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(11)

EP 3 572 580 A1

(12)

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

(43) Date of publication:

27.11.2019 Bulletin 2019/48

(51) Int Cl.:

D06N 3/00 (2006.01)

D06N 3/14 (2006.01)

(21) Application number: **17892458.5**

(86) International application number:

PCT/JP2017/046354

(22) Date of filing: **25.12.2017**

(87) International publication number:

WO 2018/135243 (26.07.2018 Gazette 2018/30)

(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**

Designated Extension States:

BA ME

Designated Validation States:

MA MD TN

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(54) **SHEET-LIKE OBJECT**

(57) The present invention provide a sheet-like material having a highly soft texture, and further having high crease resistance while being soft. The sheet-like material of the present invention is a sheet-like material comprising a nonwoven fabric containing ultrafine fibers hav-

ing an average single fiber diameter of 0.3 to 7 μm , and an elastomer, and having nap on a surface, in which the elastomer has a porous structure, and the porous structure has a proportion of micropores with a pore size of 0.1 to 20 μm of 60% or more in all pores.

EP 3 572 580 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a sheet-like material, particularly to a napped leather-like sheet-like material.

BACKGROUND ART

[0002] It is widely known to obtain a suede-like or nubuck-like, napped leather-like sheet-like material by buffing with sandpaper a surface of a sheet-like material in which a base material such as a nonwoven fabric composed of fibers is impregnated with a polyurethane resin to stand the fibers. Desired properties of the napped leather-like sheet-like material can be arbitrarily and widely designed by combination of a base material composed of fibers and a polyurethane resin.

[0003] For example, it is proposed that when a polycarbonate-based polyurethane resin is used which is obtained by a reaction of a polycarbonate polyol having a specific structure with an aromatic polyisocyanate, softness of the polycarbonate-based polyurethane resin is improved, grindability obtained by using sandpaper is improved whereby a preferable nap length of a ultrafine fiber is expressed, and an artificial leather having an elegant appearance, a supple surface touch and soft texture due to nap can be obtained (see Patent Document 1).

[0004] The napped leather-like sheet-like material has an appearance and a surface closely resembling to natural leather, and is recognized to have advantages which do not exist in the natural leather, such as uniformity and color fastness. Use of the napped leather-like sheet-like material has recently been spread to long-term uses such as covering materials for furniture such as sofa and seat covers for automobiles, in addition to clothing use. In the clothing use among them, artificial leather having both excellent softness and crease resistance has been required.

[0005] According to the proposal described above, it is proposed that soft artificial leather can be obtained by making a structure of the polycarbonate polyol forming the polyurethane resin specific to the hardness of the polycarbonate-based polyurethane resin which is the conventional problem. In the use requiring the soft texture as in the clothing use, however, the softness has been still insufficient.

[0006] It is also proposed that when a polyurethane resin including a bio-based polycarbonate polyol is used, synthetic leather having excellent low-temperature flexing and contributing to environmental loading reduction can be obtained (see Patent Document 2). According to this proposal, however, synthetic leather composed of layers of nonporous polyurethane resins having various molecular weights and a fiber fabric has been studied in detail, but napped artificial leather having a soft texture and crease resistance has not been studied at all.

[0007] A method for obtaining a suede-like, leather-like sheet whose color tone is not changed and which has an elegant appearance is proposed, the sheet being obtained in a manner in which a porous layer having micropores is formed by adding a specific coagulation modifier to a polyurethane resin and the layer is napped by grinding (see Patent Document 3). According to this proposal, a good texture has been attained by controlling pore sizes in layers of nonporous polyurethane resins having various molecular weights, and in portions close to the surface layer and the fibrous base layer, but coexistence of softness and crease resistance has not been studied at all, and softness is impaired because of porous polyurethane resin layer.

[0008] Separately, a method for obtaining a sheet-like material having nap and elegant appearance in a manner in which a polyurethane resin having good grindability is obtained by containing pores having a diameter of 10 to 200 μm inside a water-dispersible polyurethane resin, and a sheet obtained therefrom is ground with sandpaper, or the like is proposed (see Patent Document 4). According to this proposal, however, when the pores inside the polyurethane resin layer have a large pore size of more than 20 μm , the thickness of the polyurethane resin layer between the pores is thick, so that an effect of improving the grindability of the polyurethane resin and an effect of improving softness are insufficiently exhibited. Accordingly, it has been difficult to obtain sufficient softness in the use requiring flexible deformation along a complicated shape such as in clothing use. It has been also difficult to obtain ultrafine and uniform pores.

