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(54) METHOD OF MANUFACTURING SHEET ARTICLE

(57) The present invention provides a method of manufacturing a sheet article achieving both an elegant appearance and a flexible feel and having good wear resistance even when a conventional low-polymerization, low-viscosity polyvinyl alcohol aqueous solution which is highly soluble in water is used in a manufacturing step considering the environment. The method of manufacturing a sheet article of the present invention is to sequentially perform the following steps 1 to 4:
1. a polyvinyl alcohol-adding step of adding a polyvinyl alcohol aqueous solution, which is an aqueous solution of polyvinyl alcohol having the following characteristics, to a fibrous substrate having microfiber expression type fibers as its main constituent to add the polyvinyl alcohol in an amount of 0.1 to 50% by mass based on a mass of the fibers contained in the fibrous substrate
(polyvinyl alcohol: a saponification degree is 90% or more, and an rrr composition abundance ratio is 14.5% or more in a heavy water solvent in tacticity evaluation measured by ^{13}C-NMR),
2. microfiber expression step,
3. polyurethane-adding step, and
4. polyvinyl alcohol removal step.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a method of manufacturing a sheet article that uses water-dispersible polyurethane for a binder resin to reduce an amount of an organic solvent used in a manufacturing process, achieves both good flexibility and high-grade surface appearance in an environment-friendly sheet article, and has good wear resistance.

BACKGROUND ART

[0002] Sheet articles made up mainly of a fibrous substrate and polyurethane have excellent features that natural leathers do not have, and are widely utilized in various uses. In particular, a leather-like sheet article that employs a polyester-based fibrous substrate is excellent in light resistance, and therefore its use has spread year by year to clothing, chair upholstery, automotive interior finishing material uses, etc.

[0003] To produce such a sheet article, a process in which a fibrous substrate is impregnated with an organic solvent solution of polyurethane, and then the obtained fibrous substrate is dipped in water or a mixed solution of organic solvent and water that is a non-dissolving medium for polyurethane, so as to cause polyurethane to undergo wet coagulation is generally adopted. As the organic solvent used to dissolve the polyurethane, a water miscible organic solvent such as N,N-dimethylformamide (hereinafter referred to as "DMF") is used. There has been proposed, for example, a process for producing a sheet article, the process including impregnating a nonwoven fabric with a polyvinyl alcohol aqueous solution to prepare a fibrous sheet article, immersing the fibrous sheet article in a polyurethane-impregnating solution, subjecting the polyurethane to wet coagulation in a 45% DMF aqueous solution at 20°C, and then removing the DMF and the polyvinyl alcohol in hot water at 85°C (see Patent Document 1) .

[0004] In recent years, a technique for reducing the use of the organic solvent has attracted much attention in consideration of health conditions of workers, safety, and surrounding environment in the production of sheet articles.

[0005] By way of a specific means for solving this problem, for example, studies have been performed for development of a method using water-dispersible polyurethane, which is produced by dispersing polyurethane in water, in place of conventional polyurethane dissolved in an organic solvent. In addition, there has been proposed a process including, as in the case of a production process using a conventional polyurethane dissolved in an organic solvent, the following steps: adding polyvinyl alcohol to a fibrous substrate in advance in order to form voids between fibers and the polyurethane, then adding the polyurethane, and then removing the polyvinyl alcohol (see Patent Document 2).

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0006]

Patent Document 1: Japanese Patent Laid-open Publication No. 2002-30579
Patent Document 2: International Publication No. 2014/084253

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] A conventional sheet article which is formed by impregnating a fibrous substrate with water-dispersible polyurethane and adding the polyurethane has a problem in that the feel tends to be hard because the polyurethane strongly adheres to fibers of the fibrous substrate.

[0008] As in the technique disclosed in Patent Document 2, in the method of adding polyvinyl alcohol to a fibrous substrate in advance, then adding polyurethane, and then removing the polyvinyl alcohol, the polyvinyl alcohol is water-soluble, and therefore, after the polyvinyl alcohol is added to the fibrous substrate, when the fibrous substrate is wetted with water, the polyvinyl alcohol may dissolved away and lost in the water. Thus, for example, in Patent Document 2, it is attempted to suppress the loss of polyvinyl alcohol into water by using an aqueous solution of polyvinyl alcohol having a saponification degree of 98% or more and a degree of polymerization of 800 to 3500 and a small amount of impurities.

[0009] However, by using polyvinyl alcohol having a high degree of polymerization, there is a problem that a viscosity of the polyvinyl alcohol aqueous solution is increased, and an impregnation property into the fibrous substrate and handleability of the polyvinyl alcohol aqueous solution are lowered.

[0010] Thus, an object of the present invention is to provide a sheet article that reduces use of an organic solvent in a manufacturing process and thereby to consider the environment, achieves both an elegant, napped appearance and a flexible feel even when a polyvinyl alcohol aqueous solution having a low degree of polymerization and a low viscosity is used, and has good wear resistance.

SOLUTIONS TO THE PROBLEMS

[0011] As a result of repeated studies by the present inventors to achieve the above object, it has been found that a sheet article having excellent flexibility is obtained by applying polyvinyl alcohol having a high saponification degree, adding polyvinyl alcohol, and then adding polyurethane, and when tacticity of polyvinyl alcohol is made a structure having higher syndiotactic properties, solubility of polyvinyl alcohol in water can be effectively reduced.

[0012] That is, the present invention aims to solve the above problems, and is a method of manufacturing a sheet article including a fibrous substrate including microfibers and polyurethane, and a method of manufacturing a sheet article including the following steps (1) to (4):

(1) a polyvinyl alcohol-adding step of adding a polyvinyl alcohol aqueous solution, which is an aqueous solution of polyvinyl alcohol having the following characteristics, to a fibrous substrate having microfiber expression type fibers as its main constituent to add the polyvinyl alcohol in an amount of 0.1 to 50% by mass based on a mass of the fibers contained in the fibrous substrate
(polyvinyl alcohol: a saponification degree is 90% or more, and an rrr composition abundance ratio is 14.5% or more in a heavy water solvent in tacticity evaluation measured by 13C-NMR),
(2) a microfiber expression step of, after the preceding step, making microfiber expression type fibers of the fibrous substrate into microfibers having an average single fiber diameter of 0.1 μm to 10 μm,
(3) a polyurethane-adding step of, after the preceding step, adding water-dispersible polyurethane to the fibrous substrate having the added polyvinyl alcohol, and
(4) a polyvinyl alcohol removal step of, after the preceding step, removing the polyvinyl alcohol from the fibrous substrate having the added water-dispersible polyurethane.

[0013] According to a preferred mode of the manufacturing method of the present invention, a degree of polymerization of the polyvinyl alcohol is 200 to 3500.

[0014] According to a preferred embodiment of the method of manufacturing a sheet article of the present invention, in the microfiber expression step, the fibrous substrate having the microfiber expression type fibers as its main constituent is treated with an alkaline aqueous solution.

[0015] According to a preferred embodiment of the manufacturing method of the present invention, in the polyvinyl alcohol-adding step, after adding the polyvinyl alcohol, heating is performed at 80 to 190°C.

[0016] According to a preferred embodiment of the manufacturing method of the present invention, in the polyvinyl alcohol-adding step, the fibrous substrate having the microfiber expression type fibers as its main constituent in which the fibers and a woven fabric and/or a knitted fabric are integrated by entanglement is used.

EFFECTS OF THE INVENTION

[0017] According to the present invention, even when a low-polymerization, low-viscosity polyvinyl alcohol aqueous solution which is highly soluble in water is used in a manufacturing step considering the environment, a sheet article achieving both an elegant appearance and a flexible feel and having good wear resistance can be obtained.

EMBODIMENTS OF THE INVENTION

[0018] The method of manufacturing a sheet article of the present invention is to perform the following steps (1) to (4) :

(1) a polyvinyl alcohol-adding step of adding a polyvinyl alcohol aqueous solution, which is an aqueous solution of polyvinyl alcohol having the following characteristics, to a fibrous substrate having microfiber expression type fibers as its main constituent to add the polyvinyl alcohol in an amount of 0.1 to 50% by mass based on a mass of the fibers contained in the fibrous substrate
(polyvinyl alcohol: a saponification degree is 90% or more, and an rrr composition abundance ratio is 14.5% or more in a heavy water solvent in tacticity evaluation measured by 13C-NMR),
(2) a microfiber expression step of, after the preceding step, making microfiber expression type fibers of the fibrous substrate into microfibers having an average single fiber diameter of 0.1 μm to 10 μm,
(3) a polyurethane-adding step of, after the preceding step, adding water-dispersible polyurethane to the fibrous substrate having the added polyvinyl alcohol, and

(4) a polyvinyl alcohol removal step of, after the preceding step, removing the polyvinyl alcohol from the fibrous substrate having the added water-dispersible polyurethane.

[0019] The components thereof will be described in detail below. However, the present invention is not limited to the scope described below as long as the gist thereof is not exceeded.

(Method of manufacturing sheet article)

[0020] In the method of manufacturing a sheet article of the present invention, the above steps (1) to (4) are performed in this order. A step (for example, a dissolution step) of adding the polyvinyl alcohol aqueous solution to a fibrous substrate having microfiber expression type fibers as its main constituent and then expressing microfibers from the microfiber expression type fibers (for example, islands-in-the-sea fibers) is performed. Then, a water-dispersible polyurethane liquid is added to the fibrous substrate having the microfibers as its main constituent and having the added polyvinyl alcohol. In addition, the polyvinyl alcohol is removed from the fibrous substrate. Large voids derived from the removed polyvinyl alcohol and the removed sea component are formed between the fibers and the polyurethane. In addition, the microfibers are partially in direct contact with and held by the polyurethane, so that an elegant appearance, a flexible feel, and good wear resistance can be exhibited.

[0021] When a polyvinyl alcohol aqueous solution is added to the fibrous substrate and the fibrous substrate is heat-dried, a so-called migration phenomenon occurs in which the polyvinyl alcohol in water migrates along with the migration of the water during drying toward the surface and the polyvinyl alcohol concentrates in the surface layer of the fibrous substrate. As a result, a large amount of the polyvinyl alcohol adheres to the surface layer of the fibrous substrate and its vicinity, and a small amount of the polyvinyl alcohol adheres to the inside. In such a state, the water-dispersible polyurethane to be added later mainly adheres to the inside of the fibrous substrate. Then, after the polyvinyl alcohol is removed, large voids are present between the fibers and the polyurethane in the surface layer of the fibrous substrate, where a large amount of the polyvinyl alcohol once adhered, and in its vicinity. After a napping step, the resulting sheet article can give an elegant surface appearance where a raised nap is unlikely to be bundled but uniformly separated.

[0022] On the other hand, when the dissolution treatment is performed after removing the polyvinyl alcohol, both voids derived by the removal of the polyvinyl alcohol and voids derived by the dissolved sea component are formed between the polyurethane and the microfibers. Thus, the area where the surface of the microfibers is in direct contact with and held by the polyurethane is further reduced. Although the feel of the sheet article is flexible, characteristics such as wear resistance tend to be deteriorated.

[0023] The details of each step are shown below.

[Polyvinyl alcohol-adding step]

[0024] First, as a first step, there will be described the polyvinyl alcohol-adding step of adding the polyvinyl alcohol aqueous solution, which is the aqueous solution of polyvinyl alcohol having the following characteristics, to the fibrous substrate having microfiber expression type fibers as its main constituent to add the polyvinyl alcohol in an amount of 0.1 to 50% by mass based on the mass of the fibers contained in the fibrous substrate. The polyvinyl alcohol used here has a saponification degree of 90% or more and an rrr composition abundance ratio of 14.5% or more.

