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(57) [PROBLEM TO BE SOLVED]

To provide an artificial leather which can be suitable used as the upholstery or inner material of seats for interior, automobiles, aircraft, and railway vehicles, as well as clothing products and which has both a suitable texture (stiffness) and crease recovery.

[MEANS TO SOLVE THE PROBLEM]

The artificial leather includes a fiber sheet and a poly-

urethane resin, wherein the fiber sheet includes at least a fiber layer (A) constituting a first outer surface of the artificial leather, a cross-sectional polyurethane resin area ratio in the thickness direction of the fiber layer (A) is 15% to 30%, and standard deviation of the cross-sectional polyurethane resin area ratio of the fiber layer (A) is 25% or less.

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Description

[TECHNICAL FIELD]

- 5 **[0001]** The present invention relates to an artificial leather having both suitable texture (stiffness) and crease recovery (crease recovery rate).

[BACKGROUND ART]

- 10 **[0002]** Artificial leathers which are mainly composed of a fibrous substrate (fiber sheet) such as a nonwoven fabric and a polyurethane (hereinafter also referred to as PU resin) resin have excellent features such as easy care, functionality, and homogeneity that are difficult to achieve with natural leather, and are suitably used for clothing, shoes, and bags, as well upholstery and interior materials for seats for interior, automobiles, aircraft, trains, and clothing materials such as ribbon and patch substrates.
- 15 **[0003]** As a method for producing such an artificial leather, conventionally, a method in which a fiber sheet is impregnated with an organic solvent solution of a PU resin, and thereafter immersing the fiber sheet in a PU antisolvent (e.g., water or an organic solvent) to wet-coagulate the PU resin is generally used. For example, in Patent Document 1 below, an organic solvent-based PU resin using N,N-dimethylformamide, which is a PU resin solvent, is used as an organic solvent. However, since organic solvents are generally highly harmful to the human body and the environment, there is
- 20 a strong demand for a method for producing an artificial leather in which an organic solvent is not used.
- [0004]** In Patent Document 2 below, there is examined a method in which a water-dispersed PU resin dispersion in which a PU resin is dispersed in water is used instead of a conventional organic solvent-based PU resin. However, there is a problem in that in sheet-like materials in which a fiber sheet is impregnated with a water-dispersed PU resin dispersion and the PU resin is coagulated, the texture tends to be hard. One of the primary reasons is the difference between the
- 25 coagulation methods. In other words, the coagulation method of the organic solvent-based PU resin dispersion is a "wet coagulation method" in which PU molecules are aggregated, precipitated, and coagulated by substituting an organic solvent in which PU molecules are dissolved in water, and from the viewpoint of a PU film, a porous film having a low density is formed. Thus, even when the fiber sheet is impregnated with the PU resin and coagulated, the points of
- 30 adhesion between the fiber and the PU resin are present in a dot-like state, and the PU resin tends to have a porous structure, whereby it becomes a soft sheet-like material. Conversely, the water-dispersed PU resin is a "dry heat coagulation method" in which, mainly by heating, the hydration state of the PU molecules dispersed in water is collapsed and the PU molecules are coagulated by aggregating the PU molecules with each other, and the obtained PU film structure becomes a non-porous film having a high density. Therefore, the points of adhesion between the fiber and the PU resin become dense, and since the entangled portions of the fibers is strongly held, the texture becomes hard. In order to
- 35 improve texture by adopting such a water-dispersed PU resin, i.e., to suppress the hold of the fiber entangled portions by the PU resin, recognizing that a technique of making the PU resin in the sheet-like material a porous structure has been proposed, a sheet-like material in which the porous structure of the PU resin inside the sheet-like material can be expressed regardless of the types of foaming agent and PU resin, and which has the same uniform nap length as an artificial leather to which an organic solvent-based PU resin is applied, has an elegant surface quality with excellent fiber
- 40 dense feeling, has a good texture, and which is flexible and has excellent resilience can be produced by a method for producing a sheet-like material is characterized in that a fiber sheet is impregnated with a PU resin dispersion containing a water-dispersed PU resin, a foaming agent, an anionic surfactant and/or a zwitterionic surfactant.
- [0005]** However, in the sheet-like material obtained by the method described in Patent Document 2, voids between the ultrafine fiber bundles and the PU resin become large (porous-structuralization of the PU resin), whereby the PU
- 45 resin is controlled to adhere to the ultrafine fiber bundles, and as a result, though the flexibility of the texture is partially recognized. However, the cross-sectional PU resin area ratio is still relatively high, and the dispersibility of the PU resin is not sufficient. The crease recovery and the dispersibility of single fibers have not also been examined.
- [0006]** Furthermore, Patent Document 3 below discloses a sheet-like material comprising a nonwoven fabric composed of ultrafine fibers having an average single fiber diameter of 0.3 to 7 μm and an elastic resin in order to provide a brushed-leather sheet-like material having an excellent texture as well as excellent crease resistance while maintaining flexibility, wherein the sheet-like material has nap on the surface of the sheet-like material, the elastic resin has a porous structure, and the ratio of micropores having a pore diameter of 0.1 to 20 μm with respect to all pores of the porous structure is 60% or more. Patent Document 3 describes that in such a porous structure, continuous holes and closed cells can also be adopted, and by selecting a certain ratio or more of micropores in the elastic resin, when the flexibility of the elastic
- 55 resin is increased and the sheet-like material is creased and deformed, since the force of deformation can be dispersed and received not over only a part of the elastic resin but across the entirety thereof, the occurrence of creases accompanied by buckling of the elastic resin is suppressed, whereby a sheet-like material having excellent crease resistance can be obtained. Furthermore, Patent Document 3 describes that such a porous structure can be obtained by immersing the

non-woven fabric in a solution of a PU resin dissolved in an organic solvent such as N,N'-dimethylformamide or dimethylsulfoxide, and, after applying the PU resin to the non-woven fabric, carrying out wet-coagulation, in which the fabric is immersed in an insoluble solvent or a mixture of a solvent and an antisolvent.

[0007] As described above, in Patent Document 3, since an organic solvent (dimethylformamide)-based PU resin is used as the PU resin with which the nonwoven fabric is impregnated, rather than a water-dispersed PU resin, the problem of the case of water-dispersed PU resins described above, i.e., the problem wherein "the PU resin film structure obtained by the dry-heat coagulation method, in which the hydration state of the PU resin dispersion liquid, which is dispersed in water, is primarily removed and the PU is coagulated by aggregating the PU, becomes a non-porous film having a high density, whereby the dispersibility of the PU resin masses is deteriorated" is avoided, and adhesion between the fibers and the PU resin becomes point-like, whereby a soft sheet-like material can be obtained.

[0008] As described above, though Patent Document 3 describes that flexibility and crease resistance are compatible with each other due to the porous structure of the PU resin, the described artificial leather does not relate to an artificial leather filled with a water-dispersed PU resin, and the cross-sectional PU resin area ratio and the dispersibility of single fibers have not been examined.

[0009] Patent Document 4 below discloses a sheet-like material having high mechanical properties, flexibility, light weight, and quality, and a production method therefor, and discloses a sheet-like material comprising a nonwoven fabric composed mainly of ultrafine hollow fibers having an average single fiber diameter of 0.05 to 10 μm and an elastic resin in order to provide a grain artificial leather having high mechanical properties, texture (flexibility), light weight, and having high bending resistance, wherein the ultrafine hollow fibers each have 2 to 60 hollows. Patent Document 4 describes that by applying ultrafine fibers having hollows to an artificial leather, a sheet-like material suitable for an artificial leather having both high mechanical properties and a texture (flexibility) similar to those of solid fibers and having light weight due to the hollow fibers can be obtained and that by applying the same to a grain artificial leather, a grain artificial leather having both high mechanical properties and a texture (flexibility) similar to those of solid fibers and having light weight due to the hollow fibers, quality due to flexible fibers, and excellent bending resistance can be obtained. Patent Document 4 describes that hollows can be obtained from a precisely controlled sea-island type composite fiber, and a coating layer (grain surface layer) is formed using a method of coating a fiber sheet with a PU resin solution. In Patent Document 4, PU resin masses are obtained by wet-coagulation in which a PU resin is applied to a fiber sheet by immersing the fiber sheet in a solution of a PU resin dissolved in an organic solvent such as N,N'-dimethylformamide or dimethyl sulfoxide, and then immersing in an antisolvent or a mixture of a solvent and an antisolvent.

[0010] As described above, in Patent Document 4, since an organic solvent (dimethylformamide) based PU resin is used as the PU resin to be used to impregnate the nonwoven fabric, rather than a water-dispersed PU resin, the above problem of the case in which a water-dispersed PU resin is used, i.e., the problem wherein "the PU resin film structure obtained by the dry-heat coagulation method, in which the hydration state of the PU resin dispersion liquid, which is dispersed in water, is primarily removed and the PU is coagulated by aggregating the PU, becomes a non-porous film having a high density, whereby the dispersibility of the PU resin masses is deteriorated" is avoided, whereby adhesion between the fibers and PU resin becomes point-like, and a soft sheet-like material can be obtained.

[0011] In Patent Document 4, though the relationship between the number of hollows and texture and bending resistance of the obtained artificial leather has been examined, the artificial leather described therein does not relate to an artificial leather filled with a water-dispersed PU resin, and the cross-sectional PU resin area ratio and the dispersibility of single fibers have not been examined.

[0012] Furthermore, Patent Literature 5 below discloses an artificial leather consisting of a non-woven fabric composed of ultrafine fibers and polymer elastic materials, wherein in order to provide the artificial leather with no dyeing unevenness between the ultrafine fibers and a PU resin, an elastic and smooth feeling, and uniform and excellent surface qualities, the artificial leather is composed of a non-woven fabric comprising ultrafine fibers having an average single fiber fineness of 0.01 to 0.50 dtex and an elastomer, the elastomer is contained in a ratio of 10 to 50% by mass, in a cross-section when the artificial leather is cut perpendicularly to the surface direction, the number of elastomer per cross-section length in the surface direction of a mass of elastomer having a size of 100 μm or more in the thickness direction, which is within 200 μm in the thickness direction from the surface of the artificial leather excluding the napped portion, is 0.1 to 2.5 pieces/mm, and the method for the production thereof includes a step of passing a water stream through the non-woven fabric composed of ultrafine fibers to disperse the ultrafine fibers. Patent Document 5 describes that in order to eliminate the color spots on the surface of artificial leather caused by the difference in color tone between the ultrafine fibers and the elastomer, it is effective to disperse the ultrafine fibers during the manufacturing process so that the size of the resin masses of the elastomer present inside the artificial leather is within an appropriate range, as a treatment for dispersing the ultrafine fibers, a method of passing a water stream inside the ultrafine fiber sheet in the liquid bath is preferably used, the water stream imparts a mechanical impact to the bundle of the ultrafine fibers, and by dispersing the ultrafine fibers, specifically, a device such as a vibro-washer can be used. A vibro-washer is preferable because it can perform a uniform disperse treatment over the entire sheet, but a method such as water jet punching which imparts a mechanical impact by a local high-pressure water stream outside the liquid bath is not preferable because the water jet punching

process is difficult to uniformly perform due to the local flow of liquid, and even when the number of nozzles is increased, it tends to cause regular streaky appearance defects in the length direction, which results in an artificial leather having an artificial texture. The Examples of Patent Document 5 describe an ultrafine fiber dispersion treatment in which, after removing the sea component of a sea-island type composite fiber and exposing the ultrafine fibers, the fiber sheet after a sea component dissolution is treated with a vibro-washer, and in water, the water stream was passed through the inside of the fiber sheet to disperse the ultrafine fibers. However, the details of the treatment conditions are not described. In general dispersion treatments, fiber bundles remain, and the presence of disperse fibers along with the fiber bundles after brushing prevents the dense feeling and uniformity of the brushing. Furthermore, Patent Document 5 describes that as long as the obtained artificial leather has "0.1 to 2.5 pieces/mm per cross-section length in the surface direction of the resin masses of elastomer having a size of 100 μm or more in the thickness direction within 200 μm in the thickness direction from the surface", the appearance (color tone) was more uniform. However, the cross-sectional PU resin area ratio and the standard deviation thereof have not been examined, and the dispersibility of single fibers has not been examined.

[0013] Further, in Patent Document 5, since an organic solvent (dimethylformamide) based PU resin is used as the PU resin to be used to impregnate the sheet, rather than a water-dispersed PU resin, the problem of the case in which a water-dispersed PU resin is used described above, i.e., the problem wherein "the PU resin film structure obtained by the dry-heat coagulation method, in which the hydration state of the PU resin dispersion liquid, which is dispersed in water, is primarily removed and the PU is coagulated by aggregating the PU, becomes a non-porous film having a high density, whereby the dispersibility of the PU resin masses is deteriorated" is avoided, whereby adhesion between the fibers and PU resin becomes point-like, and a soft sheet-like material can be obtained.

[0014] In order to obtain an artificial leather which is flexible and has a product quality close to natural leather using an water-dispersed PU resin dispersion without the use of an organic solvent, Patent Document 6 below discloses a method for producing an artificial leather, wherein a polymer solution in a dispersion state of a PU resin which exhibits elasticity when affixed is applied onto or used to impregnate a fibrous substrate to be used as an artificial leather, and the polymer solution contained in the fibrous substrate is then affixed in the fibrous substrate using wet-heating and microwaves in combination. Patent Document 6 describes that the affixation of the PU resin, which is an elastic polymer, can be more uniformly carried out by irradiating with microwaves, and a large number of voids (porosity) are formed in the affixed PU resin itself, whereby the texture of the sheet-like material immediately after the wet-heat affixation is softer and smoother than by conventional drying methods (curing).

[0015] In Patent Document 6, though it is described that the texture of the artificial leather is imparted by the microwave treatment, the crease recovery, as well as the cross-sectional PU resin area ratio and the dispersibility of single fibers have not been investigated at all.

[0016] Cushioning properties are required for artificial leather used in car seats for automotive applications. Thus, by using a PU resin which is a rubber elastic body in a leather, and increasing the amount of PU resin, the cushioning property and crease recovery become high, but the leather becomes hard and the texture (stiffness) is impaired.

[0017] As described above, in Patent Document 3, by subjecting an organic solvent type PU resin to a foaming process, the amount of PU resin adhering to the fiber can be suppressed, and while stiffening of the leather is suppressed, the amount of PU resin, which is an elastic body, inside the leather is increased, whereby leather having suitable crease recovery is obtained, but when a water-dispersed PU resin is used, the obtained artificial leather tends to be harder than when an organic solvent type PU resin is used, and further improvement is required.

[0018] As described above, in the prior art, attempts have been made to provide an artificial leather which is excellent in texture (stiffness) and crease recovery in an artificial leather obtained by wet-coagulation of an organic solvent-based PU resin on a fiber sheet using sea-island fibers, or to provide an artificial leather which is excellent in texture (stiffness) in an artificial leather obtained by applying microwaves during drying to a sheet-like material obtained by dry-heat coagulation of a water-dispersed PU resin, but also in artificial leather obtained using a water-dispersed PU resin, a level of artificial leather which can satisfy both texture (stiffness) and crease recovery has not yet been achieved.

[RELATED ART]

[Patent Document]

[0019]

[Patent Document 1] Japanese Patent No. 4089324 [Patent Document 2] Japanese Unexamined Patent Publication (Kokai) No. 2014-25165 [Patent Document 3] WO 2018/135243
[Patent Document 4] WO 2016/031624
[Patent Document 5] Japanese Unexamined Patent Publication (Kokai) No. 2016-69790
[Patent Document 6] WO 99/18281

[SUMMARY OF THE INVENTION]

[Problems to be Solved by the Invention]

[0020] In light of the problems of the prior art described above, an object of the present invention is to provide an artificial leather which is less harmful to the human body and the environment and which has both a texture (stiffness) and crease recovery at satisfactory levels.

[Means to Solve the Problems]

[0021] As a result of rigorous investigation and experimentation in order to solve the problems, the present inventors have unexpectedly discovered that an artificial leather having the below features can solve the problems, and have completed the present invention.

[0022] In other words, the present invention is as described below.

[1] An artificial leather comprising a fiber sheet and a polyurethane resin, wherein the fiber sheet includes at least a fiber layer (A) constituting a first outer surface of the artificial leather, a cross-sectional polyurethane resin area ratio in a thickness direction cross-section of the fiber layer (A) is 15% to 30%, and standard deviation of the cross-sectional polyurethane resin area ratio is 25% or less.

[2] The artificial leather according to [1], wherein a k-nearest neighbor ratio value ($k = 9$, radius $r = 20 \mu\text{m}$) between single-fiber cross-sections constituting the fiber layer (A) in a thickness direction cross-section of the artificial leather is 10% to 80%.

[3] The artificial leather according to [1] or [2], wherein the fiber sheet has a two-or-more-layer structure composed of the fiber layer (A) constituting the first outer surface and a scrim and/or fiber layer (B) contacting the fiber layer (A).

