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(54) METHOD FOR PRODUCING LIQUID-REPELLENT FIBERS

(57) The present invention addresses the problem of providing a method for imparting liquid repellency to fibers even when the amount of water and/or a surfactant is reduced, preferably without using water and/or a surfactant. Provided is a method for producing liquid-repellent fibers, the method comprising a fiber treatment step in which supercritical carbon dioxide is used as a treatment medium and a fiber base material is treated with a repellent containing a liquid-repellent compound, whereby liquid repellency can be imparted to the fibers even when the amount of water and/or a surfactant is reduced, preferably without using water and/or a surfactant.

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Description

Technical Field

[0001] The present disclosure relates to a method for producing a liquid-repellent fiber, and particularly relates to a method for producing a liquid-repellent fiber by using supercritical carbon dioxide as a treatment medium.

Background Art

[0002] In recent years, research and development of technology for applying supercritical carbon dioxide to treatment of fabrics have been progressing.

[0003] Patent document 1 discloses a fiber treatment method for using a fiber treatment agent that contains supercritical carbon dioxide or liquefied carbon dioxide, water, and a surfactant to form reverse micelles in treating fibers or textile products.

Citation List

Patent Literature

[0004] [Patent Literature 1] JP2004-76190A

Summary of Invention

Technical Problem

[0005] However, the cited Patent document 1 does not specifically describe how to impart liquid repellency to fibers. Moreover, combined use of water and a surfactant is essential, which may be industrially disadvantageous from the viewpoint of productivity. Furthermore, water is a precious resource accompanying recent worsening of environmental problems, and reduction of the amount of water used industrially and the amount of wastewater discharged have been of major concern.

[0006] An object of the present disclosure is to provide a novel method for imparting liquid repellency to fibers in spite of reducing the amount of water and/or a surfactant and preferably without using water and/or surfactant.

Solution to Problem

[0007] The present disclosure includes the following embodiments.

[Item 1]

[0008] A method for producing a liquid-repellent fiber, comprising a fiber treatment of treating a fiber substrate with a repellent containing a liquid-repellent compound using supercritical carbon dioxide as a treatment medium.

[Item 2]

[0009] The method for producing a liquid-repellent fiber according to item 1, wherein a water contact angle of the liquid-repellent compound is 35° or more.

[Item 3]

[0010] The method for producing a liquid-repellent fiber according to item 1 or 2, wherein the liquid-repellent compound has a group represented by the following formula:

$$-X-R_n$$

wherein

X is a direct bond or a 1 + n valent group,
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms

and optionally having a substituent, or a polysiloxane group, and
n is 1 or more and 3 or less.

[Item 4]

[0011] The method for producing a liquid-repellent fiber according to item 3, wherein R is an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, and R has 12 or more carbon atoms.

[Item 5]

[0012] The method for producing a liquid-repellent fiber according to item 3 or 4, wherein X is a 1 + n valent group composed of one or more selected from the group consisting of X^1 composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -S(=O)$_2$-, -NR'-, -C(OR')R'-, and -C(OR')(-)$_2$, wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms, and
X^2 which is a hydrocarbon group having 1 to 40 carbon atoms.

[Item 6]

[0013] The method for producing a liquid-repellent fiber according to any one of items 3 to 5, wherein X is a group represented by -X^1- or

$$-X^1-X^2-X^1-$$

wherein

X^1 is independently at each occurrence
a direct bond;
-O-;
-O-C(=O)-;
-O-C(=O)-O-;
-O-C(=O)-NR'-;
-NR'-;
-NR'-C(=O)-;
-NR'-C(=O)-O-;
-NR'-C(=O)-NR'-;
-C(=O)-;
-C(=O)-O-;
-C(=O)-NR'-;
-SO$_2$- ;
-SO$_2$NR'-;
-C(OR')R'- or
-C(OR')(-)$_2$
wherein
R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms; and
X^2 is a hydrocarbon group having 1 to 40 carbon atoms.

