



(11)

EP 2 966 218 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

28.08.2024 Bulletin 2024/35

(21) Application number: **14756855.4**

(22) Date of filing: **25.02.2014**

(51) International Patent Classification (IPC):

D06N 3/00 ^(2006.01) **D06M 13/02** ^(2006.01)
D06M 13/224 ^(2006.01) **D06M 15/643** ^(2006.01)
D06M 23/08 ^(2006.01) **D06M 15/564** ^(2006.01)
D06N 3/14 ^(2006.01)

(52) Cooperative Patent Classification (CPC):

D06N 3/14; D06M 15/564; D06M 23/08;
D06N 3/0004; D06N 3/0011; D06N 3/0061;
D06N 3/0063; D06N 2211/28

(86) International application number:

PCT/JP2014/000991

(87) International publication number:

WO 2014/132630 (04.09.2014 Gazette 2014/36)

(54) **ARTIFICIAL LEATHER SUBSTRATE, GRAIN-FINISHED ARTIFICIAL LEATHER, ARTIFICIAL LEATHER SUBSTRATE MANUFACTURING METHOD, AND ARTIFICIAL LEATHER SUBSTRATE MODIFYING AGENT**

KUNSTLEDERSUBSTRAT, KUNSTLEDER MIT KÖRNUNGSFINISH,
HERSTELLUNGSVERFAHREN FÜR KUNSTLEDERSUBSTRAT UND MODIFIZIERUNGSMITTEL
FÜR KUNSTLEDERSUBSTRAT

SUBSTRAT EN CUIR ARTIFICIEL, CUIR ARTIFICIEL À FAUSSE FLEUR, PROCÉDÉ DE
FABRICATION D'UN SUBSTRAT EN CUIR ARTIFICIEL ET AGENT DE MODIFICATION DE
SUBSTRAT EN CUIR ARTIFICIEL

(84) Designated Contracting States:

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

(30) Priority: **27.02.2013 JP 2013037475**

(43) Date of publication of application:
13.01.2016 Bulletin 2016/02

(73) Proprietor: **Kuraray Co., Ltd.**
Okayama 710-0801 (JP)

(72) Inventors:

- **YOSHIMOTO, Shinichi**
Minami-ku, Okayama-shi,
Okayama702-8601 (JP)
- **FUJISAWA, Michinori**
Minami-ku, Okayama-sh,i
Okayama 702-8601 (JP)

- **HASHIMOTO, Koji**
Minami-ku, Okayama-shi,
Okayama702-8601 (JP)
- **SUGIURA, Hideo**
Kita-ku, Osaka-shi,
Osaka 530-8611 (JP)

(74) Representative: **Vossius & Partner**
Patentanwälte Rechtsanwälte mbB
Siebertstrasse 3
81675 München (DE)

(56) References cited:

EP-A1- 1 518 959 EP-A2- 1 079 015
DE-A1- 4 444 306 JP-A- 2000 017 581
JP-A- 2002 030 580 JP-A- 2002 302 879
JP-A- 2004 044 068 JP-A- 2004 324 012
JP-A- 2007 291 565 JP-A- 2007 291 565
JP-A- 2012 117 154 US-A- 3 203 921
US-A- 3 558 538

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 2 966 218 B1

- DATABASE WPI Week 200366, 2003 Derwent World Patents Index; AN 2003-692050, XP002760088

Description

[Technical Field]

5 **[0001]** The present invention relates to an artificial leather having suppleness and also considerable fullness.

[Background Art]

10 **[0002]** From the past, artificial leather including a non-woven fabric has been known. As an alternative to natural leather, artificial leather has been used in fields of footwear, clothing, gloves, bags, balls, interior goods, vehicle application, and the like.

15 **[0003]** Artificial leather is produced by subjecting an artificial leather substrate that is obtained by adding an elastic polymer into the voids in a non-woven fabric by impregnation, to a surface treatment for imparting a desired appearance. The elastic polymer imparts fullness to the non-woven fabric. As artificial leather, for example, artificial leather that is given a grain-like appearance, and suede-like or nubuck-like artificial leather with fuzzed-up fibers at the non-woven fabric surface, are known.

20 **[0004]** Natural leather comprises very fine collagenous fibers and therefore has suppleness and also considerable fullness. The considerable fullness of natural leather allows roundness and formation of fine fold creases with a luxurious appearance, when bent, as well as realization of excellent drape.

25 **[0005]** However, it has been difficult to use natural leather, for example, in an application such as vehicle upholstery that requires heat resistance and water resistance. This is because collagenous fibers have poor heat resistance and water resistance. For imparting heat resistance and water resistance to natural leather, there is a method for forming a thick resin layer on the leather surface. However, when a thick resin layer is formed, the suppleness of natural leather would be lost.

30 **[0006]** In contrast, compared to natural leather, artificial leather has better heat resistance, water resistance, quality stability, and wear resistance; and also, it is easier to maintain. However, regarding artificial leather, in the non-woven fabric, there are pores not packed with an elastic polymer; therefore, artificial leather is inferior to natural leather, in extreme fineness and fullness. Therefore, when bent, artificial leather does not bend with roundness as in the case of natural leather, and instead, bends sharply as if in breaking. There is no luxurious quality to this kind of bending. Moreover, when the number of pores is reduced by increasing the proportion of the elastic polymer in the non-woven fabric, resiliency increases and texture becomes rigid like rubber.

35 **[0007]** Also known is artificial leather that uses a non-woven fabric formed of ultrafine fibers, in order to more closely imitate the suppleness of natural leather (e.g., Patent Literature 1 listed below). However, in the case of artificial leather using a non-woven fabric formed of ultrafine fibers, artificial leather with sufficient suppleness and also sufficient fullness was not obtained. Moreover, Patent Literature 2 listed below discloses a leather-sheet-like product comprising: a fibrous substrate; and an oily substance with a viscosity at 30°C of 50 to 10000 mPa·s and a retaining body such as an olefin-based elastomer or the like, both included in at least the inner part of the fibrous substrate. Patent Literature 2 discloses that such leather-sheet-like product has natural-leather-like flexibility (suppleness) and fullness, and exhibits few occurrences of oil migration.

40 **[0008]** Incidentally, although not related to the field of artificial leather, for example, Patent Literature 3 listed below discloses a wiping sheet comprising: a wet-laid acrylic non-woven fabric; and a chemical agent with a dust-collecting function retained in the non-woven fabric in an amount of 1 to 30 wt% of the weight of the non-woven fabric, the chemical agent used being synthetic oil, such as liquid paraffin, mineral oil, silicone oil, or alkyl benzene oil.

45 **[0009]** Patent Literature 4 discloses a leather-like sheet including an entangled nonwoven fabric of ultrafine filament bundles and a first polymer elastic body imparted inside the entangled nonwoven fabric, and the first polymer elastic body is unevenly distributed in a surface layer. Patent Literature 5 discloses a leathery sheet comprising a mixture comprising (a) powder consisting essentially of a protein, (b) an oily substance having a viscosity of 50-100,000 mPa s at 30 °C, and (c) a supporter for an oily substance. Patent Literature 6 discloses a leather-like sheet containing, at least in its fibrous substrate, a block copolymer composed of (A) a block composed of at least one vinyl aromatic monomer and and (B) a block composed of isoprene, butadiene or isoprene-butadiene.

[Prior Art]

[Patent Literatures]

55 **[0010]**

[Patent Literature 1] WO2008/120702 pamphlet

[Patent Literature 2] WO2003/06212 pamphlet

[Patent Literature 3] Japanese Laid-Open Patent Publication No. Hei 9-313418

[Patent Literature 4] JP 2012 117154 A

[Patent Literature 5] JP 2002 302879 A

[Patent Literature 6] JP 2007 291565 A

[Summary of Invention]

[Technical Problem]

[0011] The present invention provides an artificial leather having suppleness and also considerable fullness.

[Solution to Problem]

[0012] The present invention is as defined in the appended claims.

[Advantageous Effects of Invention]

[0013] According to the present invention, there is obtained an artificial leather having suppleness and also considerable fullness.

[Brief Description of Drawings]

[0014]

Fig. 1 is a schematic sectional view of a grain-like-finish artificial leather 10 of one embodiment according to the present invention.

Fig. 2 is a schematic sectional view of a grain-like-finish artificial leather 20 of another embodiment according to the present invention.

Fig. 3 is a sectional image of when a sectional surface of the entangled fiber body in Example 6, before adding thereto the first filler, the non-volatile oil, and the first elastic polymer by impregnation, was observed with a scanning electron microscope (SEM).

Fig. 4 is a sectional image of when a sectional surface of the artificial leather substrate in Example 6 obtained by adding the first filler, the non-volatile oil, and the first elastic polymer to the non-woven fabric by impregnation, was observed with an SEM.

Fig. 5 is a sectional image of when a sectional surface of the grain-like-finish artificial leather substrate in Example 6 was observed with an SEM.

Fig. 6 is an SEM image of an oblique sectional surface of the artificial leather substrate obtained in Example 13, before formation of the smoothing layer.

Fig. 7 is an SEM image of an oblique sectional surface of the artificial leather substrate obtained in Example 13, after formation of the smoothing layer.

Fig. 8 is a sectional SEM image of an oblique sectional surface of the grain-like-finish artificial leather substrate obtained in Example 13.

Fig. 9 is an SEM image of an oblique sectional surface of the artificial leather substrate obtained in Example 22, after formation of the smoothing layer.

Fig. 10 is a sectional SEM image of an oblique sectional surface of the grain-like-finish artificial leather substrate obtained in Example 22.

[Description of Embodiment]

[0015] Fig. 1 is a schematic sectional view of a grain-like-finish artificial leather 10 of an embodiment according to the present invention. The grain-like-finish artificial leather 10 includes: an artificial leather substrate 1 including an entangled fiber body; and a grain-like resin layer 2 including an elastic polymer, formed on the surface of the artificial leather substrate 1. The artificial leather substrate 1 includes the entangled fiber body 1a; and into the voids among the fibers of the entangled fiber body 1a, as illustrated in the enlarged view in Fig. 1, a non-volatile oil 3 in liquid form, a first filler 4, and as necessary, a first elastic polymer 5 are added by impregnation. The non-volatile oil in liquid form, the first filler, and the first elastic polymer combined together is referred to as a modifying agent.

[0016] The artificial leather of the present embodiment will now be described in detail, in accordance with an example

of a production method of the same.

[0017] For the entangled fiber body, any kind can be used without particular limitation as long as the entangled fiber body is a fibrous structure, such as a non-woven fabric, a woven fabric, a woven product, or a knitted product. Among these, a non-woven fabric, particularly that of ultrafine fibers, is preferred. Since a non-woven fabric of ultrafine fibers has a high fiber density, unevenness in coarseness and fineness is low and uniformity is high. Therefore, an artificial leather with suppleness and considerable fullness that are particularly excellent is obtained. For the present embodiment, the case where a non-woven fabric of ultrafine fibers is used as the entangled fiber body will be described in detail in a typical example.

[0018] A non-woven fabric of ultrafine fibers is obtained, for example, by subjecting ultrafine-fiber-forming fibers such as sea-island-type (matrix-domain-type) conjugated fibers to an entanglement treatment and then to an ultrafine-fiber-forming treatment. Note that for the present embodiment, although a detailed description is given of when sea-island-type conjugated fibers are used, ultrafine-fiber-forming fibers other than sea-island-type conjugated fibers may be used; or alternatively, instead of using ultrafine-fiber-forming fibers, ultrafine fibers may be directly spun. Note that specific examples of ultrafine-fiber-forming fibers other than sea-island-type conjugated fibers include: separating-and-splitting-type fibers formed such that ultrafine fibers immediately after spinning lightly adhere to one another and are then unraveled by mechanical manipulation, thereby to form a plurality of ultrafine fibers; and petal-shaped fibers that are formed in a melt spinning process, by alternately arranging pieces of resin to form an aggregate similar to that of petals, and if capable of forming ultrafine fibers, any kind of fibers can be used without particular limitation.

