of 1.0 cm and regarded as peeling strength. Note that the peeling strength obtained when the superficial layer side was adhered was the peeling strength of the superficial layer side, and the peeling strength obtained when the bottom layer side was adhered was the peeling strength of the bottom layer side.

<Tensile storage elastic modulus of leather-like sheet>

[0098] The viscoelasticities of the sheet in the longitudinal direction and the horizontal direction, which is perpendicular thereto, were measured under conditions of a frequency of 11 Hz, a tensile mode, and a heating rate of 3°C/min using a viscoelasticity measuring apparatus (FT Rheospectra "DVE-V4" manufactured by Rheology Co., Ltd.) to obtain the storage elastic modulus at 20°C.

<State of adhesion of polymer elastic body>

[0099] The cross-sections at random 10 points that are in parallel with the thickness direction of a leather-like sheet dyed with a premetallized dye were observed under an optical microscope (100 to 200 magnification) and the average of the 10 points was calculated after image processing through binarization to measure the volume ratio of the fiber and the polymer elastic body. Then, the mass ratio was calculated from the obtained volume ratio and the specific gravities of the resins constituting the fiber and the polymer elastic body to determine the state of adhesion and the mass proportion of the polymer elastic body.

<Texture determination>

[0100] A test piece cut out to 20cm x 20cm was regarded as an evaluation sample. Five people in the field of artificial leather touched the test piece and evaluated the texture thereof according to the following criteria, and the evaluation submitted by the largest number of people was regarded as the result of texture evaluation.

A: Ideal natural leather-like texture demonstrating softness while having relatively very good stiffness when compared with B, which represents an ordinary texture
B: Ordinary texture of artificial leather widely used as an upper material of a sports shoe
C: Texture too hard or too soft without any stiffness, making it difficult to use in sports shoe applications

<Crease in grain leather-like sheet>

[0101] A test piece cut out to 20cm x 20cm was regarded as an evaluation sample. The shape of a crease created when the test sample was valley-folded such that the upper end meets the lower end in the longitudinal direction was visually inspected. Then, evaluations were made according to the following criteria.

A: A fine and uniform crease was created in the valley-folded surface similar to that found on cowhide.
B: An ordinary crease often observed in the upper material of a sports shoe or a partially fine crease was created in the valley-folded surface.
C: A crude crease similar to that created when cardboard is folded was created.

<Evaluation of appearance of napped leather-like sheet surface>

[0102] Five people in the field of artificial leather visually inspected the appearance of a napped leather-like sheet and evaluated it according to the following criteria, and the evaluation submitted by the largest number of people was regarded as the result of appearance evaluation.

A: Overall deneseness of the napped surface is very high, and the surface has absolutely no rough feel and is smooth when touched by hand.
B: Overall deneseness of the napped surface is slightly poor, or portions where deneseness is clearly low and poor are scattered while overall deneseness is relatively high, and slight roughness is felt when touched by hand.
C: A crude napped surface overall, and considerable roughness is felt when touched by hand.

[Example 1-1]

[0103] Modified PVA (water-soluble thermoplastic polyvinyl alcohol-based resin: sea component) and isophthalic acid-modified polyethylene terephthalate having a degree of modification of 6 mol% (island component) were discharged from a spinneret for melt spinning of a multi-component fiber set at 260°C (the number of islands: 25 islands/fiber) such that the mass ratio of sea component/island component was 25/75. Then, the ejector pressure was adjusted so as to have a spinning rate of 4000 m/min, and a sea-island (matrix-domain) type multi-component fiber having an average fineness of 2.5 dtex was deposited on a net, thus giving a spunbond sheet having a weight per unit area of 30 g/m^2.

[0104] Next, the obtained spunbond sheet was folded into 12 layers by cross wrapping, and a web having a total weight per unit area of 360 g/m^2 was prepared. Then, a needle break preventing oil was sprayed onto the web.

[0105] Then, using No.40 count needles (the number of barbs: 9), a needle punching treatment was performed from the front surface side of the web at 600 punches/cm^2 and from the back surface side at 400 punches/cm^2. Moreover, using No.42 count needles, a needle punching treatment was performed from the front surface side of the web at 600 punches/cm^2 and from the back surface side at 300 punches/cm^2. In this manner, an entangled sheet was obtained. Note that the degree of area shrinkage of the web due to the needle punching treatment was 25%. The weight per unit area of the needle-punched entangled sheet was 450 g/m^2, and the resistance to interlayer separation of the needle-punched entangled sheet was 11.0 kg/2.5 cm.