[Item 7]

[0014] The method for producing a liquid-repellent fiber according to any one of items 1 to 6, wherein the liquid-repellent compound has a repeating unit derived from a compound represented by the following formula:

$$CH_2=C(-Q)-C(=O)-X-R_n$$

wherein

Q is a hydrogen atom, a monovalent organic group, or a halogen atom;
X is a 1 + n valent group composed of one or more selected from the group consisting of

X^1 composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, $-S(=O)_2-$, -NR'-, -C(OR')R'-, and $-C(OR')(-)_2$, wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms, and
X^2 which is a hydrocarbon group having 1 to 40 carbon atoms; R is an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent; and n is 1 to 3.

[Item 8]

[0015] The method for producing a liquid-repellent fiber according to item 7, wherein X is a group represented by the following formula:

$$-X^1- \text{ or } -X^1-X^2-X^1-$$

wherein
X^1 is independently at each occurrence -O-, -NR'-, -C(=O)-NR'-, -NR'-C(=O)-, or -NR'-C(=O)-NR'-, wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms; and X^2 is a hydrocarbon group having 1 to 40 carbon atoms.

[Item 9]

[0016] The method for producing a liquid-repellent fiber according to any one of items 1 to 6, wherein the liquid-repellent compound is a compound in which one or more base material compounds selected from the group consisting of a monosaccharide, a polysaccharide, an alcohol, a polyol, a carboxylic acid, a polyvalent carboxylic acid, and derivatives thereof are modified with a group represented by the following formula:

$$-X-R_n$$

wherein

X is a direct bond or a 1 + n valent group,
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, and
n is an integer of 1 to 3.

[Item 10]

[0017] The method for producing a liquid-repellent fiber according to item 9, wherein the base material compound is one or more selected from the group consisting of starch, cellulose, curdlan, pullulan, carrageenan, guar gum, chitin, chitosan, locust bean gum, kappa carrageenan, iota carrageenan, isomaltodextrin, xanthan gum, gellan gum, tamarind seed gum, cycloamylose, glucose, sucrose, mannitol, sorbitol, sorbitan, maltitol, stevioside, dextrin, cyclodextrin, glycerin, polyglycerin, menthol, xylitol, sucralose, fructose, maltose, trehalose, lactosucrose, erythritol, vanillin, cholesterol, glucosamine, catechin, anthocyanin, quercetin, citric acid, malic acid, gluconic acid, alginic acid, butyric acid, lactic acid, tartaric acid, oxalic acid, malonic acid, succinic acid, fumaric acid, maleic acid, chlorogenic acid, aldonic acid, uronic acid, aldaric acid, phytic acid, ascorbic acid, and derivatives thereof.

[Item 11]

[0018] The method for producing a liquid-repellent fiber according to item 9 or 10, wherein the base material compound is a glycerin polymer or a citric acid polymer.

[Item 12]

[0019] The method for producing a liquid-repellent fiber according to any one of items 9 to 11, wherein the base material compound has a hydroxy group, and
the hydroxy group forms a group represented by the following formula:

$$-O-;$$

-O-C(=O)-;

-O-C(=O)-NR'-

or

-O-C=S-NR'-

wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms,
in the liquid-repellent compound.

[Item 13]

[0020] The method for producing a liquid-repellent fiber according to any one of items 9 to 12, wherein the base material compound has a carboxyl group, and
the carboxyl group forms a group represented by the following formula:

-C(=O)-;

-C(=O)-O-;

-C(=O)-NR'-

or

-C(=O)-S-

wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms,
in the liquid-repellent compound.

[Item 14]

[0021] The method for producing a liquid-repellent fiber according to any one of items 1 to 6, wherein the liquid-repellent compound is a compound represented by the following formula:

$$A(-X-R_n)_m$$

wherein

A is an m valent group obtained by removing m hydrogen atoms from an aromatic ring or a nitrogen-containing heterocyclic ring optionally having a substituent;
X is independently at each occurrence a direct bond or a 1 + n valent group;
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent;
n is independently at each occurrence 1 or more and 3 or less; and
m is 1 or more and 6 or less.