[0019] In production of a non-woven fabric of ultrafine fibers, first, a thermoplastic resin for forming a selectively-removable sea component (matrix component) of sea-island-type conjugated fibers, and a thermoplastic resin for forming island components (domain components), i.e., resin components for forming ultrafine fibers, of the sea-island-type conjugated fibers, are melt spun and then drawn, thereby to obtain sea-island-type conjugated fibers.

[0020] For the thermoplastic resin for the sea component, a thermoplastic resin that differs from the resin for the island components in solubility in a solvent and decomposability in a decomposing agent, is selected. Specific examples of the thermoplastic resin that forms the sea component include water-soluble polyvinyl alcohol-based resin, polyethylene, polypropylene, polystyrene, ethylene propylene resin, ethylene-vinyl acetate resin, styrene ethylene resin, and styrene acrylic resin.

[0021] For the thermoplastic resin being the resin component that forms the island components and the ultrafine fibers, there is no particular limitation if the resin is capable of forming sea-island-type conjugated fibers and ultrafine fibers. Specific examples include: aromatic polyesters, such as polyethylene terephthalate (PET), isophthalic acid-modified PET, sulfoisophthalic acid-modified PET, polybutylene terephthalate, and polyhexamethylene terephthalate; aliphatic polyesters such as polylactic acid, polyethylene succinate, polybutylene succinate, polybutylene succinate adipate, and polyhydroxybutyrate-polyhydroxyvalerate resin; polyamides, such as polyamide 6, polyamide 66, polyamide 10, polyamide 11, polyamide 12, and polyamide 6-12; and polyolefins, such as polypropylene, polyethylene, polybutene, polymethylpentene, and chlorinated polyolefin. These may be used singly or in a combination of two or more.

[0022] For the production method of the non-woven fabric of ultrafine fibers, for example, there is a method wherein a web of sea-island-type conjugated fibers is produced by melt spinning, the web undergoes an entanglement treatment, and thereafter the sea component is selectively removed from the sea-island-type conjugated fibers to form ultrafine fibers. For the production method of the web, there is a method wherein long fibers of the sea-island-type conjugated fibers that have been spun by a spunbonding method or the like are captured on a net, without being cut, thereby to form a web of long fibers; a method wherein the long fibers are cut into staple fibers, thereby to form a web of short fibers; or the like. Among these, a web of long fibers is particularly preferable in terms of having excellent fineness and fullness. Moreover, fusion bonding treatment may be conducted on the web formed, in order to impart structural stability thereto.

[0023] Note that long fibers are meant to be continuous fibers and not short fibers obtained by cutting intentionally after spinning. Further specifically, long fibers are meant, for example, not to be short fibers obtained by cutting intentionally such that the fiber length becomes about 3 to 80 mm. The fiber length of the sea-island-type conjugated fibers before undergoing ultrafine fiber formation, is preferably 100 mm or more; and as long as the fibers are technically producible and are not inevitably cut in the production process, the fiber length may be several meters, several hundred meters, several kilometers, or of a higher value. Note that by needle punching at the time of entanglement described below, or by buffing of the surface of the non-woven fabric, one part of the long fibers may be inevitably cut in the production process and become short fibers.

[0024] In any of the processes until the sea component of the sea-island-type conjugated fibers is removed to form ultrafine fibers, by conducting fiber shrinkage treatment, such as entanglement treatment and heat shrinkage treatment using water vapor, the sea-island-type conjugated fibers can be made closely-packed. For entanglement treatment, for example, there is a method wherein about 5 to 100 layers of the web are overlapped and then subjected to needle punching or high-pressure water jetting treatment.

[0025] The sea component of the sea-island-type conjugated fibers is removed by dissolution or decomposition at an

appropriate stage after the web is formed. By such removal by decomposition or by dissolution and extraction, the sea-island-type conjugated fibers undergo ultrafine fiber formation, and ultrafine fibers in the form of fiber bundles are formed.

[0026] The fineness of the ultrafine fibers are not particularly limited, and are preferably 0.001 to 0.9 dtex, further preferably 0.01 to 0.6 dtex, and particularly preferably 0.02 to 0.5 dtex. When the fineness is too high, a non-woven fabric with insufficient close-packedness tends to be obtained. Moreover, the fibers with excessively low fineness are difficult to use in production. Moreover, such fibers tend to bundle together and increase rigidity of the non-woven fabric.

[0027] The non-woven fabric of the ultrafine fibers obtained as above undergoes thickness adjustment and planarization treatment, as necessary. Specifically, slicing treatment or buffing treatment is conducted. As such, the non-woven fabric of the ultrafine fibers, i.e., the entangled fiber body, is obtained.

[0028] The thickness of the entangled fiber body is not particularly limited, and is preferably about 100 to 3000 μm and further preferably about 300 to 2000 μm . Moreover, the apparent density of the entangled fiber body is not particularly limited, and is preferably about 0.25 to 0.70 g/cm^3 , further preferably about 0.45 to 0.65 g/cm^3 , and particularly preferably about 0.55 to 0.60 g/cm^3 , in terms of obtaining an artificial leather substrate with fullness and also supple texture.

[0029] A description will now be given of a process of adding the first filler and the non-volatile oil in liquid form into the voids in the entangled fiber body, by impregnation.

[0030] In the present step, first, a dispersion containing the non-volatile oil and the first filler is prepared.

[0031] For the dispersion, for example, the non-volatile oil in liquid form and the first filler are uniformly mixed and dispersed in a dispersion medium of water, or of a mixed liquid of water and a polar solvent such as alcohol, or the like.

[0032] The non-volatile oil in liquid form in the present embodiment is a liquid with a boiling point of 150°C or more and that substantially does not dissolve in a polar solvent. Specific examples include liquid paraffin, paraffin-based or naphthene-based process oil, mineral oil, silicone oil, and phthalate esters. These may be used singly or in a combination of two or more. Among these, liquid paraffin is preferred in terms of having excellent chemical stability and not tending to be easily oxidized.

[0033] Moreover, the first filler according to the invention includes at least one of an inorganic filler, a metal filler, a metal oxide filler, a semimetal oxide filler, a flame-retardant filler and a carbon-based filler.

[0034] For the inorganic filler, for example, various fillers, such as of metals, metal oxides, inorganic compounds, with an average particle size of preferably about 0.1 to 15 μm and further preferably about 0.5 to 10 μm , are used without particular limitation. Specific examples thereof include: fillers of metal oxides or semimetal oxides, such as alumina (Al_2O_3), titanium dioxide (TiO_2), zinc oxide (ZnO), cerium dioxide (CeO_2), and silica (SiO_2); fillers of inorganic compounds, such as talc, clay, aluminum hydroxide, mica, calcium carbonate, and cage-like polysilsesquioxane (POSS); flame-retardant fillers, such as ammonium polyphosphate, aluminum dialkyl phosphinate, and melamine polyphosphate; and carbon-based fillers, such as carbon nanotubes (CNT), carbon fibers (CF), carbon black (CB), graphite (GF), and acetylene black (AB). These may be used singly or in a combination of two or more. Among these, various flame-retardant fillers are particularly preferred in terms of being capable of also imparting flame retardancy.

[0035] Moreover, into the voids in the entangled fiber body, in addition to the first filler and the non-volatile oil in liquid form, a first elastic polymer is further added by impregnation. In that case, a dispersion containing the non-volatile oil, the first filler, and the first elastic polymer is used.

[0036] Specific examples of the first elastic polymer include polyurethanes, acrylic-based elastomers, silicone-based elastomers, diene-based elastomers, nitrile-based elastomers, fluorine-including elastomers, polystyrene-based elastomers, polyolefin-based elastomers, polyamide-based elastomers, and halogen-including elastomers. These may be used singly or in a combination of two or more. Among these, polyurethanes are preferred in terms of having excellent wear resistance and mechanical properties.

[0037] For the polyurethane, water-based polyurethane, such as an emulsion of polycarbonate-based polyurethane, polyester-based polyurethane, polyether-based polyurethane, or polycarbonate/ether-based polyurethane, or the like is preferable. These polyurethanes are particularly preferable in terms of easy preparation of their dispersions, easy formation of a crosslinked structure, and easy realization of a soft texture by allowing voids to be present without allowing too much contact among fibers.

[0038] Moreover, to the extent of not adversely affecting the effect of the present invention, as necessary, a component such as a surfactant, a dispersant, or a coloring agent, may be added into the dispersion.

[0039] The concentration of each of the components in the dispersion is adjusted as appropriate in view of the intended characteristic, the viscosity and stability of the dispersion, or the like. Specifically, regarding the proportion of the non-volatile oil in the dispersion, for example, preferably about 1 to 50 mass% and further preferably about 3 to 30 mass% are preferably added therein. Moreover, regarding the proportion of the total of the filler and the elastic polymer in the dispersion, for example, preferably about 5 to 99 mass% and further preferably about 7 to 80 mass% are preferably contained therein.

[0040] The method of impregnating the entangled fiber body with the dispersion is not particularly limited. Specifically, for example, preferably used is a method of impregnating the entangled fiber body by dipping and nipping in the dispersion. The viscosity of the dispersion is not particularly limited, if impregnation of the entangled fiber body with a desired amount

of the dispersion is possible. Specifically, for example, in values obtained by measuring with a rotational viscometer, the solution viscosity is preferably about 10 to 1000 mPa·s (millipascal-second) and further preferably about 50 to 500 mPa·s.

[0041] Subsequently, the entangled fiber body is dried after being impregnated with the dispersion, thereby to dry and remove the volatile components, such as the dispersion medium, in the dispersion. This allows the first filler, the non-volatile oil, and the like to remain in the voids among the fibers of the entangled fiber body. The drying conditions are not particularly limited, and for example, there is a condition of drying at 70 to 150°C for about 1 to 10 minutes. As such, the first filler, the non-volatile oil, and the like are added into the voids among the fibers of the entangled fiber body. These are present in the voids, for example, in clay or paste form.

[0042] The proportion of the non-volatile oil relative to the entangled fiber body is preferably 0.5 to 10 mass%, further preferably 1 to 10 mass%, and particularly preferably 3 to 8 mass%. When the proportion of the non-volatile oil relative to the entangled fiber body is less than 0.5 mass%, a supple texture cannot be easily obtained sufficiently. Moreover, when the proportion of the non-volatile oil relative to the entangled fiber body is too high, the entangled fiber body becomes unable to retain the non-volatile oil, and the non-volatile oil tends to become easily detached.

[0043] The proportion of the first filler relative to the entangled fiber body is not particularly limited, and is preferably 1 to 60 mass%, 10 to 50 mass%, and further preferably 10 to 40 mass%. When the proportion of the first filler relative to the entangled fiber body is too low, fullness tends to lessen. Moreover, when the proportion of the first filler relative to the entangled fiber body is too high, supple texture tends to lessen.

[0044] Moreover, the proportion of the first elastic polymer relative to the entangled fiber body is preferably 0 to 15 mass%, further preferably 1 to 14 mass%, and particularly preferably 1 to 10 mass%. When the proportion of the first elastic polymer relative to the entangled fiber body is too high, rubberiness increases and resilience becomes high, and therefore, supple texture tends to lessen. Note that the first elastic polymer is not an indispensable component, but by being added, structural stability can be further increased and elasticity can be further adjusted.

