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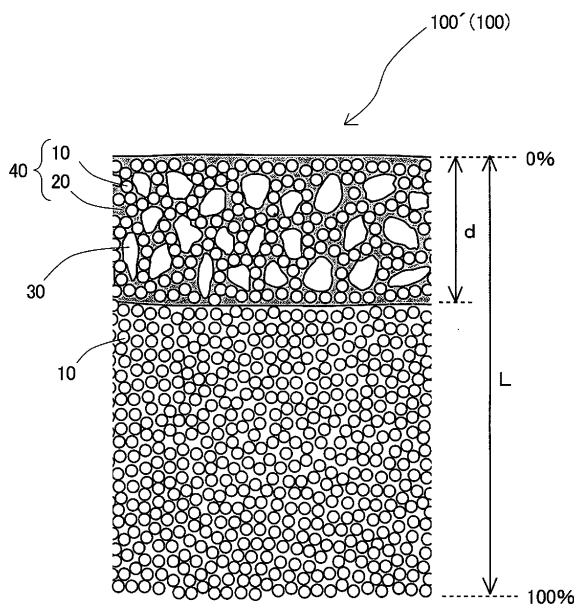
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(54) **NUBUCK-LIKE ARTIFICIAL LEATHER, AND METHOD FOR PRODUCING NUBUCK-LIKE ARTIFICIAL LEATHER**

(57) Provided is a nubuck-like artificial leather having a moist feel and nap close to those of natural leather, and superior abrasion resistance. A nubuck-like artificial leather 100 is provided with a flexible sheet 100' including a base material containing tangled fibers 10 to which a resin 20 is added. Voids 30 are formed in the flexible sheet 100', the voids 30 being surrounded by cross-sections of the fibers 10 as viewed in a cross-section parallel

to a thickness direction of the flexible sheet 100', and the voids being held by the fibers 10 being bonded together by the resin 20. In a region having a unit area of the cross-section of the flexible sheet 100', a ratio (A/B) of a cross-sectional area (A) of a continuous structure 40 formed by the fibers 10 being bonded together by the resin 20 to a cross-sectional area (B) of the voids is 15/85-90/10.

[FIG.1]



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a nubuck-like artificial leather including a flexible sheet obtained by adding a resin to a base material containing tangled fibers, and a method for producing the nubuck-like artificial leather.

BACKGROUND ART

10 **[0002]** Nubuck-like artificial leather is desired to have tactile feel and texture close to those of natural leather. Natural leather contains a moderate amount of voids, which structure provides a characteristic tactile feel (a smooth, soft, and supple feel called "moist feel") and texture (nap). It is considered that nubuck-like artificial leather that has a structure (voids) similar to that of natural leather can have a moist feel and nap similar to those of natural leather. Meanwhile, natural leather has a drawback that it easily wears, and therefore, nubuck-like artificial leather is desired to have superior
15 abrasion resistance that cannot be achieved by natural leather. To this end, suitable materials should be selected for nubuck-like artificial leather.

[0003] As a technique of producing nubuck-like artificial leather; commonly known are a wet method of immersing a fiber sheet impregnated with a solvent-based polyurethane resin in a solidification liquid so that the solvent-based polyurethane resin is solidified (see, for example, Patent Document 1), and a dry method of drying a fiber sheet impregnated with a water-based polyurethane resin in a gas phase so that the water-based polyurethane resin is solidified
20 (see, for example, Patent Document 2).

[0004] Patent Document 1 describes a method for producing a nubuck-like sheet that includes impregnating a fiber base material with a polycarbonate polyurethane resin, which is a solvent-based polyurethane resin, immersing the resulting fiber base material in an aqueous dimethyl formamide solution so that the polycarbonate polyurethane resin
25 in the fiber base material is solidified, washing the resulting fiber base material in hot water, and drying the resulting fiber base material. According to Patent Document 1, the polycarbonate polyurethane resin does not ooze from the back surface of the sheet, and therefore, the nubuck-like sheet has excellent appearance and texture.

[0005] Patent Document 2 describes a method for producing a nubuck-like sheet that includes impregnating a fiber base material with a W/O urethane resin, which is a water-based polyurethane resin, thermally drying the resulting base material, and subjecting the resulting base material to embossing and raising. According to Patent Document 2, the raising allows for formation of a raised region and a non-raised region on the sheet, resulting in a tactile feel and texture close to those of natural leather.
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CITATION LIST

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PATENT LITERATURE

[0006]

40 Patent Document 1: Japanese Unexamined Patent Application Publication No. H07-42082
Patent Document 2: Japanese Unexamined Patent Application Publication No. H07-60885

SUMMARY OF INVENTION

45 TECHNICAL PROBLEM

[0007] However, the wet method, exemplified by Patent Document 1, and the dry method, exemplified by Patent Document 2, have the following respective problems. In the nubuck-like sheet of Patent Document 1, voids are formed as an empty space where the solvent (aqueous dimethyl formamide solution) has been removed from the solvent-based polyurethane resin. In other words, voids are formed in the solvent-based polyurethane resin. Therefore, when the solvent-based polyurethane resin is worn away from the sheet surface by abrasion, etc., the voids also disappear, easily leading to a deterioration in moist feel and nap. Thus, in the nubuck-like sheet of Patent Document 1, the solvent-based polyurethane resin having voids formed therein is exposed on the sheet surface and is therefore easily worn away. Therefore, the nubuck-like sheet of Patent Document 1 has a problem with its durability.

55 **[0008]** In the nubuck-like sheet of Patent Document 2, the fibers and the water-based polyurethane resin reinforce each other. Therefore, the nubuck-like sheet of Patent Document 2 is superior to a nubuck-like sheet produced by the wet method in terms of durability. However, in the nubuck-like sheet of Patent Document 2, the water-based polyurethane resin has high affinity to fibers, and therefore, easily forms a coating film on the surface of the fiber base material. This

makes it difficult to impart a sufficient moist feel and nap to the nubuck-like sheet.

[0009] Thus, in the conventional art, it is difficult to provide a nubuck-like artificial leather that has a moist feel and nap close to those of natural leather, and at the same time, has high abrasion resistance. With this in mind, the present invention has been made. It is an object of the present invention to provide a nubuck-like artificial leather that has not only a moist feel and nap close to those of natural leather but also superior abrasion resistance, and a method for producing the nubuck-like artificial leather.

SOLUTION TO PROBLEM

[0010] To achieve the above object, a nubuck-like artificial leather according to the present invention, comprises:

a flexible sheet including a base material containing tangled fibers, and a resin added to the base material, wherein

voids are formed in the flexible sheet, the voids being surrounded by cross-sections of the fibers as viewed in a cross-section parallel to a thickness direction of the flexible sheet, and the voids being held by the fibers being bonded together by the resin.

[0011] According to the nubuck-like artificial leather thus configured, voids surrounded by cross-sections of the fibers are formed in the flexible sheet, and in addition, the fibers are bonded together by the resin. Therefore, the voids are distributed in the flexible sheet to a suitable extent and are fixed. Such a structure is similar to that of natural leather. Therefore, the nubuck-like artificial leather thus configured can have a moist feel and nap close to those of natural leather. Furthermore, the fibers in the flexible sheet are reinforced by the resin, and therefore, a strength greater than that of natural leather is provided, resulting in an artificial leather product having superior abrasion resistance.