[0025] In the present invention, as the polyvinyl alcohol added to the fibrous substrate, a polyvinyl alcohol containing polyvinyl acetate as a raw material is preferable. In addition, a polyvinyl alcohol containing poly(trifluorovinyl acetate) as a raw material is also preferable. Polyvinyl alcohol has a saponification degree of 90% or more. The saponification degree is preferably 95% or more, and more preferably 98% or more. By setting the saponification degree of polyvinyl alcohol to a certain value or more, it is possible to prevent the polyvinyl alcohol from being dissolved in the water-dispersible polyurethane liquid when the water-dispersible polyurethane is added after the polyvinyl alcohol is added to the fibrous substrate. On the other hand, if the saponification degree is low, when the water-dispersible polyurethane liquid is added to the fibrous substrate, the polyvinyl alcohol is dissolved in the water-dispersible polyurethane liquid, and polyvinyl alcohol is taken into the polyurethane, which makes it difficult to remove the polyvinyl alcohol later. Thus, an adhesive state between the polyurethane and the fibers cannot be controlled stably, and the feel is hard.

[0026] In the present invention, the saponification degree of polyvinyl alcohol can be calculated as follows as described in 3.5 "Saponification Degree" in JIS K 6726: 1994 "Polyvinyl Alcohol Test Method".

(1) Weigh polyvinyl alcohol, put the polyvinyl alcohol in an Erlenmeyer flask, add water and a phenolphthalein solution, and completely dissolve the mixture at a temperature of 90°C or higher.
(2) After allowing to cool to room temperature, add an aqueous sodium hydroxide solution with a burette, shake the mixture well, and hold the solution at room temperature for 2 hours or more. Here, when the saponification degree is less than 97%, a 0.5 mol/L aqueous sodium hydroxide solution is used, and when the saponification degree is

97% or more, a 0.1 mol/L aqueous sodium hydroxide solution is used.
(3) Add sulfuric acid or hydrochloric acid having the same molar concentration (unit: mol/L) as the aqueous sodium hydroxide solution in the same amount as the aqueous sodium hydroxide solution with a bullet, and shake the mixture well.
(4) Carry out titration with an aqueous sodium hydroxide solution until the solution turns pale red.
(5) Perform a blank test without adding polyvinyl alcohol.
(6) Calculate a saponification degree H from the following formula.

[Formula 1]

$$X_1 = \frac{(b-a) \times f \times D \times 0.06050}{S \times \frac{P}{100}} \times 100$$

$$X_2 = \frac{44.05 \times X_1}{60.05 - 0.42 \times X_1}$$

$$H = 100 - X_2$$

[0027] Here,

X_i: the amount of acetic acid corresponding to residual acetic acid groups (%),
X_2: residual acetic acid groups (mol %),
H: the saponification degree (mol %),
a: the amount of the aqueous sodium hydroxide solution used in (4) (mL),
b: the amount of the aqueous sodium hydroxide solution used in the blank test of (5) (mL),
f: the factor of the aqueous sodium hydroxide solution,
D: the concentration of the aqueous sodium hydroxide solution (mol/L),
S: the amount of the polyvinyl alcohol taken (g), and
P: the purity of the polyvinyl alcohol (%).

[0028] When the raw material before saponification is a carboxylic acid vinyl ester polymer other than polyvinyl acetate, the above formula should be read as follows:

X_1: the amount of carboxylic acid corresponding to residual carboxylic acid groups (%), and
X_2: residual carboxylic acid groups (mol %).

[0029] Instead of 60.05 (molecular weight of acetic acid) in the formula for calculating X_2, the molecular weight of the carboxylic acid constituting vinyl carboxylic acid ester is used.

[0030] In the present invention, the polyvinyl alcohol added to the fibrous substrate has an rrr composition abundance ratio of 14.5% or more in a heavy water solvent in the tacticity evaluation measured by ^{13}C-NMR.

[0031] In a repeated structure of a vinyl alcohol unit, a structure in which an "r" (racemo) structure having adjacent hydroxyl groups being in different directions is repeated is a partially syndiotactic structure. In the syndiotactic structure, hydroxyl groups are arranged alternately one above the other on a plane formed by a carbon chain in a polymer, so that the syndiotactic structure is a structure likely to form many hydrogen bonds due to a hydroxyl group in a molecule of polyvinyl alcohol in the syndiotactic structure. As a result, the hydroxyl groups that contribute to the formation of hydrogen bonds with water molecules are reduced, solubility in water is reduced, and solubility in warm water is also reduced.

[0032] In ^{13}C-NMR measurement in a heavy water solvent, the arrangement of "m" in which adjacent hydroxyl groups of vinyl alcohol units are in the same direction and "r" in which the adjacent hydroxyl groups of vinyl alcohol units are in different directions can be evaluated as arrangement of m and r corresponding to four units of vinyl alcohol because a peak derived from methylene carbon in a polyvinyl alcohol skeleton splits into five peaks. It is known that the arrangements of m and r are "mmm", "mmr", "mrr", "rmr", and "rrr" from the peak on the high magnetic field side. The abundance ratio of each arrangement is expressed as a percentage, assuming that a sum of the integrated values of absorptions is 100%. Polyvinyl alcohol having an abundance ratio of the rrr structure having the highest syndiotactic properties of 14.5% or more can effectively reduce the solubility in water. The abundance ratio of the rrr structure is preferably 14.7% or more, and more preferably 15.0% or more. A high abundance ratio of the rrr structure means a high ratio of the syndiotactic structure, and the solubility in water can be further reduced. When the abundance ratio of the rrr structure is less than 14.5%, the formation of hydrogen bonds between polyvinyl alcohols is reduced, and the polyvinyl alcohol is dissolved away and lost in water during the dissolution step, etc. An area where fibers are in direct contact with and held by the polyurethane increases, and flexibility and surface appearance of the sheet article decrease.

[0033] From the viewpoint of reducing the solubility of polyvinyl alcohol in water, other than the rrr structure, the abundance ratio of the mrr structure is preferably 25% or more. The abundance ratio is more preferably 25.5% or more, still more preferably 26% or more. A total of the abundance ratio of the rrr structure and the abundance ratio of the mrr structure is preferably 39.5% or more. The total is more preferably 40% or more, still more preferably 40.5% or more. On the other hand, a total of the abundance ratio of the mmm structure and the abundance ratio of the mmr structure is preferably 50% or less. The total is more preferably 48% or less, still more preferably 45% or less.

[0034] Although there is no particular preferred upper limit of the rrr structure, the upper limit is 28.0% or less, and preferably 20.0% or less, from the viewpoint of easy availability or easy production.

[0035] The rrr composition abundance ratio of polyvinyl alcohol is measured as follows, and the calculated value is adopted.

[0036] First, polyvinyl alcohol is dissolved in a heavy water solvent at a temperature of 80°C, and ^{13}C-NMR measurement at a measurement temperature of 80°C and a resonance frequency of 100 MHz is performed. Of two groups of peaks corresponding to a carbon atom of polyvinyl alcohol, the group of peaks observed at 45 to 49 ppm is the group of peaks corresponding to methylene carbon in the polyvinyl alcohol skeleton. The group of peaks on the low magnetic field side is a methine carbon peak group to which the hydroxyl group in the polyvinyl alcohol skeleton is bonded. For the carbon peak group constituting this methylene group, in five peaks detected, if the peaks overlap, the peaks are vertically divided in a peak valley to calculate an integrated value, and the abundance ratio of each arrangement is calculated as a percentage. The peak of the rrr structure is observed on the lowest magnetic field side of the group of peaks.

[0037] The abundance ratio of the rrr structure can be adjusted by appropriately changing the polymerization conditions and polymerization catalyst of polyvinyl alcohol or polyvinyl acetate which can be a raw material.

[0038] The solubility of polyvinyl alcohol in water and the viscosity of the polyvinyl alcohol aqueous solution change depending on the degree of polymerization. The smaller the degree of polymerization of polyvinyl alcohol, the lower the viscosity of the polyvinyl alcohol aqueous solution, and the better an impregnation property of the aqueous solution into the fibrous substrate and handleability of the aqueous solution. On the other hand, the higher the degree of polymerization of polyvinyl alcohol, the lower the solubility in water. When the water-dispersible polyurethane is added, the dissolution of polyvinyl alcohol in the water-dispersible polyurethane liquid can be further suppressed. Since the polyvinyl alcohol of the present invention has a high rrr composition abundance ratio as described above, it is possible to effectively suppress the dissolution of polyvinyl alcohol in the water-dispersible polyurethane liquid even when the degree of polymerization of polyvinyl alcohol is low. Thus, an average degree of polymerization of polyvinyl alcohol is preferably 200 or more, more preferably 300 or more, and still more preferably 400 or more. By setting the degree of polymerization of polyvinyl alcohol to 200 or more, it is possible to suppress the dissolution of polyvinyl alcohol in water. The average degree of polymerization of polyvinyl alcohol is preferably 3500 or less, more preferably 2500 or less, still more preferably 1500 or less, and particularly preferably 1000 or less. By setting the degree of polymerization of polyvinyl alcohol to 3500 or less, it is possible to prevent the viscosity of the polyvinyl alcohol aqueous solution from becoming too high, and to improve the impregnation property into the fibrous substrate and the handleability of the polyvinyl alcohol aqueous solution.

[0039] In the present invention, the average degree of polymerization of polyvinyl alcohol is measured as shown in the following (1) to (7) according to 3.7 "Average Degree of Polymerization" in JIS K 6726: 1994 "Polyvinyl Alcohol Test Method" and refers to the average degree of polymerization calculated in the present invention in (8).

(1) Put polyvinyl alcohol in an Erlenmeyer flask, add methanol, then add aqueous sodium hydroxide solution, and stir the mixture.
(2) Heat the mixture in a water bath at 40 ± 2°C for 1 hour and completely saponify the residual carboxylic acid groups.
(3) Wash with methanol, remove sodium hydroxide and sodium carboxylate, and dry at a temperature of 105 ± 2°C for 1 hour.
(4) Weigh the sample obtained in (3), add water to heat and dissolve the mixture, allow the mixture to cool to room temperature, and then filter.
(5) Determine a relative viscosity of a filtrate of (4) with respect to water at the same temperature at 30.0 ± 0.1°C using an Ostwald viscometer.

(6) Determine a concentration of the filtrate whose viscosity has been measured by drying at 105 ± 2°C for 4 hours or more.

(7) Calculate an average degree of polymerization P_A from the following formula.

[Formula 2]

$$C = \frac{W_2 - W_3}{V} \times 100$$

$$\eta_{rel} = \frac{t_1}{t_0}$$

$$[\eta] = \frac{2.303 \log_{10} \eta_{rel}}{C}$$

$$\log_{10} P_A = 1.613 \log_{10} \frac{[\eta] \times 10^4}{8.29}$$

C: Concentration of test solution (g/L)
W_2: Mass of dried sample and evaporating dish (g)
W_3: Mass of evaporating dish (g)
V: Filtrate volume (mL)
P_A: Average degree of polymerization [η]: Limiting viscosity
η_{rel}: Relative viscosity
t_0 : Dropping time of water (s)
t_1: Dropping time of test solution (s)

(8) Round the obtained average degree of polymerization after the decimal point to an integer. Express that value as n + 50* m. n is an integer from 0 to 49. m is an integer greater than or equal to zero. When n is 0 to 24, the average degree of polymerization is 50* m. When n is 25 to 49, the average degree of polymerization is 50* (m + 1).