[Item 15]

[0022] The method for producing a liquid-repellent fiber according to any one of Items 1 to 6, wherein the liquid-repellent compound is a compound obtained by polymerizing a compound represented by the following formula:

$$A(-X-R_n)_m$$

wherein

A is an m valent group obtained by removing m hydrogen atoms from an aromatic ring or a nitrogen-containing heterocyclic ring optionally having a substituent;

X is independently at each occurrence a direct bond or a 1 + n valent group;
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent;
n is independently at each occurrence 1 or more and 3 or less; and
m is 1 or more and 6 or less,
via a substituent of A.

[Item 16]

[0023] The method for producing a liquid-repellent fiber according to item 14 or 15, wherein X is a group represented by the following formula:

$$-X^1-$$

or

$$-X^1-X^2-X^1-$$

wherein

X^1 is independently at each occurrence
a direct bond;
-O-;
-O-C(=O)-;
-O-C(=O)-O-;
-O-C(=O)-NR'-;
-NR'-;
-NR'-C(=O)-;
-NR'-C(=O)-O-;
-NR'-C(=O)-NR'-;
-C(=O)-;
-C(=O)-O-;
-C(=O)-NR'-;
-C(OR')R'- or
$-C(OR')(-)_2$
wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms, and
X^2 is a hydrocarbon group having 1 to 40 carbon atoms.

[Item 17]

[0024] The method for producing a liquid-repellent fiber according to any one of items 1 to 6, wherein the liquid-repellent compound is a reaction product of an isocyanate group-containing compound and an isocyanate-reactive compound.

[Item 18]

[0025] The method for producing a liquid-repellent fiber according to any one of items 1 to 6, wherein the liquid-repellent compound has a polysiloxane group.

[Item 19]

[0026] The method for producing a liquid-repellent fiber according to item 18, wherein the liquid-repellent compound has the polysiloxane group in a side chain.

[Item 20]

[0027] The method for producing a liquid-repellent fiber according to any one of the items 1 to 6, wherein the liquid-repellent compound is an amine modified product having:

an amine backbone; and
one or more aliphatic hydrocarbon-containing groups represented by the following formula:

$$-X^N-R_n$$

wherein
X^N is a direct bond or a 1 + n valent group,
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and to 40 or less carbon atoms and optionally having a substituent, and
n is an integer of 1 or more and 3 or less,
wherein at least one of the aliphatic hydrocarbon-containing groups is bonded to a nitrogen atom of the amine backbone.

[Item 21]

[0028] The repellent according to item 20, wherein the amine backbone is composed of a monovalent to trivalent amino group and a chain saturated aliphatic hydrocarbon group or aromatic hydrocarbon group optionally interrupted by an oxygen atom and/or a sulfur atom.

[Item 22]

[0029] The method for producing a liquid-repellent fiber according to any one of claims 1 to 21, wherein the fiber is a polyester or polyester blended fiber.

[Item 23]

[0030] The method for producing a liquid-repellent fiber according to any one of claims 1 to 22, wherein a water concentration in a treatment agent for treating the fiber substrate is 0.001 mol/L or less.

[Item 24]

[0031] A composition comprising the liquid-repellent compound defined in any one of items 1 to 21 and supercritical carbon dioxide.

[Item 25]

[0032] A repellent comprising the liquid-repellent compound defined in any one of items 1 to 21 and supercritical carbon dioxide.

[Item 26]

[0033] A fiber subjected to water-repellent treatment with a composition or repellent comprising the liquid-repellent compound defined in any one of items 1 to 21.

Advantageous Effect of Invention

[0034] According to the method for producing a liquid-repellent fiber in the present disclosure, liquid repellency can be imparted to the fibers by using various liquid-repellent compounds in spite of reducing the amount of water and/or surfactant and preferably without using water and/or a surfactant.

Description of Embodiments

<Definition of Terms>

[0035] As used herein, the "n valent group" refers to a group having n bonds, i.e., a group forming n bonds. The "n valent organic group" refers to a n valent group containing carbon. Such organic groups are not limited, but can be hydrocarbon groups or derivatives thereof. The derivative of the hydrocarbon group refers to a group that has one or more of N, O, S, Si, amide, sulfonyl, siloxane, carbonyl, carbonyloxy, etc., at an end or in a molecular chain of a hydrocarbon group.