[0106] Next, the obtained entangled sheet was immersed in hot water at 70°C for 90 seconds to perform a heat-moisture shrinking treatment, thus giving a shrunk web. Moreover, the web was immersed in hot water at 95°C for 10 minutes to remove by dissolution the modified PVA from the sea-island (matrix-domain) type multi-component fiber and was further subjected to drying, thus giving a leather-like sheet A.
Note that the degree of area shrinkage before and after the heat-moisture shrinking treatment was 48%.
Regarding the leather-like sheet A, the average fiber fineness of ultrafine filaments was 0.1 dtex, the weight per unit area was 640 g/m^2, the thickness was 1.07 mm, and the apparent density was 0.60 g/cm^3.
Then, the obtained leather-like sheet A was evaluated in accordance with the evaluation methods described above. Results are shown in Table 1.

[0107]

[Table 1]

Example Number	Example									
	1-1	1-2	1-3	2-1	3-1	3-2	4-1	4-2	5-1	6-1
Leather-like sheet	A	B	C	D	E	F	G	H	I	J

(continued)

Example Number	Example									
	1-1	1-2	1-3	2-1	3-1	3-2	4-1	4-2	5-1	6-1
Weight per unit area (g/m^2)	640	580	710	660	645	720	610	720	620	525
Thickness (mm)	1.07	1.00	1.15	1.07	1.07	1.15	1.07	1.15	0.93	1.04
Apparent density (g/cm^3)	0.60	0.58	0.62	0.62	0.60	0.63	0.57	0.63	0.67	0.50
Average fineness (dtex)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Fiber occupancy of superficial layer (A1) (vol%)	46	46	46	46	46	46	47	47	55	39
Fiber occupancy of bottom layer (A2) (vol%)	40	40	40	42	40	40	36	36	32	35
Fiber occupancy of outermost layer (A3) (vol%)	47	47	47	44	47	47	47	47	59	37
Fiber occupancy ratio (A1/A2)	1.15	1.15	1.15	1.10	1.15	1.15	1.31	1.31	1.72	1.11
Fiber occupancy ratio (A3/A1)	1.02	1.02	1.02	0.96	1.02	1.02	1.00	1.00	1.07	0.95
Peeling strength on superficial layer side (kg/ 1.0 cm)	5.5	5.5	5.5	5.7	5.7	5.7	5.5	5.5	5.5	4.0
Peeling strength on bottom layer side (kg/ 1.0cm)	3.6	3.6	3.6	4.5	4.0	4.0	4.0	4.0	3.2	3.4
Ratio of peeling strength (superficial layer/bottom layer)	1.53	1.53	1.53	1.27	1.43	1.43	1.38	1.38	1.72	1.18

(continued)

Example Number	Example									
	1-1	1-2	1-3	2-1	3-1	3-2	4-1	4-2	5-1	6-1
Logarithmic value of tensile storage elastic modulus (Pa)	7.2	7.2	7.2	7.4	7.3	7.2	7.0	7.0	7.6	6.5
Proportion of polymer elastic body (mass%)	0	0	0	0	1	1	4	4	4	0
Texture	A	A	A	A	A	A	A	A	A	A
Crease of grain leather sheet	-	-	A	-	-	A	-	A	-	-
Tactile feel of suede leather sheet	-	A	-	-	-	-	-	-	-	-

[0108]

[Table 2]

Comparative Example Number	Comparative Example											
	1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	5-1	5-2	6-1	6-2
Leather-like sheet	K	L	M	N	0	P	Q	R	S	T	U	V
Weight per unit area (g/m^2)	670	735	410	460	620	685	350	420	670	735	360	430
Thickness (mm)	1.07	1.15	1.02	1.10	1.08	1.20	1.00	1.10	1.00	1.08	0.72	0.79
Apparent density (g/cm^3)	0.63	0.64	0.40	0.42	0.57	0.57	0.35	0.38	0.67	0.68	0.50	0.54
Average fineness (dtex)	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1
Fiber occupancy of superficial layer (A1) (vol%)	46	46	33	33	47.5	47.5	26	26	49	49	37	37
Fiber occupancy of bottom layer (A2) (vol%)	46	46	25	25	25	25	25	25	46	46	35	35

(continued)