[0040] If the value of the average degree of polymerization PA itself calculated in (7) above is outside the range specified in the present invention, it is not considered to be polyvinyl alcohol having the average degree of polymerization specified in the present invention.

[0041] In the present invention, the viscosity of the polyvinyl alcohol aqueous solution refers to the viscosity at 20°C of the polyvinyl alcohol aqueous solution having a concentration of 4% by mass, which is measured as follows in 3.11.1 "Rotary Viscometer Method" in JIS K 6726: 1994 "Polyvinyl Alcohol Test Method".

(1) Weigh polyvinyl alcohol and put the polyvinyl alcohol in an Erlenmeyer flask. Prepare three of these.

(2) Add water so that the respective concentrations are 3.8% by mass, 4.0% by mass, and 4.2% by mass, heat and dissolve completely, allow to cool to a temperature of 20°C, and completely defoam.

(3) Measure the viscosity at a temperature of 20.0 ± 0.1°C using a rotary viscometer.

(4) Measure the concentration (% by mass) of the liquid used for the measurement, create a graph with the viscosity on the y-axis and the concentration on the x-axis, and obtain the viscosity (mPa·s) at a concentration of 4% by mass.

[0042] In the present invention, the polyvinyl alcohol preferably has a viscosity of a 4% by mass aqueous solution of the polyvinyl alcohol at 20°C of 2 to 70 mPa·s. When the viscosity of the polyvinyl alcohol is within this range, an appropriate migration structure can be obtained inside the fibrous substrate during drying, and it is possible to obtain a balance between the flexibility of the sheet article and the physical properties such as surface appearance and wear resistance. By setting the viscosity to 2 mPa·s or more, more preferably 3 mPa·s or more, and still more preferably 4 mPa·s or more, it is possible to suppress an extreme migration structure. On the other hand, by setting the viscosity to 70 mPa·s or less, more preferably 50 mPa·s or less, and still more preferably 40 mPa·s or less, the fibrous substrate can be easily impregnated with polyvinyl alcohol.

[0043] In the present invention, a glass transition temperature (Tg) of polyvinyl alcohol is preferably 70 to 100°C or lower. By setting the glass transition temperature of polyvinyl alcohol to 70°C or higher, and more preferably 75°C or higher, softening in a drying step can be prevented, dimensional stability of the fibrous substrate can be obtained, and deterioration of the surface appearance of the sheet article can be suppressed. On the other hand, by setting the glass transition temperature to 100°C or lower, and more preferably 95°C or lower, it is possible to prevent the fibrous substrate from becoming too hard and thereby preventing deterioration in the handleability.

[0044] In the present invention, a melting point of polyvinyl alcohol is preferably 200 to 250°C. By setting the melting point of polyvinyl alcohol to 200°C or higher, and more preferably 210°C or higher, softening in the drying step can be prevented, the dimensional stability of the fibrous substrate can be obtained, and deterioration of the surface appearance of the sheet article can be suppressed. On the other hand, by setting the melting point of polyvinyl alcohol to 250°C or lower, and more preferably 240°C or lower, it is possible to prevent the fibrous substrate from becoming too hard and thereby preventing deterioration in the handleability.

[0045] In the present invention, the glass transition point and melting point of polyvinyl alcohol refer to as, respectively, the glass transition temperature and the melting temperature measured in differential scanning calorimetry (DSC) in JIS K 7121: 1987 "Testing Methods for Transition Temperatures of Plastics".

(1) Weigh polyvinyl alcohol and put the polyvinyl alcohol in an aluminum container.
(2) Obtain a DSC curve at a heating rate of 20°C/min for the glass transition temperature and 10°C/min for the melting temperature, and read each temperature from the DSC curve.

[0046] Next, there will be described the polyvinyl alcohol-adding step of adding a polyvinyl alcohol aqueous solution to a fibrous substrate having microfiber expression type fibers as its main constituent to add the polyvinyl alcohol in an amount of 0.1 to 50% by mass based on the mass of the fibers contained in the fibrous substrate.

[0047] The fibrous substrate in the present invention typically has microfiber expression type fibers as its main constituent. The content of the microfiber expression type fibers in the fibrous substrate is preferably 50 to 100% by mass. The content of the microfiber expression type fibers in the fibrous substrate is more preferably 60% by mass or more, and still more preferably 70% by mass or more, because an elegant surface appearance of a sheet article can be obtained. The microfiber expression type fibers are used to generate microfibers through the subsequent step of ultra-fining fibers, and an elegant surface appearance can be obtained.

[0048] The microfiber expression type fibers may be (a) "islands-in-the-sea fibers", which are prepared using two types of thermoplastic resins having different solvent solubilities as the sea and island components and which can generate microfibers from the island component through the dissolution and removal of the sea component with a solvent or the like. Alternatively, the microfiber expression type fibers may be (b) "peelable composite fibers", which are prepared by alternately arranging two types of thermoplastic resins in radial segments or multi-layered segments in the cross-section and which generate microfibers through splitting the fibers by peeling and separating the segments. Of the two types, the islands-in-the-sea fibers can give voids in an appropriate size between the island components, i.e., between the microfibers, through the removal of the sea component, and thus are preferably used from the viewpoint of the flexibility and feel of the sheet article.

[0049] The islands-in-the-sea fibers include, for example, islands-in-the-sea conjugated fiber prepared by using a nozzle for islands-in-the-sea conjugation, mutually aligning two components, namely, the sea component and the island component, and spinning the aligned sea and island components from the nozzle, and mix-spun fiber prepared by spinning a mixture of two components, namely, the sea component and the island component. The islands-in-the-sea conjugated fiber described first is preferably used in view of producing microfibers having uniform fineness as well as the production of microfibers with sufficient length contributing for the strength of the resulting sheet article.

[0050] The island component of the islands-in-the-sea fibers is not particularly limited, and the following are exemplified.

[0051] Polyesters such as polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate and polylactic acid.

[0052] Polyamides such as polyamide 6 and polyamide 66; acryl; polyethylene; and polypropylene. Thermoplastic resins that can be melt-spun, such as thermoplastic cellulose.

[0053] Particularly, it is preferable to use polyester fibers from the viewpoint of strength, dimensional stability, and light resistance. Due to environmental concerns, the fibers are preferably fibers obtained from recycled materials or bio-base materials. The fibrous substrate may include mixed fibers made from different materials.

[0054] The sea component of the islands-in-the-sea fibers is not particularly limited, and the following are exemplified.

[0055] Addition polymers of hydrocarbons such as polyethylene, polypropylene and polystyrene.

[0056] Copolymerized polyester prepared by copolymerizing sodium sulfoisophthalic acid, polyethylene glycol, etc. Polylactic acid. Polyvinyl alcohol.

[0057] Particularly, due to environmental concerns, preferred are copolymerized polyesters prepared by copolymerizing sodium sulfoisophthalate, polyethylene glycol, or the like, and polylactic acid, because these polymers are alkali-degradable and can be degraded without any organic solvent. Also preferred is polyvinyl alcohol because it is soluble in hot water.

[0058] The cross-sectional shape of the fibers constituting the fibrous substrate is not particularly limited, and may be a circular shape, an oval shape, a flat shape, a polygonal shape such as a triangular shape, or a modified cross-sectional shape such as fan and cross shapes.

[0059] The fibrous substrate in the present invention may be a woven fabric, a knitted fabric, a nonwoven fabric, or the like. Among them, a nonwoven fabric is preferably used because it gives a sheet article having a good surface appearance after buffing treatment on the surface.

[0060] The nonwoven fabric may be a staple nonwoven fabric or a filament nonwoven fabric. However, a filament nonwoven fabric has a smaller amount of fibers which lie in the thickness direction of a resulting sheet article and which is to form a raised nap by buffing, as compared with a staple nonwoven fabric. A filament nonwoven fabric thus tends to give a less dense nap, resulting in a poor surface appearance. Therefore, a staple nonwoven fabric is preferably used.

[0061] The fiber length of the staples in the staple nonwoven fabric is preferably 25 to 90 mm. When the fiber length is 25 mm or more, and more preferably 30 mm or more, the fibers can be entangled to yield a sheet article having an excellent wear resistance. When the fiber length is 90 mm or less, and more preferably 80 mm or less, the fibers can yield a sheet article having excellent feel and quality.

[0062] The method for entangling the fibers or fiber bundles to yield a nonwoven fabric may be needle punching or water jet punching.

[0063] In the present invention, when the fibrous substrate including microfiber expression type fibers is a nonwoven fabric, a preferred embodiment of the nonwoven fabric is a nonwoven fabric having a structure in which microfiber expression type fibers are entangled with each other in advance. Consequently, the fibrous substrate including microfibers has a structure in which bundles of the microfibers are entangled, and the strength of the sheet article is improved by the entangled microfibers in the bundle state.

[0064] When the fibrous substrate having microfiber expression type fibers as its main constituent is a nonwoven fabric, a woven fabric or a knitted fabric may be further integrated inside the nonwoven fabric by entanglement for the purpose of improving the strength and other properties. Examples of the woven fabric include plain woven fabrics, twill woven fabrics, and satin woven fabrics, and preferred is plain woven fabrics in view of the cost. Examples of the knitted fabric include circular knitted fabrics, tricot fabrics, and raschel fabrics. The fibers constituting such woven and knitted fabrics preferably have an average single fiber diameter of 0.3 to 20 μm.

[0065] When fibers and a woven fabric and/or a knitted fabric are integrated inside the fibrous substrate having microfiber expression type fibers as its main constituent by entanglement, the addition of the polyvinyl alcohol before addition of the water-dispersible polyurethane reduces the area where the woven fabric or the knitted fabric is in direct contact with and held by the water-dispersible polyurethane, the feel of the resulting sheet article is unlikely to be hard. Especially when the woven fabric and/or the knitted fabric to be used is made of fibers other than microfiber expression type fibers, a sheet article having remarkably excellent flexibility can be obtained.

[0066] The amount of polyvinyl alcohol to be added to the fibrous substrate is 0.1 to 50% by mass based on the total mass of the fibers in the fibrous substrate. When the amount of polyvinyl alcohol to be added is 0.1% by mass or more, preferably 1% by mass or more, a sheet article having good flexibility and feel is obtained. When the amount of polyvinyl alcohol to be added is 50% by mass or less, preferably 45% by mass or less, a sheet article having good processability and good physical properties including wear resistance is obtained.

[0067] In the present invention, the method of adding polyvinyl alcohol to the fibrous substrate is not particularly limited, and various methods commonly used in the art can be adopted. Among the methods, preferred is a method involving dissolving polyvinyl alcohol in water, impregnating the fibrous substrate with the polyvinyl alcohol solution, and heat-drying the substrate, so that the polyvinyl alcohol can be uniformly added. If the drying temperature is too low, a longer drying time is required, and if the drying temperature is too high, polyvinyl alcohol becomes completely insoluble, making it difficult to dissolve and remove the polyvinyl alcohol later. Thus, the drying temperature is preferably 80 to 140°C, and more preferably 110 to 130°C. The drying time is usually 1 to 20 minutes, and is preferably 1 to 10 minutes and more preferably 1 to 5 minutes in view of the processability. Further, in order to make polyvinyl alcohol more insoluble, heat treatment may be performed after drying. The heating treatment is preferably performed at 80 to 190°C. By the heat treatment, insolubilization of polyvinyl alcohol proceeds simultaneously with thermal degradation of the polyvinyl alcohol, and thus the heating temperature is more preferably 90°C to 170°C.