[0036] As used herein, the "hydrocarbon group" refers to a group containing carbon and hydrogen and a group in which a hydrogen atom is removed from the hydrocarbon. Such a hydrocarbon group is not limited, but examples thereof include $C_{1\text{-}20}$ hydrocarbon groups, such as an aliphatic hydrocarbon group and an aromatic hydrocarbon group. The "aliphatic hydrocarbon group" may be either linear, branched chain, or cyclic, and may be either saturated or unsaturated. The hydrocarbon group may contain one or more ring structures. The hydrocarbon group may be substituted with one or more substituents.

[0037] In the present description, regardless of whether "independently at each occurrence," "independently with each other," "each independently," or similar expressions are explicitly stated, with the exception of case where they are exceptions, when a term (symbol) that may occur a plurality of times in a chemical structure is defined, the definition applies independently at each occurrence.

<Repellent>

[0038] The repellent in the present disclosure can impart liquid repellency to a fiber substrate, and can function as at least one selected from the group consisting of a water-repellent agent, an oil-repellent agent, an oil-resistant agent, and a water-resistant agent. According to the present disclosure, the repellent can satisfactorily impart liquid repellency to a fiber substrate in spite of reducing the amount of water and/or a surfactant in the repellent, resulting in being advantageous from an industrial viewpoint and/or an environmental protection viewpoint.

[0039] The repellent in the present disclosure contains a liquid-repellent compound. For example, the repellent in the present disclosure may be a liquid-repellent compound singly. The repellent according to the present disclosure may contain, in addition to the liquid-repellent compound, supercritical carbon dioxide as a treatment medium and/or other components.

[0040] The repellent in the present disclosure may be free of any selected from the group consisting of a compound having a fluoroalkyl group having 8 or more carbon atoms, a compound having a perfluoroalkyl group having 8 or more carbon atoms, a compound having a fluoroalkyl group having 4 or more carbon atoms, a compound having a perfluoroalkyl group having 4 or more carbon atoms, a compound having a perfluoroalkyl group, a compound having a fluoroalkyl group and a compound having a fluorine atom. The repellent in the present disclosure can impart liquid repellency to a substrate even free of these fluorine compounds.

{Liquid-Repellent Compound}

[0041] The liquid-repellent compound in the present disclosure is capable of adhering to a fiber substrate and imparting liquid repellency to a fiber substrate.

[0042] A water contact angle of the liquid-repellent compound may be 35° or more, 40° or more, 45° or more, 50° or more, 55° or more, 65° or more, 75° or more, 85° or more, 90° or more, or 100° or more. The water contact angle of the liquid-repellent compound may be 160° or less, 140° or less, 130° or less, 120° or less, 110° or less, 100° or less, or 90° or less. The liquid-repellent compound having a water contact angle of the above lower limit or more can favorably impart liquid repellency (particularly water-repellency) to a fiber substrate. The water contact angle is a static contact angle of the liquid-repellent compound to a spin-coated film, as shown in Example, and is obtained by dropping 2 μL of water onto the spin-coated film and measuring a contact angle one second after the drop.

[0043] A solubility parameter (SP value) of the liquid-repellent compound may be 6 or more, 7 or more, 7.5 or more, 8 or more, 8.5 or more, 9 or more, 9.5 or more, 10 or more, 10.5 or more, 11 or more, 11.5 or more, or 12 or more, and is preferably 8 or more and more preferably 9 or more. The solubility parameter (SP value) of the liquid-repellent compound may be 18 or less, 16 or less, 15.5 or less, 15 or less, 14.5 or less, 14 or less, 13.5 or less, 13 or less, 12.5 or less, 12 or less, 11.5 or less, or 11 or less, and is preferably 14 or less and more preferably 12 or less. The solubility parameter is defined as a square root of a cohesive energy density obtained by dividing cohesive energy by a molar molecular volume.