[0012] In the nubuck-like artificial leather of the present invention, in a region having a unit area of the cross-section of the flexible sheet, a ratio (A/B) of a cross-sectional area (A) of a continuous structure formed by the fibers being bonded together by the resin to a cross-sectional area (B) of the voids is preferably 15/85-90/10.

[0013] According to the nubuck-like artificial leather thus configured, the ratio (A/B) of the cross-sectional area (A) of the continuous structure to the cross-sectional area (B) of the voids is adjusted within a suitable range. Therefore, a well-balanced combination of superior abrasion resistance attributed to the continuous structure that is not provided by natural leather, and a moist feel and nap attributed to the voids that are comparable to those of natural leather, can be provided.

[0014] In the nubuck-like artificial leather of the present invention, the fibers preferably have a mono-fineness of 0.1-0.7 dtex.

[0015] According to the nubuck-like artificial leather thus configured, the fibers have a suitable mono-fineness. Therefore, necessary and sufficient abrasion resistance can be provided, and at the same time, a particularly good nap can be provided.

[0016] In the nubuck-like artificial leather of the present invention, a ratio (a/b) of a length (a) to a diameter (b) of each of the fibers is preferably 2-1700.

[0017] According to the nubuck-like artificial leather thus configured, the ratio (a/b) of the length (a) to the diameter (b) of each of the fibers is adjusted within a suitable range. Therefore, necessary and sufficient abrasion resistance can be provided, and at the same time, a good moist feel and nap can be provided.

[0018] In the nubuck-like artificial leather of the present invention, the resin is preferably at least one selected from the group consisting of polyurethane resins, silicone resins, and acrylic resins.

[0019] According to the nubuck-like artificial leather thus configured, the resin is suitably selected. Therefore, the artificial leather product can have suitable flexibility in addition to superior abrasion resistance.

[0020] In the nubuck-like artificial leather of the present invention, the voids are preferably present in a region of the flexible sheet extending from a front surface of the flexible sheet toward a back surface of the flexible sheet, the region ranging from a 0-15% region to a 0-40% region, where a position of the front surface of the flexible sheet is 0%, and a position of the back surface of the flexible sheet is 100%.

[0021] According to the nubuck-like artificial leather thus configured, the voids are formed in a suitable region in the flexible sheet. Therefore, necessary and sufficient abrasion resistance can be maintained, and at the same time, a good moist feel and nap can be provided.

[0022] In the nubuck-like artificial leather of the present invention, a front surface of the nubuck-like artificial leather preferably has a surface roughness of 0.2-1.55 μm .

[0023] According to the nubuck-like artificial leather thus configured, the surface roughness is adjusted within a suitable range. Therefore, a nubuck-like nap, and smoothness peculiar to artificial leather, can be provided.

[0024] To achieve the above object, a nubuck-like artificial leather production method according to the present invention,

comprising:

an impregnation step of impregnating a base material containing tangled fibers and having a weight of 150-1000 g/m², with 15-40 wt% of a resin with respect to the weight of the base material in terms of solid content; and
 a drying step of drying the base material impregnated with the resin at 80-150°C for 50-1200 sec.

[0025] According to the nubuck-like artificial leather production method of the present invention thus configured, by carrying out the impregnation step and the drying step under the above conditions, voids surrounded by cross-sections of the fibers are formed in the flexible sheet, and in addition, the fibers are bonded together by the resin. As a result, the voids are distributed in the flexible sheet to a suitable extent and are fixed. Such a structure is similar to that of natural leather. Therefore, a moist feel and nap close to those of natural leather can be provided. Furthermore, the fibers in the flexible sheet are reinforced by the resin, and therefore, a strength greater than that of natural leather is provided, resulting in an artificial leather product having superior abrasion resistance.

[0026] The nubuck-like artificial leather production method of the present invention preferably further comprises:

a finishing step of, after the drying step, finishing the base material impregnated with the resin.

[0027] According to the nubuck-like artificial leather production method of the present invention thus configured, by carrying out the finishing step, a moist feel and nap closer to those of natural leather can be provided.

[0028] In the nubuck-like artificial leather production method of the present invention, the drying step is preferably carried out by dry-heat drying or moist-heat drying.

[0029] According to the nubuck-like artificial leather production method of the present invention thus configured, by carrying out dry-heat drying or moist-heat drying on the base material impregnated with the resin, the resin can be reliably solidified in every part including inner parts of the base material, resulting in an artificial leather product having superior strength and abrasion resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0030]

[FIG. 1] FIG. 1 is an illustrative diagram showing a microscopic internal structure of a nubuck-like artificial leather according to the present invention.

[FIG. 2] FIG. 2 is a flowchart showing steps of a method for producing the nubuck-like artificial leather of the present invention.

[FIG. 3] FIG. 3 are SEM images at 1000 times magnification of a cross-section parallel to the thickness direction and the front surface of: (a) the nubuck-like artificial leather of the present invention; (b) a conventional artificial leather; and (c) natural leather.

DESCRIPTION OF EMBODIMENTS

[0031] Environmental awareness has in recent years gained momentum, and therefore, in the textile industry, there has been a demand for environmentally friendly manufacturing technologies. For nubuck-like artificial leather, it is expected that the dry method, in which a solvent is basically not used, will go mainstream instead of the wet method, in which a large amount of a solvent is used. With this in mind, in the present invention, attention has been paid to the dry method as a method for producing a nubuck-like artificial leather. In particular, improvements to the conventional dry method, which has a problem with a moist feel and a nap, have been extensively studied. Embodiments of a nubuck-like artificial leather according to the present invention and a production method therefor will now be described in detail with reference to the accompanying drawings. Note that the present invention is in no way intended to be limited to the embodiments described below.

(Nubuck-like Artificial Leather)

[0032] FIG. 1 is an illustrative diagram showing a microscopic internal structure of a nubuck-like artificial leather 100 according to the present invention. Note that FIG. 1 is not to scale, i.e., the shapes, sizes, positional relationship, etc., of parts shown in FIG. 1 are not the same as the actual ones. The nubuck-like artificial leather 100 includes a flexible sheet 100' that is obtained by impregnating a base material formed of fibers 10 as a base with a resin 20. Note that the nubuck-like artificial leather 100 may be commercially produced in a form in which a lining or the like is attached to the flexible sheet 100'. For the sake of simplicity, the flexible sheet 100' itself without a lining or the like being attached thereto is herein regarded as the nubuck-like artificial leather 100.

[0033] The base material is a nonwoven fabric formed of a plurality of tangled fibers 10. The weight (per unit area) of

the base material is adjusted to 150-1000 g/m². If the weight (per unit area) of the base material is less than 150 g/m², the resin 20 easily passes through the fibers 10 included in the base material. If the weight (per unit area) of the base material is more than 1000 g/m², it is difficult to sufficiently impregnate the base material with the resin 20, i.e., the resin is less likely to be held between the fibers 10 included in the base material. A thickness L of the base material is adjusted to 0.5-3.7 mm. If the thickness L of the base material is less than 0.5 mm, a nubuck-like artificial leather as a final product is less likely to have a moist feel and a nap, i.e., is likely to have paper-like texture. If the thickness L of the base material is more than 3.7 mm, the workability of the base material as an industrial material is likely to deteriorate, leading to problems with its production, such as sewing difficulties, etc. Examples of the fibers 10 in the base material include synthetic fibers, such as polyesters, nylons, acrylic fibers, vinylons, urethanes, etc., semisynthetic fibers, such as acetates, triacetates, Promix, etc., and regenerated fibers, such as rayons, cupra, polynosic, etc. The above fibers may be used alone or in combination as commingled fibers. A material for the fibers 10 is preferably polyester, nylon, acrylic, or rayon in terms of versatility and durability, more preferably polyester, which has superior strength.