[0009] It is also proposed that a leather-like base material having lightweight and supple texture is obtained which is composed of a porous elastomer having a specific pore size and a nonwoven fabric of porous hollow fibers (see Patent Document 5). According to this proposal, the material has a soft texture because of the porous structure and is uniform, but it has been difficult to have both softness and crease resistance due to remaining creases.

[0010] As described above, it has been very difficult to stably obtain a napped leather-like sheet-like material having both excellent softness and excellent crease resistance according to the conventional techniques.

PRIOR ART DOCUMENT

PATENT DOCUMENTS

[0011]

Patent Document 1: WO2005/095706

Patent Document 2: Japanese Patent Laid-open Publication No. 2014-1475

Patent Document 3: Japanese Patent Laid-open Publication No. 2000-303368

Patent Document 4: Japanese Patent Laid-open Publication No. 2011-214210

Patent Document 5: Japanese Patent Laid-open Publication No. 2012-214944

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0012] In view of the background of the prior art described above, an object of the present invention is to provide a napped leather-like sheet-like material having both a texture of excellent softness and high crease resistance while it is soft.

SOLUTIONS TO THE PROBLEMS

[0013] The present invention is to solve the problems described above, and the sheet-like material of the present invention is a sheet-like material comprising a nonwoven fabric containing ultrafine fibers having an average single fiber diameter of 0.3 to 7 μm , and an elastomer, and having nap on a surface, wherein the elastomer has a porous structure, and the porous structure has a proportion of micropores with a pore size of 0.1 to 20 μm of 60% or more in all pores.

[0014] According to a preferable embodiment of the sheet-like material of the present invention, the elastomer exists in an interior space in the nonwoven fabric.

[0015] According to a preferable embodiment of the sheet-like material of the present invention, the elastomer is a polycarbonate-based polyurethane resin.

[0016] According to a preferable embodiment of the sheet-like material of the present invention, the polyurethane resin has a weight-average molecular weight of 30,000 to 150,000.

[0017] According to a preferable embodiment of the sheet-like material of the present invention, a number of pores per unit area in section is 50 pores/1600 μm^2 or more in the porous structure in the elastomer.

EFFECTS OF THE INVENTION

[0018] According to the present invention, a napped leather-like sheet-like material having both a highly soft texture and crease resistance can be obtained. Specifically, a napped leather-like sheet-like material having an elegant appearance obtained by buffing, and further having excellent softness and crease resistance can be obtained by the present invention. Here, the term "highly soft texture" means, in clothing use, that the sheet-like material can be tailored into a complicated three-dimensional shape and can provide good feeling of wearing by deformation along with the physical movement, and means, in use of furniture, automobile interior materials, or the like, that the sheet-like material can be molded or processed along with a complicated three-dimensional shape and can provide good feeling of use by flexibly following deformation caused, for example, when a person sits. The term "crease resistance" refers to an excellent recovery from the crease, and means that even if wrinkles are caused by applying a load, for example, a deformation caused upon the use as described above, the wrinkles disappear without leaving any trace after removing the load. It is necessary to apply appropriate elasticity to the sheet-like material in order to express the crease resistance, which is conflict with the softness, and thus it has been difficult to obtain both the softness and the crease resistance.

EMBODIMENTS OF THE INVENTION

[0019] The sheet-like material of the present invention is a sheet-like material comprising a nonwoven fabric containing an ultrafine fibers having an average single fiber diameter of 0.3 to 7 μm , and an elastomer, and having nap on a surface, in which the elastomer has a porous structure, and the porous structure has a proportion of micropores with a pore size of 0.1 to 20 μm of 60% or more in all pores.

[0020] The sheet-like material of the present invention comprises, as described above, a nonwoven fabric containing ultrafine fiber, and an elastomer.

[0021] As a material of the ultrafine fiber forming the nonwoven fabric used in the present invention, it is possible to use thermoplastic resins capable of melt-spinning, for example, polyesters such as polyethylene terephthalate, polybutylene terephthalate, and polytrimethylene terephthalate, polyamides such as 6-nylon and 66-nylon, and the like. Of these, a polyester is preferably used from the viewpoint of the strength, dimensional stability, and light resistance. The nonwoven fabric may be mixed with ultrafine fibers of different other materials.

[0022] The cross-sectional shape of a single fiber forming the nonwoven fabric may have a circular cross-section, and

may be an elliptical, plane, or polygonal such as triangle shape. A single fiber having a modified cross-section such as a sector or cruciform may also be used.

[0023] It is important that the ultrafine fibers that form the non-woven fabric have an average single fiber diameter of 7 μm or less from the viewpoint of the softness and nap appearance of the sheet-like material. The average single fiber diameter is preferably 6 μm or less, and more preferably 5 μm or less. On the other hand, it is important that the average single fiber diameter is 0.3 μm or more from the viewpoint of the chromogenic property after dyeing, the dispersibility of fiber bundles during buffing, and the easy handling. The average single fiber diameter is preferably 0.7 μm or more, and more preferably 1 μm or more.