[0044] The amount of the liquid-repellent compound dissolved relative to supercritical carbon dioxide (25 MPa, 120°C) may be 0.001 mg/mL or more, 0.005 mg/mL or more, 0.01 mg/mL or more, 0.05 mg/mL or more, 0.1 mg/mL or more, 0.5 mg/mL or more, or 1 mg/mL or more, and is preferably 0.005 mg/mL or more and more preferably 0.01 mg/mL or more. The amount of the liquid-repellent compound dissolved relative to supercritical carbon dioxide (25 MPa, 120°C) may be 50 mg/mL or less, 10 mg/mL or less, 5 mg/mL or less, 1 mg/mL or less, 0.5 mg/mL or less, or 0.1 mg/mL or less, and is preferably 5 mg/mL or less and more preferably 1 mg/mL or less.

[0045] A dust absorption rate of the liquid-repellent compound may be 40% or more, 50% or more, 60% or more, 70% or more, 80% or more, or 90% or more, and is preferably 50% or more, more preferably 80% or more, and particularly preferably 90% or more. Herein, the dust absorption rate is a percentage obtained by dividing the weight of the liquid-repellent compound adhered to a fiber by the weight of the liquid-repellent compound dissolved in supercritical carbon dioxide during treatment and then multiplying the product by 100.

[0046] A melting point of the liquid-repellent compound may be 60°C or higher, 80°C or higher, 100°C or higher, 110°C or

higher, 120°C or higher, 130°C or higher, 140°C or higher, or 150°C or higher, and the melting point of the liquid-repellent compound is preferably higher than a treatment temperature.

[0047] Examples of the liquid-repellent compounds include, but are not limited to, an acrylic polymer type liquid-repellent compound, a base material-modified liquid-repellent compound, a ring-modified liquid-repellent compound, an isocyanate-based liquid-repellent compound, a polysiloxane group-containing liquid-repellent compound, etc., as described in detail below. The liquid-repellent compound may be combinations of a plurality of types (for example, two types or three types) of liquid-repellent compounds.

[0048] In the present disclosure, the liquid-repellent compound preferably has a monovalent hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent. The hydrocarbon group may be an aromatic hydrocarbon group or an aliphatic hydrocarbon group, is preferably an aliphatic hydrocarbon group), and is preferably an aliphatic hydrocarbon group, particularly a saturated aliphatic hydrocarbon group (alkyl group). The hydrocarbon group may be cyclic, linear, or a branched chain, and is preferably linear. The number of carbon atoms in the hydrocarbon group may be 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, or 18 or more, and is preferably 10 or more and more preferably 12 or more. The number of carbon atoms in the hydrocarbon group may be 40 or less, 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, or 10 or less, and is preferably 30 or less and more preferably 25 or less. It is to be noted that the monovalent hydrocarbon group used herein, which has 6 or more and 40 or less carbon atoms and optionally has a substituent, may correspond to R described below.

[0049] The hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, in the present disclosure may be a hydrocarbon group having a substituent, or may be an unsubstituted hydrocarbon group. Herein, examples of the substituents include -OR', $-N(R')_2$, -COOR', and a halogen atom, and the like (wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms). The substituent may have or be free of active hydrogen. The number of substituent may be 6 or less, 5 or less, 4 or less, 3 or less, 2 or less, 1 or less, or 0. In the hydrocarbon group having a substituent, the amount of carbon atoms relative to the total amount of carbon atoms and heteroatoms may be 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and is preferably 75 mol% or more. In the hydrocarbon group having a substituent, the amount of carbon atoms relative to the total amount of carbon atoms and heteroatoms may be 95 mol% or less, 90 mol% or less, 85 mol% or less, or 80 mol% or less. For example, the group having 6 or more and 40 or less carbon atoms may have 1 to 3 (for example, 1) -OR' (particularly -OH) as substituents (for example, other than an end).

[0050] The liquid-repellent compound may have 2 or more, 5 or more, 10 or more, 25 or more, 50 or more, 75 or more, 100 or more, 300 or more, or 500 or more hydrocarbon groups per molecule, and preferably has 10 or more hydrocarbon groups. The liquid-repellent compound may have 1,000 or less, 500 or less, 300 or less, 100 or less, 75 or less, or 50 or less hydrocarbon groups per molecule.