Comparative Example Number	Comparative Example											
	1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2	5-1	5-2	6-1	6-2
Fiber occupancy of outermost laver (A3) (vol%)	46	46	28	28	55	55	25	25	66	66	54	54
Fiber occupancy ratio (A1/A2)	1.0	1.0	1.32	1.32	1.9	1.9	1.04	1.04	1.07	1.07	1.06	1.06
Fiber occupancy ratio (A3/A1)	1.0	1.0	0.85	0.85	1.22	1.22	0.96	0.96	1.35	1.35	1.46	1.46
on superficial layer side (kg/ 1.0 cm)	4.8	4.8	2.4	2.4	2.0	2.0	1.0	1.0	5.0	5.0	2.2	2.2
Peeling strength on bottom layer side (kg/1.0 cm)	4.8	4.8	1.2	1.2	0.8	0.8	0.7	0.7	4.8	4.8	2	2
Ratio of peeling strength (superficial layer/bottom layer)	1.00	1.00	2.00	2.00	2.50	2.50	1.43	1.43	1.04	1.04	1.10	1.10
Logarithmic value of tensile storage elastic modulus (Pa)	7.4	7.4	5.8	5.8	6.7	6.7	5.6	5.6	7.6	7.6	6.2	6.2
Proportion of polymer elastic body (mass%)	0	0	0	0	0	0	15	15	0	0	0	0
Texture	B	B	B	B	C	C	C	C	B	B	B	B
Crease of grain leather sheet	-	B	-	B	-	B	-	C	-	B	-	B
Tactile feel of suede leather sheet	-	-	-	-	-	-	-	-	-	-	-	-

[Example 1-2]

[0109] The front surface of the leather-like sheet A obtained in Example 1-1 was subjected to a buffing treatment with#240 paper, and moreover the sheet was dyed in gray with a disperse dye of 2% owf. Moreover, a finishing buffing treatment was performed to raise the front surface (a napping treatment), thus giving a napped leather-like sheet B.

Note that falling out or loosening of fiber during dying or falling out fiber during buffing barely occurred.

[0110] The leather-like sheet B had a weight per unit area of 580 g/m^2, a thickness of 1.00 mm, and an apparent density of 0.58 g/cm^3. Flexibility, stiffness, surface fluffiness, and the state of dense creases were favorable. Results are shown in Table 1.

[Example 1-3]

[0111] The front surface of the leather-like sheet A obtained in Example 1-1 was subjected to a buffing treatment with #240 paper. Separately, a grain resin layer having a thickness of 30 μm was formed by coating a release paper with aqueous polyurethane for a surface layer and drying it. Moreover, the surface of the grain resin layer was coated with aqueous polyurethane for an adhesive layer and dried, thus forming an adhesive layer having a thickness of 70 μm. Then, the adhesive layer and the buffing-treated surface were dry-laminated, thus performing a dry coating treatment Then, the release paper was peeled off, thus giving a grain leather-like sheet C.

[0112] The leather-like sheet C had a weight per unit area of 710 g/m^2, a thickness of 1.15 mm, and an apparent density of 0.62 g/cm^3. Flexibility, a crease appearance, and roundish voluminousness were favorable.

[Example 2-1]

[0113] A leather-like sheet D was obtained in the same manner as in Example 1-1 except that the needle punching treatment conditions of Example 1-1 were changed to the following conditions. Specifically, a needle punching treatment was performed from the front surface side of the web at 600 punches/cm^2 and from the back surface side at 500 punches/cm^2. Moreover, using No.42 count needles, a needle punching treatment was performed from the front surface side at 600 punches/cm^2 and from the back surface side at 400 punches/cm^2. In this manner, an entangled sheet was obtained. Note that the degree of area shrinkage of the web due to the needle punching treatment was 28%. The weight per unit area of the needle-punched entangled sheet was 470 g/m^2, and the resistance to interlayer separation of the needle-punched entangled sheet was 12.0 kg/2.5 cm.

[0114] The leather-like sheet D had a weight per unit area of 660 g/m^2, a thickness of 1.07 mm, and an apparent density of 0.62 g/cm^3. Then, the obtained leather-like sheet was evaluated in accordance with the evaluation methods described above. Results are shown in Table 1.

[Example 3-1]

[0115] The leather-like sheet A obtained in Example 1-1 was immersed in a 2% aqueous liquid of a polyurethane-based aqueous resin (an aqueous resin of a polymer elastic body) and then dried, thus giving a leather-like sheet E. When the cross-section in the thickness direction of the leather-like sheet E was observed under a scanning electron microscope (200 magnification), the polymer elastic body was mainly present inside the fiber bundle, and the mass ratio of the non-woven fabric to the polymer elastic body was 99:1.

[0116] The leather-like sheet E had a weight per unit area of 645 g/m^2, a thickness of 1.07 mm, and an apparent density of 0.60 g/cm^3. The polymer elastic body mainly present inside the fiber bundle contributed to further providing stiffness. Then, the obtained leather-like sheet E was evaluated in accordance with the evaluation methods described above. Results are shown in Table 1.

[Example 3-2]

[0117] A buffing treatment and a dry coating treatment were performed on the first surface of the leather-like sheet E in the same manner as in Example 1-3. Then, the release paper was peeled off, thus giving a grain leather-like sheet F. The leather-like sheet F had a weight per unit area of 720 g/m^2, a thickness of 1.15 mm, and an apparent density of 0.63 g/cm^3. Then, the obtained leather-like sheet F was evaluated in accordance with the evaluation methods described above. Results are shown in Table 1. The leather-like sheet F had favorable stiffness, was in the state of having fine creases, and thus was favorable.