[Microfiber expression step]

[0068] Next, as a second step, there will be described the microfiber expression step of expressing microfibers having an average single fiber diameter of 0.1 to 10 μm from a fibrous substrate including microfiber expression type fibers.

[0069] As described above, the microfiber expression type fiber is preferably an islands-in-the-sea fiber. A microfiber expression treatment of a fibrous substrate having such fibers as its main constituent is a dissolution treatment. The dissolution treatment can be performed by immersing the fibrous substrate in a solvent, dissolving a sea component in the solvent, and wringing out the fibrous substrate. In cases where the microfiber expression type fibers are islands-in-the-sea fibers and where the sea component is polyethylene, polypropylene or polystyrene, the solvent may be an organic solvent such as toluene and trichloroethylene. In cases where the sea component is a copolymerized polyester or polylactic acid, the solvent may be an aqueous solution of alkali such as sodium hydroxide. When the sea component is polyvinyl alcohol, the solvent may be hot water. Due to environmental concerns regarding the process, dissolution treatment is preferably performed with an aqueous solution of alkali such as sodium hydroxide or with hot water.

[0070] In a preferred embodiment of the present invention, the average single fiber diameter of the microfibers generated from the microfiber expression type fibers through the step of ultra-fining fibers is 0.1 to 10 μm. When the average single fiber diameter is 10 μm or less, more preferably 7 μm or less, and still more preferably 5 μm or less, a sheet article having excellent flexibility and an excellent nap quality can be obtained. When the average single fiber diameter is 0.1 μm or more, more preferably 0.3 μm or more, and still more preferably 0.7 μm or more, the resulting sheet article will exhibit an excellent chromogenic property for dyeing, an excellent separability of fibers aggregated into bundles during napping treatment by, for example, grinding with a sandpaper or the like, and an excellent loosening property of fibers.

[0071] In the present invention, as the average single fiber diameter, a value obtained by the following procedure is adopted.

(1) Cut out a sample part from the fibrous substrate, a dissolution sheet, and the sheet article.

(2) For the sample, observe three cross sections, including fibers and perpendicular to the thickness direction, at 3000 times using a scanning electron microscope (SEM), and measure the single fiber diameters of 50 microfibers, randomly extracted within a field of 30 μm × 30 μm per cross section, in μm units to the first decimal place.

(3) Measure the diameters of a total of 150 single fibers with three cross sections, and calculate the average value to the first decimal place.

(4) However, if fibers with a fiber diameter of more than 50 μm are mixed, the fibers are to be excluded from measurement targets for the average fiber diameter, assuming that the fibers clearly do not correspond to microfibers. When the microfiber has a modified cross section, a cross-sectional area (S) of the single fiber is first measured, and a diameter (D) of a circle corresponding to the cross-sectional area is calculated as follows to obtain the diameter of the single fiber. An average value using the diameter as a population is calculated and taken as the average single fiber diameter.

$$S = \pi D^2/4.$$

[Polyurethane-adding step]

[0072] Next, as a third step, there will be described a polyurethane-adding step of adding water-dispersible polyurethane to the fibrous substrate having the microfibers as its main constituent and having the added polyvinyl alcohol.

[0073] The water-dispersible polyurethane includes (I) emulsified polyurethanes, which have been forced to be stably dispersed in water with use of a surfactant, and (II) self-emulsifying polyurethanes, which have hydrophilic structures in their molecular structures and are capable of being dispersed and then stabilized in water without use of any surfactant. Both types of polyurethanes can be used in the present invention.

[0074] The method of adding the water-dispersible polyurethane to the fibrous substrate is not particularly limited. Preferred is a method in which a water-dispersible polyurethane liquid is impregnated into or applied to the fibrous substrate, then coagulated and heat-dried, because the water-dispersible polyurethane is uniformly added by this method.

[0075] In view of storage stability of the water-dispersible polyurethane liquid, the concentration of polyurethane is preferably 10 to 50% by mass and more preferably 15 to 40% by mass in the water-dispersible polyurethane.

[0076] The water-dispersible polyurethane liquid used in the present invention may contain a water-soluble organic solvent in an amount of 40% by mass or less based on the total amount of the polyurethane liquid for the purpose of improving the storage stability of the polyurethane dispersion and the productivity of the sheet. However, the amount of the organic solvent is preferably 1% by mass or less in view of the environmental safety at the production site for the sheet, and the like.

[0077] The water-dispersible polyurethane liquid used in the present invention preferably has a heat-sensitive coagulation property. When the water-dispersible polyurethane liquid having a heat-sensitive coagulation property is used, the polyurethane can be added uniformly in the thickness direction of the fibrous substrate.

[0078] In the present invention, the heat-sensitive coagulation property refers to a property that, when the polyurethane liquid is heated and reaches a certain temperature, reduces the flowability of the polyurethane liquid and then coagulates the polyurethane. A temperature at which this occurs refers to as a heat-sensitive coagulation temperature. In the production of the sheet article having the polyurethane added, the polyurethane liquid is added to the fibrous substrate, then coagulated by dry coagulation, wet-heat coagulation, wet coagulation, or any combination thereof, and dried to give the fibrous substrate having the added polyurethane. In industrial production, a realistic method for coagulating a water-dispersible polyurethane liquid not exhibiting a heat-sensitive coagulation property is dry coagulation. In this method, a migration phenomenon occurs in which the polyurethane concentrates in the surface layer of the fibrous substrate, and the feel of the resulting sheet article having the polyurethane added tends to be hardened. In that case, the migration can be prevented by adjusting the viscosity of the water-dispersible polyurethane liquid by a thickener. Also when a water-dispersible polyurethane liquid exhibiting a heat-sensitive coagulation property is used, the migration can be prevented by the addition of a thickener and dry coagulation.

[0079] The heat-sensitive coagulation temperature of the water-dispersible polyurethane liquid is preferably 40 to 90°C. When the heat-sensitive coagulation temperature is 40°C or higher, the polyurethane liquid has good storage stability, and the adhesion of the polyurethane to the machines during operation can be prevented. When the heat-sensitive coagulation temperature is 90°C or lower, the migration phenomenon of the polyurethane toward the surface layer of the fibrous substrate can be suppressed.

[0080] In one embodiment of the present invention, in order to achieve the above heat-sensitive coagulation temperature, a heat-sensitive coagulant may be added, as appropriate. Examples of the heat-sensitive coagulant include inorganic salts such as sodium chloride, potassium chloride, sodium sulfate, magnesium sulfate, calcium sulfate, and calcium chloride; and radical initiators such as sodium persulfate, potassium persulfate, ammonium persulfate, azobisisobutyronitrile, and benzoyl peroxide.

[0081] In a preferred embodiment of the present invention, the polyurethane liquid can be added to the fibrous substrate by impregnation, application, or other methods, and the polyurethane can be coagulated by dry coagulation, wet-heat coagulation, wet coagulation, or any combination thereof.

[0082] The temperature for the wet-heat coagulation is preferably equal to or higher than the heat-sensitive coagulation temperature of the polyurethane and is preferably 40 to 200°C. When the temperature for the wet-heat coagulation is 40°C or higher, and more preferably 80°C or higher, the polyurethane can coagulate in a shorter period of time, and the migration phenomenon can be more efficiently prevented. On the other hand, when the temperature for the wet-heat coagulation is 200°C or lower, and more preferably 160°C or lower, thermal degradation of the polyurethane and of the polyvinyl alcohol can be prevented.

[0083] The temperature for the wet coagulation is equal to or higher than the heat-sensitive coagulation temperature of the polyurethane and is preferably 40 to 100°C. When the temperature for the wet coagulation in hot water is 40°C or higher, and more preferably 80°C or higher, the polyurethane can coagulate in a shorter period of time, and the migration phenomenon can be more efficiently prevented.

[0084] The temperature for the dry coagulation and the drying temperature are preferably 80 to 140°C. When the temperature for the dry coagulation and the drying temperature are 80°C or higher, and more preferably 90°C or higher, the productivity is excellent. On the other hand, when the temperature for the dry coagulation and the drying temperature are 140°C or lower, and more preferably 130°C or lower, thermal degradation of the polyurethane and of the polyvinyl alcohol can be prevented.

[0085] In the present invention, after being subjected to the coagulation, the polyurethane may be subjected to heat treatment. The heat treatment reduces the number of interfaces between the polyurethane molecules, thereby strengthening the polyurethane. In a preferred embodiment, the heat treatment is performed after removing the polyvinyl alcohol from a sheet having water-dispersible polyurethane added. The temperature for the heat treatment is preferably 80 to 170°C.

[0086] The polyurethane used in the present invention is preferably obtained by reaction of a polymer diol and an organic diisocyanate with a chain extender.

[0087] Examples of the polymer diol include, but are not particularly limited to, polycarbonate diols, polyester diols, polyether diols, silicone diols, and fluorine diols, and copolymers obtained by combining them. In view of hydrolysis resistance, polycarbonate diols and polyether diols are preferably used. In view of light resistance and heat resistance, polycarbonate diols and polyester diols are preferably used. In view of the balance among hydrolysis resistance, heat resistance and light resistance, polycarbonate diols and polyester diols are more preferably used, and polycarbonate diols are particularly preferably used.

[0088] The polycarbonate diols can be produced by, for example, transesterification of an alkylene glycol and a carbonate or reaction of phosgene or a chloroformate with an alkylene glycol.

[0089] The alkylene glycol is not particularly limited, and examples thereof include the following alkylene glycols.

[0090] Linear alkylene glycols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, and 1,10-decanediol.

[0091] Branched alkylene glycols such as neopentyl glycol, 3-methyl-1,5-pentanediol, 2,4-diethyl-1,5-pentanediol, and 2-methyl-1,8-octanediol.

[0092] In addition, alicyclic diols such as 1,4-cyclohexanediol; aromatic diols such as bisphenol A; glycerin; trimethylolpropane; pentaerythritol; and the like.

[0093] The polycarbonate diol may be either a polycarbonate diol obtained from a single type of alkylene glycol or a copolymerized polycarbonate diol obtained from two or more types of alkylene glycols.

[0094] The polyester diols are exemplified by polyester diols obtained by condensation of various low molecular weight polyols and polybasic acids.

[0095] Examples of the low molecular weight polyols include, but are not particularly limited to, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,8-octanediol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, cyclohexane-1,4-diol, and cyclohexane-1,4-dimethanol. These polyols may be used singly or in combination of two or more of them. Adducts prepared by adding various alkylene oxides to bisphenol A are also usable.

[0096] Examples of the polybasic acids include, but are not particularly limited to, succinic acid, maleic acid, adipic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and hexahydroisophthalic acid. These acids may be used singly or in combination of two or more of them.

[0097] Examples of the polyether diols include, but are not particularly limited to, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and copolymerized diols obtained by combining them.

[0098] A number average molecular weight of the polymer diol used in the present invention is preferably 500 to 4000. When the number average molecular weight is 500 or more, and more preferably 1500 or more, the feel of the sheet article is prevented from becoming hard. When the number average molecular weight is 4000 or less, or more preferably 3000 or less, the polyurethane can maintain its strength.