[0051] The amount of the hydrocarbon group (particularly aliphatic hydrocarbon group) having 6 or more and 40 or less carbon atoms and optionally having a substituent may be 1% by weight or more, 3% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, or 30% by weight or more, and is preferably 5% by weight or more in the liquid-repellent compound. The amount of hydrocarbon group (particularly aliphatic hydrocarbon group) having 6 or more and 40 or less carbon atoms and optionally having a substituent may be 80% by weight or less, 70% by weight or less, 60% by weight or less, 50% by weight or less, 40% by weight or less, 30% by weight or less, or 25% by weight or less, and is preferably 70% by weight or less in the liquid-repellent compound.

[0052] The liquid-repellent compound in the present disclosure may be free of any one selected from the group consisting of a fluoroalkyl group having 8 or more carbon atoms, a perfluoroalkyl group having 8 or more carbon atoms, a fluoroalkyl group having 4 or more carbon atoms, a perfluoroalkyl group having 4 or more carbon atoms, a perfluoroalkyl group, a fluoroalkyl group, and a fluorine atom. The liquid-repellent compound can impart liquid repellency to a substrate, even free of these fluorine-containing groups.

[0053] The liquid-repellent compound in the present disclosure preferably has the group represented by the following formula:

$$-X-R_n$$

[wherein

X is a direct bond or a 1 + n valent group,
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, and
n is 1 or more and 3 or less.]. The liquid-repellent compound having this group can impart favorable liquid repellency to a fiber substrate.

[X]

[0054] X is a direct bond or a 1 + n valent group. n may be 1 to 3, 2 or 3, 1 or 2, 1, 2, or 3.

[0055] The molecular weight of X may be 3,000 or less, 2,500 or less, 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, or 500 or less. The molecular weight of X may be 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, 500 or more, or 750 or more.

[0056] X may be a 1 + n valent group composed of one or more selected from the group consisting of

X^1 composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -S(=O)$_2$-, -NR'-, -C(OR')R'-, and -C(OR')(-)$_2$ (wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms), and
X^2 which is a hydrocarbon group having 1 to 40 carbon atoms. It is to be noted that the group represented as X used herein on the right side thereof is bonded to R.

[X^1]

[0057] X^1 is a non-hydrocarbon linker.

[0058] X^1 is a direct bond or a divalent or higher group. A valence of X^1 may be 2 to 4, 2 to 3, or 2. X^1 is preferably not a direct bond singly.

[0059] The molecular weight of X^1 may be 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, or 500 or less. The molecular weight of X^1 may be 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, or 500 or more.

[0060] X^1 is composed of one or more selected from the group consisting of -O-, -C(=O)-, -S(=O)$_2$-, -NR'-, -C(OR')R'-, and -C(OR')(-)$_2$ (wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms) . Examples of X^1 include, for example,

a direct bond;
-O-;
-O-C(=O)-;
-O-C(=O)-O-;
-O-C(=O)-NR'-;
-NR'-;
-NR'-C(=O)-;
-NR'-C(=O)-O-;
-NR'-C(=O)-NR'-;
-C(=O)-;
-C(=O)-O-;
-C(=O)-NR'-;
-SO$_2$- ;
-SO$_2$NR'-;
-C(OR')R'-; and
-C(OR')(-)$_2$
(wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms).

[X^2]

[0061] X^2 is a hydrocarbon linker and is a hydrocarbon group having 1 to 40 carbon atoms.

[0062] X^2 is a divalent or higher group. A valence of X^2 may be, for example, 2 to 4, 2 to 3, or 2.

[0063] The number of carbon atoms of X^2 may be 1 or more, 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, or 18 or more. The number of carbon atoms in X^2 may be 40 or less, 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, 10 or less, or 5 or less.

[0064] X^2 may be a cyclic, branched chain, or linear hydrocarbon group. X^2 may be an aromatic hydrocarbon group or an aliphatic hydrocarbon group, for example, an aliphatic hydrocarbon group (for example, a saturated aliphatic hydrocarbon group).

[0065] Examples of X^2 include, for example,

-(CH_2)$_p$- (p is 1 to 40, for example, 1 to 10),
a linear hydrocarbon group having 1 to 40 carbon atoms, for example 1 to 10 unsaturated bonds;

a hydrocarbon group with a branched structure, having 1 to 40 carbon atoms, for example 1 to 10 carbon atoms; and $-(CH_2)_q-C_6H_4-(CH_2)_r-$ (q and r are each independently 0 to 40, for example 1 to 10, and $-C_6H_4-$ is a phenylene group).