[Example 4-1]

[0118] The procedure up to the production of a shrunk web was carried out in the same manner as in Example 1-1. Then, the shrunk web as obtained in Example 1-1 was immersed in a 5% aqueous liquid of a polyurethane-based aqueous resin and dried, and the superficial layer side was subjected to a pressing treatment at 150°C. The degree of area shrinkage of the shrunk web relative to the entangled sheet in the above-described processing was 44%. The pressed shrunk web had a weight per unit area of 840 g/m^2, a thickness of 1.4 mm, and an apparent density of 0.70 g/cm^3.

Then, after the pressed shrunk web was immersed in hot water at 95°C for 10 minutes to remove by dissolution the modified PVA, and the web was dried, thus giving a leather-like sheet G Regarding the leather-like sheet G, the average fineness of ultrafine filaments was 0.1 dtex, the weight per unit area was 610 g/m^2, the thickness was 1.07 mm, and the apparent density was 0.57 g/cm^3. When the cross-section in the thickness direction of the leather-like sheet G was observed under a scanning electron microscope (200 magnification), the polymer elastic body was mainly present outside the fiber bundle, and the mass ratio of the non-woven fabric to the polymer elastic body was 96:4. The polymer elastic body mainly present outside the fiber bundle contributed to providing stiffness and supple flexibility. Then, the obtained leather-like sheet G was evaluated in accordance with the evaluation methods described above. Results are shown in Table 1.

[Example 4-2]

[0119] A buffing treatment and a dry coating treatment were performed on the front surface of the leather-like sheet G obtained in Example 4-1 in the same manner as in Example 1-3. Then, the release paper was peeled off, thus giving a grain leather-like sheet H. The leather-like sheet H had a weight per unit area of 720 g/m^2, a thickness of 1.15 mm, and an apparent density of 0.63 g/cm^3. Then, the obtained leather-like sheet H was evaluated in accordance with the evaluation methods described above. Results are shown in Table 1. The leather-like sheet H had excellent stiffness, flexibility, and uniformity between the sheet and the coated surface, was in the state of having fine creases, and thus was favorable.

[Example 5-1]

[0120] A leather-like sheet I was obtained in the same manner as in Example 1 except that a leather-like sheet obtained by changing the needle punching treatment conditions of Example 1-1 to the following conditions was immersed in a 5% aqueous liquid of a polyurethane-based aqueous resin and then dried, and the superficial layer side was subjected to a pressing treatment at 170°C. Specifically, a needle punching treatment was performed from the front surface side of the web at 600 punches/cm^2 and from the back surface side at 300 punches/cm^2. Moreover, using No.42 count needles, a needle punching treatment was performed from the front surface side at 600 punches/cm^2 and no needle punching treatment was performed from the back surface side. In this manner, an entangled sheet was obtained. Note that the degree of area shrinkage of the web due to the needle punching treatment was 20%. The weight per unit area of the needle punched entangled sheet was 430 g/m^2, and the resistance to interlayer separation was 10.0 kg/2.5 cm.

[0121] The leather-like sheet I had a weight per unit area of 620 g/m^2, a thickness of 0.93 mm, and an apparent density of 0.67 g/cm^3. Then, the obtained leather-like sheet was evaluated in accordance with the evaluation methods described above. Results are shown in Table 1.

[Example 6-1]

[0122] A leather-like sheet J was obtained in the same manner as in Example 1-1 except that the ejector pressure was adjusted such that the spinning rate was 4400 m/min instead of the spinning rate of 4000 m/min in order to achieve a degree of area shrinkage of 38% before and after the heat-moisture shrinking treatment in which an needle-punched entangled sheet was immersed in hot water at 70°C for 90 seconds as in Example 1-1.

[0123] The leather-like sheet J had a weight per unit area of 525 g/m^2, a thickness of 1.04 mm, and an apparent density of 0.50 g/cm^3. Then, the obtained leather-like sheet J was evaluated in accordance with the evaluation methods described above. Results are shown in Table 1.

[Comparative Example 1-1]

[0124] A leather-like sheet K was obtained in the same manner as in Example 1 except that the needle punching treatment conditions of Example 1-1 were changed to the following conditions. Specifically, using No.40 count needles (the number of barbs: 9), a needle punching treatment was performed from the front surface side and the back side of the web both under the condition of 500 punches/cm^2, and then using No.42 count needles (the number of barbs: 6), a needle punching treatment was performed from the front surface side and the back surface side of the web both under the condition of 500 punches/cm^2. Note that the degree of area shrinkage of the entangled sheet due to the needle punching treatment was 28%. The weight per unit area of the needle punched entangled sheet was 470 g/m^2, and the resistance to interlayer separation was 12.0 kg/2.5 cm.