[0099] Examples of the organic diisocyanate include, but are not particularly limited to, aliphatic diisocyanates such as hexamethylene diisocyanate, dicyclohexylmethane diisocyanate, isophorone diisocyanate, and xylylene diisocyanate; and aromatic diisocyanates such as diphenylmethane diisocyanate and tolylene diisocyanate. These diisocyanates may be used in combination. Among them, in view of light resistance, aliphatic diisocyanates such as hexamethylene diisocyanate, dicyclohexylmethane diisocyanate, and isophorone diisocyanate are preferably used.

[0100] Examples of the chain extender include, but are not particularly limited to, amine chain extenders such as ethylenediamine and methylenebisaniline; and diol chain extenders such as ethylene glycol. Polyamines prepared by reacting a polyisocyanate with water may also be used as the chain extender.

[0101] The polyurethane, if desired, may be used in combination with a crosslinker for the purpose of improving water resistance, wear resistance, hydrolysis resistance, and other characteristics. The crosslinker may be an external crosslinker, which is added to the polyurethane as a third component, or an internal crosslinker, which previously introduces reaction points into the molecular structure of the polyurethane to form crosslinked structure. In the present invention, an internal crosslinker is preferably used because it can form crosslinking points uniformly throughout the molecular structure of the polyurethane and alleviates the reduction in flexibility.

[0102] As the crosslinker, a compound having an isocyanate group, an oxazoline group, a carbodiimide group, an epoxy group, a melamine resin, a silanol group and the like can be used. However, if crosslinking proceeds excessively, the polyurethane is hardened, resulting in a sheet article with a hard feel. Therefore, a crosslinker having a silanol group is preferably used in view of the balance between reactivity and flexibility.

[0103] The polyurethane used in the present invention preferably has a hydrophilic group in the molecular structure. When a hydrophilic group exists in the molecular structure, dispersibility and stability as the water-dispersible polyurethane can be improved.

[0104] The hydrophilic group may be any hydrophilic groups including cationic groups such as quaternary amine groups; anionic groups such as a sulfonate group and a carboxylate group; nonionic groups such as a polyethylene glycol group; combinations of a cationic group and a nonionic group; and combinations of an anionic group and a nonionic group. Among them, particularly preferred are the nonionic hydrophilic groups, which are free from concerns of yellowing by light or harmful effects by a neutralizer.

[0105] When the polyurethane has an anionic hydrophilic group, a neutralizer is required. For example, when the neutralizer used is a tertiary amine such as ammonia, triethylamine, triethanolamine, triisopropanolamine, trimethylamine, and dimethylethanolamine, the amine is generated and volatilized by heating during the sheet production or drying and is released outside the system. Thus, in order to prevent the emission to the atmosphere or the deterioration of working environment, a device for recovering the volatilized amine is required to be installed. If the amine is not volatilized by the heating but remains in a sheet article as the end product, the amine may be released in the environment when, for example, the product is burned. On the other hand, when the polyurethane has a nonionic hydrophilic group, no neutralizer is used, and thus the installment of an amine-recovering device is not required. In addition, there is no need for concerns about a remaining amine in the sheet article. Therefore, the polyurethane having a nonionic hydrophilic group can be preferably used.

[0106] When the neutralizer for the anionic hydrophilic group is a hydroxide of an alkali metal or an alkaline earth metal, such as sodium hydroxide, potassium hydroxide, and calcium hydroxide, if a polyurethane portion is wetted with water, alkalinity is demonstrated. However, since the polyurethane having a nonionic hydrophilic group requires no neutralizer, there is no need for concerns about the deterioration of the polyurethane by hydrolysis.

[0107] The water-dispersible polyurethane used in the present invention, if desired, may contain various additives, including pigments such as carbon black; flame retardants such as phosphoric flame retardants, halogen flame retardants, silicone flame retardants, and inorganic flame retardants; antioxidants such as phenol antioxidants, sulfur-containing antioxidants, and phosphorus-containing antioxidants; ultraviolet absorbers such as benzotriazole ultraviolet absorbers, benzophenone ultraviolet absorbers, salicylate ultraviolet absorbers, cyanoacrylate ultraviolet absorbers, and oxalic acid anilide ultraviolet absorbers; light stabilizers such as hindered amine light stabilizers and benzoate light stabilizers; hydrolysis inhibitors such as polycarbodiimide; plasticizers; antistatic agents; surfactants; softening agents; water repellents; coagulation modifiers; viscosity modifiers; dyes; antiseptics; antimicrobials; deodorants; fillers such as cellulose particles and microballoons; and inorganic particles such as silica particles and titanium oxide particles. The water-dispersible polyurethane may also contain inorganic foaming agents such as sodium hydrogen carbonate and organic foaming agents such as 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] in order to form large voids between the fibers and the polyurethane.

[0108] The amount of the polyurethane contained in the fibrous substrate having microfibers as its main constituent according to the present invention is preferably 1 to 80% by mass. When the amount of the polyurethane contained in the sheet article is 1% by mass or more, and more preferably 5% by mass or more, the sheet strength can be obtained, and, at the same time, a loss of the fibers can be prevented. When the amount of the polyurethane contained in the sheet article is 80% by mass or less, and more preferably 70% by mass or less, the feel is prevented from becoming hard, and a good nap quality can be obtained.

[Polyvinyl alcohol removal step]

[0109] Next, as a fourth step, there will be described the step of removing the polyvinyl alcohol from the fibrous substrate including the polyvinyl alcohol and the microfibers having the added water-dispersible polyurethane.

[0110] In a preferred embodiment of the present invention, the polyvinyl alcohol is removed from the fibrous substrate having the added polyurethane, and a flexible sheet article is obtained. The method for removing the polyvinyl alcohol is not particularly limited, but in a preferred embodiment, the polyvinyl alcohol is dissolved and removed by, for example, immersing the sheet in hot water at 60 to 100°C, and wringing out the water from the sheet with a mangle or the like.

[0111] The method of manufacturing a sheet article of the present invention may include, after at least the addition of the water-dispersible polyurethane to the fibrous substrate having the added polyvinyl alcohol is performed, a step of cutting the fibrous substrate in half thickness-wise. In the step of adding the polyvinyl alcohol, a large amount of the polyvinyl alcohol adheres to the surface layer of the fibrous substrate by migration, whereas a small amount of the polyvinyl alcohol adheres to the inside of the fibrous substrate. Subsequently, the water-dispersible polyurethane is added and the fibrous substrate is cut in half thickness-wise to give a sheet article having a structure in which a small amount of the water-dispersible polyurethane adheres to the side to which a large amount of the polyvinyl alcohol has adhered, whereas a large amount of the water-dispersible polyurethane adheres to the side to which a small amount of the polyvinyl alcohol has adhered. When the side to which a large amount of the polyvinyl alcohol once adhered, in other words, the side to which a small amount of the water-dispersible polyurethane has adhered is used as a nap face of the sheet article, the following effects can be obtained. The previous presence of the polyvinyl alcohol allows the formation of large voids between the polyurethane and the nap-forming microfibers. Such large voids give the freedom of movement to the nap-forming fibers, so that the feel of the surface becomes flexible, and a good surface appearance and soft-touch texture can be obtained.

[0112] On the other hand, when the side to which a small amount of the polyvinyl alcohol once adhered, that is, the side to which a large amount of the water-dispersible polyurethane has adhered is used as a nap face of the sheet article, the following effects can be obtained. The nap-forming fibers are strongly held by the polyurethane. This provides a good surface appearance with a short nap with a more density and also provides a good wear resistance. When the process includes the step of cutting the sheet in half thickness-wise, the production efficiency can be improved.

[0113] In the present invention, at least one side of the sheet article may be subjected to buffing treatment to raise a nap on the surface. The method of raising a nap is not particularly limited, and it is possible to use various methods usually performed in the art, such as buffing with a sandpaper or the like. An excessively short nap is unlikely to provide an elegant appearance, whereas an excessively long nap is likely to cause pilling. Therefore, the length of the raised nap is preferably 0.2 to 1 mm.

[0114] In one embodiment of the present invention, before the buffing treatment, silicone or the like may be added as a lubricant to the sheet article. The addition of a lubricant is preferred because it facilitates buffing by surface grinding and provides the surface with excellent quality. An antistatic agent may also be added before the buffing treatment. The addition of an antistatic agent is preferred because a grinding powder generated from the sheet article by grinding is unlikely to deposit on the sandpaper.

[0115] In one embodiment of the present invention, the sheet article can be dyed. As the dyeing method, various methods commonly used in the art can be adopted, and preferred is a method using a jet dyeing machine because, at the same time of dyeing the sheet article, the sheet article can be softened by kneading.

[0116] The dyeing temperature varies with the type of the fibers but is preferably 80 to 150°C. When the dyeing temperature is 80°C or higher, and more preferably 110°C or higher, the attachment of dye to the fibers is efficiently performed. On the other hand, when the dyeing temperature is 150°C or lower, and more preferably 130°C or lower, deterioration of the polyurethane can be prevented.

[0117] The dye used in the present invention is not particularly limited as long as the dye is appropriately selected depending on the type of the fibers constituting the fibrous substrate. For example, when the fibers are polyester fibers, a disperse dye can be used. When the fibers are polyamide fibers, an acid dye, a metal complex dye, or a combination thereof may be used. When the sheet article is dyed with a disperse dye, the sheet article may be subjected to reduction cleaning after the dyeing.

[0118] In a preferred embodiment, a dyeing aid is used during the dyeing. When a dyeing aid is used, uniform dyeing is achieved and reproduction of color is improved. Simultaneously with the dyeing or after the dyeing, finishing treatment can be performed using a fabric softener such as silicone, an antistatic agent, a water repellent, a flame retardant, a light stabilizer, an antimicrobial agent, or other finishing agents.

(Sheet article)

[0119] The sheet article obtained by the above-mentioned manufacturing method achieves an elegant appearance and a flexible feel and has good wear resistance.

[0120] In the present invention, the surface appearance of the sheet article will be evaluated by the following method.

[0121] The surface appearance of a sheet article is evaluated by 20 panelists including 10 healthy adult males and 10 healthy adult females. Visual evaluation and sensory evaluation are performed and scored based on the following criteria with 5 grades. The grade which had the largest number of the panelists is taken as the grade for the surface appearance of the sheet article. Grades 3 to 5 are regarded as good surface appearance.

[0122] Grade 5: a uniform nap of the fibers is observed, a scattered state of the fibers is good, and the appearance is good.

[0123] Grade 4: the material is evaluated as between Grade 5 and Grade 3.

[0124] Grade 3: as the scattered state of the fibers, some of the fibers are not well separated, but the fibers are napped and the appearance is rather good.

[0125] Grade 2: the material is evaluated as between Grade 3 and Grade 1.

[0126] Grade 1: the scattered state of the fibers is very poor throughout the whole surface or the napped fibers have a long length, and the appearance is poor.

[0127] In the present invention, the flexibility of the sheet article will be evaluated by the magnitude of stiffness (mm) measured as follows, based on 8.21 "Stiffness" and "A method (45° cantilever method)" described in 8.21.1 in JIS L 1096: 2010 "Fabric Testing Methods for Woven and Knit Fabrics".

(1) Prepare 2 cm × 15 cm test pieces long in the longitudinal direction or long in the transverse direction.
(2) Place the test piece on a horizontal platform with a 45° sloped surface.
(3) Slide the test piece and, when a central point of one end of the test piece comes into contact with the sloped surface, measure a position of the other end by a scale.
(4) Express a distance that the test piece has moved at this time as (mm) and calculate an average value of the distances of the movement of the five test pieces to determine the stiffness (mm).