[Example of X]

[0066] Examples of X will be described. It is to be noted that in the following, R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms.

[0067] Preferred examples of X include X^1- or $-X^1-X^2-X^1--X^1-$.

[0068] X is preferably the group represented by

$$-X^1- \text{ or } -X^1-X^2-X^1-$$

[wherein

X^1 is independently at each occurrence
a direct bond;
-O-;
-O-C(=O)-;
-O-C(=O)-O-;
-O-C(=O)-NR'-;
-NR'-;
-NR'-C(=O)-;
-NR'-C(=O)-O-;
-NR'-C(=O)-NR'-;
-C(=O)-;
-C(=O)-O-;
-C(=O)-NR'-;
$-SO_2-$;
$-SO_2NR'-$;
-C(OR')R'- or
$-C(OR')(-)_2$
(wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms); and X^2 is a hydrocarbon group having 1 to 40 carbon atoms.].

[0069] X may have an amide group, a urea group, or a urethane group. Specific examples of such X include, for example,

-O-C(=O)-NR'-;

NR'-C(=O)-;

-NR'-C(=O)-O-;

NR'-C(=O)-NR'-;

-C(=O)-NR'-.

[0070] When X is divalent, examples of X include, for example, $-X^1-$, $-X^1C(=O)-$, $-C(=O)-X^1-$, $-X^1-C(=O)-X^1-$, $-X^1-X^2-$, $-X^1-X^2-X^1-$, $-X^1-X^2-X^1-C(=O)-$, $-X^1-X^2-C(=O)-X^1-$, $-X^1-X^2-X^1-C(=O)-X^1-$, and $-X^1-X^2-X^1-X^2-$.

[0071] When X is trivalent, examples of X include, for example, $-X^1(-)_2$, $-X^1-X^1(-)_2$, $-X^1-X^2(-X^1-)_2$, $-X^2(-X^1-)_2$, $-X^2(-X^1-C(=O)-)_2$, $-X^2(-C(=O)-X^1-)_2$, $-X^2(-X^1-C(=O)-X^1-)_2$, $-X^2(-X^1-X^2-)_2$, $-X^2(-X^1-X^2-X^1)_2$, $-X^2(-X^1-X^2-X^1-C(=O)-)_2$, $-X^2(-X^1-X^2-C(=O)-X^1-)_2$, $-X^2(-X^1-X^2-X^1-C(=O)-X^1-)2$, and $-X^2(-X^1-X^2-X^1-X^2-)_2$.

[0072] When X is tetravalent, examples of X include, for example, $-X^1-X^2(-X^1-)_3$, $-X^2(-X^1-)_3$, $-X^2(-X^1-C(=O)-)_3$, $-X^2(-C(=O)-X^1-)_3$, $-X^2(-X^1-C(=O)-X^1-)_3$, $-X^2(-X^1-X^2-)_3$, $-X^2(-X^1-X^2-X^1-)_3$, $-X^2(-X^1-X^2-X^1-C(=O)-)_3$, $-X^2(-X^1-X^2-C(=O)-X^1-)_3$, $-X^2(-X^1-X^2-X^1-C(=O)-X^1-)_3$, and $-X^2(-X^1-X^2-X^1-X^2-)_3$.

[0073] When X is divalent, specific examples of X include, for example, -O-, -O-C(=O)-, -O-C(=O)-O-, -O-C(=O)-NR'-, $-O-X^2-S(=O)_2-NR'-$, $-O-X^2-NR'-$, $-O-X^2-NR'-S(=O)_2-$, $-O-X^2-NR'-C(=O)-$, $-OX^2-NR'-C(=O)-O-$, $-O-X^2-NR'-C(=O)-NR'-$,