[0034] Examples of the resin 20 include polyurethane resins, silicone resins, and acrylic resins. Of these resins, polyurethane resins are preferable. Polyurethane resins are roughly organized into non-water-based polyurethane resins (solvent-based polyurethane resins) and water-based polyurethane resins. Although water-based polyurethane resins are suitably used herein because the present invention is directed to the dry method, non-water-based polyurethane resins for use in the conventional wet method may be used. Note that a method for producing the nubuck-like artificial leather 100 of the present invention using the dry method is described in detail in the section "Method for Producing Nubuck-like Artificial Leather" below. Examples of polyurethane resins include polyether polyurethane resins, polyester polyurethane resins, polycarbonate polyurethane resins, etc. These polyurethane resins may be used alone or in combination. Of these polyurethane resins, polycarbonate polyurethane resins are preferable in terms of abrasion resistance. Polyurethane resins are organized, by how they are cured, into one-part, two-part, and wet-curable polyurethane resins, etc. Of these polyurethane resins, aqueous one-part polyurethane resins are preferable because their environmental impact and operation load are small. Examples of aqueous one-part dispersion polyurethane resins include self-emulsification and forced-emulsification polyurethane resins. Note that each of the above polyurethane resins may additionally contain various additives, such as catalysts, crosslinking agents, lubricating agents, gelation accelerating agents, fillers, waxes, light resistance improvers, foaming agents, thermoplastic resins, thermosetting resins, dyes, pigments, flame retardants, electrical conductivity-imparting agents, antistatic agents, moisture permeability improvers, water repellents, oil repellents, hollow foams, water absorbents, protein powders, moisture absorbents, deodorants, foam stabilizers, defoamers, antifungal agents, antiseptics, pigment dispersing agents, inert gases, antiblocking agents, hydrolysis inhibitors, matting agents, tactile feel improvers, thickeners, etc.

[0035] The amount of the resin 20 with which the base material is impregnated is adjusted to 15-40 wt%, preferably 20-30 wt%, with respect to the weight (per unit area) of the base material in terms of solid content. If the amount of the resin 20 with which the base material is impregnated is less than 15 wt%, the bonding force between the fibers 10 is insufficient, and therefore, it is difficult to form voids 30 described below, so that a nubuck-like artificial leather as a final product is less likely to have a moist feel. If the amount of the resin 20 with which the base material is impregnated is more than 40 wt%, a nap is likely to be impaired, leading to a coarse and hard artificial leather.

[0036] The nubuck-like artificial leather 100 of the present invention is configured to have a structure similar to that of natural leather, which is a porous material. Specifically, a large number of microscopic spaces surrounded by a plurality of fibers 10 bonded together by the resin 20 are formed in the flexible sheet 100' included in the nubuck-like artificial leather 100. The microscopic space is herein referred to as a void 30. In the flexible sheet 100', the fibers 10 are fixed to each other by the resin 20 at a portion where the fibers 10 intersect, and in addition, the resin 20 adheres to the surfaces of the fibers 10 to a suitable extent, and therefore, a continuous structure 40 is formed in which the fibers 10 are bonded together by the resin 20. The continuous structure 40 thus formed substantially fixes a relative positional relationship between the fibers 10 in the flexible sheet 100'. As a result, the form of each void 30 surrounded by the fibers 10 is maintained, and the voids are fixed in the flexible sheet 100'.

[0037] As shown in FIG. 1, in the nubuck-like artificial leather 100 of the present invention, the voids 30, each of which is surrounded by a large number of cross-sections extending perpendicularly to a longitudinal direction of the fibers 10, are dispersed in the flexible sheet 100' to a suitable extent. Such a structure is similar to that of natural leather. As a result, a tactile feel (moist feel) and texture (nap) close to those of natural leather can be provided. In addition, in the flexible sheet 100', the fibers 10 are reinforced by the resin 20, and therefore, the strength is greater than that of the natural leather, resulting in superior abrasion resistance.

[0038] Various nubuck-like characteristics, such as "moist feel," "nap," "abrasion resistance," etc., that are imparted to the artificial leather, are affected by a state of the presence of the continuous structure 40 and the voids 30 in the flexible sheet 100', specifically, the amount of space in the flexible sheet 100' that is occupied by the continuous structure 40 (also referred to as the occupancy rate of the continuous structure 40 or the continuous structure occupancy rate). Here, the nubuck-like characteristics can be provided by adjusting a ratio A/B within a suitable range, where, in a region having a unit area of an image of a cross-section of the flexible sheet 100' captured by an electronic microscope, "A"

represents the cross-sectional area of the continuous structure 40, and "B" represents the cross-sectional area of the voids 30. Note that "A" (%) corresponds to the occupancy rate of the continuous structure 40 in the nubuck-like artificial leather 100. In the nubuck-like artificial leather 100 of the present invention, the ratio A/B is adjusted to 15/85-90/10, preferably 20/80-80/20. The ratio A/B can be changed by adjusting the amount of the resin 20 with which the fibers 10 (base material) are impregnated. In the nubuck-like artificial leather 100 of the present invention having a ratio A/B within the above range, the continuous structure 40 improves the abrasion resistance of the flexible sheet 100', and the voids 30 impart, to the flexible sheet 100', a moist feel and nap comparable to those of natural leather. If the ratio A/B is less than 15/85, the relative proportion of the continuous structure 40 in the flexible sheet 100' is small, and voids are excessive, and therefore, the strength of the flexible sheet 100' is reduced, and the flexible sheet 100' easily wears. If the ratio A/B is more than 90/10, the relative proportion of the continuous structure 40 in the flexible sheet 100' is large, and voids are insufficient, and therefore, the elasticity of the flexible sheet 100' is lost, and it is difficult to impart a sufficient moist feel and nap.

[0039] In the nubuck-like artificial leather 100 of the present invention, it is not essential that the voids 30 are distributed throughout the flexible sheet 100'. The voids 30 may only need to be present from the front surface of the flexible sheet 100' up to a suitable depth. As shown in FIG. 1, assuming that the position of the front surface of the flexible sheet 100' is 0%, and the position of the back surface is 100%, a region d where the voids 30 are present may extend from the front surface toward the back surface of the flexible sheet 100', the region d ranging from a 0-15% region to a 0-40% region, preferably from a 0-20% region to a 0-35% region. In this case, the nubuck-like artificial leather 100 has a moist feel and nap similar to those of natural leather, and at the same time, can maintain good abrasion resistance. If the region where the voids 30 are present extends from the front surface (0%) to less than 15% of the flexible sheet 100', voids are insufficient, and therefore, the elasticity is lost, and it is difficult to impart a sufficient moist feel and nap. If the region where the voids 30 are present is extends from the front surface (0%) to more than 40% of the flexible sheet 100', voids are excessive, and therefore, the strength of the flexible sheet 100' is reduced, and the flexible sheet 100' easily wears.