[4] The artificial leather according to any one of [1] to [3], wherein the average diameter of single fibers constituting the fiber layer (A) is $1.0 \mu\text{m}$ to $8.0 \mu\text{m}$.

[5] The artificial leather according to any one of [1] to [4], wherein the polyurethane resin is a water-dispersed polyurethane resin.

[6] The artificial leather according to any one of [1] to [5], wherein an adhesion rate of the polyurethane resin to the fiber sheet is 15% by mass to 50% by mass.

[7] The artificial leather according to any one of [1] to [6], having a stiffness of 28 cm or less.

[8] The artificial leather according to any one of [1] to [7], wherein the fiber sheet has a crease recovery rate, as measured in accordance with JIS L1059-1:2009 "Methods for Evaluating Crease Recovery of Textiles - Part 1: Measurement of Recovery from Horizontal Creasing", of 60% or greater.

[9] The artificial leather according to any one of [1] to [8], wherein the fiber sheet is composed of polyester fibers.

[10] A production method of the artificial leather according to any one of [1] to [9], the method comprising the steps of:

forming a fiber web from sea-island cut fibers, thereafter performing needle-punch processing, and de-sea treating the obtained fiber sheet to obtain a fiber sheet in which island component single fibers are exposed, and subjecting the obtained fiber sheet to water stream dispersion treatment to obtain a fiber sheet in which the single fibers are dispersed.

[11] The production method according to [10], further comprising the step of:

impregnating the fiber sheet in which the single fibers are dispersed with a water-dispersed polyurethane resin dispersion containing hot-water-soluble resin fine particles.

[12] The production method according to [10] or [11], further comprising the step of:

after impregnation with the water-dispersed polyurethane resin dispersion and performing wet-heat treatment, affixing the polyurethane resin to the fibers by drying with microwaves to obtain a sheet-like material in which the polyurethane resin is filled.

[13] The production method according to any one of [10] to [12], wherein the fiber web contains hot-water-soluble resin fibers.

[14] The production method according to [13], wherein both the hot-water-soluble resin fine particles and a hot-water soluble resin of the hot-water-soluble resin fibers are a polyvinyl alcohol resin.

[15] The production method according to any one of [10] to [14], wherein the water stream dispersion treatment is carried out using a plurality of nozzles having a nozzle hole interval of 1.0 mm or less and a nozzle hole diameter of 0.05 mm to 0.30 mm .

[16] The production method according to any one of [10] to [15], wherein the water stream dispersion treatment is carried out using a plurality of nozzles which discharge water streams having a turbulence of 10% or more.

[17] The production method according to any one of [11] to [16], wherein a solid content concentration of the water-dispersed polyurethane resin dispersion is 10 wt% to 35 wt%.

[18] The method according to any one of [11] to [17], wherein the content of the hot-water-soluble resin fine particles in the water-dispersed polyurethane resin dispersion is 1 wt% to 20 wt%.

[Effects of the Invention]

[0023] Since the artificial leather according to the present invention is excellent in texture (stiffness) and crease recovery, it can be suitably used as the upholstery or interior material of seats in interior applications, vehicle applications, aircraft applications, and rail applications, as well as clothing products.

[Brief Description of the Drawings]

[0024]

[FIG. 1] FIG. 1 is conceptual diagram illustrating examples of the structures of artificial leathers. Note that since the scrim of reference numeral 11 and the fiber layer (B) of reference numeral 13 are arbitrary, the artificial leather of the present embodiment includes the case of a single layer including the fiber layer (A) of reference numeral 12, the case of two layers including the fiber layer (A) and the scrim or fiber layer (B), and the case of three layers including the fiber layer (A), the scrim, and the fiber layer (B).

[FIG. 2] FIG. 2 is a conceptual diagram detailing the method for determining the average diameter of a single fiber constituting the fiber layer (A).

[FIG. 3] FIG. 3 is a conceptual diagram detailing the single fiber cross-section k-nearest neighbor ratio value (%) of the thickness direction cross-section of the fiber layer (A), the cross-sectional PU resin area ratio, the single fiber average particle diameter, the surface PU resin area ratio, and each sampling point of interval size.

[FIG. 4] FIG. 4 shows photographs illustrating a state in which each single fiber cross-section has been marked by a person for determining the single fiber cross-section k-nearest neighbor ratio value (%) of the thickness direction cross-section.

[FIG. 5] FIG. 5 is a conceptual diagram for detailing the method for determining the single fiber cross-section k-nearest neighbor ratio value (%) of the thickness direction cross-section.

[FIG. 6] FIG. 6 is a conceptual diagram for detailing the method for determining the cross-section or surface PU resin area ratio and the standard deviation thereof.

[FIG. 7] FIG. 7 is a conceptual diagram illustrating nozzle hole intervals in the cases in which a plurality of nozzle holes to be used for a water stream dispersion treatment are arranged in one row or in two or more rows.

[Mode for Carrying Out the Invention]

[0025] Though the embodiments of the present invention are described in detail below, the present invention is not limited to these embodiments. Further, unless otherwise specified, the various values in the present disclosure are values obtained by the method described in the [Examples] section of the present disclosure or methods understood by those skilled in the art to be equivalent thereto.

<Artificial Leather>

[0026] An embodiment of the present invention provides an artificial leather comprising a fiber sheet and a polyurethane resin, wherein the fiber sheet includes at least a fiber layer (A) constituting a first outer surface of the artificial leather, a PU resin area ratio (cross-sectional PU resin area ratio) in a thickness direction cross-section of the artificial leather is 15% to 30%, and standard deviation of the cross-sectional PU area ratio is 25% or less.

[0027] As used herein, the phrase "artificial leather" means "a material in which a special nonwoven fabric (primarily a fiber layer having a random three-dimensional structure which is impregnated with a PU resin or a elastomer having comparable flexibility) is used as a substrate in accordance with the Household Goods Quality Labeling Act." Furthermore, in the JIS-6601 standard, artificial leathers are classified into those which are "smooth" having a leather grain-like appearance and those which are "nap" having the appearance of suede or velour, depending on appearance. However, the artificial leather of the present embodiment relates to what is classified as "nap" (i.e., a suede-like artificial leather having a brushed appearance). A suede-like appearance can be achieved by subjecting the outer surface of a fiber layer (A) (i.e., a surface serving as a first outer surface of the artificial leather) to a buffing process (brushing) with sandpaper or the like. Note that, as used herein, the first outer surface of the artificial leather is the surface exposed to the outside when the artificial leather is used (e.g., the surface on the side which contacts with a human body in the case of chair

applications) (refer to FIGS. 1 and 3). In one aspect, in the case of suede-like artificial leather, the first outer surface is raised or napped by buffing or the like.

[0028] As used herein, unless otherwise specified, the phrase "fiber web" means a state before entanglement of cut fibers, the phrase "fiber sheet" means a state prior to PU resin filling after entanglement, the phrase "sheet-like material" means a state prior to dyeing after PU resin filling, and the phrase "artificial leather" means a state of a product after dyeing. Furthermore, the phrase "nonwoven fabric" encompasses "fiber web", "fiber sheet", "sheet-like material", and "artificial leather", and the phrase "fibrous substrate" encompasses woven fabrics in addition to the phrase "nonwoven fabric."

[Cross-sectional PU Resin Area Ratio in Thickness Direction Cross-Section of Fiber Layer (A) and Standard Deviation Thereof]

[0029] In the artificial leather of the present embodiment, the cross-sectional PU resin area ratio in a thickness direction cross-section of the fiber layer (A) is 15% to 30%, and the standard deviation of the cross-sectional PU resin area ratio is 25% or less.

[0030] When the cross-sectional PU resin area ratio exceeds 30%, the PU resin adhesion rate becomes excessively high, whereby a rubber-like feeling of the artificial leather becomes strong, and though the crease recovery is improved, the texture (stiffness) deteriorates and becomes hard. When the cross-sectional PU resin area ratio is less than 15%, though the texture (stiffness) is good, the crease recovery is reduced. Furthermore, when the artificial leather does not have scrim, from the viewpoint of easily obtaining sufficient mechanical properties in the planar direction, the cross-sectional PU resin area ratio should be 15% or more. The cross-sectional PU resin area ratio is preferably 15% to 28%, and more preferably 15% to 26%.

[0031] The PU resin may be a water-dispersed PU resin.

[0032] The cross-sectional PU resin area ratio in conjunction with the k-nearest neighbor ratio value ($k = 9$, radius $r = 20 \mu\text{m}$), which is described later, is an index of texture (stiffness) and crease recovery, which is described below. For example, when the k-nearest neighbor ratio value ($k = 9$, radius $r = 20 \mu\text{m}$) exceeds 80%, excessive single fiber bundles are present. Conversely, the water-dispersed PU resin has a significant tendency toward adhesion in a single fiber or single fiber bundle state. In other words, in the presence of excessive single fiber bundles having a k-nearest neighbor ratio value of 80% or more, the PU resin masses aggregate and adhere to the single fiber bundles, whereby crease recovery is improved, but the texture (stiffness) tends to be deteriorated. Conversely, when the k-nearest neighbor ratio value is less than 10%, since the single fibers are excessively dispersed, the PU resin is also excessively dispersed, whereby adhesion by the PU resin between the fibers becomes insufficient, crease recovery is deteriorated, and as a result, it is difficult to obtain a leather-like texture and it is difficult to obtain sufficient mechanical properties.

[0033] When the k-nearest neighbor ratio value ($k = 9$, radius $r = 20 \mu\text{m}$), which is described later, is 10% to 80%, since the single fibers are appropriately dispersed, suitable texture (stiffness) and crease recovery are easily obtained.

[0034] As will be described later (refer to FIG. 6), the cross-sectional PU resin area ratio is obtained by binarizing the SEM image to distinguish the PU resin as a black portion, determining from the obtained binarized image the area ratio of the PU resin to each compartment by the compartment method, and averaging the cross-sectional PU resin area ratio (%) for all compartments, and the standard deviation thereof indicates the variation from the average for all compartments.

[0035] The artificial leather of the present embodiment is characterized in that the standard deviation of the cross-sectional PU resin area ratio in a thickness direction cross-section of the artificial leather is 25% or less. When the standard deviation of the cross-sectional PU resin area ratio is 25% or less, since the PU resin masses adhering to the fibers are uniformly adhered, the texture (stiffness) is improved. In other words, by uniformly refining the state of adhesion of the PU resin to the fibers in the cross-section in the thickness direction of the artificial leather, fine PU resin masses serve as cushions around the fibers, whereby suitable crease recovery is obtained. Furthermore, since the portions where PU resin excessively adheres to the fibers and the portions where the PU resin masses are excessively unevenly distributed are small, a suitable texture (stiffness) is obtained, and variations in the texture (stiffness) are also reduced. The standard deviation of the cross-sectional PU resin area ratio is preferably 22% or less, more preferably 20% or less, and further preferably 16% or less. The lower limit of the standard deviation of the cross-sectional PU resin area ratio is not particularly limited, and may be 0% or more.

[0036] The PU resin may be a water-dispersed PU resin.

[0037] As will be described later, for example, after a fiber web in which single fibers are dispersed is impregnated with, for example, a water-dispersed PU resin dispersion containing hot-water-soluble resin fine particles, such as polyvinyl alcohol resin fine particles (hereinafter, also referred to as PVA resin fine particles), microwaves are used in combination at the time of drying after wet-heat treatment to obtain a fiber web in which a PU resin is filled, and/or hot-water-soluble resin fibers are mixed with sea-island cut fibers to be used, and in a subsequent step, for example, at the time of dyeing, the hot-water-soluble resin fibers and hot-water-soluble resin fine particles (e.g., PVA resin fine particles) are eluted, whereby the standard deviation of the cross-sectional PU resin area ratio can be controlled to 25% or less.

Furthermore, by performing wet-heat coagulation under the conditions of a steam temperature of 100 °C to 110 °C and a treatment time of 1 minute to 5 minutes, and microwave treatment under the conditions of a microwave output of 10 kw and a treatment time of 1 minute to 5 minutes, the PU resin becomes porous, whereby the hot-water-soluble resin fibers and the hot-water-soluble resin particles (e.g., PVA resin particles) elute during dyeing, and the PU resin becomes porous and fine as the hot-water-soluble resin fibers adjacent to the PU resin and the hot-water-soluble resin particles are removed, and as a result, point-like adhesion with the fibers progresses, whereby the texture (stiffness) becomes suitable and the crease recovery is improved.

[0038] Further, for example, after a step of forming a web from sea-island type cut fibers and then de-sea treating the entangled fibers of the fiber sheet obtained by needle punching to obtain a fiber sheet in which the single fibers of the island component are exposed, a step in which the obtained fiber web is subjected to a water stream dispersion treatment, which is described later, to obtain a fiber web in which single fibers are dispersed is performed, whereby as a result of dispersing the PU resin adhering to the fibers with the dispersion of the single fibers, the standard deviation of the cross-sectional PU resin area ratio can be controlled to 25% or less.

[k-Nearest Neighbor Ratio Value (k = 9, radius r = 20 μm) between Single Fiber Cross-Sections Constituting Fiber Layer (A)]

[0039] In the present embodiment, the k-nearest ratio value (k = 9, radius r = 20 μm) between the single fiber cross-sections constituting the fiber layer (A) in a thickness direction cross-section of the artificial leather is preferably 10% to 80%. The k-nearest ratio value (k = 9, radius r = 20 μm) indicates the density of single fibers.

[0040] Though the measurement method will be described later, the k-nearest neighbor method is a method for taking k number of single fiber cross-sections near any one single fiber cross-section and determining the kth nearest radius at the Euclidean distance (i.e., the square root of the sum of squares of the distances in the X and Y directions (= the shortest distance)), and in the present embodiment, an SEM image is captured to determine whether or not there is a single fiber cross-section near k = 9th within a distance of a radius of 20 μm from substantially the center of any one single fiber cross-section. For all single fiber cross-sections in one SEM image, to determine whether or not to exist, the single fiber cross-section k=9 near distance ratio value (%) is determined by the following equation:

$$\text{Single Fiber Cross-Section (k = 9) Nearest Neighbor Distance Ratio Value (\%)} = \left\{ \left(\frac{\text{Number of Single Fiber Cross-Sections where k = 9th nearest single fiber cross-section present within a distance of 20 } \mu\text{m radius from approximate center of single fiber cross-section}}{\text{total number of single fiber cross-sections in one SEM image}} \right) \right\} \times 100.$$

[0041] When the k-nearest neighbor ratio value (k = 9, radius r = 20 μm) between the single fiber cross-sections constituting the fiber layer (A) in the thickness direction cross-section of the artificial leather is 10% or more, the single fibers are present in a state in which the single fibers are appropriately dispersed, and as a result, the PU resin masses of the fiber layer (A) are also present in a moderately dispersed state, and when the artificial leather is touched with the fingertip, the dispersed fibers are touched by the fingertip, whereby a brushed texture can be achieved. Conversely, when the k-nearest neighbor ratio value (k = 9, radius r = 20 μm) is 80% or less, since the coarse PU resin masses are not excessive, the texture of the surface is not rough, and in the cross-section, large PU resin masses do not adhere to the fibers, whereby the texture (stiffness) is not deteriorated. The k-nearest neighbor ratio value (k = 9, radius r = 20 μm) is preferably 20% to 70%, and more preferably 30% to 60%.

[0042] As will be described later, a step of forming a fiber web from sea-island cut fibers, thereafter performing needle-punch processing to obtain a fiber sheet, and performing sea component dissolution of the fiber sheet to obtain a fiber sheet in which island component single fibers are exposed is followed by a step of subjecting the obtained fiber sheet to a water stream dispersion treatment and obtaining a fiber sheet in which a single fiber is dispersed, whereby the k-nearest neighbor ratio value (k = 9, radius r = 20 μm) can be controlled within a range of 80% or less. It is preferable that the water stream dispersion treatment be carried out by injecting high-pressure water using a plurality of nozzles having a nozzle hole interval of 1.00 mm or less. As shown in FIG. 7, the nozzle hole interval is the distance in the nozzle width direction between a nozzle hole and the nozzle hole closest to this nozzle hole in the nozzle width direction (when there are two or more rows of nozzle holes, the same as in the case of one row). By setting the nozzle hole interval to 1.00 mm or less, water stream can be discharged onto the fiber sheet at close intervals, whereby by dispersing the single fibers, which are in a single fiber bundle state, the dense feeling and the moist feeling can be easily improved. Furthermore, the water stream trajectory due to the water stream dispersion treatment is inconspicuous on the surface of the fiber sheet. The nozzle hole interval is preferably 0.60 mm or less, and more preferably 0.30 mm or less.