[0045] Moreover, the proportion of the non-volatile oil in the modifying agent being the first filler, the non-volatile oil, and the first elastic polymer added together is not particularly limited, and is 3 to 50 mass%, preferably 10 to 50 mass%, and especially 20 to 35 mass%, in terms of obtaining supple texture and fullness. When the proportion of the non-volatile oil in the modifying agent is too low, supple texture tends to lessen; and when too high, the proportion of the filler becomes relatively lower, and therefore, fullness tends to lessen.

[0046] Moreover, the proportion of the first filler in the modifying agent is 50 to 97 mass%, and preferably 50 to 90 mass%. When the proportion of the first filler is too low, fullness tends to lessen; and when too high, the proportion of the non-volatile oil becomes relatively lower, and therefore, supple texture tends to lessen.

[0047] The proportion of the first elastic polymer in the modifying agent is 0 to 20 mass% and preferably 1 to 20 mass%. When the proportion of the first elastic polymer is too high, texture tends to become rubber-like.

[0048] The proportion of the modifying agent relative to the entangled fiber body is not particularly limited, and is preferably 1 to 60 mass%, further preferably 3 to 45 mass%, particularly preferably 10 to 40 mass%, and especially 10 to 30 mass%. When the proportion of the modifying agent relative to the entangled fiber body is made too high, sufficient filling of the voids by impregnation tends to become difficult.

[0049] As the above, the modifying agent including the first filler, the non-volatile oil, and as necessary, the first elastic polymer is added into the voids among the fibers of the entangled fiber body, thereby to obtain an artificial leather substrate. Such artificial leather substrate may undergo slicing treatment or buffing treatment as necessary, for thickness adjustment and planarization treatment; or may undergo finishing treatment, such as softening treatment by rubbing, softening treatment by milling, brushing treatment by reverse sealing, stain inhibiting treatment, hydrophilization treatment, treatment with lubricant, treatment with softener, treatment with antioxidant, treatment with ultraviolet absorber, treatment with fluorescing agent, or treatment with flame retardant.

[0050] For the purpose of adjusting fullness and suppleness of the artificial leather substrate, softening processing is preferably conducted on the artificial leather substrate into which the modifying agent including the first filler, the non-volatile oil, and as necessary, the first elastic polymer, was added by impregnation. The method for the softening processing is not particularly limited, and is preferably a method wherein the artificial leather substrate is made to adhere to an elastic sheet, mechanically shrink in a vertical direction (MD on production line), and then, in such shrunken state, undergo heat treatment for heat setting. By employing this method, the artificial leather substrate can be softened, while the smoothness of its surface is enhanced.

[0051] The thickness of the artificial leather substrate obtained as the above is not particularly limited, and is preferably about 100 to 3000 μm and further preferably about 300 to 2000 μm . Moreover, the apparent density of the artificial leather substrate is not particularly limited, and is preferably 0.55 to 0.85 g/cm³ and further preferably 0.60 to 0.80 g/cm³, in terms of excellent balance between fullness and supple texture.

[0052] The artificial leather substrate obtained as the above undergoes a treatment for imparting a desired appearance, and is thereby finished as an artificial leather. Examples of the artificial leather include: grain-like-finish artificial leather comprising the artificial leather substrate and a resin layer with a grain-like surface added onto the substrate surface; napped-like-finish artificial leathers (suede, nubuck, velour, buckskin) comprising the artificial leather substrate having

a surface at which fibers are raised or napped by buffing treatment, thereby to impart a fuzzy appearance.

[0053] The grain-like-finish artificial leather is obtained by forming a resin layer with a grain-like surface on the surface of the artificial leather substrate. The method for forming the resin layer with a grain-like surface on the surface of the artificial leather substrate is not particularly limited, and for example, a dry-type surface forming method or a direct coating method is used. The dry-type surface forming method is a method wherein a coating liquid including a colored resin for forming a grain-like layer is applied to a release sheet, followed by drying to form a film; and then the film is attached to the surface of the artificial leather substrate via an adhesion layer, followed by release of the release sheet. Moreover, a direct coating method is a method wherein formation is by applying the coating liquid including the resin directly to the surface of the artificial leather substrate with a roll coater or a spray coater, followed by drying.

[0054] Conventionally, a grain-like layer has been typically formed by a method which involves dry-type surface formation wherein a film formed in advance is stacked on an artificial leather substrate via a semi-cured adhesion layer, and then hot pressed for adhesion to the substrate. The grain-like layer formed by dry-type surface formation becomes relatively thick, and moreover, the formation process is cumbersome. In contrast, according to the direct coating method, there is the advantage of the formation process being simple since a grain-like layer can be formed by coating. However, when formation of a grain-like layer by a direct coating method is attempted, since the coating liquid that enters from the voids in the surface of the artificial leather substrate permeates too much into the substrate, there is the problem of the artificial leather substrate becoming hard and the supple texture thereof being lost.

[0055] The artificial leather substrate of the present embodiment has excellent fullness as described above, and furthermore, is a substrate having a smooth surface; therefore, by a method as given below, a remarkably high degree of smoothness can be imparted to the surface. By enhancing the smoothness of the surface of the artificial leather substrate as such, even if the coating liquid is applied to the surface of the artificial leather substrate by a direct coating method, the coating liquid would not easily permeate into the substrate. Due to the above, the resin layer formed would not sink deeply into the artificial leather substrate; therefore, supple texture would be maintainable.

[0056] For a first method, as illustrated in Fig. 2, there is a method wherein a smoothing layer 6 including a second elastic polymer and a second filler is formed on the surface layer of the artificial leather substrate 1, in order to smooth the surface. Then, a grain-like layer 12 is formed on the surface of such smoothing layer 6. A method for forming such smoothing layer will be described below.

[0057] A coating liquid including a second elastic polymer and a second filler and furthermore having a thixotropic index of 2 to 4 is applied to the surface of an original fabric of the artificial leather substrate, followed by drying, thereby to form a smoothing layer. Since such coating liquid has a thixotropic index of 2 to 4, viscosity becomes low at the time of coating liquid application when there is shear application, and viscosity becomes high after coating liquid application when there is no shear application. According to such method, the coating liquid that enters the voids in the surface of the artificial leather substrate does not easily sink into the substrate; therefore, a thin smoothing layer can be easily formed on the surface of the artificial leather substrate.

[0058] The coating liquid used for forming the smoothing layer is not particularly limited, if the coating liquid includes the second elastic polymer and the second filler and furthermore has a thixotropic index of 2 to 4. Here, "thixotropic index" means the ratio between a viscosity $\eta_{0.6}$ and a viscosity $\eta_{3.0}$ ($\eta_{0.6}/\eta_{3.0}$), the viscosity $\eta_{0.6}$ measured at 0.6 rotation/sec and the viscosity $\eta_{3.0}$ measured at 3 rotations/sec by using a B-type rotational viscometer at a temperature of 25°C.

[0059] The coating liquid used for forming the smoothing layer includes the second elastic polymer and the second filler. For a specific example of the coating liquid, for example, preferably used is a mixed liquid comprising: a resin liquid, such as an emulsion, suspension, or dispersion of the second elastic polymer; and the second filler mixed into the resin liquid.

[0060] Specific examples of the second elastic polymer are similar to those given for the first elastic polymer described above, and include polyurethanes, acrylic-based elastomers, silicone-based elastomers, diene-based elastomers, nitrile-based elastomers, fluorine-including elastomers, polystyrene-based elastomers, polyolefin-based elastomers, polyamide-based elastomers, and halogen-including elastomers. The concentration of the second elastic polymer in the resin liquid is not particularly limited, and in the case of an emulsion for example, is preferably 10 to 50 mass%, further preferably 20 to 40 mass%, and particularly preferably 25 to 35 mass%.

[0061] The second filler is a component that imparts thixotropy to the coating liquid and also fills the voids in the surface of the artificial leather substrate. For a specific example of the second filler, in addition to filled particles that serve as a filler similar to the first filler described above, there are hollow particles, such as plastic beads. Among these, clay, aluminum hydroxide, calcium carbonate, hollow particles, and the like are particularly preferred, in terms of easy adjustment of the thixotropic index.

[0062] The particle size of the filled particles is preferably 0.5 to 15 μm , in terms of easy adjustment of the thixotropic index. Moreover, the particle size of the hollow particles is preferably 10 to 80 μm , in terms of easy adjustment of the thixotropic index.

[0063] For the amount of the second filler to be added, addition is preferably made such that the amount in the solid

content in the coating liquid becomes preferably 1 to 50 mass%, further preferably 5 to 50 mass%, and particularly preferably 10 to 30 mass%. Moreover, for the amount of the second filler to be added when in the form of hollow particles, addition of hollow particles corresponding to a volume of preferably 5 to 70% and further preferably 10 to 50% relative to the volume of the solid content in the coating liquid, is preferably made.

[0064] Moreover, the coating liquid used for forming the smoothing layer may include, as necessary, a thickener for adjusting the thixotropic index or the viscosity. Specific examples of the thickener include ammonium polyacrylate and polyacrylic acid. The amount of the thickener to be added is preferably 0.5 to 5 parts by mass relative to 100 parts by mass of the solid content of the second elastic polymer. Furthermore, a dispersant for improving stability of the coating liquid, a crosslinking agent for crosslinking the elastic polymer, or a coloring agent, such as a pigment, may be included. Specific examples of the dispersant include low-molecular-weight sodium polycarboxylate and sodium tripolyphosphate. The amount of the dispersant to be added is preferably 0.2 to 2 parts by mass relative to 100 parts by mass of the solid content of the second elastic polymer.

[0065] The coating liquid is prepared by adding the second filler and other additives, such as the thickener, that are added as necessary, to the resin liquid of the second elastic polymer, and then conducting stirring and mixing. The viscosity of the coating liquid prepared as such, as the viscosity $\eta_{0.6}$ measured at 0.6 rotation/sec by using a B-type rotational viscometer at a temperature of 25°C, is preferably 100 to 600 Pa·s (pascal-second) and further preferably 150 to 350 Pa·s. When the viscosity is as above, coating property of the coating liquid is excellent, and also, the coating liquid that enters the voids in the surface of the artificial leather substrate does not easily sink into the substrate.

[0066] Moreover, the proportion of the solid content in the coating liquid is not particularly limited, and is preferably about 40 to 60 mass%, in terms of excellent thixotropy which results in moderate viscousness after application, and in terms of excellent drying property.

[0067] After the above coating liquid is applied to the surface of the original fabric of the artificial leather substrate, drying is conducted, thereby to form a smoothing layer. For the coating method, various coating methods, such as reverse coating and doctor knife coating, can be used without particular limitation. The coating liquid becomes low in viscosity at the time of application due to receiving shear, and increases in viscosity after application; therefore, the coating liquid that enters the voids in the surface of the artificial leather substrate tends not to easily sink into the substrate.

[0068] By drying the coating liquid that has been applied, the smoothing layer is formed. The average thickness of the smoothing layer formed as such is preferably 10 to 100 μm and further preferably 20 to 70 μm . When the smoothing layer is too thick, suppleness of the artificial leather obtained tends to lessen; and when too thin, the voids in the surface of the artificial leather substrate tend not to be filled sufficiently. Moreover, the proportion of the second filler in the smoothing layer is preferably 1 to 50 mass%, further preferably 5 to 50 mass%, and particularly preferably 10 to 30 mass%.

[0069] Regarding the artificial leather substrate with the smoothing layer formed thereon, most of the voids in the surface is preferably filled and made smooth. In such case, even when the resin liquid for imparting a grain-like appearance is applied to the surface of the smoothing layer, the resin liquid tends not to easily seep into the artificial leather substrate. By using such artificial leather substrate with the smoothing layer formed thereon, a grain-like-finish artificial leather without loss of suppleness of the artificial leather substrate, can be produced.