[0024] The average single fiber diameter herein refers to a value obtained by cutting the obtained sheet-like material in a thickness direction, observing a cross-section with a scanning electron microscope (SEM), measuring a fiber diameter of 50 arbitrary ultrafine fibers at three points, and calculating an average value of fiber diameters of a total of 150 fibers.

[0025] As a method for obtaining the ultrafine fiber used in the present invention, use of an ultrafine fiber-generating fiber is a preferable embodiment. As the ultrafine fiber-generating fiber, an islands-in-the-sea fiber can be used in which two thermoplastic resin components having solubility in a solvent different from each other are used as a sea component and an island component, and the island component can be used as the ultrafine fiber by dissolving only the sea component in a solvent to be removed. A peelable composite fiber or a multilayered composite fiber can also be used in which two thermoplastic resin components are disposed alternately in a radial pattern of a fiber cross-section or in a layer pattern, and each component is peeled and divided to split the composite fiber into an ultrafine fiber.

[0026] As the nonwoven fabric, it is possible to use a nonwoven fabric in which single fibers of the ultrafine fibers are entangled with one another, and a nonwoven fabric in which fiber bundles of the ultrafine fibers are entangled. However, the nonwoven fabric in which fiber bundles of the ultrafine fibers are entangled is preferably used from the viewpoint of the strength and texture of the sheet-like material. A nonwoven fabric having appropriate voids between the ultrafine fibers inside the fiber bundle is particularly preferably used from the viewpoint of the softness and the texture. The nonwoven fabric in which fiber bundles of the ultrafine fibers are entangled, as described above, can be obtained by previously entangling the ultrafine fiber-generating fibers and then generating the ultrafine fibers. The nonwoven fabric having appropriate voids between the ultrafine fibers inside the fiber bundle can be obtained by using islands-in-the-sea fibers which can provide appropriate voids between the island components, i.e., between the ultrafine fibers inside the fiber bundle, by removing the sea component.

[0027] As the nonwoven fabric, any of a staple fiber nonwoven fabric and a filament fiber nonwoven fabric can be used, and a staple fiber nonwoven fabric is preferably used from the viewpoint of the texture and the appearance.

[0028] A staple fiber in the staple fiber nonwoven fabric preferably has a fiber length of 25 to 90 mm. When the fiber length is set to 25 mm or more, the sheet-like material having the excellent abrasion resistance can be obtained by entanglement. When the fiber length is set to 90 mm or less, the sheet-like material having a more excellent texture and appearance can be obtained. The fiber length is more preferably 35 to 80 mm, and particularly preferably 40 to 70 mm.

[0029] When the ultrafine fibers or the fiber bundles thereof form the nonwoven fabric, a woven fabric or a knitted fabric may be inserted into the fabric in order to improve the strength. Fibers that form the woven fabric or the knitted fabric used have preferably an average single fiber diameter of about 0.3 to 10 μm .

[0030] The elastomer used in the present invention has a porous structure, and a proportion of micropores with a pore size of 0.1 to 20 μm in all pores in the porous structure is 60% or more. The ratio of the micropores is more preferably 70% or more, and still more preferably 80% or more. The porous structure may have either open cells or closed cells. When the elastomer has a certain ratio or more of the micropores, the softness of the elastomer can be increased, and the sheet-like material having a highly soft texture can be obtained. In order to make the elastomer have the porous structure having micropores, it is preferable to use wet coagulation described below as a method for fixing the elastomer in the nonwoven fabric.

[0031] Further, by making the elastomer have the porous structure having micropores, a deformation force can be dispersedly received by not a part of the elastomer but by the whole elastomer when a crease deformation is applied to the sheet-like material. Accordingly, the generation of the creases with buckling of the elastomer is suppressed, and the sheet-like material having the excellent crease resistance can be obtained.

[0032] It is important that 60% or more of the pores with respect to all pores in the porous structure of the elastomer have a pore size of 0.1 μm or more. The pore size is preferably 0.5 μm or more, and more preferably 1 μm or more. When the pore size is set to 0.1 μm or more, the softness of the elastomer is increased and, at the same time, the cushioning against the deformation can be increased. On the other hand, it is also important that 60% or more of the pores with respect to all pores in the porous structure of the elastomer have a pore size of 20 μm or less. The pore size is preferably 15 μm or less, and more preferably 10 μm or less. When the pore size is set to 20 μm or less, the pore density of the porous structure can be increased, both the softness and the appropriate strength can be obtained, and a deformation force can be dispersedly received by the whole elastomer, so that the sheet-like material having the excellent softness and the crease resistance can be obtained.