[0125] The leather-like sheet K had a weight per unit area of 670 g/m^2, a thickness of 1.07 mm, and an apparent density of 0.63 g/cm^3. Then, the obtained leather-like sheet K was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2.

[Comparative Example 1-2]

[0126] A buffing treatment and a dry coating treatment were performed on the front surface of the leather-like sheet K in the same manner as in Example 1-3. Then, the release paper was peeled off, thus giving a grain leather-like sheet L. The leather-like sheet L had a weight per unit area of 735 g/m^2, a thickness of 1.15 mm, and an apparent density of 0.64 g/cm^3 . Then, the obtained leather-like sheet L was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2. The leather-like sheet L had inferior flexibility and denseness of creases.

[Comparative Example 2-1]

[0127] A leather-like sheet M was obtained in the same manner as in Example 1-1 except that the ejector pressure was adjusted such that the spinning rate was 4800 m/min instead of the spinning rate of 4000 m/min in order to achieve a degree of area shrinkage of 20% before and after the heat-moisture shrinking treatment in which an entangled sheet after needle punching was immersed in hot water at 70°C for 90 seconds as in Example 1-1.

[0128] The leather-like sheet M had a weight per unit area of 410 g/m^2, a thickness of 1.02 mm, and an apparent density of 0.40 g/cm^3. Then, the obtained leather-like sheet M was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2.

[Comparative Example 2-2],

[0129] A buffing treatment and a dry coating treatment were performed on the front surface of the leather-like sheet M in the same manner as in Example 1-3. Then, the release paper was peeled off, thus giving a grain leather-like sheet N. The leather-like sheet N had a weight per unit area of 460 g/m^2, a thickness of 1.10 mm, and an apparent density of 0.42 g/cm^3. Then, the obtained leather-like sheet N was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2. The leather-like sheet N lacked uniformity between the fiber bundle entangled body and the grain surface, exhibited large creases, and had poor stiffness.

[Comparative Example 3-1]

[0130] A leather-like sheet O was obtained in the same manner as in Example 1-1 except that the conditions of the needle punching treatment of the web obtained of Example 1-1 were changed to the following conditions, and the front surface side was subjected to a pressing treatment at 150°C after the modified PVA was removed by dissolution from the sea-island (matrix-domain) type multi-component fiber and the fiber was dried. As for the needle punching treatment conditions, using No.40 count needles (the number of barbs: 9), a needle punching treatment was performed from the front surface side and the back surface side of the web both under the condition of 1000 punches/cm^2, and then using No.42 count needles (the number of barbs: 6), a needle punching treatment was performed only from the front side under the condition of 2000 punches/cm^2. The degree of area shrinkage of the web due to the needle punching treatment was 22%. Note that the weight per unit area of the entangled sheet after needle punching was 450 g/m^2, and the resistance to interlayer separation of the entangled sheet was 5.0 kg/2.5 cm.

[0131] The leather-like sheet O had a weight per unit area of 620 g/m^2, a thickness of 1.08 mm, and an apparent density of 0.57 g/cm^3. Then, the obtained leather-like sheet O was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2.

[Comparative Example 3-2]

[0132] A buffing treatment and a dry coating treatment were performed on the front surface of the leather-like sheet O in the same manner as in Example 1-3. Then, the release paper was peeled off, thus giving a grain leather-like sheet P. The leather like sheet P had a weight per unit area of 685 g/m^2, a thickness of 1.20 mm, and an apparent density of 0.57 g/cm^3. Then, the obtained leather-like sheet O was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2. The leather-like sheet P lacked stiffness and had paper-like creases.

[Comparative Example 4-1]

[0133] A polyethylene terephthalate filament was discharged from a spinneret for melt spinning set as 260°C. Then, the ejector pressure was adjusted so as to have a spinning rate of 4500 m/min, and filaments having an average fineness of 0.2 dtex were deposited on a net, thus giving a spunbond sheet having a weight per unit area of 30 g/m^2. Note that the filaments obtained in this manner do not form a fiber bundle.

[0134] Next, the obtained spunbond sheet was folded into 12 layers, and a web having a total weight per unit area of

360 g/m^2 was prepared by cross wrapping. Then, a needle break preventing oil was sprayed on to the web.

[0135] Then, a needle punching treatment was performed in the same manner as in Example 1-1. Note that the degree of area shrinkage of the web due to the needle punching treatment was -23%. The weight per unit area of the needle-punched entangled sheet was 280 g/m^2, and the resistance to interlayer separation of the needle-punched entangled sheet was 2 kg/2.5 cm. Moreover, the entangled sheet was immersed in hot water at 70°C for 90 seconds to cause area shrinkage and was further subjected to drying, thus giving a leather-like sheet Q. Note that the degree of area shrinkage before and after immersion in hot water was 20%. Then, the leather-like sheet Q was immersed in a 20% aqueous liquid of a polyurethane-based aqueous resin and then dried.