[0043] Furthermore, the number of rows of nozzle hole rows opened in the width direction of the water stream dispersion treatment device may be either one row or two or more rows. When a water stream dispersion process is performed, it is common to remove the moisture discharged onto the fiber sheet by a water stream dispersion treatment from the viewpoint of uniformity and morphology stability of the fiber sheet, and drying is performed from the surface opposite the water stream dispersion treatment surface by a suction method or the like. In such cases, for example, in the case of one row of nozzles, when the nozzle hole interval is reduced, the drying capability is insufficient with respect to the amount of input water, and as a result, the uniformity and the morphological stability of the fiber sheet may be deteriorated. Conversely, in the case of a plurality of rows, it is preferable to reduce the amount of water discharged per row of nozzle holes by widening the nozzle hole interval per nozzle hole row since the balance between the input water amount and the drying capacity is facilitated. For example, when a drying defect occurs in one row of nozzles having a nozzle hole interval of 0.30 mm, if two row of nozzles having a nozzle hole interval of 0.60 mm in one row are used and a nozzle row having a nozzle hole interval of 0.60 mm in phase difference of 0.30 mm with respect to the first row is arranged in the second row, a water stream trajectory (nozzle hole interval) becomes 0.30 mm, and an effect of improving drying defects can be obtained. Furthermore, widening the nozzle hole interval and providing a plurality of rows are preferable because the nozzle holes are easily manufactured. The nozzle hole interval (water stream trajectory) is preferably equal because it is easy to disperse the single fibers uniformly, the water stream trajectory is inconspicuous, whereby the surface quality is suitable.

[0044] In the case of a plurality of nozzle rows, the distance between nozzle rows is preferably set to a distance equivalent to, for example, the nozzle hole interval of nozzle holes in one row from the viewpoint of drying.

[0045] The pore diameters of the high-pressure water injection nozzles of the water stream dispersion treatment are preferably 0.05 mm to 0.30 mm, more preferably 0.05 mm to 0.20 mm, and further preferably 0.08 mm to 0.13 mm from the point of view of achieving a high single fiber dispersion, inconspicuousness of the water stream trajectory, and facilitating balance of the drying ability without excessive water discharge.

[0046] Furthermore, it is preferable that the pressurized water of the water stream dispersion treatment be injected at 1.0 to 10.0 MPa. By setting the water pressure of the water stream dispersion treatment to 1.0 MPa or more, since the single fiber bundles are not excessively dispersed, it is easy to control the k-nearest neighbor ratio value to 10% to 80%. Further, by dispersing the single fibers in a single fiber bundle state, and setting the water pressure of the water stream dispersion treatment to 10.0 MPa or less, dispersion of the single fibers in single fiber bundle state is facilitated and the water stream trajectory is inconspicuous. When the water pressure of the water stream dispersion treatment is high, the water stream may pass through the fiber sheet, whereby the single fiber bundles may not be dispersed, and the single fiber bundle dispersing effect may be reduced as compared to the case in which the single fiber bundles are treated at a low water pressure. Furthermore, when the water pressure of the water stream dispersion treatment is high, the fiber sheet is densified and the texture (stiffness) tends to deteriorate. The water pressure of the water stream dispersion treatment is more preferably 1.5 to 7.0 MPa, and further preferably 2.0 to 4.5 MPa.

[0047] Regarding the shape of the water streams discharged from the nozzle hole, it is also preferable that a plurality of nozzles for discharging the water streams at a turbulence of 10% or more be used. Turbulence is an index of the fluctuation of the diameter of water stream. Since the energy of the water stream can be efficiently converted into the dispersion of the fibers, the turbulence is preferably 12% or more, and more preferably 15% or more. When the average diameter of the water streams in the range of 28 mm to 35 mm from the discharge port of the nozzle hole are defined as W , and the standard deviation of the average diameter is defined as σ , turbulence is calculated by the following equation:

$$\text{Turbulence (\%)} = \sigma \text{ (mm)} / W \text{ (mm)} \times 100.$$

[0048] Though the dispersion mechanism of the single fiber bundles as a result of turbulence has not been clarified, the inventors of the present application consider that, when the turbulence is large relative to the case where the turbulence is small, since the water stream energy is easily dispersed in multiple directions toward the horizontal direction in addition to the vertical direction of the fiber sheet, the water stream energy can be efficiently converted into single fiber bundle dispersion energy, whereby the dispersion effect is enhanced. As an example, it is considered that water stream energy, which is wasted when passing the fiber sheet at high water pressure, is easily taken in as dispersion energy.

[0049] Circular motion or reciprocating motion at right angle to the process progress direction (machine direction) of the high-pressure water injection nozzle is also preferable since it promotes single fiber dispersion and adhesion between the fibers and the PU resin, whereby crease recovery and texture (stiffness) are improved.

[0050] The distance from the high pressure water injection surface to the object to be processed is preferably 5 mm to 100 mm, more preferably 10 mm to 60 mm, and further preferably 20 mm to 40 mm from the viewpoint of the passing property of the fabric prior the water stream dispersion treatment and the process at the time of the water stream dispersion treatment, in addition to the single fiber bundle dispersing effect.

[Adhesion Ratio of PU Resin to Fiber Sheet]

[0051] In the artificial leather of the present embodiment, the adhesion ratio of the PU resin to the fiber sheet is preferably 15% by mass to 50% by mass, more preferably 22% by mass to 45% by mass, and further preferably 26% by mass to 40% by mass. The ratio of PU resin to fiber sheet affects the cross-sectional PU resin area ratio described above. When the ratio of PU resin is low, the cross-sectional PU resin area ratio tends to be low. Conversely, when the ratio of PU resin is high, the cross-sectional PU resin area ratio tends to be high. When the ratio of the PU resin to the fiber sheet is 15% by mass or more, since the fibers adhere well to the PU resin and the cushioning properties of the artificial leather are enhanced by the PU resin, mechanical strength such as abrasion resistance and crease recovery satisfying the market needs is easily obtained. Conversely, when the adhesion ratio of the PU resin to the fiber sheet is 50% by mass or less, a flexible texture can easily be obtained.

[0052] The PU resin may be a water-dispersed PU resin.

[Polyurethane (PU) Resin]

[0053] PU resins obtained by reacting a polymer diol with an organic diisocyanate and a chain extender are preferred.

[0054] As the polymer diol, for example, polycarbonate-based, polyester-based, polyether-based, silicone-based, and fluorine-based diols can be used, and a copolymer obtained by combining two or more of these may be used. From the viewpoint of hydrolysis resistance, a polycarbonate-based or polyether-based diol or a combination thereof is preferably used. Furthermore, from the viewpoint of light resistance and heat resistance, a polycarbonate-based or polyester-based diol or a combination thereof is preferably used. Furthermore, from the viewpoint of cost competitiveness, a polyether-based or polyester-based diol or a combination thereof is preferably used.

[0055] The polycarbonate-based diol can be produced by transesterification reaction of an alkylene glycol with a carbonic ester or reaction of a phosgene or a chlorformic acid ester with an alkylene glycol.

[0056] Examples of the alkylene glycol include linear alkylene glycols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, and 1,10-decanediol; branched alkylene glycols such as neopentyl glycol, 3-methyl-1,5-pentanediol, 2,4-diethyl-1,5-pentanediol, and 2-methyl-1,8-octanediol; alicyclic diols such as 1,4-cyclohexanediol; and aromatic diols such as bisphenol A; and combinations of one or two or more of these can be used.

[0057] Examples of the polyester-based diol include polyester diols obtained by condensing various low molecular weight polyols and polybasic acids.

[0058] The low molecular weight polyol may be, for example, one or more selected from ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,8-octanediol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, cyclohexane-1,4-diol, cyclohexane-1,4-dimethanol. Furthermore, an adduct obtained by adding various alkylene oxides to bisphenol A can be used.

[0059] Examples of the polybasic acid includes one or more selected from the group consisting of succinic acid, maleic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and hexahydroisophthalic acid.

[0060] Examples of the polyether-based diol include polyethylene glycol, polypropylene glycol, polytetramethylene glycol, or copolymerized diols in which these are combined.

[0061] The number average molecular weight of the polymer diol is preferably 500 to 4000. By setting the number average molecular weight to 500 or more, more preferably 1500 or more, it is possible to prevent a hard texture. Further, by setting the number average molecular weight to 4000 or less, more preferably 3000 or less, the strength of the PU resin can be maintained.

[0062] Examples of the organic diisocyanate include aliphatic diisocyanates such as hexamethylene diisocyanate, dicyclohexylmethane diisocyanate, isophorone diisocyanate, and xylylene diisocyanate; and aromatic diisocyanates such as diphenylmethane diisocyanate and tolylene diisocyanate; and these may be used in combination. Among these, aliphatic diisocyanates such as hexamethylene diisocyanate, dicyclohexylmethane diisocyanate, and isophorone diisocyanate are preferably used from the viewpoint of light resistance.

[0063] As a chain extender, an amine-based chain extender such as ethylenediamine and methylenebisaniiline, or a diol-based chain extender such as ethylene glycol can be used. Further, a polyamine obtained by reacting a polyisocyanate with water can also be used as a chain extender.

[0064] Further, the PU resin can be used in the form of a solvent type PU resin in which a PU resin is dissolved in an organic solvent such as N,N-dimethylformamide, or a water-dispersed PU resin in which a PU resin is emulsified with an emulsifier and dispersed in water. Among these, a water-dispersed PU resin is preferred from the viewpoint that the PU resin can be easily filled into a fiber sheet in a fine form, and the required performance as an artificial leather such as feeling and mechanical properties can be easily obtained even with a small amount of adhesion, and an environmental

load can be reduced without the use of an organic solvent. Specifically, since water-dispersed PU resins can be impregnated into the fiber sheet in the form of a dispersion (hereinafter, also referred to as a PU resin dispersion) in which the PU resin is dispersed with a desired particle diameter, the filling form of the PU resin in the fiber sheet can be controlled by controlling the particle diameter.

[0065] As the water-dispersed PU resin, a self-emulsifying PU resin containing a hydrophilic group in the PU molecule or a forced-emulsifying PU resin obtained by emulsifying a PU resin with an external emulsifier can be used.

[0066] In water-dispersed PU resins, a crosslinking agent can be used in combination for the purpose of improving durability such as wet-heat resistance, abrasion resistance, and hydrolysis resistance. It is preferable to add a crosslinking agent in order to improve durability at the time of jet dyeing processing, to suppress fiber loss, and to obtain excellent surface quality. The crosslinking agent may be an external crosslinking agent added as an additive component to the PU resin, and may be an internal crosslinking agent for introducing a reaction group capable of taking a crosslinked structure in the PU resin structure in advance.

[0067] Since water-dispersed PU resins used in artificial leather generally have a crosslinked structure in order to provide dyeing processing resistance, it tends to be poorly soluble in an organic solvent such as N,N-dimethylformamide. Therefore, for example, when the artificial leather is immersed in N,N-dimethylformamide for 12 hours at room temperature, then subjected to a PU resin dissolution treatment, and then its cross-section is observed with an electron microscope or the like, if a resin-like material having no fiber shape remains, it can be determined that the resin-like material is a water-dispersed PU resin.

[0068] In a preferred aspect, from the viewpoint of easily controlling the cross-sectional PU resin area ratio and the standard deviation thereof, filling of the PU resin is performed using the PU resin dispersion, and at that time, the average primary particle diameter of the PU resin in the dispersion is preferably 0.1 μm to 0.8 μm , more preferably 0.1 μm to 0.6 μm , and further preferably 0.2 μm to 0.5 μm . Note that the average primary particle diameter is a value obtained by measurement of the PU resin dispersion with a laser diffraction particle size distribution measuring device ("LA-920" manufactured by Horiba, Ltd.). By setting the average primary particle diameter of the PU resin to 0.1 μm or more, an artificial leather having excellent mechanical strength is obtained by improving the adhesion force (i.e., the binding force) of the fibers in the fiber sheet by the PU resin. Further, by setting the average primary particle diameter of the PU resin to 0.8 μm or less, aggregation or coarsening of the PU resin can be suppressed, and the standard deviation of the cross-sectional PU resin area ratio can be easily controlled to 25% or less. By setting the average primary particle diameter of the PU resin in the PU resin dispersion to 0.1 μm to 0.8 μm , a large number of the fibers constituting the artificial leather (particularly, the surface layer thereof) are held each other, whereby a flexible texture (stiffness) and excellent crease recovery can be achieved.

[Solid Concentration of PU Resin Dispersion]

[0069] As will be described later, in a typical aspect, the PU resin is impregnated in the form of an impregnating liquid such as a solution (e.g., in the case of a solvent dissolving type) or a dispersion (e.g., in the case of a water-dispersed). For example, the solid concentration of the water-dispersed PU resin dispersion may be 10 wt% to 35 wt%, more preferably 15 to 30% by mass, and further preferably 15 to 25% by mass. In one aspect, preparation of the impregnation liquid and impregnation into the fiber sheet are performed so that the ratio of the PU resin to 100% by mass of the fiber sheet is 15% to 50% by mass.

[0070] The PU resin may be a water-dispersed PU resin.

[0071] Additives such as a stabilizer (such as ultraviolet absorber, or antioxidant), a flame retardant, an antistatic agent, or a pigment (such as carbon black) may be added to the impregnation liquid containing the PU resin (e.g., a water-dispersed PU resin) if necessary. The total amount of these additives present in the artificial leather may be, for example, 0.1 to 10.0 parts by mass, or 0.2 to 8.0 parts by mass, or 0.3 to 6.0 parts by mass, per 100 parts by mass of the PU resin. Note that such additives will be distributed in the PU resin of the artificial leather. In the present disclosure, the value when referring to the size of the PU resin and the mass ratio to the fiber sheet is intended to mean values including the additives (if used).

[Hot Water-Soluble Resin Fine Particles]

[0072] When a PU resin is filled in the fiber sheet by impregnating a fiber sheet with an impregnation liquid containing a PU resin, it is preferable to perform a step of impregnating the fiber sheet with a water-dispersed PU resin dispersion containing hot water-soluble resin fine particles, and then further affixing the PU resin by heating to obtain a sheet-like material filled with a PU resin. In a subsequent step or a dyeing step, by removing the hot water-soluble resin fine particles from the obtained fiber sheet using hot water, an effect of partially dividing and aerating a portion of a continuous layer of PU resin and miniaturizing an adhesion state of PU resin is obtained.

[0073] Examples of the hot water-soluble resin fine particles include partially saponified PVA resin fine particles and

fully saponified PVA resin fine particles. Since the fully saponified PVA resin fine particles tend to be resistant to elution into water at ambient temperature (20 °C) as compared with partially saponified PVA resin fine particles, it is preferable to use fully saponified PVA resin fine particles as the hot water-soluble resin fine particles. From the viewpoint of resistance to elution into water at ambient temperature (20 °C), the degree of saponification of the fully saponified PVA resin fine particles is preferably 95 mol% or more, and more preferably 98 mol% or more. In order to achieve both fiber adhesion force and the refinement of the state of adhesion of the PU resin, the average particle diameter (size) of the hot water-soluble resin fine particles is preferably 1 μm to 8 μm, more preferably 2 μm to 6 μm, and further preferably 2 μm to 4 μm. By setting the average particle diameter to 1 μm or more, the hot water-soluble resin fine particles are unlikely to aggregate, and by setting the average particle diameter to 8 μm or less, the hot water-soluble resin fine particles can easily impregnate the fiber sheet. NL-05 manufactured by Mitsubishi Chemical Co., Ltd., can be used as the fine particles, or the fine particles can be obtained by the method described in Japanese Unexamined Patent Publication (Kokai) No. 07-82384.

[0074] The content of the hot water-soluble resin fine particles in the water-dispersed PU resin dispersion is preferably 1 wt% to 20 wt%, more preferably 2 wt% to 15 wt%, and further preferably 3 wt% to 10 wt%. When 1% by mass or more of the hot water-soluble resin fine particles are contained in the water-dispersed PU resin dispersion, dispersion of the PU resin mass is easily accelerated. Conversely, when the hot water-soluble resin fine particles are contained in the water-dispersed PU resin dispersion in a quantity of 20 wt% or less, the fine particles do not aggregate and the stability of the dispersion is easily maintained.

[0075] Note that, as used herein, the phrase "hot water-soluble resin" refers to resistant to dissolution in ambient temperature water.

[Hot Water-Soluble Resin]

[0076] When the fiber sheet is impregnated with a water-dispersed PU resin dispersion containing hot water-soluble resin fine particles, and the PU resin is then affixed by heating to obtain a sheet-like material filled with PU resin, a step of adhering the hot water-soluble resin to the fiber sheet before impregnating the fiber sheet with the water-dispersed PU resin dispersion containing hot water-soluble resin fine particles can also be performed. As the method of adhering the hot water-soluble resin (e.g., PVA resin), a hot water-soluble resin aqueous solution can be prepared, and the aqueous solution can be adhered by a method such as impregnation into the fiber sheet and then drying. In a subsequent step or a dyeing step, by removing the hot water-soluble resin together with the hot water-soluble resin fine particles from the obtained sheet material using hot water, adhesion between the fibers and the PU resin is suppressed, and a portion of the continuous layer of the PU resin is fragmented, whereby the effect of miniaturizing the adhesion state of the PU resin is obtained, so that the texture of the artificial leather is easily improved.