[0033] The number of pores per unit area in the porous structure of the elastomer is 50 pores/1600 μm^2 or more,

preferably 70 pores/1600 μm^2 or more, and more preferably 100 pores/1600 μm^2 or more. On the other hand, the number of pores per unit area in the porous structure of the elastomer is preferably 1000 pores/1600 μm^2 or less, and more preferably 800 pores/1600 μm^2 or less.

[0034] When the number of pores per unit area is set to 50 pores/1600 μm^2 or more, the porous structure having a soft texture is obtained and a crease deformation force of the sheet can be received by a plurality of pores. Accordingly, the excellent crease resistance can be obtained. When the number of pores per unit area is too small, the deformation force is concentrated to specific pores to cause buckling, and the crease recovery is poor. When the number of pores per unit area is too large, a deformation space of the pores is too small, the deformation force cannot be dispersed, and the crease recovery is poor.

[0035] The elastomer used in the present invention holds the ultrafine fibers in the sheet-like material. It is a preferable embodiment that the elastomer exists in an interior space of the nonwoven fabric from the viewpoint of having nap on at least one surface of the sheet-like material.

[0036] As the elastomer used in the present invention, a polyurethane resin is preferably used in the point of obtaining uniform micropores in the sheet-like material. As the polyurethane resin, a polyurethane resin obtained by a reaction of a polymer diol with an organic diisocyanate is preferably used.

[0037] Examples of the polymer diol may include polycarbonate-based, polyester-based, polyether-based, silicone-based, and fluorine-based polymer diols, and copolymers of combinations of these may also be used.

[0038] A polycarbonate-based polymer diol is preferably used, because it can provide the appropriate rigidity to the polyurethane resin, the excellent softness can be exhibited by forming the porous structure having micropores, and the high crease resistance can be exhibited without buckling of the polyurethane resin.

[0039] The polycarbonate-based diol can be produced by transesterification of an alkylene glycol with a carbonic acid ester, or a reaction of phosgene or chloroformic acid ester with an alkylene glycol, or the like.

[0040] Examples of the alkylene glycol include linear alkylene glycols such as ethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,9-nonane diol, and 1,10-decane diol, branched alkylene glycols such as neopentyl glycol, 3-methyl-1,5-pentane diol, 2,4-diethyl-1,5-pentane diol, and 2-methyl-1,8-octane diol, alicyclic diols such as 1,4-cyclohexane diol, aromatic diols such as bisphenol A, glycerol, trimethylol propane, and pentaerythritol. Either polycarbonate-based diols obtained from alkylene glycol alone, or copolymerized polycarbonate-based diol obtained from two or more kinds of alkylene glycols may be used.

[0041] Examples of the polyester-based diol may include polyester diols obtained by condensation of a polybasic acid with various low molecular weight polyols.

[0042] As the low molecular weight polyols, it is possible to use one or more kinds of polyols selected from, for example, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butane diol, 1,4-butane diol, 2,2-dimethyl-1,3-propane diol, 1,6-hexane diol, 3-methyl-1,5-pentane diol, 1,8-octane diol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, cyclohexane-1,4-diol, and cyclohexane-1,4-dimethanol. As the low molecular weight polyols, it is possible to use an adduct in which bisphenol A is added with various alkylene oxides.

[0043] Examples of the polybasic acid include one or more kinds of acids selected from, for example, succinic acid, maleic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecane dicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and hexahydroisophthalic acid.

[0044] Examples of the polyether-based diol may include polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and copolymerized diols obtained by combination of these.

[0045] The polymer diol preferably has a number-average molecular weight of 500 to 5000. When the number-average molecular weight is set to 500 or more, and more preferably 1500 or more, it is possible to prevent the texture from being hardened. When the number-average molecular weight is set to 5000 or less, and more preferably 4000 or less, the strength as the polyurethane resin can be maintained.

[0046] Examples of the organic diisocyanate used in the synthesis of the polyurethane resin may include aromatic diisocyanates such as 4,4'-diphenylmethane diisocyanate, paraphenylene diisocyanate, 1,5-naphthalene diisocyanate, paraxylene diisocyanate, and methylene diisocyanate, alicyclic diisocyanates such as 4,4'-dicyclohexylmethane diisocyanate and isophorone diisocyanate, and aliphatic diisocyanates such as 1,6-hexamethylene diisocyanate. Of these, aromatic diisocyanates, particularly 4,4'-diphenylmethane diisocyanate, are preferably used from the viewpoint of the strength and durability such as heat resistance of the obtained polyurethane resin.