[0128] In the present invention, the stiffness of the sheet article is preferably 20 to 45 mm. The stiffness of the sheet article is more preferably 25 mm or more. In places where the stiffness is high, 40 mm or less is preferable.

[0129] In the present invention, the wear resistance will be evaluated by a small amount of wear loss (mg) measured by the following method.

(1) Cut out a circular sample (diameter: 45 mm) of a sheet article and measure the mass.

(2) Cut polyamide fibers, made of polyamide 6 and having a diameter of 0.4 mm, perpendicularly to the longitudinal direction of the fibers into a length of 11 mm, and align and bundle 100 fibers. Next, use a circular brush (the number of nylon yarns is 9700 in total) in which 97 bundles are arranged so that six concentric circles are formed inside a circle of a diameter of 110 mm (one bundle is placed at the center, six bundles are arranged centering around it to form a circle with a diameter of 17 mm, 13 bundles are arranged centering around it to form a circle with a diameter of 37 mm, 19 bundles are arranged centering around it to form a circle with a diameter of 55 mm, 26 bundles are arranged centering around it to form a circle with a diameter of 74 mm, and 32 bundles are arranged centering around it to form a circle with a diameter of 90 mm; in each circle, the bundles are arranged at equal intervals) and abrade a surface of a circular sample (diameter: 45 mm) of the sheet article under conditions of a load of 8 pounds (about 3629 g), a rotation speed of 65 rpm, and a rotation time of 50 times.
(3) Measure the sample mass after abrasion and calculate a mass change of the sample before and after abrasion.
(4) Define the wear loss (mg), which is an average value of mass changes of five samples, as the wear resistance.

[0130] In the present invention, the wear loss of the sheet article is preferably 30 mg or less. The wear loss is more preferably 25 mg or less.

[0131] The density of the sheet article obtained by the above-mentioned manufacturing method is preferably 0.2 to 0.7 g/cm^3. When the density is 0.2 g/cm^3 or more, and more preferably 0.3 g/cm^3 or more, the surface is provided with density and high quality appearance. On the other hand, when the density is 0.7 g/cm^3 or less, and more preferably 0.6 g/cm^3 or less, the sheet article can be prevented from having a hard feel.

EXAMPLES

[0132] The method of manufacturing a sheet article of the present invention will be described in further detail with reference to examples, but the present invention is not limited to these examples. Various modifications can be made within the technical idea of the present invention by a person skilled in the art.

[Evaluation methods]

[0133] The evaluation method will be described in detail below. If there is no particular description in the measurement of each physical property, the measurement is performed based on the method described above.

(1) Tacticity of polyvinyl alcohol

[0134] A sample obtained by dissolving 10 mg of polyvinyl alcohol in 1 mL of heavy water (D_2O) at a temperature of 80°C was placed in a straight tube, and ^{13}C-NMR measurement was performed at a measurement temperature of 80°C, a resonance frequency of 100 MHz, and an integration number of 20000 times or more. For the measurement, ECA400 manufactured by JEOL RESONANCE Inc. was used.

(2) Average single fiber diameter

[0135] As a scanning electron microscope, VE-7800 type manufactured by KEYENCE CORPORATION was used.

[Example 1]

(Step of forming nonwoven fabric for fibrous substrate)

[0136] A polyethylene terephthalate copolymerized with 8 mol % of sodium 5-sulfoisophthalate was provided as the sea component, and a polyethylene terephthalate was provided as the island component. The sea and island components were used at a ratio of 45% : 55% by mass to give islands-in-the-sea composite fibers with 36 islands per filament and an average single fiber diameter of 17 μm. The obtained islands-in-the-sea composite fibers were cut into a length of 51 mm to prepare staples. The staples were subjected to carding and cross wrapping to form a fibrous web. The fibrous web was needle punched to give a nonwoven fabric. The thus obtained nonwoven fabric was shrunk by being immersed in hot water at a temperature of 98°C for 2 minutes and was dried at a temperature of 100°C for 5 minutes to give a nonwoven fabric for a fibrous substrate.

(Polyvinyl alcohol aqueous solution preparation step)

[0137] Polyvinyl alcohol having a saponification degree of 98%, an rrr composition abundance ratio of 15.5%, and a degree of polymerization of 450 obtained from polyvinyl acetate was provided. The polyvinyl alcohol was added to water at 25°C, and the mixture was heated to 90°C. The mixture was stirred for 2 hours while the temperature was maintained at 90°C to give a polyvinyl alcohol aqueous solution with a solid content of 10% by mass.

(Polyvinyl alcohol-adding step)

[0138] The nonwoven fabric for a fibrous substrate was impregnated with the polyvinyl alcohol aqueous solution, heat-dried at a temperature of 140°C for 10 minutes, and then heat-treated at a temperature of 160°C for 5 minutes. A sheet to which the polyvinyl alcohol was added in an amount of 30% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained.

(Microfiber expression step)

[0139] The sheet having the added polyvinyl alcohol was immersed in a 10 g/L aqueous sodium hydroxide solution heated to a temperature of 60°C and treated for 30 minutes to give a dissolution sheet from which the sea component of the islands-in-the-sea composite fibers was removed. The average single fiber diameter of a cross section of the dissolution sheet was 3 μm.

(Polyurethane solution preparation step)

[0140] Polyhexamethylene carbonate was used as a polyol and dicyclohexylmethane diisocyanate was used as an isocyanate to give a self-emulsifying polycarbonate polyurethane liquid. To the self-emulsifying polycarbonate polyurethane liquid was added 1 part by mass of magnesium sulfate as a heat-sensitive coagulant relative to 100 parts by mass of the solid content of the polyurethane liquid. Water was then added to adjust the overall solid content to 20% by mass to give a water-dispersible polyurethane. The heat-sensitive coagulation temperature was 65°C.

(Polyurethane-adding step)

[0141] The dissolution sheet having the added polyvinyl alcohol was impregnated with the polycarbonate polyurethane liquid. The sheet was treated in a dry-heat atmosphere at a temperature of 120°C for 10 minutes, then dried, and dry-heated at a temperature of 150°C for 2 minutes. A sheet in which the amount of the polyurethane adhering to the sheet was 30% by mass relative to the mass of the fibers in the nonwoven fabric was obtained.

(Polyvinyl alcohol removal step)

[0142] The sheet to which the polyurethane was adhered was immersed in water heated to 95°C and treated for 10 minutes to give a sheet from which the added polyvinyl alcohol was removed.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0143] The polyvinyl alcohol-removed sheet was cut in half thickness-wise. The surfaces opposite to the cut surfaces were subjected to buffing treatment by grinding with a 240-mesh abrasive belt. Thereafter, the sheet was dyed with a disperse dye by using a circular dyeing machine and subjected to reduction cleaning to give a sheet article.

[0144] The obtained sheet article had a good surface appearance and a flexible feel.

[Example 2]

(Step of forming nonwoven fabric for fibrous substrate)

[0145] A polyethylene terephthalate copolymerized with 8 mol % of sodium 5-sulfoisophthalate was provided as the sea component, and a polyethylene terephthalate was provided as the island component. The sea and island components were used at a ratio of 45% : 55% by mass to give islands-in-the-sea composite fibers with 16 islands per filament and an average single fiber diameter of 12 μm. The obtained islands-in-the-sea composite fibers were cut into a length of 51 mm to prepare staples. The staples were subjected to carding and cross wrapping to form a fibrous web. The fibrous web was needle punched to give a nonwoven fabric. The thus obtained nonwoven fabric was shrunk by being immersed in hot water at a temperature of 98°C for 2 minutes and was dried at a temperature of 100°C for 5 minutes to give a nonwoven fabric for a fibrous substrate.

(Polyvinyl alcohol aqueous solution preparation step)

[0146] A polyvinyl alcohol aqueous solution was obtained in the same manner as in Example 1.

(Polyvinyl alcohol-adding step)

[0147] The same polyvinyl alcohol aqueous solution as in Example 1 was used, and a sheet to which the polyvinyl alcohol was added in an amount of 30% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained.

(Microfiber expression step)

[0148] The nonwoven fabric for a fibrous substrate was treated in the same manner as in Example 1 to obtain a dissolution sheet from which the sea components of the islands-in-the-sea composite fibers were removed. The average single fiber diameter of a cross section of the dissolution sheet was 2 μm.

(Polyurethane solution preparation step)

[0149] In the same manner as in Example 1, a water-dispersible polyurethane was obtained.

(Polyurethane-adding step)

[0150] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0151] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning)

[0152] In the same manner as in Example 1, a sheet article was obtained.
[0153] The obtained sheet article had a good surface appearance, a flexible feel, and good wear resistance.

[Example 3]

(Step of forming nonwoven fabric for fibrous substrate)

[0154] A polyethylene terephthalate copolymerized with 8 mol % of sodium 5-sulfoisophthalate was provided as the sea component, and a polyethylene terephthalate was provided as the island component. The sea and island components were used at a ratio of 20% : 80% by mass to give islands-in-the-sea composite fibers with 16 islands per filament and an average single fiber diameter of 20 μm. The obtained islands-in-the-sea composite fibers were cut into a length of 51 mm to prepare staples. The staples were subjected to carding and cross wrapping to form a fibrous web. The fibrous web was needle punched to give a nonwoven fabric. The thus obtained nonwoven fabric was shrunk by being immersed in hot water at a temperature of 98°C for 2 minutes and was dried at a temperature of 100°C for 5 minutes to give a nonwoven fabric for a fibrous substrate.

(Polyvinyl alcohol aqueous solution preparation step)

[0155] A polyvinyl alcohol aqueous solution was obtained in the same manner as in Example 1.

(Polyvinyl alcohol-adding step)

[0156] The same polyvinyl alcohol aqueous solution as in Example 1 was used, and a sheet to which the polyvinyl alcohol was added in an amount of 30% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained.

(Microfiber expression step)

[0157] The nonwoven fabric for a fibrous substrate was treated in the same manner as in Example 1 to obtain a dissolution sheet from which the sea components of the islands-in-the-sea composite fibers were removed. The average single fiber diameter of a cross section of the dissolution sheet was 4.4 μm.

(Polyurethane solution preparation step)

[0158] In the same manner as in Example 1, a water-dispersible polyurethane was obtained.

(Polyurethane-adding step)

[0159] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0160] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0161] In the same manner as in Example 1, a sheet article was obtained.

[0162] The obtained sheet article had a good surface appearance, a flexible feel, and good wear resistance.

[Example 4]

(Step of forming nonwoven fabric for fibrous substrate)

[0163] A polyethylene terephthalate copolymerized with 8 mol % of sodium 5-sulfoisophthalate was provided as the sea component, and a polyethylene terephthalate was provided as the island component. The sea and island components were used at a ratio of 10% : 90% by mass to give islands-in-the-sea composite fibers with 16 islands per filament and an average single fiber diameter of 24 μm. The obtained islands-in-the-sea composite fibers were cut into a length of 51 mm to prepare staples. The staples were subjected to carding and cross wrapping to form a fibrous web. The fibrous web was needle punched to give a nonwoven fabric. The thus obtained nonwoven fabric was shrunk by being immersed in hot water at a temperature of 98°C for 2 minutes and was dried at a temperature of 100°C for 5 minutes to give a nonwoven fabric for a fibrous substrate.

(Polyvinyl alcohol aqueous solution preparation step)

[0164] A polyvinyl alcohol aqueous solution was obtained in the same manner as in Example 1.

(Polyvinyl alcohol-adding step)

[0165] The same polyvinyl alcohol aqueous solution as in Example 1 was used, and a sheet to which the polyvinyl alcohol was added in an amount of 30% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained.