[0040] In the nubuck-like artificial leather 100 of the present invention, to suitably select or adjust a size of the fibers 10 is effective in providing a well-balanced combination of a moist feel and nap, and abrasion resistance. The thickness of the fibers 10 that is measured as a mono-fineness is 0.1-0.7 dtex, preferably 0.1-0.5 dtex. If the mono-fineness is less than 0.1 dtex, it is difficult to ensure sufficient abrasion resistance. If the mono-fineness is more than 0.7 dtex, it is difficult to provide a moist feel and a nap. A ratio a/b (so-called aspect ratio) of a length (a) to a diameter (b) of each of the fibers 10 that are measured when a cross-section parallel to the thickness direction of the nubuck-like artificial leather 100 is observed using a microscope is adjusted to 2-1700, preferably 5-1700, and more preferably 8-1700. If the ratio a/b is less than 2, the fibers 10 have an excessively short fiber length, and therefore, it is difficult to form a sufficient number of portions where the fibers 10 intersect, so that the strength of the flexible sheet 100' is reduced, and the flexible sheet 100' easily wears. In addition, the nonwoven fabric has an insufficient thickness, and it is difficult to form voids. If the ratio a/b is more than 1700, the fibers 10 has an excessively long fiber length, and therefore, portions where the fibers 10 intersect are not uniformly distributed, so that the artificial leather is likely to have non-uniform color and physical properties. Note that, as long as the fibers 10 used satisfy the above conditions, the fibers 10 may be commingled fibers including fibers having different sizes.

[0041] The nubuck-like artificial leather 100 of the present invention thus configured has a porous structure in which the voids 30 are formed and stacked over top of each other in a cross-sectional view taken parallel to the thickness direction. The porous structure is similar to that of natural leather, which is a porous material. Therefore, according to the nubuck-like artificial leather 100 of the present invention, a moist feel and nap close to those of natural leather can be provided. Furthermore, in the nubuck-like artificial leather 100 of the present invention, the fibers 10 included in the flexible sheet 100' are reinforced by the resin 20, and therefore, abrasion resistance superior to that of natural leather can be provided.

(Method for Producing Nubuck-like Artificial Leather)

[0042] FIG. 2 is a flowchart showing steps of a method for producing the nubuck-like artificial leather of the present invention. A symbol "S" added to each block means a step. The nubuck-like artificial leather of the present invention is produced by carrying out a fleece formation step (S1), a fiber bonding step (S2), an impregnation step (S3), a drying step (S4), and a finishing step (S5) described below. Of these steps, the impregnation step (S3) and the drying step (S4) are a characteristic feature of the present invention. By carrying out the two steps, a moist feel and nap close to those of natural leather can be provided, and an artificial leather product having superior abrasion resistance can be obtained. In addition, by carrying out the finishing step (S5), the moist feel and nap of the nubuck-like artificial leather as a final product can be further improved. The steps will now be described.

[0043] Initially, a base material (nonwoven fabric) that is a base for the nubuck-like artificial leather is prepared. The base material is produced by the fleece formation step (S1) of forming a layer including a set of fibers, which is called

fleece (may also be called a web), and the fiber bonding step (S2) of bonding the fibers together using a binder. The fleece formation step is carried out by a technique, such as drylaying, wetlaying, spunbonding, etc. The fiber bonding step is carried out by a technique, such as chemical bonding, needle punching, spunlacing, stitch bonding, steam jet, etc. When the fleece formation step (S1) and the fiber bonding step (S2) are carried out, the amount of the fibers and a condition for bonding the fibers are adjusted so that the weight (per unit area) of the base material is 150-1000 g/m².

[0044] Next, the impregnation step (S3) of impregnating the base material with a resin is carried out. The impregnation step is carried out by a mangle-pad technique of immersing a base material in a resin solution containing a resin, and squeezing the base material through a mangle, a coating technique of applying a resin solution to a base material using a spray coater, a gravure coater, a reverse coater, a doctor-knife coater, etc. Of these techniques, the mangle-pad technique is preferable because a base material can be uniformly impregnated with a resin. A condition for impregnation with the resin is adjusted so that 30-300 g/m² of the resin is added to the base material having a weight (per unit area) of 150-1000 g/m² in terms of solid content. As a result, the resin adheres to portions where the fibers intersect. In addition, the resin adheres to the surfaces of the fibers to a suitable extent. The amount of the resin added to the base material is adjusted to 15-40 wt%, preferably 20-30 wt%, in terms of solid resin content.

[0045] Next, the drying step (S4) of drying the base material impregnated with the resin is carried out. The drying step is carried out by a technique, such as dry-heat drying using a pintenter, a loop dryer, a net dryer, an oven, etc., moist-heat drying using a high-temperature steamer, a high-pressure steamer, etc., drying using infrared, drying using micro-waves, etc. Of these techniques, dry-heat drying and moist-heat drying are preferable because the resin can be reliably solidified in every part including inner parts of the base material. The base material dried by dry-heat drying or moist-heat drying can be processed into an artificial leather product having superior strength and abrasion resistance. As a condition for drying of the base material, the drying temperature is adjusted to 80-150°C, preferably 100-130°C. If the drying temperature is less than 80°C, the resin is insufficiently dried (cured), and therefore, the resin migrates and has difficulty in adhering to a predetermined position of the fiber. If the drying temperature is more than 150°C, the moist feel of a nubuck-like artificial leather as a final product is reduced, and the nap is likely to be coarse and hard. The drying time is adjusted to 50-1200 sec, preferably 100-600 sec. If the drying time is less than 50 sec, the resin is insufficiently dried (cured), and therefore, the resin migrates and has difficulty in adhering to a predetermined position of the fiber. If the drying time is more than 1200 sec, the moist feel of a nubuck-like artificial leather as a final product is reduced, and the nap is likely to be coarse and hard. After completion of the drying step, the fibers in the base material are bonded by the resin and are thereby hardened, and therefore, the base material can be directly used as a flexible sheet for a nubuck-like artificial leather. In the flexible sheet, formed are a large number of voids surrounded by the fibers. In other words, in the nubuck-like artificial leather of the present invention, voids are distributed in the flexible sheet to a suitable extent, and therefore, a structure similar to that of natural leather is formed.

[0046] Finally, the finishing step (S5) of finishing the flexible sheet is carried out. The finishing step is any suitable step that is carried out if necessary, including a raising process of raising the front surface of the flexible sheet. By carrying out the finishing step, the front surface of the finished nubuck-like artificial leather has a suitable friction coefficient (MIU) and surface roughness (SMD), and therefore, a moist feel and nap closer to those of natural leather can be provided. The friction coefficient of the front surface of the nubuck-like artificial leather is preferably 0.15-0.35, more preferably 0.20-0.30. If the friction coefficient is less than 0.15, the abrasion resistance is likely to be insufficient. If the friction coefficient is more than 0.35, the moist feel is likely to be insufficient. The surface roughness of the front surface of the nubuck-like artificial leather is preferably 0.2-1.55 μm, more preferably 0.2-1.4 μm, and even more preferably 0.3-1.2 μm. If the surface roughness of the front surface is less than 0.2 μm, the nubuck-like nap is likely to be insufficient. If the surface roughness of the front surface is more than 1.55 μm, smoothness peculiar to artificial leather is likely to be impaired.