[0136] The leather-like sheet Q had a weight per unit area of 350 g/m^2, a thickness of 1.00 mm, and an apparent density of 0.35 g/cm^3. The mass ratio of the non-woven fabric to the polymer elastic body of the leather-like sheet Q was 85:15. Then, the obtained leather-like sheet Q was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2.

[Comparative Example 4-2]

[0137] A buffing treatment and a dry coating treatment were performed on the front surface of the leather-like sheet Q in the same manner as in Example 1-3. Then, the release paper was peeled off, thus giving a grain leather-like sheet R.

[0138] The leather-like sheet R had a weight per unit area of 420 g/m^2, a thickness of 1.10 mm, and an apparent density of 0.38 g/cm^3. Then, the obtained leather-like sheet R was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2. The leather-like sheet R had poor stiffness, exhibited large creases, and lacked a dassy texture.

[Comparative Example 5-1]

[0139] A leather-like sheet S was obtained in the same manner as in Example 1-1 except that the front surface side of a leather-like sheet as obtained in Comparative Example 1-1 was subjected to a pressing treatment at 150°C.

[0140] The leather-like sheet S had a weight per unit area of 670 g/m^2, a thickness of 1.00 mm, and an apparent density of 0.67 g/cm^3. Then, the obtained leather-like sheet S was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2. Note that regarding the fiber occupancy, the density over 1/3 of the thickness from the front surface was high, the leather-like sheet S had a hard, paper-like texture.

(Comparative Example 5-2]

[0141] A buffing treatment and a dry coating treatment were performed on the front surface of the leather-like sheet S in the same manner as in Example 1-3. Then, the release paper was peeled off, thus giving a grain leather-like sheet T. The leather-like sheet T had a weight per unit area of 735 g/m^2, a thickness of 1.08 mm, and an apparent density of 0.68 g/cm^3. Then, the obtained leather-like sheet T was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2. The leather-like sheet T had paper-like creases.

[Comparative Example 6-1]

[0142] Modified PVA (sea component) and isophthalic add-modified polyethylene terephthalate having a degree of modification of 6 mol% (island component) were discharged from a spinneret for melt spinning of a multi-component fiber set at 260°C (the number of islands: 25 islands/fiber) such that the sea component/island component was 30/70 (mass ratio). The ejector pressure was adjusted so as to have a spinning rate of 4500 m/min, and filaments having an average fineness of 2.0 dtex were collected on a net, thus giving a spunbond sheet (a filament web) having a weight per unit area of 30 g/m^2.

[0143] Next, the obtained spunbond sheet was folded into 6 layers, and a stacked web having a total weight per unit area of 180 g/m^2 was prepared by cross wrapping. Then, a needle break preventing oil was sprayed onto the web. Then, using a single-barb needle on which the distance from the needle tip to the barb was 5 mm, the stacked web was needle-punched alternately from both surfaces at 3600 punches/cm^2 to the needle depth of 10 mm, and thus the stacked web was entangled. The degree of area shrinkage due to this needle punching treatment was 53%, and the needle-punched filament entangled sheet had a weight per unit area of 340 g/m^2 and a resistance to interlayer separation of 9.2 kg/2.5 cm.

[0144] This filament entangled sheet was immersed in hot water at 70°C for 90 seconds to cause area shrinkage by the relaxation of stress on the island component. Thereafter, one-side hot-pressing was performed at a surface temperature of 150°C under a pressure of 50 kg/cm^2, and then the sheet was immersed in hot water at 95°C for 10 minutes to remove by dissolution the modified PVA, thus giving a leather-like sheet U. The degree of area shrinkage measured after drying was 30%, the weight per unit area was 360 g/m^2, the apparent density was 0.50 g/cm^3, and the average single fiber fineness of the ultrafine filaments was 0.1 dtex. Then, the obtained leather-like sheet U was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2.

[Comparative Example 6-2]

[0145] A buffing treatment and a dry coating treatment were performed on the front surface of the leather-like sheet U in the same manner as in Example 1-3. Then, the release paper was peeled off, thus giving a grain leather-like sheet V. The leather-like sheet V had a weight per unit area of 430 g/m^2, a thickness of 0.82 mm, and an apparent density of 0.54 g/cm^3. Then, the obtained leather-like sheet V was evaluated in accordance with the evaluation methods described above. Results are shown in Table 2. The leather-like sheet V had poor stiffness, exhibited large creases, and lacked a dassy texture.