[0070] The surface of the artificial leather substrate with the smoothing layer formed thereon, as above, preferably has, for example, a surface water absorption rate in compliance with the water drop test of JIS L 1907-7.1.1, of preferably 100 seconds or more, further preferably 150 seconds or more, and particularly preferably 180 seconds or more. When the surface water absorption rate is less than 100 seconds, since there are voids remaining, the resin liquid tends to easily seep into the substrate.

[0071] Moreover, for a second method for smoothing the surface of the artificial leather substrate of the present embodiment, there is a method wherein the surface of the artificial leather substrate of the present embodiment is hot pressed to make the surface closely packed. In that case, particularly when the modifying agent is contained such that its proportion becomes 10 mass% or more relative to the entangled fiber body, the voids in the surface become filled with the modifying agent, and the number of the voids in the surface becomes less. Therefore, even when the resin liquid for imparting a grain-like appearance is applied to the surface of the artificial leather substrate that has been hot pressed, sinking of the resin liquid into the artificial leather substrate is suppressed. Therefore, even by using the artificial leather substrate having a hot-pressed surface, a grain-like-finish artificial leather can be produced without loss in suppleness.

[0072] Subsequently, the coating liquid for forming a resin layer is applied to the surface of the smoothing layer formed; and thereafter, by a direct coating method for drying, a resin layer with a grain-like surface is formed. The coating liquid for forming the resin layer is applied to the surface of the smoothing layer, for example, by a method of spray coating, reverse coating, or the like. Among these, spray coating is preferred, in terms of being capable of uniformly applying a small amount of the resin.

[0073] Examples of the resin component for forming the resin layer with a grain-like surface by a direct coating method, include resin liquids, such as emulsions, suspensions, dispersions, and liquids of elastomers, such as polyurethane, acrylic-based elastomer, silicone-based elastomer, diene-based elastomer, nitrile-based elastomer, fluorine-including

elastomer, polystyrene-based elastomer, polyolefin-based elastomer, polyamide-based elastomer, and halogen-including elastomer. These may be used singly or in a combination of two or more. Among these, emulsions of polyurethanes are preferred, in terms of excellent wear resistance and mechanical properties. Moreover, the resin component for forming the grain-like layer may contain, as necessary, a coloring agent, an ultraviolet absorber, a surfactant, a flame retardant, an antioxidant, or the like.

[0074] The thickness of the resin layer with a grain-like surface is preferably 10 to 1000 μm and further preferably 50 to 300 μm . Moreover, the resin layer may have a stacked structure wherein layers, such as basecoat layers, colored layers, and top clear layers, are stacked as appropriate. Moreover, the resin layer preferably has a wrinkle pattern formed by embossing processing, in terms of designability. For the embossing processing, there is a method wherein a wrinkle pattern is transferred to the grain-like layer in a semi-cured state, followed by complete curing of the grain-like layer.

[0075] The grain-like-finish artificial leather of the present embodiment has suppleness and also considerable fullness as with natural leather. Specifically, for example, the grain-like-finish artificial leather preferably exhibits suppleness corresponding to stiffness measured by a softness tester as 1.5 mm or more and preferably 1.8 to 2.5 mm. Moreover, the grain-like-finish artificial leather preferably has fullness corresponding to apparent density of 0.55 to 0.85 g/cm^3 and further preferably 0.60 to 0.80 g/cm^3 .

[0076] Moreover, a napped-like-finish artificial leather (suede, nubuck, velour, buckskin) is obtained by subjecting the surface of the artificial leather substrate to buffing treatment by using sandpaper or the like, for treatment to raise the fibers or to nap the fibers.

[0077] Moreover, finishing treatment, such as softening treatment by rubbing, softening treatment by milling, brushing treatment by reverse sealing, stain inhibiting treatment, hydrophilization treatment, treatment with lubricant, treatment with softener, treatment with antioxidant, treatment with ultraviolet absorber, treatment with fluorescing agent, or treatment with flame retardant, may be conducted.

[Examples]

[0078] The present invention will now be specifically described by way of Examples. The following Examples, however, are not to be construed as limiting in any way the scope of the present invention.

[Example 1]

(Production of non-woven fabric)

[0079] By using water-soluble thermoplastic polyvinyl alcohol (PVA) as a sea component and isophthalic acid-modified polyethylene terephthalate with a degree of modification of 6 mol% as island components, molten resin was fed to a plurality of spinnerets for spinning set to a spinneret temperature of 260°C and having nozzle holes arranged in parallel, the nozzle holes being capable of forming a sectional surface comprising a sea component and 25 island components all with a uniform sectional surface area distributed in the sea component; and the molten resin was ejected from the nozzle holes. At that time, the molten resin was fed while pressure was adjusted, such that the mass ratio between the sea component and the island components became sea component/island components = 25/75.

[0080] Subsequently, the molten fibers ejected were drawn by suction with a suction machine, such that the average spinning rate became 3700 m/min; and long fibers of sea-island-type conjugated fibers with a fineness of 2.1 dtex were spun. The long fibers of the sea-island-type conjugated fibers that were spun, were continuously deposited on a mobile net, and then lightly pressed with a metal roller at 42°C to suppress fuzzing at the surface. Then, the long fibers of the sea-island-type conjugated fibers were separated from the net and passed between a grid-patterned metal roller with a surface temperature of 55°C and a back roller. As such, hot pressing was conducted at a linear pressure of 200 N/mm, thereby to obtain a web of the long fibers with a mass per unit area of 31 g/m^2 .

[0081] Subsequently, the web was overlapped into eight layers by using a cross-lapper machine such that the total mass per unit area became 250 g/m^2 , thereby to produce an overlapped web; and furthermore, an anti-needle-breakage oiling agent was sprayed to the overlapped web. Then, by using a needle with 6 barbs and a distance of 3.2 mm from the needle tip to the first barb, both surfaces of the overlapped web were needle punched alternatively at 3300 punches/ cm^2 , with the needle penetration depth at 8.3 mm. The area shrinkage due to this needle punching treatment was 68%, and the mass per unit area of the entangled web after the needle punching was 550 g/m^2 .

[0082] The entangled web was immersed in hot water at 70°C for 14 seconds and at a take-up line velocity of 10 m/min, thereby to cause area shrinkage. Then, dip-nip treatment was conducted repeatedly in hot water at 95°C to dissolve and remove the PVA, thereby to produce a non-woven fabric wherein fiber bundles with a fineness of 2.5 dtex each comprising 25 ultrafine fibers with a fineness of 0.1 dtex were interlaced three-dimensionally. The area shrinkage measured after drying was 52%. Then, the non-woven fabric was sliced and buffed to adjust the thickness to 1.05 mm. The non-woven fabric of the ultrafine fibers, i.e., the entangled fiber body obtained as above, had a mass per unit area

of 576 g/m² and an apparent density of 0.565 g/cm³.

(Addition of modifying agent by impregnation)

[0083] Components of a modifying agent being 38%owf of a flame-retardant filler, 3.75%owf of liquid paraffin, and 5%owf of water-based polyurethane were dispersed in water, thereby to prepare a dispersion. Then, the non-woven fabric of the ultrafine fibers was impregnated with the dispersion at a pick-up rate of 80%, followed by drying of moisture, thereby to uniformly add the modifying agent into the non-woven fabric by impregnation. Then, the non-woven fabric of the ultrafine fibers with the addition of the modifying agent by impregnation, was shrunk 5.5% in a vertical direction (longitudinal direction), by using a shrinkage processing machine (sanforizing machine available from Komatsubara Tekko K.K.) for treatment at 120°C as the drum temperature of its shrinking unit, 120°C as the drum temperature of its heat setting unit, and 10 m/min as the transferring rate, thereby to obtain an artificial leather substrate. The artificial leather substrate obtained had a mass per unit area of 676 g/m² and an apparent density of 0.633 g/cm³.

[0084] For the flame-retardant filler, a dispersion (solid content: 40%) of aluminum dialkylphosphinate with an average particle size of 5 μm was added. Moreover, for the water-based polyurethane, an emulsion of crosslink-type polyurethane (solid content: 30 mass%, melting point: 180 to 190°C, peak temperature for loss elastic modulus: -15°C, swelling rate in hot water at 130°C: 35%) wherein the soft segment included a mixture of polyhexylene carbonate diol and polymethyl pentanediol in a ratio of 70:30, and the hard segment mainly included hydrogenated methylene diisocyanate.

(Formation of grain-like layer)

[0085] A basecoat liquid was applied to the surface of the artificial leather substrate by roll coating at a rate of applied amount 140 g/m², by using STARPLUS available from Gemata, thereby to form a basecoat layer with a film thickness of 28 μm. Note that for the basecoat liquid, a polyurethane emulsion (LCC Binder UB1770 available from DIC Corporation, solid content: 30 mass%) adjusted with a thickener such that the viscosity via the Ford Cup No. 4 55S became 195 mPa·s, was used. Then, a colorcoat liquid was further applied to the surface of the basecoat layer formed, by spray coating at a rate of applied amount 70 g/m², by using STARPLUS available from Gemata, thereby to form a colorcoat layer with a film thickness of 14 μm. Note that for the colorcoat liquid, a polyurethane emulsion (LCC Binder UB1770 available from DIC Corporation, solid content: 30%) adjusted such that the viscosity became 30 mPa·s via the Iwata Cup (IWATA NK-2 12s), was used. Then, milling treatment was further conducted at 40 to 50°C for 2 to 4 hours. Then, by using embossing rollers at 125°C and 50 kg/cm², embossing treatment was conducted on the surface layer, at a line velocity of 7.0 m/min. Then, a topcoat coating material (clear coating material, available from Tohpe Corporation) adjusted to 30 mPa s via the Iwata Cup (IWATA NK-2 12s), was applied to the surface, thereby to form a topcoat with a film thickness of 13.5 μm. As such, a grain-like-finish artificial leather with a mass per unit area of 777 g/m² and an apparent density of 0.762 g/cm³ was obtained.

(Evaluation of grain-like-finish artificial leather)

[0086] The grain-like-finish artificial leather obtained was evaluated by in accordance with the evaluation methods below.

(Stiffness)

[0087] Stiffness was measured by using a softness tester (leather softness measuring equipment ST300, available from MSA Engineering Systems Limited of the United Kingdom). Specifically, a predetermined, 25 mm-diameter ring was set to the lower holder of the equipment, and thereafter, the grain-like-finish artificial leather was set to the lower holder. Then, the metal pin (diameter: 5 mm) fixed to the upper lever was pushed down toward the grain-like-finish artificial leather. Then, the value at the time the upper lever was pushed down and locked, was read. Note that the value indicated penetration depth and also indicated that the greater the value became, the more supple the leather became.

(Texture)

[0088] The grain-like-finish artificial leather was cut to a size of 20 × 20 cm to prepare a sample. Then, the appearance of the leather when bent inward at the center portion thereof and the appearance of the leather when held, were evaluated based on the following criteria.

A: When bent, the leather bent as if with roundness, and also formed a pattern of very fine and minute fold wrinkles. Moreover, drape was excellent.

EP 2 966 218 B1

- B: When bent, the leather bent sharply, and also formed a pattern of coarse wrinkles, as well as deep creases. Moreover, drape was poor.
C: The texture had a remarkably low degree of fullness.

5 (Coatability of grain-like layer)

[0089]

- 10 A: Sinking of the grain-like layer was slight, and a flat and smooth surface was formed.
B: There was a small amount of sinking of the grain-like layer, and roughness of the fibers at the surface was slightly felt.
C: Most of the grain-like layer sunk, and the fibers were exposed and fuzzed at the surface.