[0077] Examples of the hot water-soluble resin include partially saponified PVA resins and fully saponified PVA resins. Since fully saponified PVA resins tend to be resistant to elution into water at ambient temperature (20 °C) as compared with partially saponified PVA resins, it is preferable to use a fully saponified PVA resin as the hot water-soluble resin. From the viewpoint of resistance to elution into water at ambient temperature (20 °C), the degree of saponification of the fully saponified PVA resin is preferably 95 mol% or more, more preferably 98 mol% or more. Furthermore, in order to enhance the permeability of the hot water-soluble resin aqueous solution at the time of impregnation, the degree of polymerization is preferably 1000 or less, and more preferably 700 or less.

[Fiber Sheet]

[0078] As shown in FIG. 1, the fiber sheet 1 includes at least a fiber layer (A) 12, and the scrim 11 and the fiber layer (B) 13 are optional and not indispensable elements. Therefore, the artificial leather of the present embodiment includes the case of a single layer of the fiber layer (A), the case of two layers including the fiber layer (A) and scrim or the fiber layer (B), the case of three layers including the fiber layer (A), scrim, and the fiber layer (B).

[0079] When the scrim 11 and/or the fiber layer (B) 13 are not included, the fiber layer (A) may be a single layer fiber sheet which is sliced in half horizontally and filled with PU resin, as will be described later. In one aspect, the fiber sheet is a scrim-free single layer structure. This is because the productivity is increased by slicing in half horizontally.

[0080] In other aspects, the fiber sheet has a three-layer structure and the scrim is an intermediate layer. For example, a three-layer structure in which the scrim 11 as a woven or knit fabric is interposed between the fiber layer (A) 12 constituting a first outer surface of the artificial leather and the fiber layer (B) 13 constituting the second outer surface of the artificial leather, and fibers are entangled between these layers is preferable in terms of dimensional stability, tensile strength, and tear strength. Furthermore, according to the three-layer structure including the fiber layer (A), the fiber layer (B), and the scrim interposed therebetween, since the fiber layer (A) and the fiber layer (B) can be individually designed, it is preferable that the diameter, the type, and the sort of the fibers constituting these layers be freely customized according to the function and the application required for the artificial leather. For example, when ultrafine fibers are

used for the fiber layer (A) and flame-retardant fibers are used for the fiber layer (B), respectively, compatibility between excellent surface quality and high flame retardancy can be achieved.

[0081] When the fiber sheet contains scrim, it is preferable that the scrim, which is a woven or knit fabric, is constituted of the same type of polymer as the fibers constituting the fiber layer (A) from the viewpoint of color unification by dyeing. For example, if the fibers constituting the fiber layer (A) are polyester-based, the fibers constituting the scrim are also preferably polyester-based, and if the fibers constituting the fiber layer (A) are polyamide-based, the fibers constituting the scrim are also preferably polyamide-based. In the case in which the scrim is a knit fabric, the scrim is preferably a single knit knitted at 22 gauge to 28 gauge. When the scrim is a woven fabric, higher dimensional stability and strength than a knitted fabric can be realized. The textile structure may be plain weave, twill weave, or satin weave, and plain weave is preferred from the viewpoint of cost, entanglement, etc.

[0082] The yarn constituting the fabric may be a monofilament or a multifilament. The single fiber fineness of the yarn is preferably 5.5 dtex or less from the viewpoint wherein a flexible artificial leather can be easily obtained. As the form of the yarn constituting a fabric, a yarn obtained by twisting a raw yarn of a multifilament such as polyester or polyamide or a machining yarn subjected to a false twisting treatment at a twist number of 0 to 3000 T/m is preferred. The multifilament may be conventional, and, for example, a 33dtex/6f, 55dtex/24f, 83dtex/36f, 83dtex/72f, 110dtex/36f, 110dtex/48f, 167dtex/36f, 166dtex/48f polyester or polyamide is preferably used. The yarn constituting the fabric may be a long fiber of a multifilament. The woven density of yarns in the fabric is preferably 30 to 150 yarns per inch, and more preferably 40 to 100 yarns per inch, in terms of obtaining an artificial leather which is flexible and excellent in mechanical strength. In order to impart suitable mechanical strength and a moderate texture, a basis weight of 20 to 150 g/m² is preferred. Note that the presence or absence of false twisting machining in the fabric, the number of twists, the single fiber fineness of the multifilament, and the weave density contribute to mechanical properties such as stitch strength, tear strength, tensile strength, stretchability, and elasticity in addition to entanglement of the fibers constituting the fiber layer (A) and the fibers constituting the fiber layer (B), which is an optional layer, and the texture of the artificial leather, and may be appropriately selected according to the desired physical properties and application.

[0083] From the viewpoint of obtaining an artificial leather having high level abrasion resistance, dyeability, and surface quality, in the artificial leather of the present embodiment, the fiber layer (A) is preferably composed of fibers having an average diameter of 1 μ m to 8 μ m, more preferably 2 μ m to 6 μ m, and further preferably 2 μ m to 5 μ m. When the average diameter of the fibers is 1 μ m or more, the abrasion resistance, color developability after dyeing, and light fastness are suitable. Conversely, when the average diameter of the fibers is 8 μ m or less, since the number density of the fibers is large, an artificial leather having a dense feeling, a smooth surface feeling, and superior surface qualities can be obtained.

[0084] As the fibers constituting the fiber layers constituting the artificial leather (the fiber layer (A), and the fiber layer (B) and the additional layer as an optional layer), synthetic fibers including polyester-based fibers such as polyethylene terephthalate, polybutylene terephthalate, and polytrimethylene terephthalate; polyamide-based fibers such as nylon 6, nylon 66, and nylon 12 are suitable. Among these, polyethylene terephthalate is preferred from the viewpoint that the fibers themselves do not yellow even when exposed to direct sunlight for long periods of time, and the dyeing fastness thereof is excellent, and in consideration of applications requiring durability, such as in the application of automobile seats. Further, from the viewpoint of reducing the environmental impact, as the fibers constituting the fiber layers constituting the artificial leather, polyethylene terephthalate which has been chemically recycled or material recycled, or polyethylene terephthalate using plant-derived raw materials is further preferred.

[0085] As used herein, the phrase "dispersed single fiber" means that the fibers do not form a fiber bundle, for example, an island component in the sea-island composite fibers described below. For example, a fiber obtained by using filaments capable of ultrafine fiber generating such as a sea-island type composite fiber (e.g., a copolymerized polyester is used as the sea component and a conventional polyester is used as the island component), subjecting it to a three-dimensional entanglement with scrim, and subsequently subjecting it to a sea component dissolution (removing the sea component of the sea-island type composite fiber by dissolution or decomposition) is present as a fiber bundle in the fiber layer (A), and is not a dispersed single fiber. As an example, an ultrafine fiber having a single fiber fineness of 0.2 dtex is obtained by producing a sea-island type composite cut fiber in which an island component is 24 islands/lf corresponding to a single fiber fineness of 0.2 dtex, thereafter forming a fiber layer (A) with the sea-island type composite cut fiber, forming a three dimensional entangled body with a scrim by needle-punch processing, filling the three dimensional entangled body with PU resin, and then dissolving or decomposing the sea component. In this case, the single fibers are present in the fiber layer (A) in a state of 24 convergent fibers (corresponding to 4.8 dtex in a convergent state)

[0086] When the fiber layer (A) is composed of dispersed single fibers, it is excellent in surface smoothness, and, for example, uniform nap can be easily obtained when the outer surface of the fiber layer (A) is raised by buffing, and even when the adhesion ratio of the PU resin is relatively small, a lint-like appearance called pilling is not readily generated by friction, whereby an artificial leather having superior surface quality and abrasion resistance is obtained. Furthermore, when the fibers are dispersed single fibers, since the fiber interval tends to be narrow and uniform, good abrasion resistance can be obtained even if the PU resin is adhered in a fine state. Examples of the method for dispersing a fibers

in single fibers include a method of converting a fiber produced by a direct spinning method into a fiber sheet by a papermaking method, a method of promoting a single fiber conversion of an ultrafine fiber bundle by dissolving or decomposing the sea component of a fiber sheet composed of a sea-island type composite fiber to generate an ultrafine fiber bundle, and thereafter subjecting the ultrafine fiber bundle surface to the aforementioned water stream dispersion treatment.

[0087] In fiber layers other than the fiber layer (A) among the fiber layers constituting the artificial leather, the fibers may or may not be dispersed single fibers. However, in a preferred aspect, the layers other than the fiber layer (A) are also composed of dispersed single fibers. Since the fibers constituting the layers other than the fiber layer (A) are dispersed single fibers, it is preferable from the viewpoint that the thickness of the artificial leather becomes homogeneous, the processing accuracy is improved, and quality is stabilized and from the viewpoint of homogenizing the appearances of the front and back surfaces of the artificial leather.

[0088] When the artificial leather is composed only of the fiber layer (A), the basis weight of the fibers constituting the fiber layer (A) is preferably 40 g/m² to 500 g/m², more preferably 50 g/m² to 370 g/m², and further preferably 60 g/m² to 320 g/m², from the viewpoint of mechanical strength such as abrasion resistance.

[0089] When the artificial leather has a three-layer structure including the fiber layer (A), scrim, and the fiber layer (B), the basis weight of the fibers constituting the fiber layer (A) is preferably 10 g/m² to 200 g/m², more preferably 30 g/m² to 170 g/m², and further preferably 60 g/m² to 170 g/m², from the viewpoint of mechanical strength such as abrasion resistance. Further, from the viewpoint of cost and ease of production, the basis weight of the fibers constituting the fiber layer (B) is preferably 10 g/m² to 200 g/m², and more preferably 20 g/m² to 170 g/m². The basis weight of the scrim is preferably 20 g/m² to 150 g/m², more preferably 20 g/m² to 130 g/m², and further preferably 30 g/m² to 110 g/m², from the viewpoint of mechanical strength and entanglement between the fiber layer and the scrim.

[0090] The basis weight of artificial leather filled with PU is preferably 50 g/m² to 550 g/m², more preferably 60 g/m² to 400 g/m², and further preferably 70 g/m² to 350 g/m².

[0091] In one aspect, the texture (stiffness) of the artificial leather is preferably 28 cm or less, more preferably 6 cm to 26 cm, and further preferably 8 cm to 22 cm or less. The stiffness is an index of the texture of the artificial leather. By setting the stiffness to 28 cm or less, the formability as the upholstery or interior material of a seat for interior, automobiles, aircraft, and railway vehicles is improved, and the consumption performance is also suitable, whereby the needs required from the market with respect to texture can be easily satisfied.

[0092] In one aspect, the crease recovery rate, as measured in accordance with JIS L1059-1:2009 "Methods for Evaluating Crease Recovery of Textiles - Part 1: Measurement of Recovery from Horizontal Creasing", is preferably 60% or more, more preferably 70% or more, and further preferably 80% or more. Crease recovery (crease recovery rate) is an index indicating the recovery of creasing of the artificial leather. For example, when the artificial leather is used as the upholstery of a seat such as in an automobile, aircraft, or railway vehicle, a fine creases are formed on the back portion due to sitting on the seat for long periods of time, but by setting the crease recovery (crease recovery rate) to 60% or more, the creases can easily recover, whereby the surface quality is easily maintained, even when the seat is used for long periods of time.

[0093] In one aspect, in accordance with an evaluation method which is described later, it is preferable that the brushed texture of the artificial leather be grade 3 or higher. The surface quality of the artificial leather becomes satisfactory when the brushed texture is grade 3 class or higher.

<Method for Producing Artificial Leather>

[0094] An example of the method for producing the artificial leather of the present embodiment will be described below.

[0095] The example of the method for producing the artificial leather of the present embodiment further comprises the following steps:

forming a fiber web by combining sea-island cut fibers with hot-water-soluble resin fibers, if necessary, thereafter performing needle-punch processing to obtain a fiber sheet, and performing a sea component dissolution of the fiber sheet to obtain a fiber sheet in which island component single fibers are exposed, and
subjecting the obtained fiber sheet to a water stream dispersion treatment to obtain a fiber sheet in which the single fibers are dispersed, and may comprise the following steps:

impregnating the fiber sheet in which the single fibers are dispersed with a water-dispersed PU resin dispersion containing hot-water-soluble resin fine particles, and thereafter affixing the PU resin by combining wet-heating and microwaves, if necessary, to obtain a sheet-like material in which the polyurethane resin is filled, and removing the hot-water-soluble resin fine particles and/or the water-soluble resin fibers from the sheet-like material using hot water.

[0096] It is preferable that the PU resin be affixed to the fibers using both wet-heating and microwaves under the conditions of a steam temperature of 100 °C to 110 °C, a microwave output of 10 kW, and a treatment time of 1 minute to 5 minutes.

[0097] Each step will be described below in order.

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[Step of Forming Fiber Web by Combining Sea-Island Cut fibers with Hot-Water-Soluble Resin Fibers, if Necessary, Performing Needle-Punch Processing to Obtain Fiber Sheet, and Performing Sea Component Dissolution of Fiber Sheet to Obtain Fiber Sheet in which Island Component Single Fibers are Exposed]

10 **[0098]** Examples of the method for producing each fiber layer (fiber layer (A) and optional fiber layer (B)) constituting a fiber sheet of the artificial leather include spinning direct coupling methods (e.g., the spunbond method and melt blowing method), and a method of forming a fiber sheet using cut fibers (e.g., dry methods such as carding or the airlaid method, and wet methods such as a papermaking method), and any of these can be suitably used. However, in the present embodiment, hot-water-soluble resin fibers, if necessary, and sea-island (SIF) cut fibers are used as raw materials. After
15 fiber sheet formation, the fiber web is subjected to water stream dispersion treatment, which is described later, and the hot-water-soluble resin fibers in the sheet-like material in which the PU resin is filled are removed from the obtained fiber sheet, whereby the PU resin surrounding the hot water-soluble resin fibers achieves a porous structure, and a flexible sheet-like material is obtained. When the artificial leather is composed of only the fiber layer (A), from the viewpoint of mechanical physical properties and texture (flexibility), the content of hot water-soluble resin fibers is preferably 5 to
20 40% by mass, more preferably 5 to 30% by mass, and further preferably 5 to 20% by mass, based on the total fiber content.

[0099] When the fiber layer has a two-or-more layer structure, the same mixing ratio as in the case of the fiber layer (A) may be used. In addition, in the case of two or more layers, in order to obtain a softer artificial leather, it is preferable to also combine hot-water-soluble resin fibers in the fiber layer (B) in the same manner as in the fiber layer (A). Fiber sheets produced using cut fibers are suitable in terms of improving the surface quality of the artificial leather because
25 they have a small basis weight and are excellent in uniformity, whereby uniform nap can easily be obtained.

[0100] As the means for forming the ultrafine fibers of the fiber sheet, filaments capable of ultrafine fiber generating can be used. By using filaments capable of ultrafine fiber generating, a state in which ultrafine fiber bundles are entangled can be stably obtained.

[0101] As the filaments capable of ultrafine fiber generating, a sea-island type fiber in which two thermoplastic resins having different solvent solubilities are used as the sea component and island component, and the island component is formed into ultrafine fibers by dissolving and removing the sea component with a solvent or a peelable composite fiber in which a thermoplastic resin having two components which alternately arranged in a fiber cross-section in a radial or multilayered manner, and each component is peeled and divided into ultrafine fibers can be used. Among these, sea-island type fibers are preferably used from the viewpoint of flexibility and texture of the sheet-like material because
30 suitable voids can be imparted between the island components, i.e., between the ultrafine fibers, by removing the sea component.

[0102] Examples of sea-island type fibers include sea-island type composite fibers which are spun by arranging two components including the sea component and the island component using a sea-island type composite spinneret, and sea-island type composite fibers which are spun by mixing the two components including the sea component and the island component. In view of obtaining ultrafine fibers of uniform fineness, obtaining ultrafine fibers of sufficient length, and imparting the sheet-like material with strength, a sea-island type composite fiber is preferably used.

[0103] Polyethylene, polypropylene, polystyrene, a copolymerized polyester obtained by copolymerizing sodium sulfoisophthalic acid or polyethylene glycol, and polylactic acid can be used as the sea component of the sea-island fiber. Among these, from the viewpoint of environmental considerations, a copolymerized polyester or a polylactic acid obtained
45 by copolymerizing an alkali-decomposable sodium sulfoisophthalic acid or polyethylene glycol which can be decomposed without the use of an organic solvent is preferred.

[0104] It is preferable that the sea component dissolution is performed prior to the application of the PU resin onto the fiber sheet when a sea-island fiber is used. If the sea component dissolution is performed prior to the application of the PU resin, the PU resin is adhered directly with the ultrafine fibers, whereby the ultrafine fibers can be strongly adhered,
50 improving the abrasion resistance of the sheet-like material.

[0105] As the method for entangling the fibers or fiber bundles of the fiber web, a method in which the sea-island fibers are cut into predetermined fiber lengths to form staple fibers, a fiber web is formed with a card and a cross-lapper, and the fiber web is entangled by a needle punching process or a water stream entanglement process referred to as the spunlace method can be used.