(Microfiber expression step)

[0166] The nonwoven fabric for a fibrous substrate was treated in the same manner as in Example 1 to obtain a dissolution sheet from which the sea components of the islands-in-the-sea composite fibers were removed. The average single fiber diameter of a cross section of the dissolution sheet was 5.5 μm.

(Polyurethane solution preparation step)

[0167] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0168] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0169] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0170] In the same manner as in Example 1, a sheet article was obtained. The obtained sheet article had a good surface appearance, a flexible feel, and good wear resistance.

[Example 5]

(Nonwoven fabric for fibrous substrate)

[0171] The same nonwoven fabric for a fibrous substrate as in Example 1 was used.

(Preparation of polyvinyl alcohol aqueous solution)

[0172] A polyvinyl alcohol aqueous solution was obtained in the same manner as in Example 1.

(Addition of polyvinyl alcohol)

[0173] The same polyvinyl alcohol aqueous solution as in Example 1 was used, and a sheet having the added polyvinyl alcohol was obtained in the same manner as in Example 1 except that the amount of the polyvinyl alcohol adhering was changed by controlling the degree of wringing after the impregnation. In the sheet, the amount of polyvinyl alcohol adhering was 20% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate.

(Microfiber expression step)

[0174] In the same manner as in Example 1, a dissolution sheet was obtained from the nonwoven fabric for a fibrous substrate.

(Polyurethane solution preparation step)

[0175] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0176] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0177] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0178] In the same manner as in Example 1, a sheet article was obtained.
[0179] The obtained sheet article had a good surface appearance, a flexible feel, and good wear resistance.

[Example 6]

(Step of forming nonwoven fabric for fibrous substrate)

[0180] A polyethylene terephthalate copolymerized with 8 mol % of sodium 5-sulfoisophthalate was provided as the sea component, and a polyethylene terephthalate was provided as the island component. The sea and island components were used at a ratio of 20% : 80% by mass to give islands-in-the-sea composite fibers with 16 islands per filament and an average single fiber diameter of 20 μm. The obtained islands-in-the-sea composite fibers were cut into a length of 51 mm to prepare staples. The staples were subjected to carding and cross wrapping to form a fibrous web. On each face of the web, a plain woven fabric using a polyethylene terephthalate (PET) hard twist yarn of 84 dtex and 72 filaments with a twist of 2000 T/m was stacked, and needle punching was performed to give a nonwoven fabric. The thus obtained nonwoven fabric was shrunk by being immersed in hot water at a temperature of 98°C for 2 minutes and was dried at a temperature of 100°C for 5 minutes to give a nonwoven fabric for a fibrous substrate.

(Polyvinyl alcohol aqueous solution preparation step)

[0181] A polyvinyl alcohol aqueous solution was obtained in the same manner as in Example 1.

(Polyvinyl alcohol-adding step)

[0182] The same polyvinyl alcohol aqueous solution as in Example 1 was used, and a sheet having the added polyvinyl alcohol was obtained in the same manner as in Example 1 except that the amount of the polyvinyl alcohol adhering was changed by controlling the degree of wringing after the impregnation. In the sheet, the amount of polyvinyl alcohol adhering was 15% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate.

(Microfiber expression step)

[0183] The nonwoven fabric for a fibrous substrate was treated in the same manner as in Example 1 to obtain a dissolution sheet from which the sea components of the islands-in-the-sea composite fibers were removed. The average single fiber diameter of a cross section of the dissolution sheet was 4.4 μm.

(Polyurethane solution preparation step)

[0184] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0185] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0186] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning)

[0187] A sheet article was obtained in the same manner as in Example 1 except that the cut surface was ground and subjected to buffing.
[0188] The obtained sheet article had a good surface appearance, a flexible feel, and good wear resistance.

[Example 7]

(Step of forming nonwoven fabric for fibrous substrate)

[0189] The same nonwoven fabric for a fibrous substrate as in Example 1 was used.

(Polyvinyl alcohol aqueous solution preparation step)

[0190] Polyvinyl alcohol having a saponification degree of 98%, an rrr composition abundance ratio of 15.2%, and a degree of polymerization of 1000 obtained from polyvinyl acetate was provided. The polyvinyl alcohol was added to water at 25°C, and the mixture was heated to 90°C. The mixture was stirred for 2 hours while the temperature was maintained at 90°C to give a polyvinyl alcohol aqueous solution with a solid content of 10% by mass.

(Polyvinyl alcohol-adding step)

[0191] A sheet to which the polyvinyl alcohol was added in an amount of 30% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 1 except that the polyvinyl alcohol aqueous solution was used.

(Microfiber expression step)

[0192] In the same manner as in Example 1, a dissolution sheet was obtained from the nonwoven fabric for a fibrous substrate.

(Polyurethane solution preparation step)

[0193] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0194] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0195] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0196] In the same manner as in Example 1, a sheet article was obtained.
[0197] The obtained sheet article had a good surface appearance, a flexible feel, and good wear resistance.

[Example 8]

(Step of forming nonwoven fabric for fibrous substrate)

[0198] A nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 6.

(Polyvinyl alcohol aqueous solution preparation step)

[0199] A polyvinyl alcohol aqueous solution was obtained in the same manner as in Example 7.

(Polyvinyl alcohol-adding step)

[0200] A sheet to which the polyvinyl alcohol was added in an amount of 15% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 6 except that the polyvinyl alcohol aqueous solution of Example 7 was used.

(Microfiber expression step)

[0201] In the same manner as in Example 1, a dissolution sheet was obtained.

(Polyurethane solution preparation step)

[0202] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0203] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0204] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0205] In the same manner as in Example 6, a sheet article was obtained.

[0206] The obtained sheet article had a good surface appearance, a flexible feel, and good wear resistance.

[Comparative Example 1]

(Step of forming nonwoven fabric for fibrous substrate)

[0207] The same nonwoven fabric for a fibrous substrate as in Example 1 was used.

(Polyvinyl alcohol aqueous solution preparation step)

[0208] Polyvinyl alcohol having a saponification degree of 98%, an rrr composition abundance ratio of 14.1%, and a degree of polymerization of 400 obtained from polyvinyl acetate was provided. The polyvinyl alcohol was added to water at 25°C, and the mixture was heated to 90°C. The mixture was stirred for 2 hours while the temperature was maintained at 90°C to give a polyvinyl alcohol aqueous solution with a solid content of 10% by mass.

(Polyvinyl alcohol-adding step)

[0209] A sheet to which the polyvinyl alcohol was added in an amount of 30% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 1 except that the polyvinyl alcohol aqueous solution was used.

(Microfiber expression step)

[0210] In the same manner as in Example 1, a dissolution sheet was obtained from the nonwoven fabric for a fibrous substrate.

(Polyurethane solution preparation step)

[0211] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0212] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0213] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0214] In the same manner as in Example 1, a sheet article was obtained.

[0215] To the obtained sheet article, the polyvinyl alcohol was not uniformly added due to partial dissolution of the polyvinyl alcohol into the aqueous alkaline solution and the water-dispersible polyurethane liquid. As a result, the sheet article had a poor surface appearance with a poor scattered state of the fibers and with no dense nap and had a hard feel.

[Comparative Example 2]

(Nonwoven fabric for fibrous substrate)

[0216] A nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 6.

(Preparation of polyvinyl alcohol aqueous solution)

[0217] A polyvinyl alcohol aqueous solution was obtained in the same manner as in Comparative Example 1.

(Addition of polyvinyl alcohol)

[0218] A sheet to which the polyvinyl alcohol was added in an amount of 15% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 6 except that the polyvinyl alcohol aqueous solution of Comparative Example 1 was used.

(Microfiber expression step)

[0219] In the same manner as in Example 1, a dissolution sheet was obtained.

(Polyurethane solution preparation step)

[0220] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0221] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0222] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0223] In the same manner as in Example 6, a sheet article was obtained.

[0224] To the obtained sheet article, the polyvinyl alcohol was not uniformly added due to partial dissolution of the polyvinyl alcohol into the aqueous alkaline solution and the water-dispersible polyurethane liquid. As a result, the sheet article had a poor surface appearance with a poor scattered state of the fibers and with no dense nap and had a hard feel.

[Comparative Example 3]

(Step of forming nonwoven fabric for fibrous substrate)

[0225] The same nonwoven fabric for a fibrous substrate as in Example 1 was used.

(Polyvinyl alcohol aqueous solution preparation step)

[0226] Polyvinyl alcohol having a saponification degree of 98%, an rrr composition abundance ratio of 13.9%, and a degree of polymerization of 500 obtained from polyvinyl acetate was provided. The polyvinyl alcohol was added to water at 25°C, and the mixture was heated to 90°C. The mixture was stirred for 2 hours while the temperature was maintained at 90°C to give a polyvinyl alcohol aqueous solution with a solid content of 10% by mass.

(Polyvinyl alcohol-adding step)

[0227] A sheet to which the polyvinyl alcohol was added in an amount of 30% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 1 except that the polyvinyl alcohol aqueous solution was used.

(Microfiber expression step)

[0228] In the same manner as in Example 1, a dissolution sheet was obtained from the nonwoven fabric for a fibrous substrate.

(Polyurethane solution preparation step)

[0229] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0230] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0231] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0232] In the same manner as in Example 1, a sheet article was obtained.

[0233] To the obtained sheet article, the polyvinyl alcohol was not uniformly added due to partial dissolution of the polyvinyl alcohol into the aqueous alkaline solution and the water-dispersible polyurethane liquid. As a result, the sheet article had a poor surface appearance with a poor scattered state of the fibers and with no dense nap and had a hard feel.

[Comparative Example 4]

(Step of forming nonwoven fabric for fibrous substrate)

[0234] The same nonwoven fabric for a fibrous substrate as in Example 1 was used.

(Polyvinyl alcohol aqueous solution preparation step)

[0235] Polyvinyl alcohol having a saponification degree of 99%, an rrr composition abundance ratio of 14.4%, and a degree of polymerization of 500 obtained from polyvinyl acetate was provided. The polyvinyl alcohol was added to water at 25°C, and the mixture was heated to 90°C. The mixture was stirred for 2 hours while the temperature was maintained at 90°C to give a polyvinyl alcohol aqueous solution with a solid content of 10% by mass.

(Polyvinyl alcohol-adding step)

[0236] A sheet to which the polyvinyl alcohol was added in an amount of 30% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 1 except that the polyvinyl alcohol aqueous solution was used.

(Microfiber expression step)

[0237] In the same manner as in Example 1, a dissolution sheet was obtained from the nonwoven fabric for a fibrous substrate.

(Polyurethane solution preparation step)

[0238] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0239] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0240] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0241] In the same manner as in Example 1, a sheet article was obtained.

[0242] To the obtained sheet article, the polyvinyl alcohol was not uniformly added due to partial dissolution of the polyvinyl alcohol into the aqueous alkaline solution and the water-dispersible polyurethane liquid. As a result, the sheet article had a poor surface appearance with a poor scattered state of the fibers and with no dense nap and had a hard feel.

[Comparative Example 5]

(Step of forming nonwoven fabric for fibrous substrate)

[0243] The same nonwoven fabric for a fibrous substrate as in Example 1 was used.

(Polyvinyl alcohol aqueous solution preparation step)

[0244] Polyvinyl alcohol having a saponification degree of 88%, an rrr composition abundance ratio of 14.2%, and a degree of polymerization of 500 obtained from polyvinyl acetate was provided. The polyvinyl alcohol was added to water at 25°C, and the mixture was heated to 90°C. The mixture was stirred for 2 hours while the temperature was maintained at 90°C to give a polyvinyl alcohol aqueous solution with a solid content of 10% by mass.