15 (Apparent density)

[0090] Thickness (mm) and mass per unit area (g/cm^2) were measured in compliance with JIS L1913, and the apparent density (g/cm^3) was calculated from the obtained values.

[0091] The evaluation results of the above are shown in Table 1.

20

25

30

35

40

45

50

55

[Table 1]

Example No.	Proportion relative to non-woven fabric (%)				Proportion in modifying agent (%)				Apparent density (g/cm ³)	Evaluation results			
	Non-volatile oil	Filler	Elastic polymer	Total	Non-volatile oil	Filler	Elastic polymer	Total		Stiffness (mm)	Texture	Coatability of grain-like layer	
1	0.5	11	1.5	13	3.8	84.6	11.5	100	0.633		1.86	A	B
2	1.5	11	1.5	14	10.7	78.6	10.7	100	0.632		1.91	A	B
3	3.5	11	1.5	16	21.9	68.8	9.4	100	0.645		2.17	A	A
4	3.5	11	0	14.5	24.1	75.9	0.0	100	0.645		2.48	A	A
6	3.5	11	0.5	15	23.3	73.3	3.3	100	0.643		2.2	A	A
7	3.5	11	3	17.5	20.0	62.9	17.1	100	0.654		1.84	A	B
RefEx. 8	3.5	3	1.5	8	43.8	37.5	18.8	100	0.607		2.3	B	C
9	3.5	25	1.5	30	11.7	83.3	5.0	100	0.656		2.15	A	A
10	6.5	11	1.5	19	34.2	57.9	7.9	100	0.662		2.23	A	A
11	3.5	5	1.5	10	35	50	15.0	100	0.601		2.24	A	A
12	3.5	11	0.5	15	23.3	73.3	3.3	100	0.657		2.2	A	A
CompEx. 1	0	0	12.5	12.5	0	0	100.0	100	0.624		0.89	B	C
CompEx. 2	-	-	-	-	-	-	-	-	0.569		2.39	C	C
CompEx. 3	0	0	1.5	1.5	0	0	100.0	100	0.563		1.98	B	C
CompEx. 4	0	11	0	11	0	100	0.0	100	0.612		2.14	B	B
CompEx. 5	0	11	1.5	12.5	0	88	12.0	100	0.626		1.76	B	B
CompEx. 6	3.5	0	1.5	5	70.0	0.0	30.0	100	0.578		2.37	B	C

[Examples 2 to 11]

[0092] The composition of the dispersion for the modifying agent prepared in Example 1 was changed to the compositions and amounts shown in Table 1, thereby to prepare modifying agents for addition into the non-woven fabric of the ultrafine fibers by impregnation; and except for the above, grain-like-finish artificial leathers were obtained as in Example 1 and then evaluated. The results are shown in Table 1. Moreover, Fig. 3 shows a sectional image of when the non-woven fabric of the ultrafine fibers obtained in Example 6 was observed with a scanning electron microscope (SEM); and Fig. 4 shows a sectional SEM image of the artificial leather substrate obtained by addition of the modifying agent by impregnation. Moreover, Fig. 5 shows a sectional SEM image of the grain-like-finish artificial leather substrate obtained in Example 6. Example 8 is a reference example.

[Example 12]

[0093] For the filler in particle form, alumina (Al_2O_3) particles instead of the aluminum dialkylphosphinate were added into the composition of the dispersion for the modifying agent prepared in Example 6; and except for the above, a grain-like-finish artificial leather was obtained as in Example 1 and then evaluated. The results are shown in Table 1.

[Comparative Example 1]

[0094] Instead of adding the dispersion for the modifying agent into the non-woven fabric of the ultrafine fibers by impregnation in Example 1, a water-based polyurethane dispersion as the one used in Example 1 was added by impregnation, such that the dispersion became 12.5 mass% as a solid content relative to the non-woven fabric of the ultrafine fibers, and was then dried at 120°C; and except for the above, a grain-like-finish artificial leather was obtained as in Example 1 and then evaluated. The results are shown in Table 1.

[Comparative Example 2]

[0095] Except that the process of adding the modifying agent by impregnation in Example 1 was omitted, a grain-like-finish artificial leather was obtained as in Example 1 and then evaluated. The results are shown in Table 1.

[Comparative Examples 3 to 6]

[0096] The composition of the dispersion for the modifying agent prepared in Example 1 was adjusted and modifying agents with the compositions and amounts shown in Table 1 were added into the artificial leather substrate by impregnation; and except for the above, grain-like-finish artificial leathers were obtained as in Example 1 and then evaluated. The results are shown in Table 1.

[0097] Regarding each of the artificial leather substrates obtained in Examples 1 to 12 according to the present invention, the apparent density was 0.6 g/cm³ or more, and also, the suppleness of the grain-like-finish artificial leather corresponded to a stiffness of 1.8 mm or more; and therefore, an artificial leather having fullness and also suppleness was obtained. In contrast, regarding the artificial leather obtained in Comparative Example 1, i.e., a conventional and typical artificial leather, wherein the non-woven fabric was given fullness by addition of the elastic polymer, although the apparent density was 0.6 g/cm³ or more and allowed fullness, the stiffness was 0.89 mm and suppleness was of a low degree. Moreover, in production of the artificial leather of Comparative Example 1, when the resin liquid for the grain-like layer was applied, the resin liquid tended to easily seep into the artificial leather substrate. This was because there were many voids remaining in the surface. Moreover, regarding the artificial leather of Comparative Example 6 which did not include the filler, apparent density was low and fullness was of a low degree.

[0098] Note that the artificial leather of Example 8 exhibited fullness of a slightly low degree due to the relatively low proportion of the modifying agent, but exhibited suppleness of a remarkably high degree. However, regarding the artificial leather of Example 8, since there were voids remaining in the surface of the artificial leather substrate, the resin liquid applied tended to easily seep into the substrate.

[0099] As shown by the above Examples, according to the present invention, there is obtained an artificial leather having a supple texture and also fullness, due to addition of the modifying agent as described above into the voids among the fibers of the entangled fiber body, by impregnation.

[Example 13]

[0100] Instead of forming the basecoat with a film thickness of 28 μm for the grain-like layer on the surface of the artificial leather substrate obtained in Example 6, a smoothing layer was formed as follows. Specifically, a filler (calcium

carbonate with average particle size of 5 μm) was added into a polyurethane emulsion (LCC Binder UB1770 available from DIC Corporation, solid content: 30 mass%), the amount of the filler being 42.9 parts by mass relative to 100 parts by mass of the solid content in the polyurethane emulsion; and this was followed by addition of a thickener and then stirring and mixing, thereby to prepare a smoothing-layer-forming coating liquid. Note that regarding the smoothing-layer-forming coating liquid obtained, according to a B-type rotational viscometer at a temperature of 25°C, a viscosity $\eta_{0.6}$ measured at 0.6 rotation/sec was 240 Pa·s, a viscosity $\eta_{3.0}$ measured at 3 rotations/sec was 75 Pa·s, and $\eta_{0.6}/\eta_{3.0}$ was 3.2. Note that when only the polyurethane emulsion was used, the viscosity $\eta_{0.6}$ was 4.2 Pa·s, the viscosity $\eta_{3.0}$ was 3.0 Pa·s, and $\eta_{0.6}/\eta_{3.0}$ was 1.4.

[0101] The smoothing-layer-forming coating liquid was applied to the surface of the artificial leather substrate obtained in Example 6, at 140 g/m² with a reverse coater, followed by drying, thereby to form a 45 μm -thick smoothing layer. The surface water absorption rate of the smoothing layer formed as such was measured by a method as below. As a result, the surface water absorption rate was 180 seconds or more. The results are shown in Table 2.

(Surface water absorption rate)

[0102] Measurement was conducted in compliance with the water drop method of JIS L1907-7.1.1. Specifically, the artificial leather substrate was cut into a size of about 200 mm $\times$ 200 mm to prepare a test piece. The prepared test piece was attached to a test piece-holding frame, which was then placed between a light source and the observer; and then, adjustment was made so that the height from the surface on the smoothing layer side of the test piece to the tip of the burette became 10 mm. Then, one drop of water was dropped from the burette to the surface on the smoothing layer side of the test piece; and then, with a stopwatch, measurement was made for time starting from when the water drop reached the test piece surface, until when the test piece reached a state where specular reflection disappeared as the water drop was absorbed and only moisture remained. The results are shown in Table 2.

[0103] Subsequently, a colorcoat layer with a film thickness of 14 μm as in Example 1 was formed on the surface of the smoothing layer on the artificial leather substrate. Then, milling treatment was further conducted at 40 to 50°C for 2 to 4 hours. Then, as in Example 1, by using embossing rollers at 125°C and 50 kg/cm², embossing processing was conducted on the surface layer, at a line velocity of 7.0 m/min. Then, as in Example 1, a topcoat with a film thickness of 13.5 μm was formed. As such, a grain-like-finish artificial leather with a mass per unit area of 665 g/m² and an apparent density of 0.629 g/cm³ was obtained. Fig. 6 shows an SEM image of an oblique sectional surface of the artificial leather substrate obtained in Example 13, before formation of the smoothing layer; and Fig. 7 shows an SEM image of an oblique sectional surface thereof after formation of the smoothing surface. Moreover, Fig. 8 shows a sectional SEM image of the grain-like-finish artificial leather substrate obtained in Example 13. Moreover, the sinking amount (g/m²) was calculated from the difference between the applied amount when forming the smoothing layer and the film thickness when the smoothing layer was actually formed. However, when the value obtained was smaller than 0, the value was regarded as 0. Moreover, the results for stiffness and texture are shown in Table 2.

[Table 2]

Example No.	Kind of filler in smoothing layer	Proportion of filler in smoothing layer (%)	Thickness of smoothing layer (μm)	$\eta_{0.6}$ (Pa·s)	$\eta_{3.0}$ (Pa·s)	$\eta_{10.0}$ (Pa·s)	Evaluation results			
							Surface water absorption rate (sec)	Sinking amount (g/m^2)	Stiffness (mm)	Texture
13	Calcium carbonate	30	45	240	75	3.2	180<	0	2.41	A
14	Calcium carbonate	5	36	170	76	2.2	162	6	2.31	A
15	Calcium carbonate	10	35	210	74	2.8	158	7	2.39	A
16	Calcium carbonate	20	38	270	77	3.5	180<	4	2.38	A
17	Calcium carbonate	40	42	300	79	3.8	180<	0	2.42	A
18	Calcium carbonate	50	47	320	82	3.9	180<	0	2.49	A
19	Calcium carbonate	30	20	240	75	3.2	126	0	2.35	A
20	Calcium carbonate	30	31	240	75	3.2	180<	0	2.37	A
21	Calcium carbonate	30	54	240	75	3.2	180<	0	2.40	A
22	Plastic balloon	1.5	60	180	86	2.1	180<	7	2.47	A
6	-	0	28	0.20	0.27	1.4	83	14	2.2	A

[Examples 14 to 18]

[0104] As shown in Table 2, except that the filler (calcium carboante) was added in amounts of 5 mass%, 10 mass%, 20 mass%, 40 mass%, and 50 mass%, respectively, smoothing-layer-forming coating liquids were prepared as in Example 13. Except that the smoothing-layer-forming coating liquids adjusted as such were used, grain-like-finish artificial leathers were obtained as in Example 13. The results are shown in Table 2.

[Examples 19 to 21]

[0105] As shown in Table 2, except that the thicknesses of the smoothing layer were changed to 20 μm , 31 μm , and 54 μm , respectively, grain-like-finish artificial leathers were obtained as in Example 13. The results are shown in Table 2.