55 **[0106]** In the needle punching method, the number of barbs of a needle used is preferably one to nine. By setting the number of barbs of a needle to one or more, the entangling effect can be obtained and damage to fibers can be suppressed. By setting the number of barbs of a needle to nine or fewer, damage to the fibers can be reduced, and additionally, needle marks remaining in the artificial leather can be reduced, whereby the appearance of the product can

be improved.

[0107] In consideration of the fiber entangling property and the influence on the appearance of the product, it is preferable that the total depth (length from the tips of the barb to the bottom of the barb) of the barbs be 0.05 mm to 0.10 mm. If the total depth of the needle is 0.05 mm or more, efficient fiber entanglement is facilitated because good hooking of the fibers is obtained. Furthermore, when the total depth of the barb is 0.10 mm or less, needle marks remaining in the artificial leather are reduced and the quality is improved. In consideration of the balance between the strength of the needles and fiber entanglement, the total depth of the barb is more preferably 0.06 mm to 0.08 mm.

[0108] When the fibers are entangled by needle punching, the range of the punch density is preferably 300 needles/cm² to 6000 needles/cm², and more preferably 1000 needles/cm² to 6000 needles/cm².

[0109] The fiber sheet obtained by the needle punch processing may be, for example, dried at a temperature of 150 °C for 2 minutes using a hot air drier to obtain a fiber sheet prior to a sea component dissolution.

[0110] The sea component dissolution can be performed by immersing the sea-island fibers in a solvent to constrict. As the solvent for dissolving the sea component, an aqueous alkali solution such as sodium hydroxide can be used when the sea component is a copolymerized polyester or a polylactic acid. From the viewpoint of environmental considerations of the treatment, a sea component dissolution with an aqueous alkali solution such as sodium hydroxide is preferred.

[0111] The cut fiber length, in the case in which a method using cut fibers (staple fibers) is selected, is preferably 13 mm to 102 mm, more preferably 25 mm to 76 mm, and further preferably 38 mm to 76 mm in dry methods (carding, airlaid method, etc.), and is preferably 1 mm to 30 mm, more preferably 2 mm to 25 mm, and further preferably 3 mm to 20 mm in wet methods (papermaking method, etc.). For example, the aspect ratio (L/D), which is a ratio of the length (L) and the diameter (D), of the cut fibers used in wet methods (such as a papermaking method) is preferably 500 to 2000, and more preferably 700 to 1500. Such an aspect ratio is preferable because when the cut fibers are dispersed in water to prepare a slurry, the dispersibility and fiber opening property of the cut fibers in the slurry are favorable, the strength of the fiber layer is suitable, and since the fiber length is short and the single fibers can be easily dispersed as compared with dry methods, a link-like phenomenon known as pilling is unlikely to be brought about by friction. For example, the fiber length of cut fibers having a diameter of 4 μm is preferably 2 mm to 8mm, and more preferably 3 mm to 6 mm.

[Step of Subjecting Obtained Fiber Sheet to Water Stream Dispersion Treatment to Obtain Fiber Sheet in which Single Fibers are Dispersed]

[0112] By subjecting the obtained fiber sheet to the aforementioned water stream dispersion treatment, a fiber sheet in which the single fibers are dispersed can be obtained. By carrying out the aforementioned water stream dispersion treatment after the sea component dissolution, the k-nearest neighbor ratio value (k = 9, radius r = 20 μm) between the single fiber cross-sections constituting the fiber layer (A) in the thickness direction cross-section of the artificial leather can be controlled to 80% or less.

[Step of Impregnating Fiber Sheet in which Single Fibers are Dispersed with Water-dispersed Polyurethane Resin Dispersion Containing Hot-Water-Soluble Resin Fine Particles, Thereafter Affixing PU Resin by Combining Wet-Heating and Microwaves, if Necessary, to Obtain Sheet-Like Material in which Polyurethane Resin is Filled]

[0113] In this step, the fiber sheet is impregnated with a water-dispersed PU resin dispersion containing hot water-soluble resin fine particles, and the PU resin is then affixed by combining wet-heating and microwaves to fill the PU resin, if necessary. In a typical aspect, the PU resin is impregnated in the form of an impregnating liquid such as a dispersion (e.g., in the case of water-dispersed PU resin). The concentration of PU resin in the impregnating liquid may be, for example, 10 to 35% by mass. In one aspect, the impregnation solution is prepared and impregnated into the fiber sheet so that the ratio of PU resin to 100% by mass of the fiber sheet is 15 to 50% by mass.

[0114] Water-dispersed PU resins are classified into forced-emulsification type PU resins which are forcibly dispersed and stabilized using a surfactant and self-emulsification type PU resins which have a hydrophilic structure in the PU molecular structure and which disperses and stabilizes in water even in the absence of a surfactant. Though any of these may be used in the present embodiment, it is preferable to use a forced-emulsification type PU resin from the viewpoint of imparting a thermal coagulation property, which is described later.

[0115] In the present embodiment, though the water-dispersed PU resin dispersion containing hot water-soluble resin fine particles is impregnated into the fiber sheet, it is not preferable that the hot water-soluble resin fine particles be dissolved in the water-dispersed PU resin dispersion. Conversely, since the hot water-dispersed resin fine particles are more likely to dissolve in an aqueous solution in which a surfactant is dissolved than in water, a forced-emulsification type PU resin dispersion containing a surfactant is preferred over a self-emulsification type PU resin dispersion containing no surfactant. The concentration of the water-dispersed PU resin (the content of the PU resin relative to the water-

dispersed PU resin dispersion) is preferably 10 to 35% by mass, more preferably 15 to 30% by mass, and further preferably 15 to 25% by mass, from the viewpoint of controlling the quantity of the water-dispersed PU resin to be adhered, and from the viewpoint of promoting adhesion of the PU resin when the concentration is high and reduction of the stability of the impregnation liquid.

[0116] Furthermore, water-dispersed PU resin dispersions having thermal coagulation properties are preferred. By using a water-dispersed PU resin dispersion having thermal coagulation properties, the PU resin can be uniformly distributed in the thickness direction of the fiber sheet. "Thermal coagulation properties" refers to the property in which when the PU resin dispersion is heated, the fluidity of the PU resin dispersion decreases and it coagulates when a certain temperature (thermal coagulation temperature) is reached. In the production of the sheet-like material filled with PU resin, the fiber sheet is impregnated with the PU resin dispersion, and the PU resin is coagulated by dry heat coagulation, wet heat coagulation, hot water coagulation, or a combination thereof, and dried to impart the fiber sheet with the PU resin. As the method of coagulating a water-dispersed PU resin dispersion which does not exhibit thermal coagulation properties, dry coagulation is conventional in industrial production, but in this case, a migration phenomenon in which PU resin is concentrated on a surface layer of the sheet-like material occurs, whereby the texture of the sheet-like material filled with PU resin tends to become hard.

[0117] The thermal coagulation temperature of the water-dispersed PU resin dispersion is preferably 40 to 90 °C. By setting the thermal coagulation temperature to 40 °C or higher, storage stability of the PU resin dispersion becomes suitable, and adhesion of the PU resin to machinery during operations can be suppressed. Further, by setting the thermal coagulation temperature to 90 °C or lower, it is possible to suppress the migration phenomenon of the PU resin in the fiber sheet.

[0118] In order to set the thermal coagulation temperature as described above, a thermal coagulation agent may be added as needed. Examples of thermal coagulation agents include inorganic salts such as sodium sulfate, magnesium sulfate, calcium sulfate, and calcium chloride, and radical reaction initiators such as sodium persulfate, potassium persulfate, ammonium persulfate, azobisisobutyronitrile, and benzoyl peroxide.

[0119] The fiber sheet is impregnated or coated with the water-dispersed PU resin dispersion, and the PU resin can be coagulated by dry heat coagulation, wet heat coagulation, hot water coagulation, or a combination thereof. The temperature of the wet heat coagulation is set to be equal to or higher than the thermal coagulation temperature of the PU resin, and is preferably 40 to 200 °C. By setting the temperature of the wet heat coagulation to 40 °C or higher, more preferably 80 °C or higher, it is possible to further suppress the migration phenomenon by shortening the time to coagulation of the PU resin. Conversely, by setting the temperature of the wet heat coagulation to 200 °C or lower, more preferably 160 °C or lower, it is possible to prevent thermal deterioration of the PU resin and the PVA resin.

[0120] Furthermore, when combining wet-heat coagulation and microwaves, porosity of the PU resin can be promoted by setting the steam temperature during the wet-heat treatment to 100 °C to 110 °C, the treatment time to 1 minute to 5 minutes, the microwave output during microwave treatment to 10 kW, and the treatment time to 1 minute to 5 minutes.

The temperature of the hot water coagulation is set to be equal to or higher than the thermal coagulation temperature of the PU resin, and is preferably set to 40 to 100 °C. By setting the temperature of hot water coagulation in hot water to 40 °C or higher, more preferably 80 °C or higher, it is possible to further suppress the migration phenomenon by shortening the time to coagulation of the PU resin. The dry coagulation temperature and the drying temperature are preferably 80 to 180 °C. By setting the dry coagulation temperature and the drying temperature to 80 °C or higher, more preferably 90 °C or higher, productivity is excellent. Conversely, by setting the dry coagulation temperature and the drying temperature to 180 °C or lower, more preferably 160 °C or lower, it is possible to prevent thermal deterioration of the PU resin or PVA resin.

[0121] As described above, when the fiber sheet in which the single fibers are dispersed is impregnated with a water-dispersed PU resin dispersion containing hot water-soluble resin fine particles, the content of the hot water-soluble resin fine particles in the water-dispersed PU resin dispersion is preferably 1 wt% to 20 wt%, preferably 2 wt% to 15 wt%, and more preferably 3 wt% to 10 wt%. By including the hot water-soluble resin fine particles in the water-dispersed PU resin dispersion, further dispersion of the PU resin mass is promoted.

[Step of Removing Hot-Water-Soluble Resin Fine Particles and/or Hot-Water-Soluble Resin Fibers from Obtained Sheet-Like Material Using Hot Water]

[0122] Examples of the means for removing the hot water-soluble resin from the sheet-like material include a method of immersion in hot water at 60 °C or higher, preferably 80 °C or higher, and a method of removing the hot water-soluble resin fine particles and/or hot-water-soluble resin fibers while circulating hot water at 80 °C or higher prior to performing dyeing processing in a jet dyeing machine. In particular, a method of removing hot water-soluble resin fine particles and/or hot-water-soluble resin fibers in a jet dyeing machine is preferred since a step of drying and winding of the sheet-like material after removing the hot water-soluble resin fine particles can be omitted, whereby production efficiency can be increased. In the present embodiment, a flexible sheet-like material is obtained by removing the hot water-soluble

resin fine particles and/or hot-water-soluble resin fibers from the sheet-like material after the PU resin has been applied. Though the method for removing the hot water-soluble resin fine particles is not particularly limited, for example, dissolving and removing the particles by immersing the sheet in hot water at 60 to 100 °C, and if necessary, wringing the sheet with a wringer is preferred.

[Finishing-Process]

[0123] After filling the fiber sheet with the PU resin and removing the hot water-soluble resin fine particles and/or hot-water-soluble resin fibers, when scrim is not included, the sheet-like material filled with the PU resin can be sliced in half horizontally. As a result, production efficiency can be improved.

[0124] Furthermore, the sheet-like material filled with a PU resin may be imparted with a lubricant such as a silicone dispersion before brushing, which is described later. Furthermore, applying an antistatic agent before brushing is preferable in order to prevent the grinding byproducts generated from the sheet-like material by grinding from accumulating on the sandpaper.

[0125] Brushing can be performed to form naps on the surface of the sheet-like material. Brushing can be performed by a method of grinding or the like using a sandpaper, a roll sander, or the like. Furthermore, applying silicone or the like as a lubricant prior to brushing easily enables brushing by surface grinding, whereby surface quality becomes very good.

[0126] It is preferable that the artificial leather be subjected to a dyeing treatment for the purpose of enhancing the surface appearance value (i.e., visual effect). The dye may be selected in accordance with the type of fiber constituting the fiber sheet, for example, a disperse dye may be used for polyester-based fibers, and an acid dye or a metal complexed dye may be used for polyamide-based fibers, and a combination thereof may be used. When dyeing is performed with a disperse dye, reduction cleaning may be performed after dyeing. As the dyeing method, a conventional method well known to dyeing processors can be used. In the dyeing method, it is preferable to use a jet dyeing machine because it is possible to soften the sheet-like material by simultaneously dyeing the sheet-like material and simultaneously imparting a kneading effect. The dyeing temperature is preferably 80 to 150 °C, depending on the type of fiber. By setting the dyeing temperature to 80 °C or higher, more preferably 110 °C or higher, dyeing of the fibers can be efficiently performed. Conversely, by setting the dyeing temperature to 150 °C or lower, more preferably 130 °C or lower, it is possible to prevent the deterioration of the PU resin.

[0127] The artificial leather dyed in this manner is preferably subjected to soaping and, if necessary, reduction cleaning (i.e., washing in the presence of a chemical reducing agent) to remove excess dye. It is also preferable to use a dyeing aid at the time of dyeing. By using a dyeing auxiliary, uniformity and reproducibility of dyeing can be improved. Further, in the same bath as used in dyeing or after dyeing, finishing using a softener such as silicone, an antistatic agent, a water repellent, a flame retardant, a light resistant agent, or an antibacterial agent can be applied.

[0128] The artificial leather of the present embodiment can also be suitably used as an upholstery or interior material requiring an elegant appearance, for example, a surface material of furniture, chairs, and walls, seats, ceilings, and interiors of vehicles such as automobiles, trains, and aircrafts, a clothing material of a part of shirts and jackets, the uppers of shoes such as casual shoes, sports shoes, men's shoes, women's shoes, various trims, bags, belts, wallets, etc., or an industrial material of wiping cloths, abrasive cloths, and CD curtains.

[Examples]

[0129] Hereinafter, the present invention will be specifically described based on Examples and Comparative Examples. However, the Examples do not limit the scope of the present invention. Regarding the artificial leather samples according to the Examples and Comparative Examples, the physical properties and grades like were evaluated by the following procedures and methods.

(1) Sampling Collection Sites

[0130] FIG. 3 shows the sample collection sites.

[0131] First, the fiber layer (A) or the artificial leather comprising the fiber layer (A) was cut at ten substantially evenly positions (sampling areas 1, 2, ...) in the machine direction (MD) into bands (indicated by dotted lines). In each sampling region, the thickness (t) cross-section was made electroconductive by coating it with osmium atom in 1nm thick. In order to determine the k-nearest neighbor ratio value (%), and the cross-sectional PU resin area ratio (%) in these cross-sections, ten substantially uniform SEM images were captured in the CD direction perpendicular to the MD direction. Furthermore, in order to obtain the surface PU resin area ratio (%) in each sampling region, ten substantially uniform SEM images of the first outer surface of the fiber layer (A) were made electroconductive by coating it with osmium atom in 1nm thick, and then were captured in the CD direction. Specifically, 100 images were prepared for each of the images

used for obtaining the single fiber cross-section k-nearest neighbor ratio value (%), and the cross-sectional PU resin area ratio (%). In this case, the average and standard deviation of each value is for 100 images.

[0132] In case where an artificial leather was napped, it can be determined that the napped direction is the MD direction. In the case where an artificial leather was not napped or the MD direction is unclear, one direction can be defined in arbitrary as MD direction, and another direction perpendicular to the defined MD direction can be defined as CD direction.

(2) Cross-sectional PU resin area ratio (%) and Standard Deviation

■ Pretreatment

[0133] 1 cm × 0.5 cm (warp (x) × weft (y)) samples were cut in a thickness direction cross-section, and an epoxy resin (primary agent: "Quetol 812" manufactured by Nissin EM Co., Ltd., adhesive agent: "MNA" manufactured by Nissin Corporation EM, Accelerator: "DMP-30" manufactured by Nissin Corporation EM) was embedded in the internal space of each sample. The obtained resin-embedded samples were cut parallel to the thickness direction with a microtome to obtain a smooth cut surface. The samples were then set in a saturated vapor of ruthenium tetroxide for 4 hours to electro-stain the PU resin adhering to the sample with ruthenium. The osmium atoms were then subjected to conductive processing by 1 nm coating processing.

■ Observation

[0134] When scrim was contained in a sample, the deepest portion (i.e., the portion on the scrim side) of the fiber layer (A) on the cut surface of the conductively treated sample was set as the observation region, the fibers constituting the scrim were excluded from the observation target, and observation was carried out with a scanning electron microscopy (SEM, "SU8220" manufactured by Hitachi, Ltd.). The observation conditions are as follows.

Acceleration voltage: 10kV

Detector: YAG-BSE (Cyclic Scintillator Reflective Electrons)

Imaging magnification: 500-fold

Observation Field of View: approximately 230 μm × approximately 173 μm

■ Image Analysis

[0135] The obtained SEM-reflected electron images were binarized by the following method using image analysis software "ImageJ (version: 1.51j8), National Institutes of Health", and the average sizes of the PU-resin was obtained.