[0047] As a chain extender used in the synthesis of the polyurethane resin, it is possible to use organic diols, organic diamines, hydrazine derivatives, and the like.

[0048] Examples of the organic diol may include aliphatic diols such as ethylene glycol, propylene glycol, 1,4-butane diol, neopentyl glycol, 1,5-pentane diol, methylpentane diol, 1,6-hexane diol, 1,7-heptane diol, 1,8-octane diol, 1,9-nonane diol, and 1,10-decane diol, alicyclic diols such as 1,4-cyclohexane diol and hydrogenated xylene glycol, and aromatic diols such as xylene glycol.

[0049] Examples of the organic diamine may include ethylene diamine, isophorone diamine, xylene diamine, phenyl diamine, and 4,4'-diaminodiphenyl methane.

[0050] Examples of the hydrazine derivative may include hydrazine, adipic acid dihydrazide, and isophthalic acid dihydrazide.

[0051] In order to improve the water resistance, the abrasion resistance, and the hydrolysis resistance, a cross-linking agent can be added to the polyurethane resin. The cross-linking agent may be an external cross-linking agent that is added to the polyurethane as a third component, or an internal cross-linking agent can be used which previously introduces a reaction point forming a cross-linked structure into a polyurethane molecular structure.

[0052] In the synthesis of the polyurethane resin, it is possible to use, as a catalyst, amines such as triethyl amine and tetramethyl butane diamine, metal compounds such as potassium acetate, zinc stearate, and tin octylate, and the like, for example.

[0053] The polyurethane resin used in the present invention preferably has a weight-average molecular weight (Mw) of 30,000 to 150,000, and more preferably 50,000 to 130,000. When the weight-average molecular weight (Mw) is set to 30,000 or more, the strength of the obtained sheet-like material can be maintained, and the loss of nap and the occurrence of pilling can be prevented. When the weight-average molecular weight (Mw) is set to 150,000 or less, the polyurethane resin in the sheet-like material can have uniform micropores. When the polyurethane resin has such a weight-average molecular weight (Mw) range, the uniform and ultrafine porous structure can be obtained by the temporary softening of the polyurethane resin with heating and the evaporation of the soluble and insoluble solvents contained in the polyurethane resin after wet coagulation described below as the starting point, in the production steps usually used where the polyurethane resin is fixed into the nonwoven fabric in the wet coagulation, and then the sheet-like material containing a insoluble solvent such as water is dried with heating.

[0054] The elastomer may contain polyester-based, polyamide-based, and polyolefin-based elastomers, acrylic resins, and ethylene-vinyl acetate resins within a range in which the performance and the texture are not impaired. In addition, the elastomer may also contain various additives, for example, pigments such as carbon black, flame retardants such as phosphorus-based, halogen-based, and inorganic flame retardants, antioxidants such as phenol-based, sulfur-based, and phosphorus-based antioxidants, UV absorbers such as benzotriazole-based, benzophenone-based, salicylate-based, cyanoacrylate-based, and oxalic acid anilide-based UV absorbers, light stabilizers such as hindered amine-based and benzoate-based light stabilizers, hydrolysis stabilizer such as polycarbodiimide, plasticizers, antistatic agents, surfactants, coagulation modifiers, dyes, and the like.

[0055] In the sheet-like material of the present invention, an amount of the elastomer in the sheet-like material is preferably 10 to 50% by mass, and more preferably 15 to 35% by mass. When the amount of the elastomer is set to 10% by mass or more, the sheet-like material obtains the strength, and it is possible to prevent fiber falling. When the amount of the elastomer is set to 50% by mass or less, it is possible to prevent the texture from being hardened, and the desired good nap appearance can be obtained.

[0056] Examples of the method of fixing the elastomer into the nonwoven fabric include methods in which the nonwoven fabric is impregnated with a solution of the elastomer, followed by wet coagulation or dry coagulation. The wet coagulation is preferably used from the viewpoint of obtaining the uniform and ultrafine porous structure as in the present invention. As the solvent used when the polyurethane resin is given as the elastomer, N,N'-dimethyl formamide, dimethyl sulfoxide, and the like may be used. Specifically, the nonwoven fabric is immersed in a solution in which the elastomer is dissolved in the solvent to give the elastomer to the nonwoven fabric, and is immersed in the insoluble solvent for the coagulation. It is also possible to perform the coagulation by immersing the nonwoven fabric in a mixture of the soluble solvent and the insoluble solvent.

[0057] The sheet-like material of the present invention may also be obtained by dividing the material in half or into several sections in the thickness direction of the sheet-like material before buffing.