[Example 22]

[0106] As shown in Table 2, instead of adding 30 mass% of the filler (calcium carbonate), a filler (vinylidene chloride nitrile-based plastic balloon with average particle size of 30 μm) was added into the polyurethane emulsion, the amount of the filler being 1.5 parts by mass relative to 100 parts by mass of the solid content in the polyurethane emulsion and being 50% in volume ratio; and except for the above, a smoothing-layer-forming coating liquid was prepared as in Example 13; and except that the smoothing-layer-forming coating liquid adjusted as such was used, a grain-like-finish artificial leather was obtained as in Example 13. The results are shown in Table 2. Moreover, Fig. 9 shows an SEM image of an oblique sectional surface of the artificial leather substrate obtained in Example 22, after formation of the smoothing layer; and Fig. 10 shows a sectional SEM image of the grain-like-finish artificial leather substrate obtained in Example 22.

[0107] Regarding each of the artificial leather substrates obtained in Examples 13 to 22, sinking of the smoothing layer and sinking of the grain-like layer were both to a small extent; and moreover, the surface water absorption rate of the artificial leather substrate was low. Therefore, it is evident that sinking of the resin layer with a grain-like surface on the surface of the artificial leather substrate can be suppressed, by providing the smoothing layer. By suppressing the sinking of the resin layer with a grain-like surface, a grain-like-finish artificial leather which maintains a remarkably supple texture is obtained. In contrast, as in Example 6, when a polyurethane emulsion without addition of a filler and having $\eta_{0.6}/\eta_{3.0}$ of 1.4 was used, a slight sinking in was apparently observed.

[0108] The artificial leather of the present invention can be used as a leather-like material for applications in footwear, clothing, gloves, bags, balls, interior decoration, vehicle upholstery, and the like.

Claims

1. An artificial leather substrate comprising:

an entangled fiber body; and

a first filler, a first elastic polymer and a non-volatile oil in liquid form, all added into the entangled fiber body by impregnation, wherein the first filler includes at least one of an inorganic filler, a metal filler, a metal oxide filler, a semimetal oxide filler, a flame-retardant filler and a carbon-based filler, and the non-volatile oil is a liquid with a boiling point of 150°C or more that substantially does not dissolve in a polar solvent, wherein a content of the first filler is 50 to 97 mass%, in the total amount of the first filler, the first elastic polymer, and the non-volatile oil.

2. The artificial leather substrate in accordance with claim 1, wherein the non-volatile oil includes at least one selected from liquid paraffin, silicone oil, mineral oil, and phthalate esters.

3. The artificial leather substrate in accordance with claim 1, wherein the entangled fiber body is a non-woven fabric of ultrafine fibers with a fineness of 0.9 dtex or less.

4. The artificial leather substrate in accordance with claim 1, wherein a content of the first filler is 1 to 60 mass% and a content of the non-volatile oil is 0.5 to 10 mass%, relative to the entangled fiber body.

5. The artificial leather substrate in accordance with claim 1, wherein 1 to 15 mass% of the first elastic polymer are present relative to the entangled fiber body.

6. The artificial leather substrate in accordance with claim 5, wherein a content of the first filler, the non-volatile oil, and the first elastic polymer in total, relative to the entangled fiber body, is 10 to 30 mass%.
7. The artificial leather substrate in accordance with claim 6, wherein a content of the first elastic polymer in the total amount of the first filler, the non-volatile oil, and the first elastic polymer, is 1 to 20 mass%.
8. The artificial leather substrate in accordance with claim 1 having an apparent density of 0.60 g/cm³ or more.
9. The artificial leather substrate in accordance with claim 1 further comprising a smoothing layer for smoothing a surface, the smoothing layer being a layer including a second elastic polymer and a second filler and having a thickness of 10 to 100 μ m.
10. The artificial leather substrate in accordance with claim 9, wherein the smoothing layer includes 1 to 50 mass% of the second filler.
11. The artificial leather substrate in accordance with claim 9, wherein a surface water absorption rate in compliance with the water drop method of JIS L1907-7.1.1 is 100 seconds or more.
12. A grain-like-finish artificial leather formed by further stacking a resin layer on the smoothing layer in the artificial leather substrate in accordance with claim 9.
13. A production method of artificial leather substrate, the method being for the artificial leather substrate in accordance with claim 9 and comprising:
 - a step of preparing an original fabric of the artificial leather substrate in accordance with claim 1; and
 - a step of forming the smoothing layer with the thickness of 10 to 100 μ m, by applying a smoothing-layer-forming coating liquid to a surface of the original fabric, followed by drying,
 - the smoothing-layer-forming coating liquid including the second elastic polymer and the second filler, as a solid content; and having a thixotropic index of 2 to 4, the thixotropic index being a ratio between a viscosity $\eta_{0.6}$ and a viscosity $\eta_{3.0}$ ($\eta_{0.6}/\eta_{3.0}$), the viscosity $\eta_{0.6}$ measured at 0.6 rotation/sec and the viscosity $\eta_{3.0}$ measured at 3 rotations/sec by using a B-type rotational viscometer at a temperature of 25°C.
14. A modifying agent for artificial leather substrate, the modifying agent comprising:
 - 3 to 50 mass% of a non-volatile oil in liquid form as a non-volatile component; and
 - 50 to 97 mass% of: a first filler; and 0 to 20 mass% of a first elastic polymer, wherein the non-volatile oil is a liquid with a boiling point of 150°C or more that substantially does not dissolve in a polar solvent, and
 - the first filler is at least one selected from an inorganic filler, a metal filler, a metal oxide filler, a semimetal oxide filler, a flame-retardant filler and a carbon-based filler.

Patentansprüche

1. Ein Kunstledersubstrat, umfassend:

einen verschlungenen Faserkörper, und
einen ersten Füllstoff, ein erstes elastisches Polymer und ein nicht-flüchtiges Öl in flüssiger Form, die alle in den verschlungenen Faserkörper durch Imprägnierung hinzugefügt werden, wobei der erste Füllstoff mindestens einen anorganischen Füllstoff, einen Metallfüllstoff, einen Metalloxidfüllstoff, einen Halbmetalloxidfüllstoff, einen flammhemmenden Füllstoff und einen Füllstoff auf Kohlenstoffbasis umfasst und das nicht-flüchtige Öl eine Flüssigkeit mit einem Siedepunkt von 150°C oder mehr ist, die sich im Wesentlichen nicht in einem polaren Lösungsmittel löst,
wobei der Gehalt des ersten Füllstoffs 50 bis 97 Massen-%, bezogen auf die Gesamtmenge des ersten Füllstoffs, des ersten elastischen Polymers und des nicht-flüchtigen Öls, beträgt.

2. Das Kunstledersubstrat nach Anspruch 1, wobei das nicht-flüchtige Öl mindestens eines, ausgewählt aus flüssigem

Paraffin, Silikonöl, Mineralöl und Phthalatestern, beinhaltet.

3. Das Kunstledersubstrat nach Anspruch 1, wobei der verschlungene Faserkörper ein Vliesstoff aus ultrafeinen Fasern mit einer Feinheit von 0,9 dtex oder weniger ist.

4. Das Kunstledersubstrat nach Anspruch 1, wobei ein Gehalt des ersten Füllstoffs 1 bis 60 Massen-% und ein Gehalt des nicht-flüchtigen Öls 0,5 bis 10 Massen-%, bezogen auf den verschlungenen Faserkörper, beträgt.

5. Das Kunstledersubstrat nach Anspruch 1, wobei 1 bis 15 Massen-% des ersten elastischen Polymers, bezogen auf den verschlungenen Faserkörper, vorhanden sind.

6. Das Kunstledersubstrat nach Anspruch 5, wobei der Gehalt des ersten Füllstoffs, des nicht-flüchtigen Öls und des ersten elastischen Polymers insgesamt, bezogen auf den verschlungenen Faserkörper, 10 bis 30 Massen-% beträgt.

7. Das Kunstledersubstrat nach Anspruch 6, wobei ein Gehalt des ersten elastischen Polymers in der Gesamtmenge des ersten Füllstoffs, des nicht-flüchtigen Öls und des ersten elastischen Polymers 1 bis 20 Massen-% beträgt.

8. Das Kunstledersubstrat nach Anspruch 1 mit einer Rohdichte von 0,60 g/cm³ oder mehr.

9. Das Kunstledersubstrat nach Anspruch 1 ferner umfassend eine Glättungsschicht zum Glätten einer Oberfläche, wobei die Glättungsschicht eine Schicht ist, die ein zweites elastisches Polymer und einen zweiten Füllstoff enthält, mit einer Dicke von 10 bis 100 µm.

10. Das Kunstledersubstrat nach Anspruch 9, wobei die Glättungsschicht 1 bis 50 Massen-% des zweiten Füllstoffs beinhaltet.

11. Das Kunstledersubstrat nach Anspruch 9, wobei eine Wasserabsorptionsrate der Oberfläche in Übereinstimmung mit der Wassertropfenmethode nach JIS L1907-7.1.1 100 Sekunden oder mehr beträgt.

12. Ein Kunstleder mit einem körnigen Finish, das durch weiteres Schichten einer Harzschicht auf der Glättungsschicht in dem Kunstledersubstrat gemäß Anspruch 9 gebildet wird.

13. Ein Verfahren zur Herstellung eines Kunstledersubstrats, wobei das Verfahren für das Kunstledersubstrat nach Anspruch 9 ist, und umfasst:

einen Schritt des Herstellens eines Originalstoffs des Kunstledersubstrats nach Anspruch 1; und
einen Schritt des Bildens der Glättungsschicht mit einer Dicke von 10 bis 100 µm durch Auftragen einer die Glättungsschicht bildenden Beschichtungsflüssigkeit auf eine Oberfläche des Originalstoffs, gefolgt von Trocknen,
die Glättungsschicht bildende Beschichtungsflüssigkeit, die das zweite elastische Polymer und den zweiten Füllstoff als Feststoffgehalt enthält, und mit einem Thixotropieindex von 2 bis 4, wobei der Thixotropieindex ein Verhältnis zwischen einer Viskosität $\eta_{0,6}$ und einer Viskosität $\eta_{3,0}$ ($\eta_{0,6}/\eta_{3,0}$) ist, wobei die Viskosität $\eta_{0,6}$ bei 0,6 Umdrehungen/Sek. und die Viskosität $\eta_{3,0}$ bei 3 Umdrehungen/Sek. unter Verwendung eines Rotationsviskosimeters vom B-Typ bei einer Temperatur von 25°C gemessen wird.

14. Ein Modifizierungsmittel für Kunstledersubstrat, wobei das Modifizierungsmittel umfasst:

3 bis 50 Massen-% eines nicht-flüchtigen Öls in flüssiger Form als eine nicht-flüchtige Komponente; und
50 bis 97 Massen-% von: einem ersten Füllstoff, und 0 bis 20 Massen-% eines ersten elastischen Polymers, wobei das nicht-flüchtige Öl eine Flüssigkeit mit einem Siedepunkt von 150°C oder mehr ist, die sich im Wesentlichen nicht in einem polaren Lösungsmittel löst, und der erste Füllstoff mindestens einer ist, ausgewählt aus einem anorganischen Füllstoff, einem Metallfüllstoff, einem Metalloxidfüllstoff, einem Halbmetalloxidfüllstoff, einem flammhemmenden Füllstoff und einem Füllstoff auf Kohlenstoffbasis.

Revendications

1. Substrat en cuir artificiel comprenant :

un corps de fibres enchevêtrées ; et
une première charge, un premier polymère élastique et une huile non volatile sous forme liquide, tous ajoutées dans le corps de fibres enchevêtrées par imprégnation, dans lequel la première charge comprend au moins une charge parmi une charge inorganique, une charge métallique, une charge d'oxyde métallique, une charge d'oxyde semi-métallique, une charge ignifugeante et une charge à base de carbone, et l'huile non volatile est un liquide ayant un point d'ébullition de 150 °C ou plus qui ne se dissout sensiblement pas dans un solvant polaire, dans lequel une teneur en première charge est de 50 à 97 % en masse, de la quantité totale de la première charge, du premier polymère élastique et de l'huile non volatile.