(i) The SEM images were filtered. The processing conditions are as follows:

Hand Path Filtering: Filter large structures down to 40 pixels, Filter small structures up to 3 pixels, Suppress stripes None, Tolerance of direction 5%, Autoscale after filtering, Saturate image when autoscaling, and in addition, as median filtering, radius: 4.0, one filtering repetition.

(ii) Binarization was performed by the MaxEntropy method, and the black portions in the SEM images after binarization were defined as PU-resin.

(iii) The area ratio of PU resin to each compartment was determined from the obtained binarized images.

[0136] As shown in FIG. 6, using the obtained binarization images (1280 × 960 pixels; 1280 × 896 pixels excluding the band below the image) were divided into 32 × 32 pixels (in this case, 1120 divisions), and the Analyze Particle function of ImageJ (conditions: Size = 0-infinity, Circularity= 0.00-1.00), the value obtained by dividing the sum of the areas of the respective PU resins distributed within each compartment by the area of each compartment was defined as the cross-sectional PU resin area ratio (%) of each compartment. The number of pixels of the x and y axes of the target image were counted, the size of the compartment was designated by the pixel size, the number of divisions of the x and y axes was determined, and the PU resin area% within each divided area was calculated.

[0137] The PU resin area ratio calculated with one SEM image was obtained by averaging the surface PU resin area ratio (%) for all compartments of the one SEM image, and the standard deviation thereof is calculated by the formula shown in FIG. 6.

[0138] The surface PU resin area ratio (%) and the standard deviation thereof were obtained by averaging the PU resin area ratio and the standard deviation thereof calculated with one SEM image. That is, as shown in FIG. 6, the standard deviation was first calculated for all compartments obtained by dividing one SEM image into compartments, and second obtained by averaging the standard deviations calculated for each of 100 SEM images.

(3) Single Fiber Cross-Section k-Nearest Neighbor Ratio Value (%)

[0139] As shown in FIG. 5, the k-nearest neighbor method is a method in which k number single fiber cross-sections are taken to any one single fiber cross-section, and the kth nearest radius in the Euclidean distance is set as the determination boundary.

[0140] In the present embodiment, in a single SEM image, a range of approximately $250\ \mu\text{m} \times$ approximately $186\ \mu\text{m}$ was taken as 640×480 pixels including the band below the image (in this case, one pixel corresponds to approximately $0.40\ \mu\text{m} \times$ approximately $0.40\ \mu\text{m}$), and it was determined whether or not a single fiber cross-section closer to $k = 9$ was present within a distance of a radius of $20\ \mu\text{m}$ from substantially the center of any one single fiber cross-section. For all single fiber cross-sections in one SEM image, presence was determined, and the single fiber cross-section $k=9$ nearest neighbor distance ratio value (%) was determined by the following equation:

$$\text{Single fiber cross-section (k=9) nearest neighbor distance ratio value (\%)} = \left\{ \frac{\text{(number of single fiber cross-sections in which k = 9th nearest single fiber cross-sections are present within a distance of a } 20\ \mu\text{m radius from substantially the center of the single fiber cross-section)}}{\text{(the total number of single fiber cross-sections in one SEM image)}} \right\} \times 100.$$

[0141] Single fiber cross-section ($k=9$) nearest neighbor distance ratio (%) was obtained by averaging each value of 100 SEM images.

[0142] Furthermore, when the sample had scrim, the deepest portion of the fiber layer (A) on the cut surface of the sample subjected to the conductive process (i.e., the most scrim-side portion) was used as the observation region, and the fibers constituting the scrim were not observed, and observation was carried out with a scanning electron microscope (SEM, "JSM-5610" manufactured by JEOL, Ltd.). When the sample did not have scrim, a central portion in the thickness direction of the artificial leather in the top cut surface of the sample subjected to the conductive process was defined as the center point of the observation region, and observation was carried out with the SEM.

[0143] Presence of the single-fiber cross-sections within SEM images can be identified regarding presence by performing markings by a person, as shown in FIG. 4. The specific procedures are as follows:

[Step 1]

[0144] In the SEM images (gray), the coordinates of the cross-sections of the fibers were calculated after the red (R) round dots were attached to the fiber cross-sections.

<Detailed Method>

[0145]

- (i) The images were read using OpenCV (cv2 module for Python).
- (ii) Pixels with RGB Rs of 220 or greater and Gs and Bs of 100 or less were extracted.
- (iii) For noise removing, the expansion processing (with `cv2.dilate` at iteration = 2) and shrinkage processing (with `cv2.erode` at iteration = 2) of the detected round dots were performed.
- (iv) The noise-removed images were processed with `cv2.connectedComponentsWithStats` to obtain the center coordinates of the detected round dots, which is the third of the four results to be obtained.
- (v) The above center coordinates were taken as the fiber cross-sectional positions.
- (vi) Further, the distances between specific positions of the coordinates were calculated. When the coordinates of the fiber cross-section A and the fiber cross-section B are defined as (A_x, A_y) and (B_x, B_y) , the two Euclidean distances R are calculated by $R = \sqrt{(A_x - B_x)^2 + (A_y - B_y)^2}$.

[Step 2]

[0146] The Euclidean distance (k-nearest neighbor distance: matrix distance) to the kth nearest fiber cross-section was calculated for all fiber cross-sections.

<Detailed Method>

[0147]

- (i) The distance between the coordinates of the fiber cross-section A and other cross-sections was calculated.
- (ii) The calculated distances were ordered in ascending order.
- (iii) The kth arranged distance was set as the k-nearest neighbor distance.

[Step 3]

[0148] The number of cross-sections with a k-nearest neighbor distance less than or equal to R was divided by the total number of fiber cross-sections, and set as the k-nearest neighbor ratio value in the SEM image.

[0149] It should be noted that when the number of SEM images becomes large, using an image containing teacher data (correct labels) with red (R) round dots on the fiber cross-sections as training data, the positions of the fiber cross-sections may be specified by machine learning (deep learning) which classifies at the pixel level by semantic segmentation using a network FCN (Fully Convolutional Networks) technique (Jonathan Long, Evan Shelhamer, and Trevor Darrel (2015): Fully Convolutional Networks for Semantic Segmentation; In The IEEE Conference on Computer Vision and Pattern Recognition (CVPR)).

(4) Average Diameter (μm) of Single Fibers Constituting Fiber Layer (A)

[0150] The average diameter of the fibers constituting the fiber layer (A) was obtained by capturing a thickness direction cross-section of the fiber layer (A) constituting the artificial leather using a scanning electron microscope (SEM, "JSM-5610" manufactured by JEOL, Ltd.) at a magnification of 1500-fold to obtain 10 SEM images, randomly selecting 100 fibers in a thickness direction cross-section of the artificial leather, measuring the diameters of the cross-sections of the single fibers, and determining the arithmetic average value of the 100 measured values.

[0151] When the observed shape of the cross-section of a single fiber was not circular, the distance between the outer circumferences on a straight line perpendicular to the middle point of the longest diameter of the single fiber cross section was taken as the fiber diameter.

[0152] FIG. 2 is a conceptual diagram detailing the method for determining fiber diameter. For example, when the cross-section A of the fiber is elliptical, as in FIG. 2, the outer peripheral distance c on the straight line b orthogonal to the midpoint p of the longest diameter a of the cross-section A in the observation image is defined as the fiber diameter.

(5) Calculation of texture (stiffness)

[0153] Samples were cut into 20 cm $\times$ 20 cm squares to obtain measurement samples. The measurement samples were placed on a horizontal plane, the vertices of the square were designated as A, B, C, and D, and the vertices A and C facing each other on the diagonal line were overlapped. Vertex A was placed on a horizontal plane, and vertex C is superimposed onto vertex A. Vertex C was then gradually moved away from the vertex A along the diagonal AC in a state in which it was brought into contact with the measurement sample, the point at which vertex C separated from the measurement sample plane was defined as point E, and the distance between point E and vertex C was defined as stiffness 1. Stiffness 2 was measured by the same procedure as described above replacing vertex A with vertex B and vertex C with vertex D. The arithmetic mean of stiffness 1 and stiffness 2 was taken as the texture (stiffness) of the sample. Note that when the artificial leather had a single-layer structure, an average value for ten samples was defined as the texture (stiffness). When the artificial leather had a two-layer structure or a three-layer structure, an average value for five samples with the fiber layer (A) constituting the artificial leather facing upwards and five samples measured with the fiber layer (A) facing downward was defined as the texture (stiffness).

(6) Crease Recovery (Crease Recovery Rate)

[0154] Based on the description of JIS L1059-1:2009 "Methods for Evaluating Crease Recovery of Textiles - Part 1: Measurement of Recovery from Horizontal Creasing" and using a 10 N loading device, when the artificial leather had a single-layer structure, the crease recovery angles of ten samples were measured, calculated was performed by the formula described in "Calculation of Crease Recovery Angle and Crease Recovery Rate", and the average value of the ten samples was defined as the crease recovery (crease recovery rate). When the artificial leather had a two-layer structure or a three-layer structure, the average value of five samples measured with the fiber layer (A) constituting the artificial leather facing upwards and five samples measured with the fiber layer (A) facing downwards was defined as the crease recovery (crease recovery rate). A crease recovery rate of 60% or more was considered suitable.

(7) Nap Texture

[0155] A total of 20 evaluators including 10 adult males and 10 adult females each in good health performed visual and sensory evaluation of the samples across seven grades according to the following criteria, and the most common evaluation was nap texture. A brushed texture of grade 3.0 to 7.0 was considered suitable (pass).

Grade 7: Nap texture was very strong and appearance was very good.

Grade 6: Evaluation between Grade 7 and Grade 5.

Grade 5: Nap texture was strong and appearance was good.

Grade 4: Evaluation between the Grade 5 and Grade 3.

Grade 3: There was a brushed texture and appearance was sufficient.

Grade 2: Evaluation between Grade 3 and Grade 1.

Grade 1: Nap texture was absent and appearance was poor.

[0156] Note that the average value for 10 samples was set as the brushed texture grade.

(8) Ratio of PU Resin to Fiber Sheet

[0157] The adhesion ratio of the PU resin to the fiber sheet was measured by the following method.

[0158] The mass of the fiber sheet before PU resin impregnation was defined as A(g). The fiber sheet was impregnated with a PU resin dispersion and then heated and dried using a pin tenter dryer at 130 °C, subsequently submerged in hot water heated to 90 °C and then dried to obtain a fiber sheet filled with PU resin (hereinafter, also referred to as a "resin filled fiber sheet"). The mass of the resin filled fiber sheet was defined as B1(g). The ratio (C1) of the PU resin was calculated by the following formula.

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

(9) Average Primary Particle Size of PU Resin in PU Resin Dispersion

[0159] Average primary particle size was measured with a laser diffraction particle size distribution measuring device ("LA-920", manufactured by HORIBA, Ltd.) according to the measuring manual of the device, and the average diameter was taken as the average primary particle diameter.

(10) Degree of Saponification of Hot-Water-Soluble Resin Fine Particles Contained in the PU Resin Dispersion

[0160] The degree of saponification was measured in accordance with the JIS K6726 (1994) 3.5 standard.

(11) Degree of Polymerization of Hot-Water-Soluble Resin Fine Particles Contained in PU Resin Dispersion

[0161] The degree of polymerization was measured in accordance with the JIS K6726 (1994) 3.7 standard.

(12) Average Particle Diameter (μm) of Hot-Water-Soluble Resin Fine Particles Contained in PU Resin Dispersion

[0162] Using "NL-05", manufactured by Mitsubishi Chemical Co., Ltd., as the fine particles, size reduction of the hot water-soluble resin fine particles was measured according to the method described in Japanese Unexamined Patent Publication (Kokai) No. 07-82384.

(13) Turbulence of Water Streams Discharged from Nozzles in Water Stream Dispersion Treatment

[0163] The turbulence of the water streams discharged from the nozzles in the water stream dispersion treatment was measured by the following method.

[0164] The water streams discharged from the nozzles were captured with a single-lens camera ("D600" manufactured by Nikon Corporation) fitted with a telecentric lens ("S5LPJ007/212" manufactured by Sill Optics GmbH & Co.KG) to obtain image data. The image data was output to a PC, water streams in the range of 25 mm to 35 mm from the nozzle discharge port were removed, and the water stream diameter was measured for each single pixel row (approximately 6 μm) in the width direction of the water streams. The average diameter W and standard deviation σ of the water streams

in the range of 25 mm to 35 mm from the discharge ports of the nozzles was calculated from all of the measured data, and the turbulence was calculated by the following equation.

$$\text{Turbulence (\%)} = \sigma \text{ (mm)} / W \text{ (mm)} \times 100$$

[0165] Note that the turbulence is the average value of the values obtained from five sets of image data.

[Example 1]

[0166] Polyethylene terephthalate obtained by copolymerizing 8 mol% of 5-sulfoisophthalic acid sodium was used as the sea component, and polyethylene terephthalate was used as the island component, and a sea-island type conjugate fiber having an island number of 16 islands/lf and an average fiber diameter of 18 μm was obtained at a composite ratio of 20% by mass of sea component and 80% by mass of island component. The obtained sea-island composite fibers were cut to a fiber length of 51 mm to form a staple, and a fiber web was formed through a card and a cross-lapper, and a fiber sheet was obtained by needle-punch processing. The obtained fiber sheet was hot-air dried using a hot-air dryer at 150 °C for 2 minutes to obtain a single layer of fiber sheet having a basis weight of 600 g/m².

[0167] The obtained fiber sheet was immersed in an aqueous sodium hydroxide solution having a concentration of 50 g/L heated to a temperature of 50 °C, subjected to treatment for 60 minutes, and subjected to a sea component dissolution to remove the sea component of the sea-island composite fibers. The average diameter of the single fibers of the fibers constituting the fiber sheet after sea component dissolution was 4 μm .

[0168] Next, high-speed water streams were discharged from the upper layer side at 4 MPa and 3 MPa pressures from the lower layer side using straight stream injection nozzles having a nozzle hole interval of 0.25 mm, a turbulence of 7%, a hole diameter of 0.10 mm, and three rows of nozzle holes to promote the formation of single fibers of the fibers constituting the fiber bundle.

[0169] Thereafter, the above fiber sheet was impregnated with an impregnation solution containing 9.0 wt%, as a quantity (% by mass of solid content) in the impregnation solution, of a polyether-based aqueous dispersion PU dispersion "AE-12" (manufactured by Nikka Chemical Co., Ltd.) (solid concentration: 35% by mass) having an average primary particle diameter of 0.3 μm , 3.0 wt%, as a quantity (% by mass of solid content) of an anhydrous sodium sulfate as an impregnation aid, and PVA resin fine particles "NL-05" (manufactured by Mitsubishi Chemical Co., Ltd.) having an average particle diameter of 3 μm , and thereafter, the impregnated sheet wet-hot coagulated at 100 °C for 5 minutes and hot air dried at 130 °C for 5 minutes using a hot air dryer.

[0170] The dried sheet was then immersed in hot water heated to 95 °C, thereby extracting and removing the impregnated anhydrous sodium sulfate and PVA resin fine particles to obtain a sheet-like material filled with a water-dispersed PU resin. The ratio of the water-dispersed PU resin to the total mass of fibers of this sheet was 30% by mass.

[0171] Thereafter, using a slicer machine having an endless band knife, the sheet-like material was sliced in half horizontally, and the surface which was not sliced was subjected to brushing using a #400 emery paper, and then dyed with a blue disperse dye having a dye density of 5.0% owf ("BlueFBL" manufactured by Sumitomo Chemical Co., Ltd.) for 15 minutes using a jet dyeing machine at 130 °C, followed by reduction cleaning. Thereafter, it was dried using a hot air dryer at 100 °C for 5 minutes to obtain a single layer of artificial leather.

[Example 2]

[0172] An artificial leather was obtained in the same manner as in Example 1, except that the water pressure from the upper layer side in the water stream dispersion treatment was changed to 4.0 MPa

[Example 3]

[0173] An artificial leather was obtained in the same manner as in Example 2, except that the ratio of PU resin to fiber sheet was 44% by mass.

[Example 4]

[0174] An artificial leather was obtained in the same manner as in Example 2, except that the ratio of PU resin to fiber sheet was 47% by mass.

[Example 5]

[0175] An artificial leather was obtained in the same manner as in Example 2, except that the ratio of PU resin to fiber sheet was 17% by mass.

[Example 6]

[0176] An artificial leather was obtained in the same manner as in Example 2, except that after PU resin impregnation, wet-heat treatment was carried out under the conditions of a steam temperature of 110 °C and a treatment time of 3 minutes, and microwave treatment was carried out under the conditions of a microwave output of 10 kW and a treatment time of 3 minutes.

[Example 7]

[0177] An artificial leather was obtained in the same manner as in Example 2, except that PVA fibers were combined with the sea-island cut fibers, and the ratio of the PVA fibers to the total fiber content was 10% by mass.

[Example 8]

[0178] An artificial leather was obtained in the same manner as in Example 2, except that PVA fibers were combined with the sea-island cut fibers, and the ratio of the PVA fibers to the total fiber content was 18% by mass.