[0047] In the raising process for the flexible sheet, for example, a roller around which card clothing or sandpaper (emery) is wrapped (a card clothing raising machine, an emery raising machine, etc.) can be used. The raising process using a roller is performed by bringing the flexible sheet into contact with the surface of the roller while moving the flexible sheet in the roller rotating direction (the longitudinal direction of the flexible sheet). In this case, the raised state of the flexible sheet can be adjusted by changing conditions, such as the type of card clothing or sandpaper, the rotational speed of the roller, the contact pressure of the flexible sheet on the roller, the frequency of contact of the flexible sheet with the roller, etc.

Examples

[0048] Examples of the nubuck-like artificial leather of the present invention will now be described. In these examples, nubuck-like artificial leathers having a characteristic feature of the present invention were produced. As comparative examples, artificial leathers that do not have any characteristic feature of the present invention were produced. The nubuck-like artificial leathers according to Examples 1-5 and the artificial leathers according to Comparative Examples 1 and 2 were produced by the following procedures.

<Example 1>

[0049] A nonwoven fabric (3071A, manufactured by Asahi Kasei Fibers Corporation) that includes a mixture of first polyester fibers (mono-fineness: 0.10 dtex) and second polyester fibers (mono-fineness: 0.15 dtex) at a weight ratio of 50:50, and has a weight (per unit area) of 269.6 g/m² and a thickness of 0.75 mm, was used. The nonwoven fabric was dyed using a disperse dye. Thereafter, the front surface of the nonwoven fabric was subjected to a buffing process. Thereafter, the nonwoven fabric was impregnated with a polyurethane resin liquid using a mangle-pad technique. The polyurethane resin liquid contained 25 wt% of a water-based polyurethane resin (SAD8·2 (solid content: 40 wt%), forced-emulsification type, manufactured by DKS Co. Ltd.), and 75 wt% of water. After the impregnation of the nonwoven fabric with the polyurethane resin liquid using a mangle-pad technique, the nonwoven fabric was subjected to dry-heat drying (thermal treatment) using a pintenter at 130°C for 150 sec. Thus, a flexible sheet including the nonwoven fabric to which a polyurethane resin was added was formed. The amount of the polyurethane resin added to this flexible sheet was 62 g/m² in terms of solid content. Thereafter, the front surface of the flexible sheet was further subjected to a buffing process. Thus, the production of the nubuck-like artificial leather of Example 1 was completed.

<Example 2>

[0050] A nonwoven fabric (3007B, manufactured by Asahi Kasei Fibers Corporation) that includes a mixture of first polyester fibers (mono-fineness: 0.15 dtex) and second polyester fibers (mono-fineness: 0.30 dtex) at a weight ratio of 50:50, and has a weight (per unit area) of 273.1 g/m² and a thickness of 0.75 mm, was used. The nonwoven fabric was dyed using a disperse dye. Thereafter, the front surface of the nonwoven fabric was subjected to a buffing process. Thereafter, the nonwoven fabric was impregnated with a polyurethane resin liquid using a mangle-pad technique. The polyurethane resin liquid was the same as that which was used in Example 1. After the impregnation of the nonwoven fabric with the polyurethane resin liquid using a mangle-pad technique, the nonwoven fabric was subjected to dry-heat drying (thermal treatment) using a pintenter at 130°C for 150 sec. Thus, a flexible sheet including the nonwoven fabric to which a polyurethane resin was added was formed. The amount of the polyurethane resin added to this flexible sheet was 50 g/m² in terms of solid content. Thereafter, the front surface of the flexible sheet was further subjected to a buffing process. Thus, the production of the nubuck-like artificial leather of Example 2 was completed.

<Example 3>

[0051] A nonwoven fabric (3007B, manufactured by Asahi Kasei Fibers Corporation) that includes polyester fibers (mono-fineness: 0.50 dtex), and has a weight (per unit area) of 273.1 g/m² and a thickness of 0.75 mm, was used. The nonwoven fabric was dyed using a disperse dye. Thereafter, the front surface of the nonwoven fabric was subjected to a buffing process. Thereafter, the nonwoven fabric was impregnated with a polyurethane resin liquid using a mangle-pad technique. The polyurethane resin liquid was the same as that which was used in Example 1. After the impregnation of the nonwoven fabric with the polyurethane resin liquid using a mangle-pad technique, the nonwoven fabric was subjected to dry-heat drying (thermal treatment) using a pintenter at 130°C for 150 sec. Thus, a flexible sheet including the nonwoven fabric to which a polyurethane resin was added was formed. The amount of the polyurethane resin added to this flexible sheet was 22 g/m² in terms of solid content. Thereafter, the front surface of the flexible sheet was further subjected to a buffing process. Thus, the production of the nubuck-like artificial leather of Example 3 was completed.

<Example 4>

[0052] A nonwoven fabric that is the same as that used in Example 3 (mono-fineness: 0.50 dtex, weight (per unit area): 273.1 g/m², and thickness: 0.75 mm) was dyed using a disperse dye. Thereafter, the front surface of the nonwoven fabric was subjected to a buffing process. Thereafter, the nonwoven fabric was impregnated with a polyurethane resin liquid by a mangle-pad technique. The polyurethane resin liquid contained 25 wt% of a water-based polyurethane resin (SAD8·2 (solid content: 40 wt%), forced-emulsification type, manufactured by DKS Co. Ltd.), 14 wt% of a dry-heat gelling agent (10-wt% aqueous ammonium acetate solution), and 61 wt% of water. After the impregnation of the nonwoven fabric with the polyurethane resin liquid using a mangle-pad technique, the nonwoven fabric was subjected to moist-heat drying (thermal treatment) using high-pressure steam at 130°C for 600 sec. This set of impregnation with the polyurethane resin liquid and moist-heat drying (thermal treatment) was performed a total of two times. Thus, a flexible sheet including the nonwoven fabric to which a polyurethane resin was added was formed. The amount of the polyurethane resin added to this flexible sheet was 43 g/m² in terms of solid content. Thereafter, the front surface of the flexible sheet was further subjected to a buffing process. Thus, the production of the nubuck-like artificial leather of Example 4 was completed.

<Example 5>

[0053] A nonwoven fabric that is the same as that used in Example 1 (a mixture of fibers having a mono-fineness of 0.10 dtex and fibers having a mono-fineness of 0.15 dtex at a weight ratio 50:50, weight (per unit area): 269.6 g/m², and thickness: 0.75 mm) was dyed using a disperse dye. Thereafter, the front surface of the nonwoven fabric was subjected to a buffing process. Thereafter, the nonwoven fabric was impregnated with a polyurethane resin liquid by a mangle-pad technique. The polyurethane resin liquid contained 50 wt% of a water-based polyurethane resin (SAD8-2 (solid content: 40 wt%), forced-emulsification type, manufactured by DKS Co. Ltd.), 27.5 wt% of a dry-heat gelling agent (10-wt% aqueous ammonium acetate solution), and 22.5 wt% of water. After the impregnation of the nonwoven fabric with the polyurethane resin liquid using a mangle-pad technique, the nonwoven fabric was subjected to moist-heat drying (thermal treatment) using high-pressure steam at 130°C for 600 sec. This set of impregnation with the polyurethane resin liquid and moist-heat drying (thermal treatment) was performed a total of two times. Thus, a flexible sheet including the nonwoven fabric to which a polyurethane resin was added was formed. The amount of the polyurethane resin added to this flexible sheet was 72 g/m² in terms of solid content. Thereafter, the front surface of the flexible sheet was further subjected to a buffing process. Thus, the production of the nubuck-like artificial leather of Example 5 was completed.