[0146] One aspect of the present invention described above is a leather-like sheet containing a fiber bundle entangled body which is an entangled body of a fiber bundle of ultrafine filaments, the fiber occupancy (A1) of the superficial layer that is a zone covering 2/3 of the thickness from the front surface of the fiber bundle entangled body being 36 to 56 vol%, the fiber occupancy (A2) of the bottom layer thereof that is a zone covering 1/3 of the thickness from the back surface being smaller than the fiber occupancy (A1 and the ratio (A1/A2) of the fiber occupancy (A1) to the fiber occupancy (A2) being 1.08 to 1.8. With this leather-like sheet, it is possible to impart a high level of stiffness to the fiber bundle entangled body due to the dense fibers of the superficial layer, and flexibility and lightweight properties to the bottom layer that has a smaller fiber density than the superficial layer. As a result, a leather-like sheet having a texture well-balanced in stiffness and flexibility is obtained. Since the bottom layer is less dense than the superficial layer and easily stretches, the bottom layer easily deforms in accordance with the superficial layer when the leather-like sheet is bent. As a result, the leather-like sheet can have a property similar to that of natural leather, i.e., is not likely to undergo loss of stiffness when bent. Also, the front surface gives a dense and smooth tactile feel and also has excellent surface abrasion resistance. Moreover, for example, if a grain coat is provided when a grain layer or the like is stacked on the superficial layer, the leather-like sheet exhibits strong adhesion, and since the fiber density of the superficial layer is high, the leather-like sheet exhibits dense creases similar to those in natural leather.

[0147] Also, when the fiber occupancy (A3) of the outermost layer that is a zone covering 1/3 of the thickness from the front surface is 36 to 60 vol%, a structure in which the difference between the fiber occupancy (A3) of 1/3 from the front surface and the fiber occupancy (A1) of 2/3 from the front surface is small and the fiber occupancy of the front surface is gradually transitioned from being high to being low is attained, thus giving an appearance and a texture more similar to those of natural leather.

[0148] It is preferable that the fiber entangled body of the ultrafine filament bundle is formed of a fiber bundle of continuously formed ultrafine filaments having a uniform fineness. With this configuration, the superficial layer and the bottom layer have excellent uniformity, and therefore the sheet demonstrates tension, firmness, and stiffness when bent.

[0149] It is preferable that the fiber entangled body of the ultrafine filament bundle has a peeling strength of 3.0 kg/1.0 cm or greater on the superficial layer side, and the peeling strength on the superficial layer side is 1.08 to 2.0 times greater than the peeling strength on the bottom layer side because an even better balance between stiffness and flexibility is obtained.

[0150] It is preferable that the logarithmic value of the tensile storage elastic modulus at 20°C is in the range of 6.0 to 7.8 Pa because the leather-like sheet has excellent shape retainability.

[0151] It is preferable that the content of the polymer elastic body relative to the total mass of the fiber bundle entangled body is 15 mass% or less, and the proportion of the polymer elastic body with which the inside of the fiber bundle of the ultrafine filaments is impregnated is 5 mass% or less relative to the total mass of the polymer elastic body with which the fiber bundle entangled body is impregnated, because the leather-like sheet has excellent shape stability and rigidity while maintaining the balance between stiffness and flexibility.

[0152] The above-described leather-like sheet is preferably used as a grain leather-like sheet provided with a grain resin layer on its front surface as well as a napped leather-like sheet in which the ultrafine filaments present on the surface of the superficial layer are napped.

Industrial Applicability

[0153] According to the present invention, a leather-like sheet having flexibility and stiffness as found in natural leather is obtained. The leather-like sheet also has excellent surface properties such as fastness and resistance to surface abrasion as well as mechanical properties such as peeling strength. Accordingly, the leather-like sheet can be preferably used as a material of leather-like products such as shoes, balls, furniture, vehicle seats, garments, gloves, baseball gloves, bags, belts, and sacks.

Description of Reference Numerals

[0154]

1	Fiber bundle entangled body
1a	Superficial layer
1 b	Bottom layer
10	Leather-like Sheet
f	Ultrafine filament

Claims

1. A leather-like sheet comprising :

   a fiber bundle entangled body which is an entangled body of a fiber bundle of ultrafine filaments,
   a fiber occupancy (A1) of a superficial layer that is a zone covering 2/3 of a thickness from a front surface of said fiber bundle entangled body being 36 to 56 vol%, and a fiber occupancy (A2) of a bottom layer thereof that is a zone covering 1/3 of a thickness from a back surface being smaller than said fiber occupancy (A1),
   a ratio (A1/A2) of said fiber occupancy (A1) to said fiber occupancy (A2) being 1.08 to 1.8.