[0058] The addition of the antistatic agent before buffing is preferably performed, because grinded powder generated from the sheet-like material by grinding tends to be hardly accumulated on the sandpaper.

[0059] The sheet-like material of the present invention is eventually used suitably as a napped leather-like sheet-like material in which ultrafine fibers are buffed on at least one surface of the sheet-like material. The buffing is performed by a method in which grinding is conducted using sandpaper, a roll sander, or the like. In order to obtain good fiber nap on the surface, it is a preferable embodiment that a lubricant such as a silicone emulsion is applied before the buffing.

[0060] The sheet-like material of the present invention is eventually used suitably as a napped leather-like sheet-like material in which ultrafine fibers are buffed on at least one surface of the sheet-like material.

[0061] The sheet-like material of the present invention can be suitably used as covering materials used in furniture, chairs, wall covering, and seats, ceilings and interior finishing products in interior of vehicles such as automobiles, trains and airplanes, and further covering materials having a very elegant appearance of clothes.

EXAMPLES

[0062] The sheet-like material of the present invention is more specifically described by way of Examples below.

[Evaluation Method]

(1) Average single fiber diameter:

[0063] A cross-section of a nonwoven fabric containing fibers of a sheet-like material, which was vertical to the thickness direction of the fabric, was observed at 3000 magnifications using a scanning electron microscope (SEM, VE-7800-type manufactured by Keyence Corporation), and diameters of 50 single fibers that were randomly extracted from a $30\ \mu\text{m} \times 30\ \mu\text{m}$ visual field were measured at a unit of μm up to the first decimal place. The measurement was performed at three points, diameters of 150 single fibers in total were measured, and an average value up to the first decimal place was calculated. In the case where fibers having a fiber diameter of more than $50\ \mu\text{m}$ are present, it is considered that those fibers do not correspond to the ultrafine fibers, and they were excluded from objects to be measured for the average fiber diameter. When the ultrafine fiber had a modified cross-section, first, a cross-sectional area of a single fiber was measured, and supposing that the cross-section had a circle, the diameter was calculated to obtain a diameter of the single fiber. An average value was calculated considering the values above as a population, which was defined as an average single fiber diameter.

(2) Pore size of porous structure of elastomer and proportion of micropores with pore size of 0.1 to $20\ \mu\text{m}$ in all pores in porous structure:

[0064] A cross-section of a nonwoven fabric containing elastomers of a sheet-like material, which was vertical to the thickness direction of the fabric, was observed at 2000 magnifications using a scanning electron microscope (SEM, VE-7800-type manufactured by Keyence Corporation), and pore sizes (diameter) of 50 pores in elastomers that were randomly extracted from a $40\ \mu\text{m} \times 40\ \mu\text{m}$ visual field were measured at a unit of μm up to the first decimal place. The measurement was performed at three points, pore sizes of 150 pores in total were measured, and the proportion of the number of pores with a pore size of 0.1 to $20\ \mu\text{m}$ in 150 pores was calculated, and the proportion was defined as the proportion of micropores with a pore size of 0.1 to $20\ \mu\text{m}$ in the porous structure. When the pores in the elastomers were variant pores, first, a cross-sectional area of a pore was measured, and supposing that the cross-section had a circle, the diameter was calculated to obtain a pore size (diameter) of the pore.

(3) The number of pores per unit area in porous structure of elastomer:

[0065] A cross-section of a nonwoven fabric containing elastomers of a sheet-like material, which was vertical to the thickness direction of the fabric, was observed at 2000 magnifications using a scanning electron microscope (SEM, VE-7800-type manufactured by Keyence Corporation), and the number of pores in the elastomer was counted in a $40\ \mu\text{m} \times 40\ \mu\text{m}$ visual field. The count was performed at three points, and an arithmetic average value of the number of pores was defined as the number of pores per unit area in the porous structure. When the area of the elastomer containing the porous structure is less than the $40\ \mu\text{m} \times 40\ \mu\text{m}$ visual field, the number of pores in the visual field was divided by an effective area of the elastomer, and the obtained value was converted into the number of pores per $1600\ \mu\text{m}^2$, which was defined as the number of pores per unit area in the porous structure. When the pore size of the pore is larger than the $40\ \mu\text{m} \times 40\ \mu\text{m}$ visual field, the number of pores in the porous structure was defined as 1.