<Comparative Example 1>

[0054] A nonwoven fabric that is the same as that used in Example 1 (a mixture of fibers having a mono-fineness of 0.10 dtex and fibers having a mono-fineness of 0.15 dtex at a weight ratio 50:50, weight (per unit area): 269.6 g/m², and thickness: 0.75 mm) was dyed using a disperse dye. Thereafter, the front surface of the nonwoven fabric was subjected to a buffing process. The resulting artificial leather was Comparative Example 1. In other words, the artificial leather of Comparative Example 1 is the nubuck-like artificial leather of Example 1 in which the nonwoven fabric is not impregnated with a polyurethane resin liquid.

<Comparative Example 2>

[0055] A nonwoven fabric that is the same as that used in Example 2 (a mixture of fibers having a mono-fineness of 0.15 dtex and fibers having a mono-fineness of 0.30 dtex at a weight ratio 50:50, weight (per unit area): 273.1 g/m², and thickness: 0.75 mm) was dyed using a disperse dye. Thereafter, the front surface of the nonwoven fabric was subjected to a buffing process. The resulting artificial leather was Comparative Example 2. In other words, the artificial leather of Comparative Example 2 is the nubuck-like artificial leather of Example 2 in which the nonwoven fabric is not impregnated with a polyurethane resin liquid.

<Reference Example 1>

[0056] Natural leather (real leather nubuck) was prepared as Reference Example 1 in order to compare it with the nubuck-like artificial leathers of Examples 1-5 and the artificial leathers of Comparative Examples 1 and 2.

[0057] Next, various characteristics of each of the above leathers were checked by various measurements and evaluations. Based on the results, relationships between the structures and the characteristics of the leathers were studied. The characteristics that were measured and evaluated are the following.

[Occupancy Rate of Continuous Structures, Voids, or Fibers]

[0058] Images of cross-sections parallel to the longitudinal direction (X direction) and the width direction (Y direction) of each leather were captured using a scanning electron microscope (S-3000N, manufactured by Hitachi High-Technologies Corporation) at 1000 times magnification. The sum of the areas of continuous structures, voids, or fibers contained in an SEM image was calculated by image analysis. The proportion of the sum of the areas of continuous structures, voids, or fibers to the area of the entire SEM image, which is 100, is referred to as the occupancy rate (%) of continuous structures, voids, or fibers included in each leather. The calculation of the occupancy rate of continuous structures, voids, or fibers was performed for two cross-sections parallel to the X direction and two cross-sections parallel to the Y direction of each leather (a total of four cross-sections), and the occupancy rate was defined as the average thereof. FIG. 3 shows SEM images at 1000 times magnification of a cross-section parallel to the thickness direction (a region where voids are formed) and the front surface of: (a) the nubuck-like artificial leather of the present invention (corresponding to Example 1); (b) a conventional artificial leather (corresponding to Comparative Example 1); and (c) natural leather (corresponding to Reference Example 1).

[Region where Voids are Formed]

[0059] An image of a cross-section parallel to the thickness direction of each leather, extending from the front surface to the back surface, was captured using a scanning electron microscope at 1000 times magnification. A region where voids were formed was identified from the SEM image. The calculation of the region where voids were formed was performed for two cross-sections parallel to the X direction and two cross-sections parallel to the Y direction of each leather (a total of four cross-sections), and the region was defined as the average thereof.

[Aspect Ratio]

[0060] Images of cross-sections parallel to the longitudinal direction (X direction) and the width direction (Y direction) of each leather were captured using a microscope (VHX-200, manufactured by Keyence Corporation) at 500 times magnification. An aspect ratio (a/b) of a length (a) and a diameter (b) of a fiber included in each leather was calculated. The calculation of the aspect ratio was performed for two cross-sections parallel to the X direction and two cross-sections parallel to the Y direction of each leather (a total of four cross-sections), and the aspect ratio was defined as the average thereof.

[Friction Coefficient and Surface Roughness]

[0061] A friction coefficient (MIU) and a surface roughness (SMD) in the longitudinal direction (X direction) of the front surface of each leather were measured using an automated surface tester (KES-FB4-AUTO-A, manufactured by Kato Tech Co., Ltd.). The measurement of the friction coefficient and the surface roughness was performed at three points of each leather, and the friction coefficient and the surface roughness were defined as the respective averages thereof.

[Tactile Feel]

[0062] The tactile feel of each artificial leather was evaluated by sensory testing according to the following criteria, in which each artificial leather was compared with the natural leather of Reference Example 1.

- 5: A soft texture and moist feel equivalent to those of natural leather are recognized
- 4: A soft texture equivalent to that of natural leather, and a slightly inferior moist feel, are recognized
- 3: A texture slightly coarser and harder than natural leather, and a slightly inferior moist feel, are recognized
- 2: A texture slightly coarser and harder than natural leather is recognized, and no moist feel is recognized
- 1: A texture coarser and harder than natural leather is recognized, and no moist feel is recognized

[Appearance]

[0063] The appearance of each artificial leather was evaluated by sensory testing according to the following criteria, in which each artificial leather was compared with the natural leather of Reference Example 1.

- 5: Soft fine fibers and minute pits and bumps similar to those of natural leather are recognized
- 4: Soft fine fibers similar to those of natural leather are recognized, and no minute pits and bumps are recognized
- 3: Fibers are recognized, and the fibers appear coarse
- 2: Long or very short fibers lying flat are recognized
- 1: A nap totally different from that of natural leather is recognized

[Abrasion Resistance]

[0064] A sample extending in the longitudinal direction (X direction) by 300 mm and in the width direction (Y direction) by 70 mm was extracted from each leather. A urethane foam having a length of 300 mm, a width of 70 mm, and a thickness of 10 mm, was attached to the back surface of the sample. An abrasion test was conducted on the resulting samples. In the abrasion test, a plane abrasion tester (T-type, manufactured by Daiei Kagaku Seiki Mfg. Co., Ltd.) was used. Each sample was pressed against a rubbing finger covered with cotton canvas with a load of 9.8 N. In this situation, the sample was abraded by the rubbing finger being moved back and forth across a 140-mm section in the longitudinal direction of the front surface of the sample at a speed of 60 round-trips per minute. Each time the number of round-trips of the rubbing finger reached 2500, the cotton canvas was replaced. A total of 10,000 round-trips were made to abrade the sample. After the end of the abrasion test, a condition of the sample was visually checked. The abrasion resistance of each leather was evaluated according to the following criteria.