2. The leather-like sheet in accordance with claim 1, wherein a fiber occupancy (A3) of an outermost layer that is a zone covering 1/3 of the thickness from the front surface is 36 to 60 vol%.

3. The leather-like sheet in accordance with claim 1 or 2, wherein said fiber bundle entangled body is formed from a fiber bundle of continuously formed ultrafine filaments having a uniform fineness.

4. The leather-like sheet in accordance with any one of daims 1 to 3, wherein a peeling strength on the superficial layer side is 3.0 kg/1.0 cm or greater, and the peeling strength on the superficial layer side is 1.08 to 2.0 times greater than a peeling strength on the bottom layer side.

5. The leather-like sheet in accordance with any one of daims 1 to 4, having a logarithmic value of a tensile storage elastic modulus at 20°C in a range of 6.0 to 7.8 Pa.

6. The leather-like sheet in accordance with any one of daims 1 to 5, having a content of a polymer elastic body of 15 mass% or less relative to a mass of said fiber bundle entangled body.

7. The leather-like sheet in accordance with claim 6, wherein a proportion of the polymer elastic body with which inside of the fiber bundle of the ultrafine filaments is impregnated is 5 mass% or less relative to a total mass of the polymer elastic body with which said fiber bundle entangled body is impregnated.

8. A grain leather-like sheet comprising the leather-like sheet in accordance with any one of daims 1 to 7 on the front surface of which a grain resin layer having a thickness of 1 to 300 μm is formed.

9. A napped leather-like sheet comprising the leather-like sheet in accordance with any one of daims 1 to 7 in which said ultrafine filaments present on a surface of the superficial layer are napped.

FIG. 1

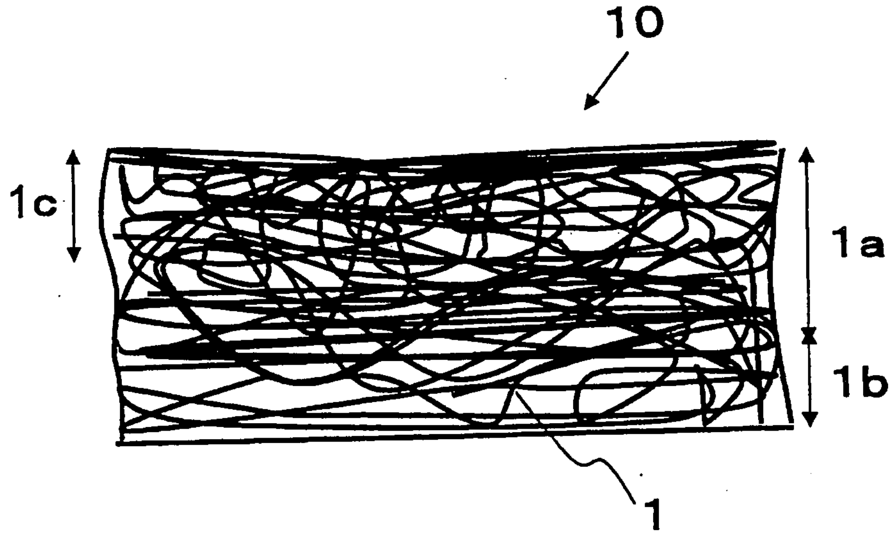
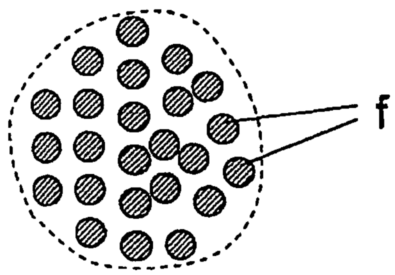


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/001705

A. CLASSIFICATION OF SUBJECT MATTER
D06N3/00(2006.01)i, *D04H3/10*(2006.01)i, *D04H3/16*(2006.01)i, *D06M15/564* (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)
D06N3/00, D04H3/10, D04H3/16, D06M15/564

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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.
A	JP 10-226968 A (Kuraray Co., Ltd.), 25 August 1998 (25.08.1998), claims; paragraphs [0005], [0007], [0009], [0021] (Family: none)	1-9
A	JP 63-3064 B2 (Hiroyuki KANAI), 21 January 1988 (21.01.1988), claims; column 4, line 6 to column 6, line 8; fig. 1 (Family: none)	1-9
A	JP 2004-169197 A (Asahi Kasei Fibers Corp.), 17 June 2004 (17.06.2004), claims; paragraphs [0013], [0014], [0020], [0024], [0027] to [0029] (Family: none)	1-9

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

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Date of the actual completion of the international search	Date of mailing of the international search report
20 June, 2011 (20.06.11)	28 June, 2011 (28.06.11)

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/001705

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REFERENCES CITED IN THE DESCRIPTION

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