(Polyvinyl alcohol-adding step)

[0245] A sheet to which the polyvinyl alcohol was added in an amount of 30% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 1 except that the polyvinyl alcohol aqueous solution was used.

(Microfiber expression step)

[0246] In the same manner as in Example 1, a dissolution sheet was obtained from the nonwoven fabric for a fibrous substrate.

(Polyurethane solution preparation step)

[0247] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0248] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0249] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0250] In the same manner as in Example 1, a sheet article was obtained.

[0251] To the obtained sheet article, the polyvinyl alcohol was not uniformly added due to partial dissolution of the polyvinyl alcohol into the aqueous alkaline solution and the water-dispersible polyurethane liquid. As a result, the sheet article had a poor surface appearance with a poor scattered state of the fibers and with no dense nap and had a hard feel.

[Comparative Example 6]

(Step of forming nonwoven fabric for fibrous substrate)

[0252] The same nonwoven fabric for a fibrous substrate as in Example 1 was used.

(Polyvinyl alcohol aqueous solution preparation step)

[0253] A polyvinyl alcohol aqueous solution was obtained in the same manner as in Example 1.

(Microfiber expression step)

[0254] The nonwoven fabric for a fibrous substrate obtained above was immersed in a 10 g/L aqueous sodium hydroxide solution heated to a temperature of 95°C and treated for 10 minutes to give a dissolution sheet from which the sea component of the islands-in-the-sea composite fibers was removed. The average single fiber diameter of the surface of the dissolution sheet was 3 μm.

(Polyvinyl alcohol-adding step)

[0255] The above dissolution sheet was impregnated with the polyvinyl alcohol aqueous solution obtained in Example 1. The sheet was heat-dried at a temperature of 140°C for 10 minutes to give a sheet to which the polyvinyl alcohol was added in an amount of 30% by mass to the dissolution sheet.

(Polyurethane solution preparation step)

[0256] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0257] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0258] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0259] In the same manner as in Example 1, a sheet article was obtained.

[0260] The obtained sheet article had a good surface appearance and a flexible feel, but the wear loss was relatively large.

[Comparative Example 7]

(Step of forming nonwoven fabric for fibrous substrate)

[0261] The same nonwoven fabric for a fibrous substrate as in Example 1 was used.

(Polyvinyl alcohol aqueous solution preparation step)

[0262] A polyvinyl alcohol aqueous solution was obtained in the same manner as in Example 1.

(Polyvinyl alcohol-adding step)

[0263] The same polyvinyl alcohol aqueous solution as in Example 1 was used, and a sheet to which the polyvinyl alcohol was added in an amount of 55% by mass relative to the mass of the fibers in the nonwoven fabric for a fibrous substrate was obtained in the same manner as in Example 1 except that the amount of the polyvinyl alcohol adhering was changed by controlling the degree of wringing after the impregnation.

(Microfiber expression step)

[0264] In the same manner as in Example 1, a dissolution sheet was obtained from the nonwoven fabric for a fibrous substrate.

(Polyurethane solution preparation step)

[0265] The same water-dispersible polyurethane liquid as in Example 1 was used.

(Polyurethane-adding step)

[0266] In the same manner as in Example 1, a sheet having the added polyurethane was obtained.

(Polyvinyl alcohol removal step)

[0267] In the same manner as in Example 1, a sheet from which polyvinyl alcohol was removed was obtained.

(Cutting in half, buffing, dyeing, and reduction cleaning step)

[0268] In the same manner as in Example 1, a sheet article was obtained. The obtained sheet article had a flexible feel. However, the excess amount of the polyvinyl alcohol resulted in insufficient holding of the fibers by the polyurethane. As a result, the sheet article had a poor surface appearance with an excessively long nap and had a poor wear resistance.

[0269] Table 1 shows the test conditions and the evaluation results for the sheet articles in Examples and Comparative Examples.

[Table 1]

	Fibrous substrate	Polyvinyl alcohol (PVA)						Amount of PVA adhering relative to mass of fibers of fibrous substrate	Sheet article			
			Abundance ratio									
	Average single fiber diameter	Saponification degree	rrr composition	mrr composition	Total of mmm composition and mmr composition	Degree of polymerization	Viscosity		Sheet density	Feel	Wear resistance	Surface appearance
Unit	(μm)	(%)	(%)	(%)	(%)	(-)	(mPa×a)	(mass%)	(g/cm^3)	(mm)	(mg)	(Grade)
Example 1	3.0	98	15.5	28.4	44.3	450	4.5	30	0.40	28	24	5
Example 2	2.0	98	15.5	28.4	44.3	450	4.5	30	0.40	25	28	5
Example 3	4.4	98	15.5	28.4	44.3	450	4.5	30	0.40	30	22	4
Example 4	5.5	98	15.5	28.4	44.3	450	4.5	30	0.40	32	20	4
Example 5	3.0	98	15.5	28.4	44.3	450	4.5	20	0.30	34	20	4
Example 6	4.4	98	15.5	28.4	44.3	450	4.5	15	0.45	32	24	5
Example 7	3.0	98	15.2	25.6	46.8	1000	10.0	30	0.40	26	26	5
Example 8	4.4	98	15.2	25.6	46.8	1000	10.0	15	0.45	30	25	5
Comparative Example 1	3.0	98	14.1	25.4	48.4	400	4.0	30	0.40	52	25	2
Comparative Example 2	4.4	98	14.1	25.4	48.4	400	4.0	15	0.45	50	29	3
Comparative Example 3	3.0	98	13.9	24.0	49.2	500	5.0	30	0.40	50	28	3
Comparative Example 4	3.0	99	14.4	24.7	48.3	500	5.5	30	0.40	48	30	3
Comparative Example 5	3.0	88	14.2	28.5	45.4	500	5.0	30	0.40	95	32	2
Comparative Example 6	3.0	98	15.5	28.4	44.3	4.50	4.5	30	0.40	20	54	4

(continued)

	Fibrous substrate	Polyvinyl alcohol (PVA)							Amount of PVA adhering relative to mass of fibers of fibrous substrate	Sheet article			
			Abundance ratio										
	Average single fiber diameter	Saponification degree	rrr composition	mrr composition	Total of mmm composition and mmr composition	Degree of polymerization	Viscosity			Sheet density	Feel	Wear resistance	Surface appearance
Unit	(μm)	(%)	(%)	(%)	(%)	(-)	(mPa×a)		(mass%)	(g/cm^3)	(mm)	(mg)	(Grade)
Comparative Example 7	3.0	98	15.5	28.9	44.3	450	4.5		55	0.15	18	74	1

[0270] In the sheet articles obtained in Examples 1 to 8, the dissolution and loss of the polyvinyl alcohol in water were suppressed in the dissolution step and the step of adding the water-dispersible polyurethane, so that fibers were held with voids in an appropriate size between the fibers and polyurethane. As a result, all the sheet articles had a good surface appearance, a flexible feel, and good wear resistance. On the other hand, in the sheet articles obtained in Comparative Examples 1 to 5, the polyvinyl alcohol was dissolved away and lost in water in the dissolution step and the step of adding the water-dispersible polyurethane, so that the area where fibers were in direct contact with and held by the polyurethane increased. As a result, these sheet articles had a hard feel. In addition, the sheet articles had a poor surface appearance with a poor scattered state of the fibers and with no dense nap. In the sheet articles obtained in Comparative Examples 6 and 7, the bonding area between the fibers and the polyvinyl alcohol increased during the manufacturing process, and the holding of the fibers by the polyurethane was weakened, resulting in poor wear resistance.

INDUSTRIAL APPLICABILITY

[0271] The sheet article obtained according to the present invention is suitable as interior materials having a very elegant appearance, such as surface materials of furniture, chairs, walls, seats in vehicles including automobiles, trains, and aircrafts, ceiling, and interior decoration; clothing materials, such as shirts, jackets, upper and trim and the like of shoes including casual shoes, sports shoes, men's shoes and ladies' shoes, bags, belts, wallets, and a part of them; and industrial materials such as wiping cloth, abrasive cloth and CD curtains.

Claims

1. A method of manufacturing a sheet article including a fibrous substrate including microfibers and polyurethane, the manufacturing method comprising the following steps (1) to (4) :

(1) a polyvinyl alcohol-adding step of adding a polyvinyl alcohol aqueous solution, which is an aqueous solution of polyvinyl alcohol having the following characteristics, to a fibrous substrate having microfiber expression type fibers as its main constituent to add the polyvinyl alcohol in an amount of 0.1 to 50% by mass based on a mass of the fibers contained in the fibrous substrate (polyvinyl alcohol: a saponification degree is 90% or more, and an rrr composition abundance ratio is 14.5% or more in a heavy water solvent in tacticity evaluation measured by ^{13}C-NMR) ;
(2) a microfiber expression step of, after the preceding step, making microfiber expression type fibers of the fibrous substrate into microfibers having an average single fiber diameter of 0.1 μm to 10 μm;
(3) a polyurethane-adding step of, after the preceding step, adding water-dispersible polyurethane to the fibrous substrate having the added polyvinyl alcohol; and
(4) a polyvinyl alcohol removal step of, after the preceding step, removing the polyvinyl alcohol from the fibrous substrate having the added water-dispersible polyurethane.

2. The method of manufacturing a sheet article according to claim 1, wherein a degree of polymerization of the polyvinyl alcohol is 200 to 3500.

3. The method of manufacturing a sheet article according to claim 1 or 2, wherein in the microfiber expression step, the fibrous substrate having the microfiber expression type fibers as its main constituent is treated with an alkaline aqueous solution.

4. The method of manufacturing a sheet article according to any one of claims 1 to 3, wherein in the polyvinyl alcohol-adding step, after adding the polyvinyl alcohol aqueous solution, heating is performed at 80 to 190°C.

5. The method of manufacturing a sheet article according to any one of claims 1 to 4, wherein in the polyvinyl alcohol-adding step, in the fibrous substrate, the fibers and a woven fabric and/or a knitted fabric are integrated by entanglement.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/024016

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. D06N3/14(2006.01)i, D06M15/564(2006.01)i
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. D06N1/00-7/06, D06M3/00-15/715, B32B1/00-43/00

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	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JMEDPlus/JST7580 (JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/084253 A1 (TORAY INDUSTRIES, INC.) 05 June 2014, entire text & US 2015/0315741 A1 & EP 2927368 A1 & CN 104838063 A & KR 10-2015-0090122 A & TW 201439398 A	1-5
A	JP 2013-234409 A (TORAY INDUSTRIES, INC.) 21 November 2013, entire text (Family: none)	1-5
A	JP 8-510796 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 12 November 1996, entire text & US 5641563 A & WO 1994/028223 A1 & CN 1124985 A	1-5
A	WO 2014/042241 A1 (TORAY INDUSTRIES, INC.) 20 March 2014, entire text & US 2015/0233050 A1 & EP 2896741 A1 & CN 104619909 A & KR 10-2015-0058268 A & TW 201425685 A	1-5
A	JP 53-50302 A (TORAY INDUSTRIES, INC.) 08 May 1978, entire text (Family: none)	1-5

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 22 August 2019 (22.08.2019)	Date of mailing of the international search report 03 September 2019 (03.09.2019)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2002030579 A **[0006]**
- JP 2014084253 A **[0006]**