[Example 9]

[0179] An artificial leather was obtained in the same manner as in Example 2, except that PVA fibers were combined with the sea-island cut fibers, and the ratio of the PVA fibers to the total fiber content was 25% by mass.

[Example 10]

[0180] An artificial leather was obtained in the same manner as in Example 2, except that PVA fibers were combined with the sea-island cut fibers, and the ratio of the PVA fibers to the total fiber content was 35% by mass.

[Example 11]

[0181] An artificial leather was obtained in the same manner as in Example 2, except that in the water stream dispersion treatment, the nozzle hole interval was changed to 0.50 mm and the number of rows of nozzle holes was changed to 2.

[Example 12]

[0182] An artificial leather was obtained in the same manner as in Example 2, except that in the water stream dispersion treatment, the nozzle hole interval was changed to 0.50 mm and the number of rows of nozzle holes was changed to 1.

[Example 13]

[0183] An artificial leather was obtained in the same manner as in Example 2, except that in the water stream dispersion treatment, the nozzle hole interval was changed to 0.90 mm and the number of rows of nozzle holes was changed to 1.

[Example 14]

[0184] An artificial leather was obtained in the same manner as in Example 1, except that in the water stream dispersion treatment, the nozzle hole interval was changed to 0.50 mm, the nozzle hole diameter was changed to 0.15 mm, and the number of rows of nozzle holes was changed to 2.

[Example 15]

[0185] An artificial leather was obtained in the same manner as in Example 1, except that in the water stream dispersion treatment, the nozzle hole interval was changed to 0.50 mm, the nozzle hole diameter was changed to 0.22 mm, and the number of rows of nozzle holes was changed to 2.

[Example 16]

[0186] An artificial leather was obtained in the same manner as Example 2, except that after PU resin impregnation, wet-heat treatment was carried out under the conditions of a steam temperature of 110 °C and a treatment time of 3 minutes, microwave treatment was carried out under the conditions of a microwave output of 10 kW and a treatment time of 3 minutes, PVA fibers were combined with the sea-island cut fibers, and the ratio of the PVA fibers to the total fiber content was 10% by mass.

[Example 17]

[0187] An artificial leather was obtained in the same manner as Example 2, except that after PU resin impregnation, wet-heat treatment was carried out under the conditions of a steam temperature of 110 °C and a treatment time of 3 minutes, microwave treatment was carried out under the conditions of a microwave output of 10 kW and a treatment time of 3 minutes, PVA fibers were combined with the sea-island cut fibers, the ratio of the PVA fibers to the total fiber content was 10% by mass, and the turbulence of the water stream dispersion treatment was set to 13%.

[Example 18]

[0188] An artificial leather was obtained in the same manner as in Example 2, except that the turbulence of the water stream dispersion treatment was set to 13%.

[Example 19]

[0189] An artificial leather was obtained in the same manner as in Example 2, except that the turbulence of the water stream dispersion treatment was set to 11%.

[Example 20]

[0190] An artificial leather was obtained in the same manner as in Example 2, except that the turbulence of the water stream dispersion treatment was set to 16%.

[Example 21]

[0191] An artificial leather was obtained in the same manner as in Example 2, except that the average particle diameter of the PVA particles in PU resin impregnation was set to 5 μm and the turbulence of the water stream dispersion treatment was set to 13%.

[Example 22]

[0192] An artificial leather was obtained in the same manner as in Example 2, except that the average particle diameter of the PVA particles in PU resin impregnation was set to 7 μm and the turbulence of the water stream dispersion treatment was set to 13%.

[Example 23]

[0193] An artificial leather was obtained in the same manner as in Example 2, except that PVA fibers were combined with the sea-island cut fibers, and the ratio of PVA fibers to the total fiber content was 45% by mass.

[Example 24]

[0194] An artificial leather was obtained in the same manner as Example 1 or 2, except that the water pressure from the upper layer side in the water stream dispersion treatment was changed to 12.0 MPa.

[Comparative Example 1]

[0195] An artificial leather was obtained in the same manner as in Example 2, except that PVA resin fine particles were not added to the PU resin impregnation liquid.

[Comparative Example 2]

[0196] An artificial leather was obtained in the same manner as in Example 2, except that the PVA resin fine particles were not added to the PU resin impregnation liquid and the turbulence of the water stream dispersion treatment was set to 13%.

[Comparative Example 3]

[0197] An artificial leather was obtained in the same manner as Example 2, except that the water stream dispersion treatment was not performed, PVA resin fine particles were not added to the PU resin impregnation liquid, and after PU resin impregnation, wet-heat treatment was carried out under the conditions of a steam temperature of 110 °C and a treatment time of 3 minutes, and microwave treatment was carried out under the conditions of a microwave output of 10 kW and a treatment time of 3 minutes.

[Comparative Example 4]

[0198] An artificial leather was obtained in the same manner as in Example 2, except that the water stream dispersion treatment was not performed.

[Comparative Example 5]

[0199] An artificial leather was obtained in the same manner as Example 2, except that PVA resin fine particles were not added to the PVA impregnation solution, PVA fibers were combined with the sea-island cut fibers, and the ratio of PVA fibers to the total fiber content was 10% by mass.

[Comparative Example 6]

[0200] An artificial leather was obtained in the same manner as in Example 2, except that the water pressure from the upper layer side in the water stream dispersion treatment was changed to 0.7 MPa.

[Comparative Example 7]

[0201] An artificial leather was obtained in the same manner as in Example 2, except that the ratio of PU resin to fiber sheet was 58% by mass.

[Comparative Example 8]

[0202] An artificial leather was obtained in the same manner as in Example 2, except that the ratio of PU resin to fiber sheet was 13% by mass.

[Comparative Example 9]

[0203] An artificial leather was obtained in the same manner as in Example 2, except that the average particle diameter of PVA particles in PU resin impregnation was set to 10 μm, the turbulence of the water stream dispersion treatment was set to 13%, and the ratio of the PU resin to fiber sheet was 13% by mass.

[0204] The results of Examples 1 to 24 and Comparative Examples 1 to 9 are shown in Table 1 below.

[Table 1-11]

		Conditions							Results			Effects				
	Water Stream Dispersion Treatment	PVA Fine Particles Added in PU Resin Impregnation	Wet-Heat Treatment and Microwave Treatment Times	Ratio of PVA Fibers to Total Fiber Content	Turbulence of Water Stream Dispersion Treatment	Nozzle Hole Interval in Water Stream Dispersion Treatment	Hole Diameter of High-Pressure Water Discharge Nozzle in Water Stream Dispersion Treatment	Row Number of High-Pressure Water Discharge Nozzle in Water Stream Dispersion Treatment	Water Pressure in Water Stream Dispersion Treatment	Ratio of PU Resin to Fiber Sheet	Cross-Sectional PU Area Ratio	Standard Deviation of PU Area Ratio	k-Near-est Neighbor Ratio Value	Crease Recovery Rate	Stiffness	Brushed Texture
		[μm]	[min]	[%]		[mm]	[mm]	[Rows]	[MPa]	[mass%]	[%]	[%]		[%]	[cm]	
Ex 1	Yes	3	N/A	N/A	7	0.25	0.10	3	5.5	30	20	16	50	75	18	4
Ex 2	Yes	3	N/A	N/A	7	0.25	0.10	3	4.0	30	20	18	65	80	20	4
Ex 3	Yes	3	N/A	N/A	7	0.25	0.10	3	4.0	44	28	23	65	85	27	3
Ex 4	Yes	3	N/A	N/A	7	0.25	0.10	3	4.0	47	28	24	64	85	27	3
Ex 5	Yes	3	N/A	N/A	7	0.25	0.10	3	4.0	17	16	13	64	65	16	5
Ex 6	Yes	3	3	N/A	7	0.25	0.10	3	4.0	30	20	13	65	87	16	4
Ex 7	Yes	3	N/A	10	7	0.25	0.10	3	4.0	30	19	14	57	82	14	4
Ex 8	Yes	3	N/A	18	7	0.25	0.10	3	4.0	30	21	14	54	82	13	3
Ex 9	Yes	3	N/A	25	7	0.25	0.10	3	4.0	30	21	13	49	83	12	3
Ex 10	Yes	3	N/A	35	7	0.25	0.10	3	4.0	30	20	13	42	83	11	3
Ex 11	Yes	3	N/A	N/A	7	0.50	0.10	2	4.0	30	20	21	70	81	22	3
Ex 12	Yes	3	N/A	N/A	7	0.50	0.10	1	4.0	30	20	21	70	81	22	3
Ex 13	Yes	3	N/A	N/A	7	0.90	0.10	1	4.0	30	21	23	79	83	24	3
Ex 14	Yes	3	N/A	N/A	7	0.50	0.15	2	4.0	30	19	21	69	81	22	3

(continued)

		Conditions							Results			Effects				
	Water Stream Dispersion Treatment	PVA Fine Particles Added in PU Resin Impregnation	Wet-Heat Treatment and Microwave Treatment Times	Ratio of PVA Fibers to Total Fiber Content	Turbulence of Water Stream Dispersion Treatment	Nozzle Hole Interval in Water Stream Dispersion Treatment	Hole Diameter of High-Pressure Water Discharge Nozzle in Water Stream Dispersion Treatment	Row Number of High-Pressure Water Discharge Nozzle in Water Stream Dispersion Treatment	Water Pressure in Water Stream Dispersion Treatment	Ratio of PU Resin to Fiber Sheet	Cross-Sectional PU Area Ratio	Standard Deviation Of PU Area Ratio	k-Near-est Neighbor Ratio Value	Crease Recovery Rate	Stiffness	Brushed Texture
		[μm]	[min]	[%]		[mm]	[mm]	[Rows]	[MPa]	[mass%]	[%]	[%]		[%]	[cm]	
Ex 15	Yes	3	N/A	N/A	7	0.50	0.22	2	4.0	30	20	21	70	81	22	3
Ex 16	Yes	3	3	10	7	0.25	0.10	3	4.0	30	20	12	58	90	10	5
Ex 17	Yes	3	3	10	13	0.25	0.10	3	4.0	30	20	10	45	92	9	7
Ex 18	Yes	3	N/A	N/A	13	0.25	0.10	3	4.0	30	19	12	49	78	16	6
Ex 19	Yes	3	N/A	N/A	11	0.25	0.10	3	4.0	30	20	14	45	78	17	5
Ex 20	Yes	3	N/A	N/A	16	0.25	0.10	3	4.0	30	20	10	43	77	15	6
Ex 21	Yes	5	N/A	N/A	13	0.25	0.10	3	4.0	30	21	16	46	78	14	5
Ex 22	Yes	7	N/A	N/A	13	0.25	0.10	3	4.0	30	20	16	45	78	14	5
Ex 23	Yes	3	N/A	45	7	0.25	0.10	3	4.0	30	20	13	40	81	21	3
Ex 24	Yes	3	N/A	N/A	7	0.25	0.10	3	12.0	30	19	18	8	80	10	5
Comp Ex 1	Yes	N/A	N/A	N/A	7	0.25	0.10	3	4.0	30	21	33	66	80	>28	2
Comp Ex 2	Yes	N/A	N/A	N/A	13	0.25	0.10	3	4.0	30	21	28	51	78	>28	4

(continued)

		Conditions							Results				Effects			
	Water Stream Dispersion Treatment	PVA Fine Particles Added in PU Resin Impregnation	Wet-Heat Treatment and Microwave Treatment Times	Ratio of PVA Fibers to Total Fiber Content	Turbulence of Water Stream Dispersion Treatment	Nozzle Interval in Water Stream Dispersion Treatment	Hole Diameter of High-Pressure Water Discharge Nozzle in Water Stream Dispersion Treatment	Row Number of High-Pressure Water Discharge Nozzle in Water Stream Dispersion Treatment	Water Pressure in Water Stream Dispersion Treatment	Ratio of PU Resin to Fiber Sheet	Cross-Sectional PU Area Ratio	Standard Deviation of PU Area Ratio	k-Near-est Neighbor Ratio Value	Crease Recovery Rate	Stiffness	Brushed Texture
		[μm]	[min]	[%]		[mm]	[mm]	[Rows]	[MPa]	[mass%]	[%]	[%]	[%]	[%]	[cm]	
Comp Ex 3	No	N/A	3	N/A	-	-	-	-	-	30	19	36	87	83	>28	2
Comp Ex 4	No	3	N/A	N/A	-	-	-	-	-	30	20	36	90	85	>28	2
Comp Ex 5	No	N/A	N/A	10	-	-	-	-	-	30	21	34	84	83	>28	2

[Table 1-2]

Comp Ex 6	Yes	3	N/A	N/A	7	0.25	0.10	3	0.7	30	21	27	81	85	>28	2
Comp Ex 7	Yes	3	N/A	N/A	7	0.25	0.10	3	4.0	58	33	34	64	85	>28	2
Comp Ex 8	Yes	3	N/A	N/A	7	0.25	0.10	3	4.0	13	12	11	64	58	14	5
Comp Ex 9	Yes	10	N/A	N/A	13	0.25	0.10	3	4.0	13	13	27	50	58	14	4

[0205] From these results, it can be seen that, in each of the Examples, the polyurethane area ratio (cross-sectional PU resin area ratio) in the thickness direction cross-section was 15% to 30%, the standard deviation of the cross-sectional PU resin area ratio was 25% or less, and the PU resin and the single fibers were distributed in a specific structure, whereby an artificial leather having both suitable texture (stiffness) and crease recovery (crease recovery rate) was obtained.

[Industrial Applicability]

[0206] Since the artificial leather according to the present invention is excellent in both texture (stiffness) and crease recovery (crease recovery rate), it can be suitably used for the upholstery or interior material of seats for interior, automobiles, aircrafts, railway vehicles, etc., garment products, or the like. Specifically, the artificial leather of the present embodiment can also be suitably used as an upholstery or interior material requiring an elegant appearance, for example, a surface material of furniture, chairs, and walls, seats, ceilings, and interiors of vehicles such as automobiles, trains, and aircrafts, a clothing material of a part of shirts and jackets, the uppers of shoes such as casual shoes, sports shoes, men's shoes, women's shoes, various trims, bags, belts, wallets, etc., or an industrial material of wiping cloths, abrasive cloths, and CD curtains..

[Description of Numerical References]

[0207]

1 fiber sheet

11 scrim (optional)

12 fiber layer (A)

13 fiber layer (B)

A fiber cross-section when cross-section is oblong

a longest diameter of cross-section A

b straight line passing through midpoint p of longest diameter a and orthogonal to longest diameter a

c distance between outer circumferences on straight line b

p midpoint of longest diameter a

MD machine direction

CD width (warp) direction

t thickness of artificial leather

Claims

1. An artificial leather comprising a fiber sheet and a polyurethane resin, wherein the fiber sheet includes at least a fiber layer (A) constituting a first outer surface of the artificial leather, a cross-sectional polyurethane resin area ratio in a thickness direction cross-section of the fiber layer (A) is 15% to 30%, and standard deviation of the cross-sectional polyurethane resin area ratio of the fiber layer (A) is 25% or less.
2. The artificial leather according to claim 1, wherein a k-nearest neighbor ratio value ($k = 9$, radius $r = 20 \mu\text{m}$) between single-fiber cross-sections constituting the fiber layer (A) in a thickness direction cross-section of the artificial leather is 10% to 80%.
3. The artificial leather according to claim 1 or 2, wherein the fiber sheet has a two-or-more-layer structure composed of the fiber layer (A) constituting the first outer surface and a scrim and/or fiber layer (B) contacting the fiber layer (A).

4. The artificial leather according to any one of claims 1 to 3, wherein the average diameter of single fibers constituting the fiber layer (A) is 1.0 μm to 8.0 μm .
- 5 5. The artificial leather according to any one of claims 1 to 4, wherein the polyurethane resin is a water-dispersed polyurethane resin.
6. The artificial leather according to any one of claims 1 to 5, wherein an adhesion rate of the polyurethane resin to the fiber sheet is 15% by mass to 50% by mass.
- 10 7. The artificial leather according to any one of claims 1 to 6, having a stiffness of 28 cm or less.
8. The artificial leather according to any one of claims 1 to 7, wherein the fiber sheet has a crease recovery rate, as measured in accordance with JIS L1059-1:2009 "Methods for Evaluating Crease Recovery of Textiles - Part 1: Measurement of Recovery from Horizontal Creasing", of 60% or greater.
- 15 9. The artificial leather according to any one of claims 1 to 8, wherein the fiber sheet is composed of polyester fibers.
10. A production method of the artificial leather according to any one of claims 1 to 9, the method comprising the steps of:
20 forming a fiber web from sea-island cut fibers, thereafter performing needle-punch processing, and de-sea treating the obtained fiber sheet to obtain a fiber sheet in which island component single fibers are exposed, and subjecting the obtained fiber sheet to water stream dispersion treatment to obtain a fiber sheet in which the single fibers are dispersed.
- 25 11. The production method according to claim 10, further comprising the step of:
impregnating the fiber sheet in which the single fibers are dispersed with a water-dispersed polyurethane resin dispersion containing hot-water-soluble resin fine particles.
- 30 12. The production method according to claim 10 or 11, further comprising the step of:
after impregnation with the water-dispersed polyurethane resin dispersion and performing wet-heat treatment, affixing the polyurethane resin to the fibers by drying with microwaves to obtain a sheet-like material in which the polyurethane resin is filled.
- 35 13. The production method according to any one of claims 10 to 12, wherein the fiber web contains hot-water-soluble resin fibers.
14. The production method according to claim 13, wherein both the hot-water-soluble resin fine particles and a hot-water soluble resin of the hot-water-soluble resin fibers are a polyvinyl alcohol resin.
- 40 15. The production method according to any one of claims 10 to 14, wherein the water stream dispersion treatment is carried out using a plurality of nozzles having a nozzle hole interval of 1.0 mm or less and a nozzle hole diameter of 0.05 mm to 0.30 mm.
- 45 16. The production method according to any one of claims 10 to 15, wherein the water stream dispersion treatment is carried out using a plurality of nozzles which discharge water streams having a turbulence of 10% or more.
17. The production method according to any one of claims 11 to 16, wherein a solid content concentration of the water-dispersed polyurethane resin dispersion is 10 wt% to 35 wt%.
- 50 18. The method according to any one of claims 11 to 17, wherein the content of the hot-water-soluble resin fine particles in the water-dispersed polyurethane resin dispersion is 1 wt% to 20 wt%.