2. Substrat en cuir artificiel selon la revendication 1, dans lequel l'huile non volatile comprend au moins une huile choisie parmi la paraffine liquide, l'huile de silicone, l'huile minérale et les esters de phtalate.

3. Substrat en cuir artificiel selon la revendication 1, dans lequel le corps de fibres enchevêtrées est un tissu non tissé de fibres ultrafines ayant une finesse de 0,9 dtex ou moins.

4. Substrat en cuir artificiel selon la revendication 1, dans lequel une teneur en première charge est de 1 à 60 % en masse et une teneur en huile non volatile est de 0,5 à 10 % en masse, par rapport au corps de fibres enchevêtrées.

5. Substrat en cuir artificiel selon la revendication 1, dans lequel de 1 à 15 % en masse du premier polymère élastique sont présents par rapport au corps de fibres enchevêtrées.

6. Substrat en cuir artificiel selon la revendication 5, dans lequel une teneur en première charge, huile non volatile et premier polymère élastique au total, par rapport au corps de fibres enchevêtrées, est de 10 à 30 % en masse.

7. Substrat en cuir artificiel selon la revendication 6, dans lequel une teneur en premier polymère élastique de la quantité totale de la première charge, de l'huile non volatile et du premier polymère élastique, est de 1 à 20 % en masse,

8. Substrat en cuir artificiel selon la revendication 1 ayant une densité apparente de 0,60 g/cm³ ou plus.

9. Substrat en cuir artificiel selon la revendication 1 comprenant en outre une couche de lissage pour lisser une surface, la couche de lissage étant une couche comprenant un deuxième polymère élastique et une deuxième charge et ayant une épaisseur de 10 à 100 μm.

10. Substrat en cuir artificiel selon la revendication 9, dans lequel la couche de lissage comprend de 1 à 50 % en masse de la deuxième charge.

11. Substrat en cuir artificiel selon la revendication 9, dans lequel un taux d'absorption d'eau de surface conformément à la méthode de la goutte d'eau de JIS L1907-7.1.1 est de 100 secondes ou plus.

12. Cuir artificiel au fini grainé formé en empilant en outre une couche de résine sur la couche de lissage dans le substrat en cuir artificiel selon la revendication 9.

13. Procédé de production d'un substrat en cuir artificiel, le procédé étant destiné au substrat en cuir artificiel selon la revendication 9 et comprenant :

une étape de préparation d'un tissu initial du substrat en cuir artificiel selon la revendication 1 ; et
une étape de formation de la couche de lissage ayant une épaisseur de 10 à 100 μm, par application d'un liquide de revêtement formant une couche de lissage sur une surface du tissu initial, suivie d'un séchage, le liquide de revêtement formant une couche de lissage comprenant le deuxième polymère élastique et la deuxième charge, en tant que contenu solide ; et ayant un indice thixotropique de 2 à 4, l'indice thixotropique étant un rapport entre une viscosité $\eta_{0,6}$ et une viscosité $\eta_{3,0}$ ($\eta_{0,6}/\eta_{3,0}$), la viscosité $\eta_{0,6}$ étant mesurée à 0,6 rotation/s et la viscosité $\eta_{3,0}$ étant mesurée à 3 rotations/s en utilisant un viscosimètre rotatif de type B à une

température de 25 °C.

14. Agent de modification pour un substrat en cuir artificiel, l'agent de modification comprenant :

5 de 3 à 50 % en masse d'une huile non volatile sous forme liquide en tant que composant non volatil ; et
de 50 à 97 % en masse de : une première charge ; et de 0 à 20 % en masse d'un premier polymère élastique,
dans lequel l'huile non volatile est un liquide ayant un point d'ébullition de 150 °C ou plus qui ne se dissout
sensiblement pas dans un solvant polaire, et
10 la première est au moins une charge choisie parmi une charge inorganique, une charge métallique, une charge
d'oxyde métallique, une charge d'oxyde semi-métallique, une charge ignifugeante et une charge à base de
carbone.