(4) Weight-average molecular weight of polyurethane resin:

[0066] The polyurethane resin was extracted from the obtained sheet-like material using N,N'-dimethylformamide (hereinafter may sometimes be referred to as "DMF"), the concentration of the polyurethane resin was set to 1% by mass, and a weight-average molecular weight of the polyurethane resin was measured by gel permeation chromatography (GPC) under the following conditions:

- Apparatus: GPC measuring apparatus HLC-8020 (manufactured by Tosoh).
- Column: TSK gel GMH-XL (manufactured by Tosoh)
- Solvent: N,N-dimethylformamide (hereinafter referred to as "DMF")
- Standard sample: polystyrene (TSK standard polystyrene manufactured by Tosoh)
- Temperature: 40°C
- Flow rate: 1.0 ml/minute

(5) Softness:

[0067] Five specimens each having a size of $2 \times 15\ \text{cm}$ (a vertical direction $\times$ a horizontal direction) were made in

accordance with the A method (45° Cantilever Method) described in 8.21.1 in 8.21 "Bending Stiffness" in JIS L 1096:2010 "Testing Methods for Woven and Knitted Fabrics". Each of the specimens was put on a horizontal table having a slope with an angle of 45°. The specimen was slid, and the scale was read when the central point on one end of the specimen was brought into contact with the slope. An average value of the five specimens was obtained. When the value was 45 mm or less, the softness was evaluated as good.

(6) Crease resistance:

[0068] Crease recovery angles for five specimens were measured using a 10 N load apparatus in accordance with JIS L 1059-1:2009 "Testing Methods for Crease Recovery of Textiles - Part 1: Determination of the Recovery from Creasing of a Horizontally Folded Specimen by Measuring the Angle of Recovery (Monsant Method)", the crease resistance was calculated by the formula of crease resistance ratio described in section 10 "Calculation of Crease Recovery Angle and Crease Resistance Ratio", and an average value of the five specimens was obtained. When the value was 90% or more, the crease resistance was evaluated as good.

[Expression of Chemical Substance]

[0069] Abbreviations of chemical substances used in Examples and Comparative Examples have the following meanings:

- PU: polyurethane
- DMF: N,N-dimethylformamide

(Example 1)

[0070] An islands-in-the-sea fiber including a polystyrene as a sea component and a polyethylene terephthalate as an island component was drawn, crimped, and cut to obtain a raw stock for a nonwoven fabric. Subsequently, the obtained raw stock was formed into fiber webs using a cross-lapper, and needle punching was performed to obtain a nonwoven fabric.

[0071] The thus obtained nonwoven fabric composed of the islands-in-the-sea fiber was impregnated with an aqueous solution of polyvinyl alcohol, dried, and then the polystyrene as the sea component was extracted in trichloroethylene to be removed. The resulting material was dried to obtain a nonwoven fabric composed of ultrafine fibers having an average single fiber diameter of 2.0 μm .

[0072] The thus obtained nonwoven fabric composed of ultrafine fibers was immersed in a resin solution in which a concentration of a solution of a polycarbonate-based polyurethane resin in DMF was adjusted to 11%, and an adhesion amount of the polyurethane (PU) resin solution was controlled by using a squeeze roll. Then, the PU resin was coagulated in an aqueous solution having a DMF concentration of 30%, subsequently, polyvinyl alcohol and DMF were removed by hot water, and the resulting material was dried to obtain a sheet-like material having a PU resin content of 17% by mass. One side of the thus obtained sheet-like material was subjected to buffing using 180-mesh endless sandpaper, and then was dyed with a dispersion dye to obtain a napped leather-like sheet-like material.

[0073] When a cross-section in the thickness direction of the inside of the obtained leather-like sheet-like material was observed with a scanning electron microscope (SEM), it was found that the polyurethane resin existed only in the inside of the nonwoven fabric, the polyurethane resin had a porous structure having micropores, the proportion of micropores with a pore size of 0.1 to 20 μm in all pores in the porous structure was 85%, and the number of pores per unit area in the porous structure was 247 pores/1600 μm . The polyurethane resin extracted from the napped leather-like sheet-like material had a weight-average molecular weight of 110,000.

[0074] The obtained napped leather-like sheet-like material had a good nap length and dispersibility of the fibers, and had the excellent softness and the crease resistance. The results are shown in Table 1.

(Examples 2 to 7 and Comparative Examples 1 to 5)

[0075] A napped leather-like sheet-like material was manufactured in the same manner as in Example 1, except that the average single fiber diameter of the ultrafine fiber, the kind of the polyurethane resin, and the weight-average molecular weight of the polyurethane resin were changed to values shown in Table 1.

[0076] When a cross-section in the thickness direction of the inside of the leather-like sheet-like material in each of Examples and Comparative Examples was observed with a scanning electron microscope (SEM), it was found that the polyurethane resin had a porous structure having micropores, and the polyurethane resin existed only in the inside of the nonwoven fabric.