FIG. 1

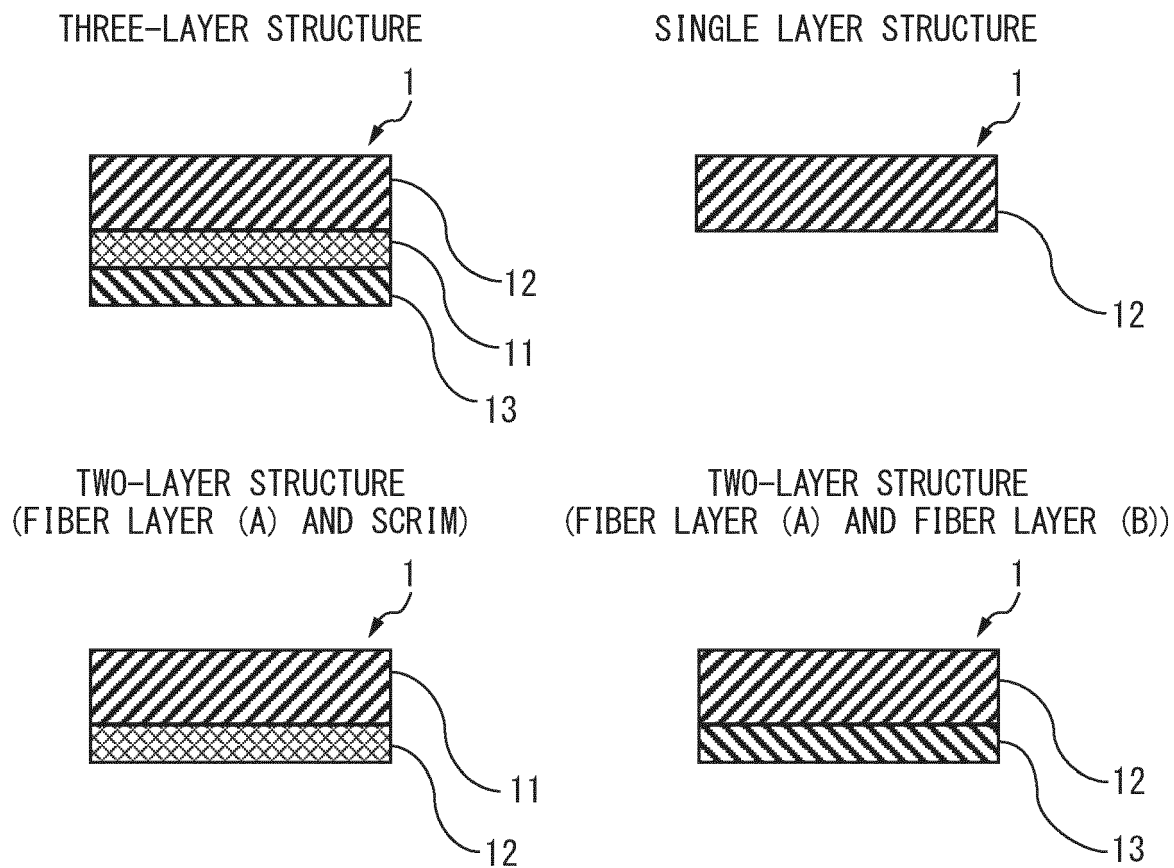


FIG. 2

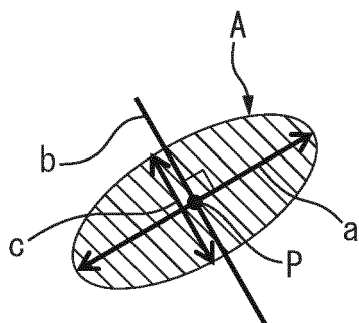


FIG. 3

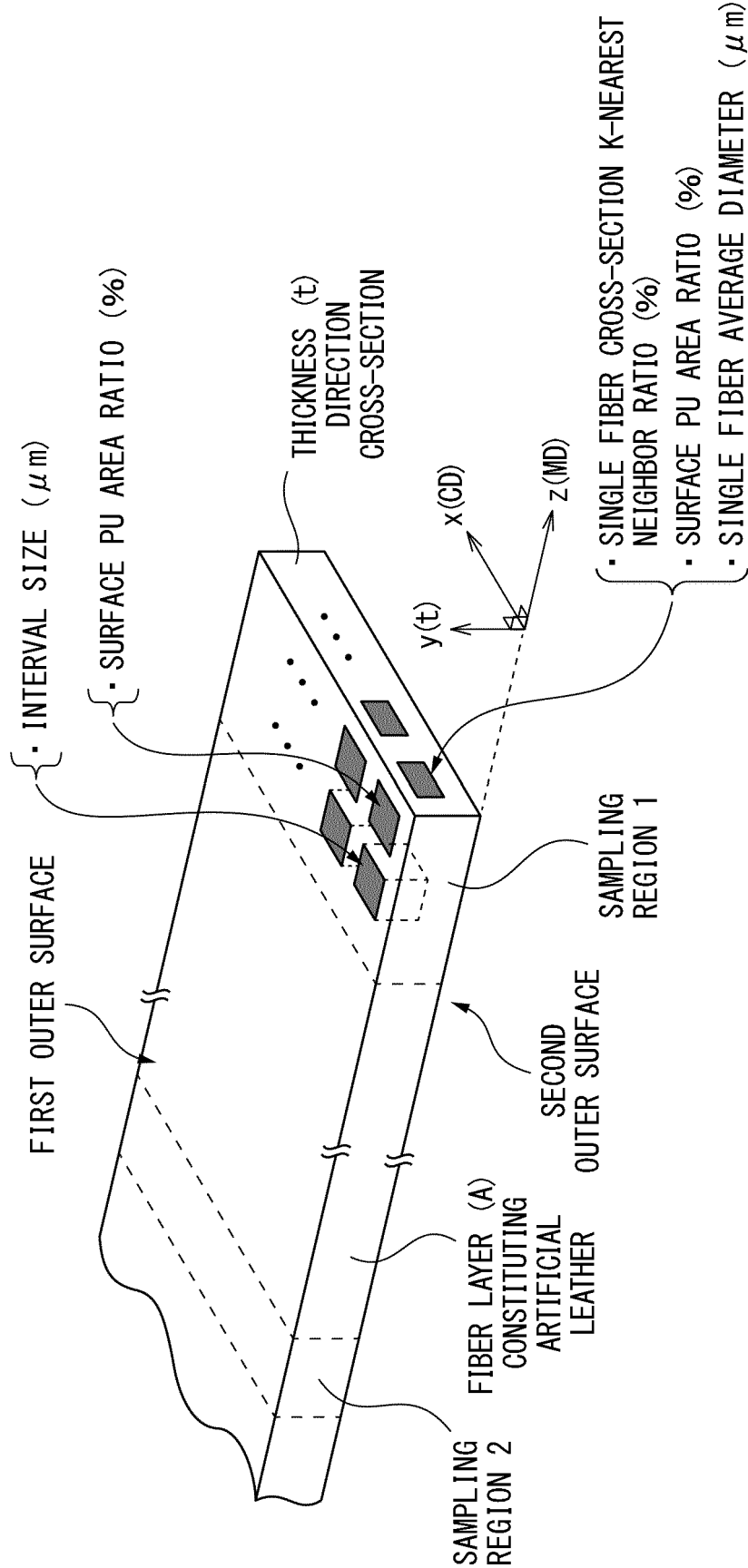


FIG. 4

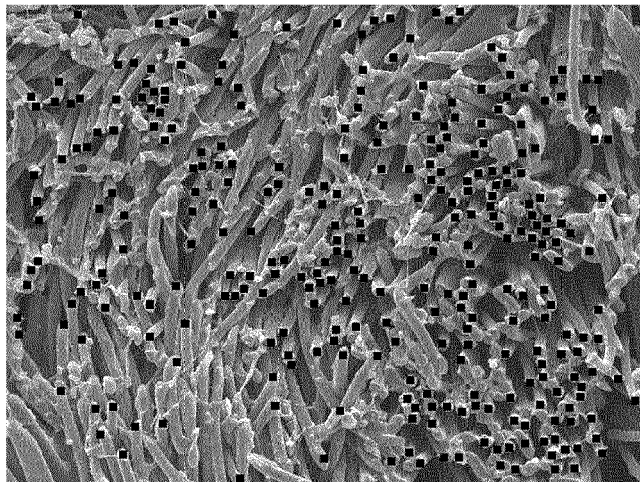
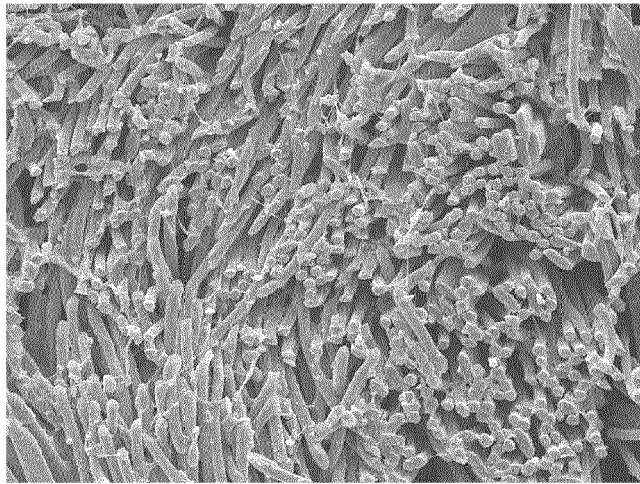


FIG. 5

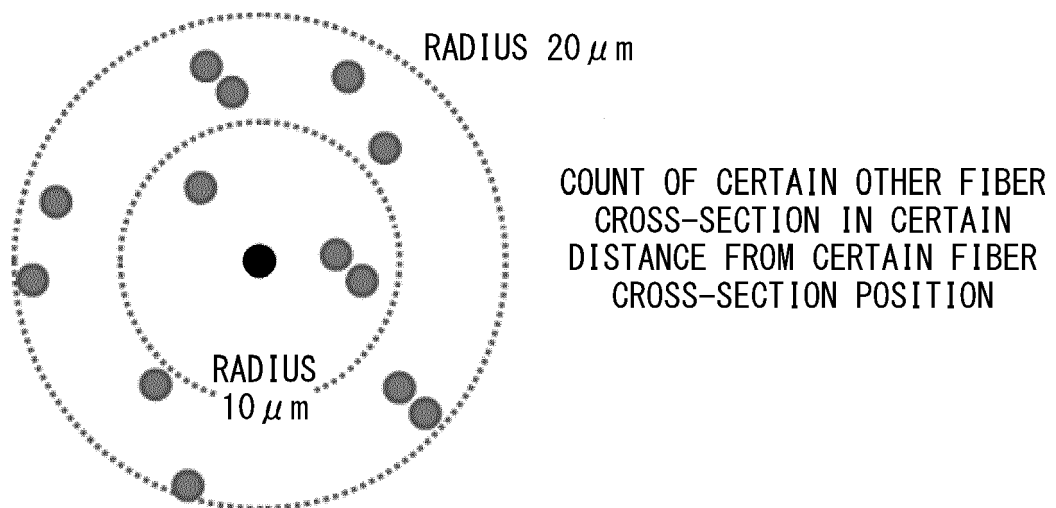
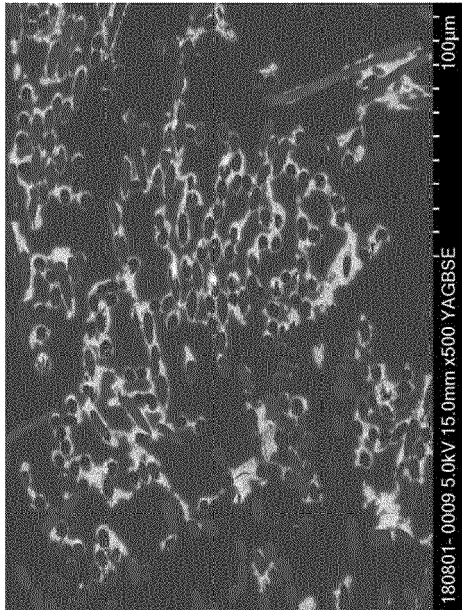
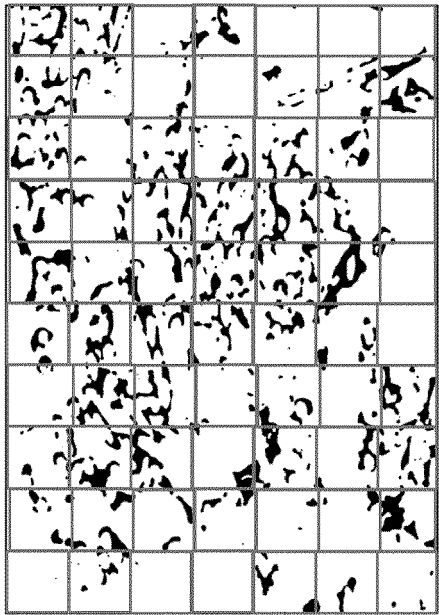


FIG. 6



BINARIZATION



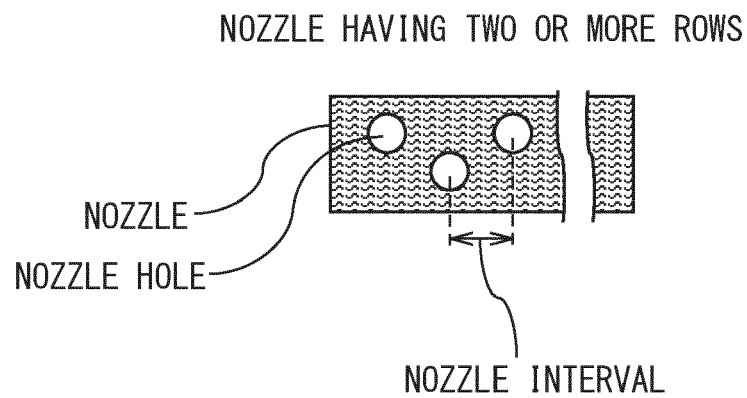
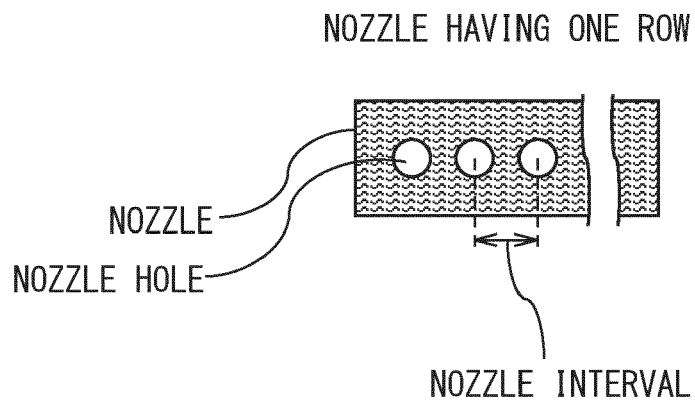
COMPARTMENT DIVIDED IMAGE

STANDARD DEVIATION $\sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (X_i - \bar{X})^2}$

STANDARD DEVIATION OF
URETHANE AREA % TARGETING
ALL COMPARTMENTS

- n : COMPARTMENT COUNT (DIVISION COUNT)
- X_i : URETHANE AREA % OF iTH COMPARTMENT
- X : AVERAGE VALUE OF URETHANE AREA % OF ALL COMPARTMENTS

FIG. 7





EUROPEAN SEARCH REPORT

Application Number
EP 20 20 4683

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EPO FORM 1503 03.82 (P04C01)

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			D06N
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		25 March 2021	Rella, Giulia
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 20 20 4683

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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25-03-2021

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