15

20

25

30

35

40

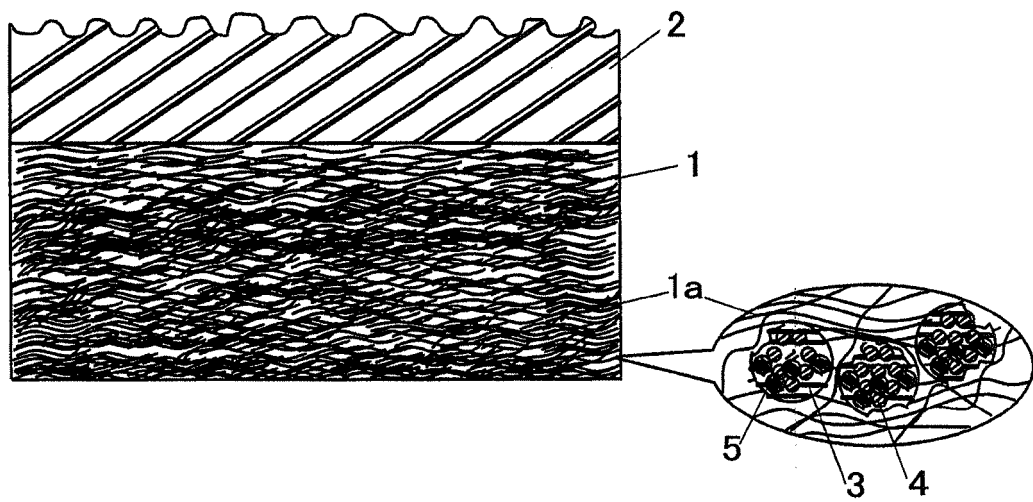
45

50

55

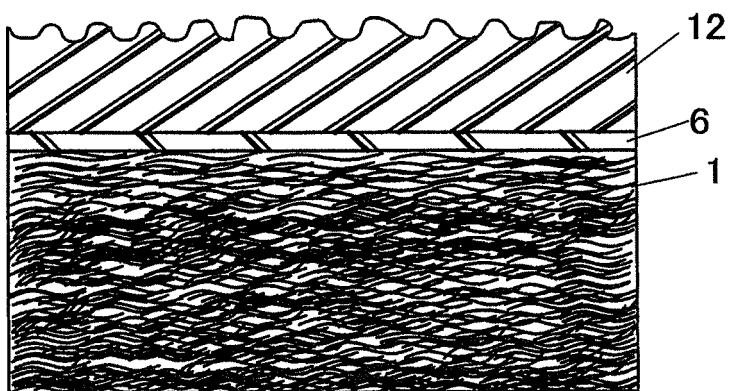
【Fig 1】

10



【Fig 2】

20



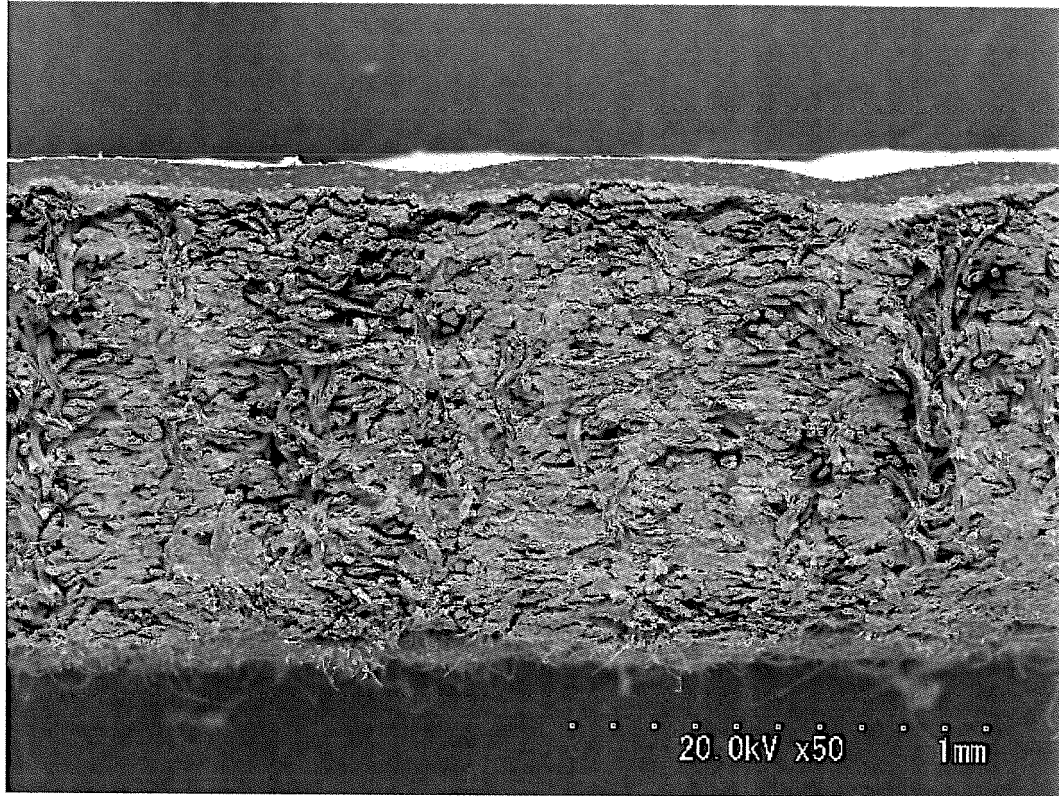
【Fig 3】



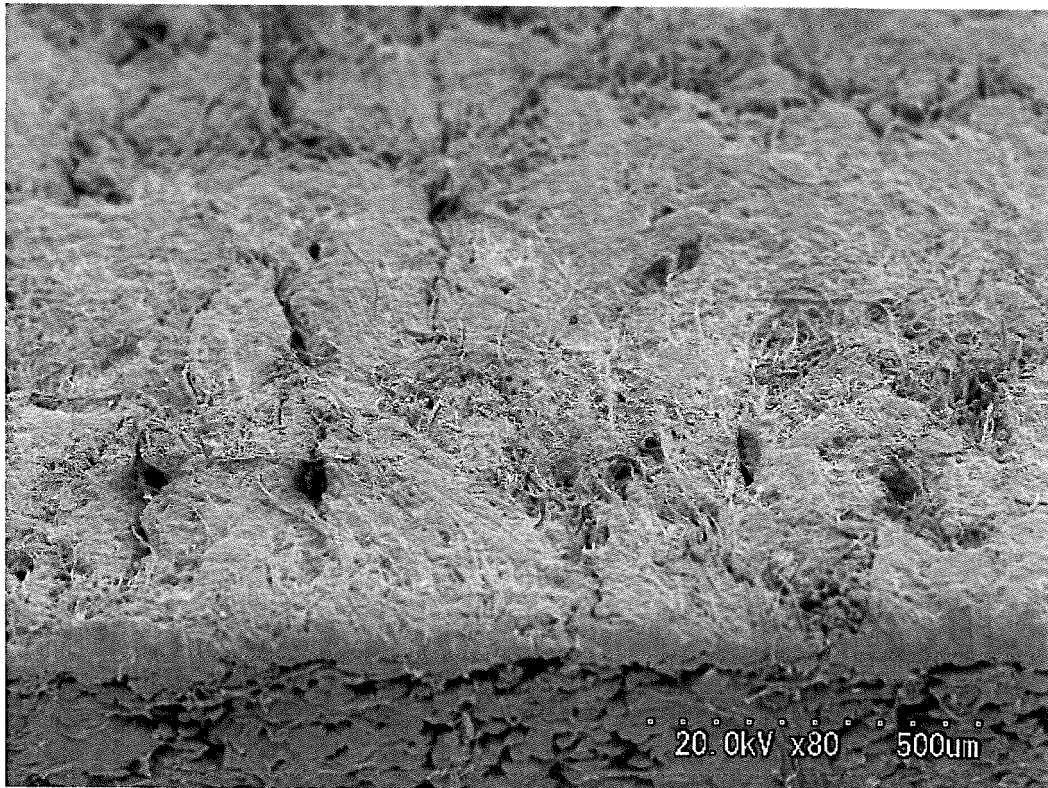
【Fig 4】



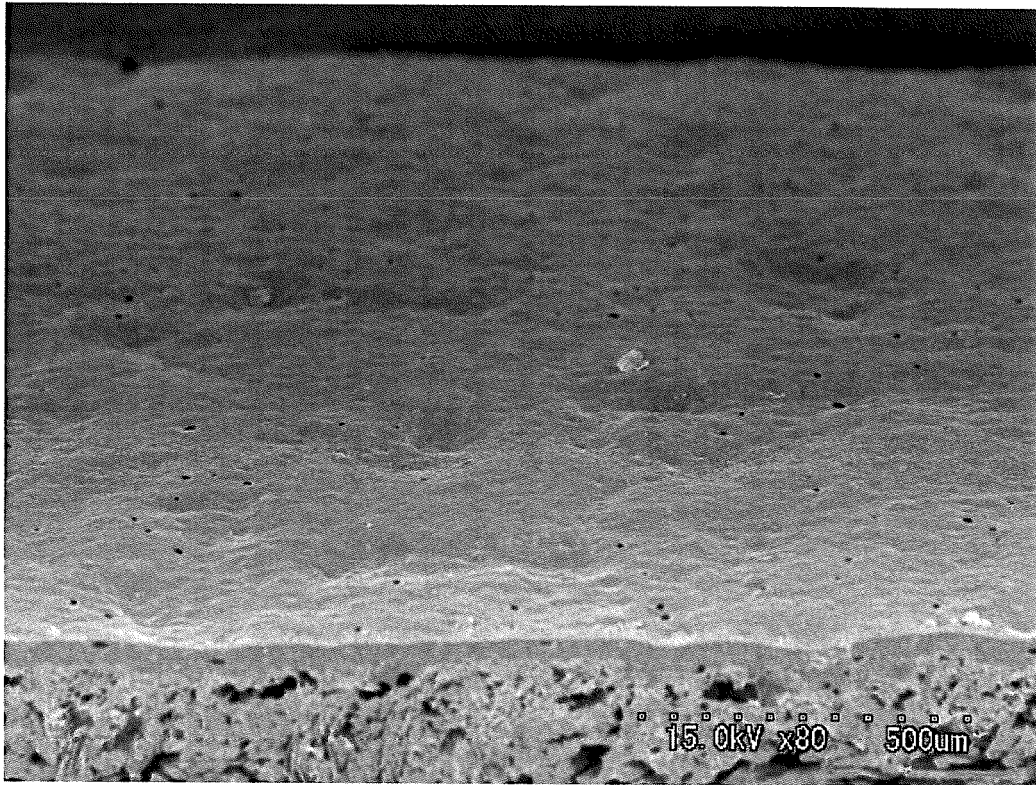
【Fig 5】



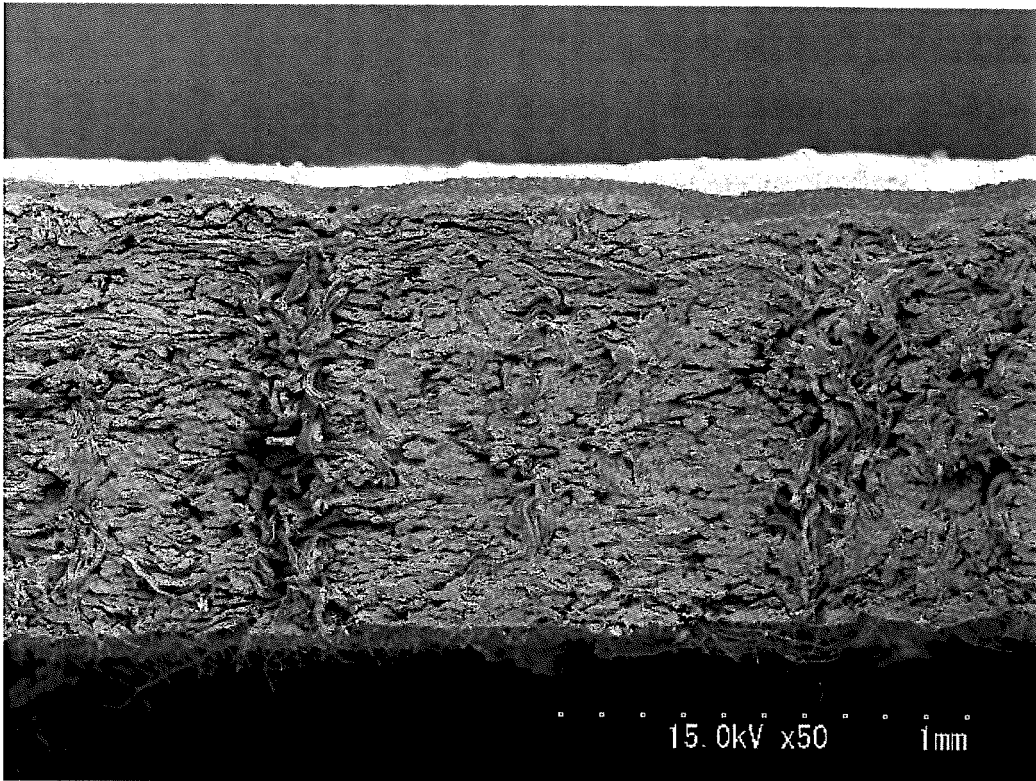
【Fig 6】



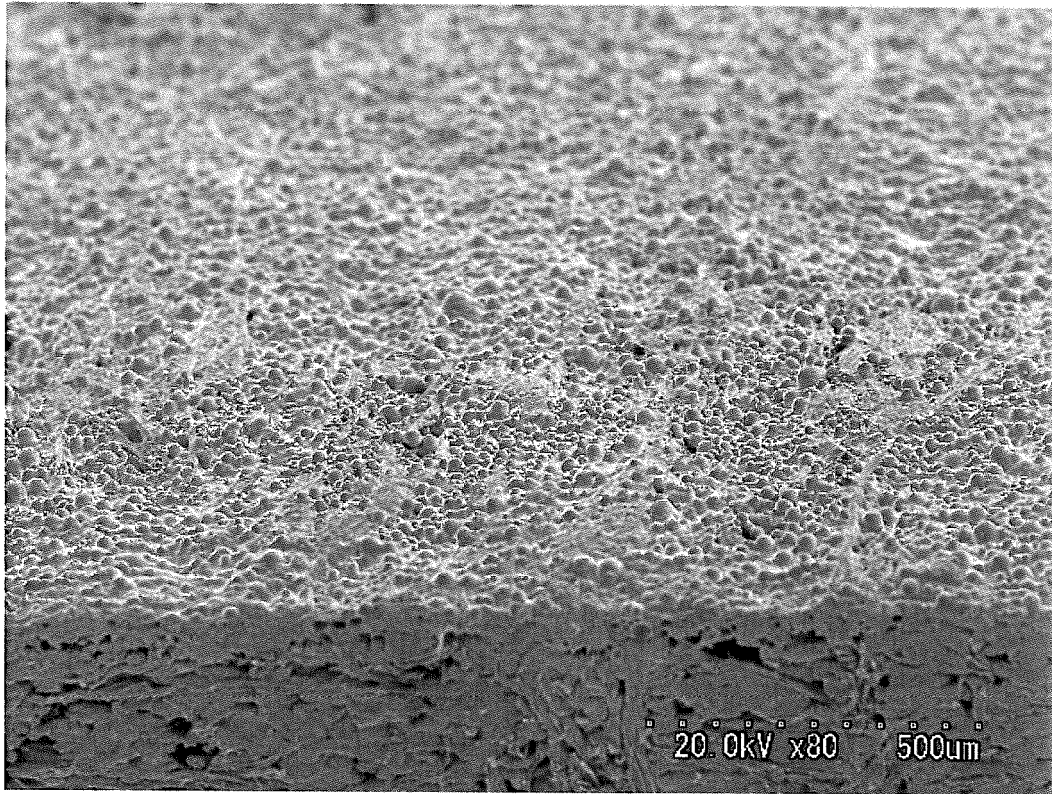
【Fig 7】



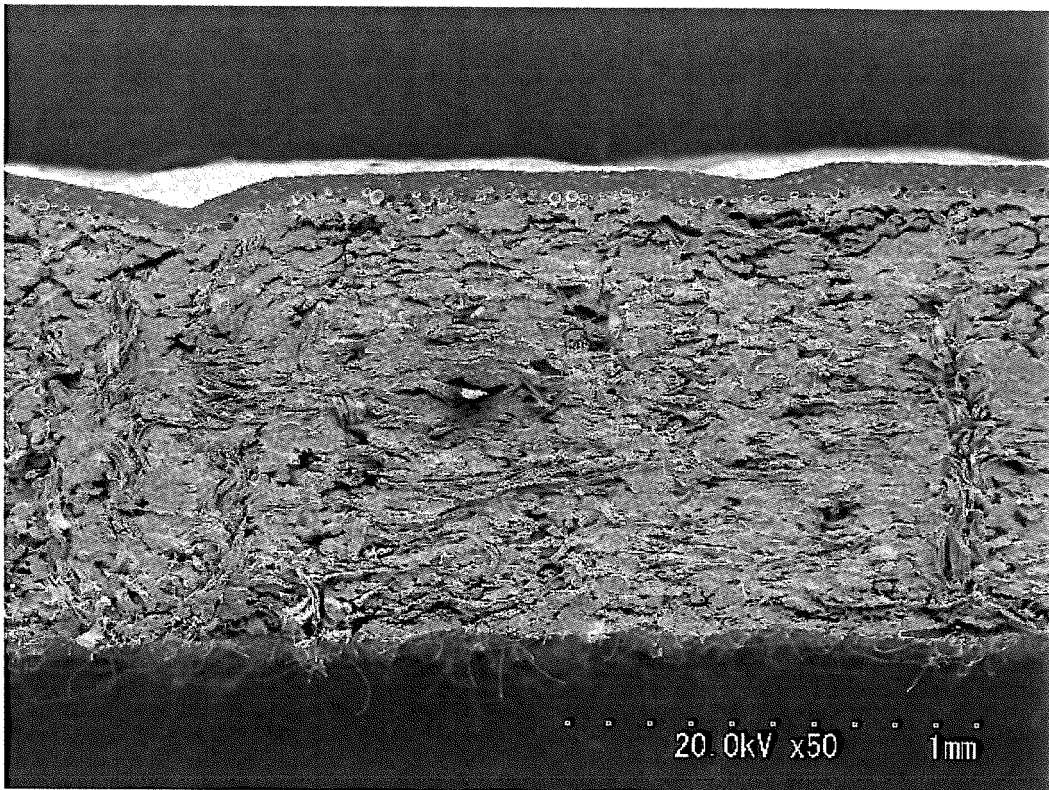
【Fig 8】



【Fig 9】



【Fig 10】



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2008120702 A [0010]
- WO 200306212 A [0010]
- JP 9313418 A [0010]
- JP 2012117154 A [0010]
- JP 2002302879 A [0010]
- JP 2007291565 A [0010]