[0077] Table 1 shows the average single fiber diameter of the ultrafine fiber, the kind of the polyurethane resin, the weight-average molecular weight of the polyurethane resin, the average particle size of the porous structure of the polyurethane in the obtained sheet-like material, the proportion of micropores with a pore size of 0.1 to 20 μm in all pores in the porous structure, the softness, and the crease resistance in each Example and each Comparative Example.

[Table 1]

[0078]

[Table 1]

	Average single fiber diameter (μm)	Kind of polyurethane resin	Weight-average molecular weight of polyurethane resin	Average pore size of porous structure (μm)	Proportion of micropores with pore size of 0.1 to 20 μm in pore structure (%)	Number of pores per unit area in porous structure (pores/1600 μm^2)	Softness (mm)	Crease resistance (%)
Example 1	2.0	polycarbonate-based	110,000	3.3	85	247	35	96
Example 2	2.0	polycarbonate-based	70,000	7.2	71	92	31	91
Example 3	2.0	polycarbonate-based	140,000	14.5	63	53	43	90
Example 4	4.4	polycarbonate-based	110,000	3.1	81	252	4	94
Example 5	5.5	polycarbonate-based	110,000	3.2	83	245	42	93
Example 6	2.0	polyether-based	110,000	8.5	68	76	30	90
Example 7	2.0	polyester-based	110,000	4.7	74	160	32	91
Comparative Example 1	2.0	polycarbonate-based	160,000	19.4	52	12	50	86
Comparative Example 2	2.0	polycarbonate-based	200,000	38.0	30	1	54	82
Comparative Example 3	2.0	polycarbonate-based	260,000	71.8	14	1	57	80
Comparative Example 4	2.0	polyether-based	200,000	58.7	19	1	48	78
Comparative Example 5	2.0	polyester-based	200,000	41.3	26	1	52	80

[0079] In all of the napped leather-like sheet-like materials in Examples 1 to 7, the polyurethane resin had the porous structure having micropores, and both the excellent softness and the excellent crease resistance were obtained by adjusting the weight-average molecular weight of the polyurethane resin, the average pore size of the pores in the porous structure, the proportion of micropores with a pore size of 0.1 to 20 μm in all pores in the porous structure, and the number of pores per unit area in the porous structure. On the other hand, in the sheet-like materials in Comparative Examples 1 to 5, the porous structure was formed in the polyurethane resin by the increase of the weight-average molecular weight of the polyurethane resin, but the pores were large and ununiform, and the thickness of the polyurethane resin between the pores became thick, thus resulting in the reduced softness. Also the pore size was not uniform, and thus the crease deformation could not be received by the whole polyurethane resin, thus resulting in the poor crease resistance.

Claims

1. A sheet-like material comprising a nonwoven fabric containing ultrafine fibers having an average single fiber diameter of 0.3 to 7 μm , and an elastomer, and having nap on a surface, wherein the elastomer has a porous structure, and the porous structure has a proportion of micropores with a pore size of 0.1 to 20 μm of 60% or more in all pores.
2. The sheet-like material according to claim 1, wherein the elastomer exists in an interior space in the nonwoven fabric.
3. The sheet-like material according to claim 1 or 2, wherein the elastomer is a polycarbonate-based polyurethane resin.
4. The sheet-like material according to claim 3, wherein the polyurethane resin has a weight-average molecular weight of 30,000 to 150,000.
5. The sheet-like material according to any one of claims 1 to 4, wherein a number of pores per unit area in section is 50 pores/1600 μm^2 or more in the porous structure in the elastomer.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/046354

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. D06N3/00 (2006.01) i, D06N3/14 (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)

Int. Cl. D06N3/00-7/06

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2018

Registered utility model specifications of Japan 1996-2018

Published registered utility model applications of Japan 1994-2018

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 A	JP 2014-65980 A (KURARAY CO., LTD.) 17 April 2014, claims 1, 4, 10, paragraphs [0035], [0081]-[0087], table 1 (Family: none)	1-3, 5 4
A	WO 2015/098271 A1 (DIC CORP.) 02 July 2015, paragraph [0035] & KR 10-2016-0067135 A & CN 105745261 A & TW 201529720 A	1-5



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

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/046354

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2000-303368 A (KURARAY CO., LTD.) 31 October 2000, claims 1, 2, paragraph [0010], embodiments (Family: none)	1-5
A	JP 2012-214944 A (KURARAY CO., LTD.) 08 November 2012, claim 1, paragraphs [0034], [0089] (Family: none)	1-5

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

REFERENCES CITED IN THE DESCRIPTION

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- JP 2011214210 A [0011]
- JP 2012214944 A [0011]