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Circle: The condition of the front surface remain unchanged

Triangle: It is recognized that the fibers partially come off the front surface

Cross: Most of the fibers on the front surface come off

5 **[0065]** The results of the measurement and evaluation are shown in Table 1 below.

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Table 1

	Example1	Example2	Example3	Example4	Example5	Comparative Example1	Comparative Example2	Reference Example1
Occupancy rate of continuous structure (%)	71.5	56.2	46.4	54.3	59.9	-	-	-
Occupancy rate of voids(%)	28.5	43.8	53.6	45.7	40.1	-	-	-
Occupancy rate of fibers(%)	31.4	35.8	38.0	38.0	31.9	31.4	35.8	-
Void-containing region(%)	26.4	32.3	19.9	25.4	324	-	-	-
Aspect ratio (a/b)	30.9	17.2	13.3	13.3	30.9	30.9	17.2	
Friction coefficient	0.260	0.303	0.320	0.290	0.272	0.327	0.335	0.228
Surface roughness(μm)	0.570	0.710	1.544	0.833	0.555	2.238	1.697	0.335
Tactile feel	4~5	4	3	3~4	4~5	2	2	5
Appearance	4-5	4	3	3~4	4~5	2~3	2	5
Abrasion resistance	○	○	○	○	○	○	○	×

[0066] The nubuck-like artificial leathers of Examples 1, 2, 4, and 5 had a friction coefficient and surface roughness close to those of the natural leather of Reference Example 1. As a result, their tactile feel and appearance were rated high, and their abrasion resistance was also good. The nubuck-like artificial leather of Example 3 had a slightly great surface roughness, but its tactile feel and texture were not such that a practical problem may arise, and its abrasion resistance was good. In contrast to this, the artificial leathers of Comparative Examples 1 and 2 had a friction coefficient and surface roughness much greater than those of the natural leather of Reference Example 1. Their abrasion resistance was good because they were artificial leather, but their tactile feel and appearance were rated low.

[0067] The SEM images of FIG. 3 demonstrate that the nubuck-like artificial leather of the present invention has a structure similar to that of natural leather. It is considered that such a structure is attributed to a moist feel and nap close to those of natural leather. In addition, the fibers included in the flexible sheet are reinforced by the resin. Therefore, the nubuck-like artificial leather of the present invention has a strength greater than that of natural leather, and therefore, has superior abrasion resistance.

INDUSTRIAL APPLICABILITY

[0068] The nubuck-like artificial leather of the present invention, and the method for producing the nubuck-like artificial leather, are applicable to various leather products, such as automotive seats, aircraft seats, watercraft seats, sofas, furniture, bags, shoes, etc.

REFERENCE SIGNS LIST

[0069]

10 FIBER
20 RESIN
30 VOID
40 CONTINUOUS STRUCTURE
100 NUBUCK-LIKE ARTIFICIAL LEATHER
100' FLEXIBLE SHEET

Claims

1. A nubuck-like artificial leather (100) **characterized in that** it comprises:

a flexible sheet (100') including a base material containing tangled fibers (10), and a resin (20) added to the base material, and
voids (30) are formed in the flexible sheet (100'), the voids (30) being surrounded by cross-sections of the fibers (10) as viewed in a cross-section parallel to a thickness direction of the flexible sheet (100'), and the voids (30) being held by the fibers (10) being bonded together by the resin (20).

2. The nubuck-like artificial leather (100) according to claim 1, **characterized in that** in a region having a unit area of the cross-section of the flexible sheet (100'), a ratio (A/B) of a cross-sectional area (A) of a continuous structure (40) formed by the fibers (10) being bonded together by the resin (20) to a cross-sectional area (B) of the voids (30) is 15/85-90/10.

3. The nubuck-like artificial leather (100) according to claim 1 or 2, **characterized in that** the fibers (10) have a mono-fineness of 0.1-0.7 dtex.

4. The nubuck-like artificial leather (100) according to any one of claims 1-3, **characterized in that** a ratio (a/b) of a length (a) to a diameter (b) of each of the fibers (10) is 2-1700.

5. The nubuck-like artificial leather (100) according to any one of claims 1-4, **characterized in that** the resin (20) is at least one selected from the group consisting of polyurethane resins, silicone resins, and acrylic resins.

6. The nubuck-like artificial leather (100) according to any one of claims 1-5, **characterized in that** the voids (30) are present in a region (d) of the flexible sheet (100') extending from a front surface of the flexible

sheet (100') toward a back surface of the flexible sheet (100'), the region (d) ranging from a 0-15% region to a 0-40% region, where a position of the front surface of the flexible sheet (100') is 0%, and a position of the back surface of the flexible sheet (100') is 100%.

- 5 7. The nubuck-like artificial leather (100) according to any one of claims 1-6, **characterized in that** a front surface of the nubuck-like artificial leather (100) has a surface roughness of 0.2-1.55 μm .
8. A nubuck-like artificial leather production method, **characterized in that** the method comprises:
 - 10 an impregnation step of impregnating a base material containing tangled fibers (10) and having a weight of 150-1000 g/m^2 , with 15-40 wt% of a resin (20) with respect to the weight of the base material in terms of solid content; and
 - a drying step of drying the base material impregnated with the resin (20) at 80-150°C for 50-1200 sec.
- 15 9. The nubuck-like artificial leather production method according to claim 8, **characterized in that** it further comprises: a finishing step of, after the drying step, finishing the base material impregnated with the resin (20) .
10. The nubuck-like artificial leather production method according to claim 8 or 9, **characterized in that** the drying step is carried out by dry-heat drying or moist-heat drying.

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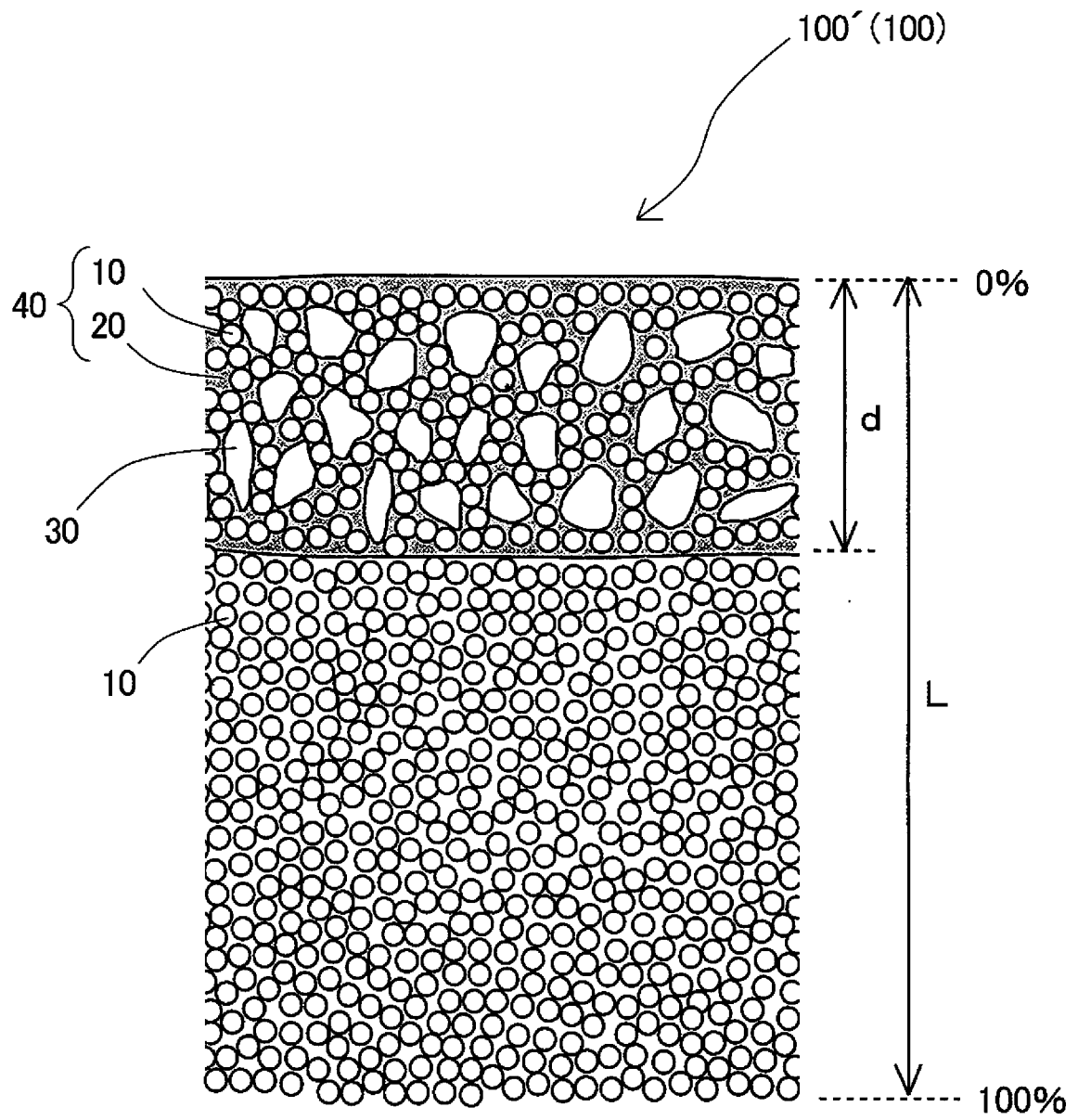
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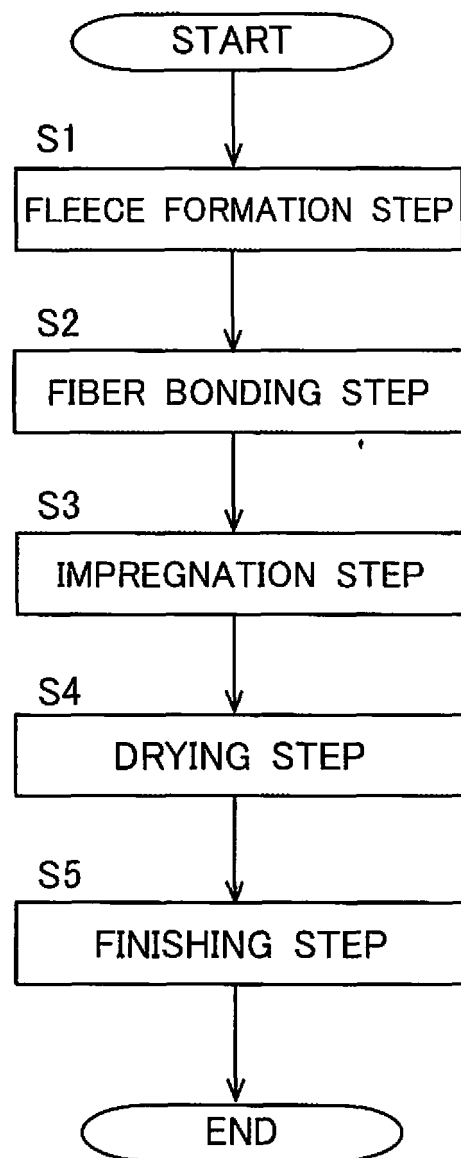
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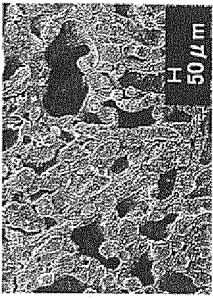
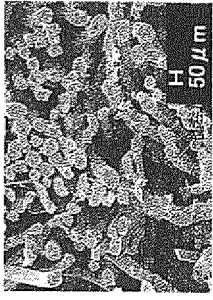
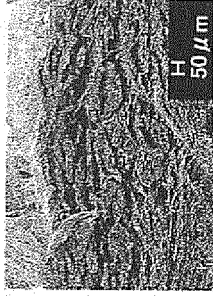
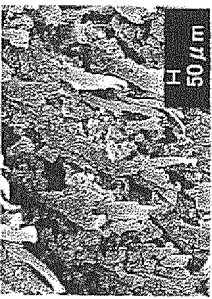
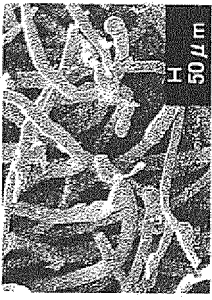
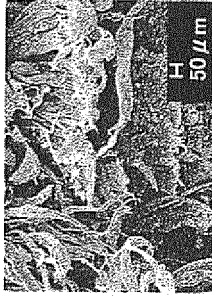
[FIG. 1]



[FIG. 2]



[FIG. 3]

	(a) NUBUCK-LIKE ARTIFICIAL LEATHER OF THE INVENTION	(b) CONVENTIONAL ARTIFICIAL LEATHER	(c) NATURAL LEATHER
CROSS-SECTION (1000 ×)	 H 50 μm	 H 50 μm	 H 50 μm
FRONT SURFACE (1000 ×)	 H 50 μm	 H 50 μm	 H 50 μm

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/074754

A. CLASSIFICATION OF SUBJECT MATTER

D06N3/00 (2006.01) i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D06N1/00-7/06

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2004-197232 A (Teijin Cordley Ltd.), 15 July 2004 (15.07.2004), claim 1; paragraphs [0020], [0022], [0024]; examples & US 2006/008631 A1 claim 1; paragraphs [0038], [0042]; examples & WO 2004/018766 A1 & EP 1550767 A1 & CN 1675428 A & KR 10-1027365 B1 & TW 200413122 A	1-6, 8-10 7
X Y A	JP 2009-052165 A (Toray Industries, Inc.), 12 March 2009 (12.03.2009), claim 1; paragraphs [0015], [0024], [0071]; fig. 1 (Family: none)	1-6 7 8-10

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

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Date of the actual completion of the international search
04 November 2016 (04.11.16)Date of mailing of the international search report
15 November 2016 (15.11.16)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/074754

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2014-145133 A (Toyobo Co., Ltd.), 14 August 2014 (14.08.2014), claim 1; paragraphs [0009], [0018], [0031] (Family: none)	7
A	WO 2015/064078 A1 (Kuraray Co., Ltd.), 07 May 2015 (07.05.2015), claims 1, 2; paragraph [0023] & US 2016/251797 A1 claims 1, 2; paragraph [0027] & EP 3064642 A1 & CN 105683441 A & TW 201533294 A & KR 10-2016-0078366 A	1-10

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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