-O-X^2-NR'-X^2-, -O-X^2-O-, - O-X^2-O-C(=O)-, -O-X^2-O-C(=O)-NR'-, -O-X^2-C(=O)-O-, -O-X^2-C(=O)-NR'-, -O-X^2-O-X^2-, -O-X^2-, -NR'-, -NR'-C(=O)-, -NR'-C(=O)-O-, - NR'-C(=O)-NR'-, -NR'-X^2-S(=O) $_2$-NR'-, -NR'-X^2-NR'-, -NR'-X^2-NR'-S(=O)$_2$-, -NR'-X^2-NR'-C(=O) -, -NR'-X^2-NR'-C(=O)-O-, -NR'-X^2-NR'-C(=O)-NR'-, -NR'-X^2-NR'-X^2-, -NR'-X^2-O-, -NR'-X^2-O-C(=O)-, -NR'-X^2-O-C(=O)-NR'-, -NR'-X^2-O-X^2-, -NR'-X^2-C(=O)-O-, -NR'-X^2-C(=O)-NR'-, -NR'-X^2-, -C(=O)-, -C(=O)-O-, -C(=O)-NR'-, -C(=O)-S-, - SO_2-, -SO_2NR'-, and -C(OR') (R') (-).

[0074] When X is trivalent, specific examples of X include, for example, -X^2(-O-)$_2$-, -X^2(-O-C(=O)-)$_2$-, -X^2(-O-C(=O)-O-)$_2$-, -X^2(-O-C(=O)-NR'-)$_2$-, -X^2(-O-X^2-S(=O)$_2$-NR'-)$_2$-, -X^2(-O-X^2-NR'-)$_2$-, - X^2(-O-X^2-NR'-S(=O)$_2$-)$_2$-, -X^2(-O-X^2-NR'-C(=O)-)$_2$-, -X^2(-O-X^2-NR'-C(=O)-O-)$_2$-, -X^2(-O-X^2-NR'-C(=O)-NR'-)$_2$-, -X^2(-O-X^2-NR'-X^2-)$_2$-, - X^2(-O-X^2-O-)$_2$-, -X^2(-O-X^2-O-C(=O)-)$_2$-, -X^2(-O-X^2-O-C(=O)-NR'-)$_2$-, -X^2(-O-X^2-C(=O)-O-)$_2$-, -X^2(-O-X^2-C(=O)-NR'-)$_2$-, -X^2(-O-X^2-O-X^2-)$_2$-, -X^2(-O-X^2-)$_2$-, -X^2(-NR-)$_2$-, -X^2(-NR'-C(=O)-)$_2$-,-X^2(-NR'-C(=O)-O-)$_2$-, -X^2(-NR'-C(=O)-NR'-)$_2$-, -X^2(-NR'-X^2-S(=O)$_2$-NR'-)$_2$-, -X^2(-NR'-X^2-NR'-)$_2$-, -X^2(-NR'-X^2NR'-S(=O) $_2$-)$_2$-, -X^2(-NR'-X^2-NR'-C(=O)-)$_2$-, -X^2(-NR'-X^2-NR'-C(=O)-O-)$_2$-, -X^2(-NR'-X^2-NR'-C(=O)- NR'-)$_2$-, -X^2(-NR'-X^2-NR'-X^2-)$_2$-, -X^2(-NR'-X^2-O-)$_2$-, -X^2(-NR'-X^2-O-C(=O)-)$_2$-, -X^2(-NR'-X^2-O-C(=O)-NR'-)$_2$-, -X^2(-NR'-X^2-O-X^2-)$_2$-, - X^2(-NR'-X^2-C(=O)-O-)$_2$-, -X^2(-NR'-X^2-C(=O)-NR'-)$_2$-, -X^2(-NR'-X^2-)$_2$-, -X^2(-C(=O)-)$_2$-, -X^2(-C(=O)-O-)$_2$-, -X^2(-C(=O)-NR-)$_2$-, -X^2(-C(=O)-S-)$_2$-, -X^2(-SO_2-)$_2$-, -X^2(-SO_2NR'-)$_2$-, -X^2(-C(OR') (R')(-))$_2$-, and - C(OR')(-)$_2$.

[0075] When X is tetravalent, specific examples of X include, for example, -X^2(-O-)3-, -X^2(-O-C(=O)-)3-, -X^2(-O-C(=O)-O-)3-, -X^2(-O-C(=O)-NR'-)$_3$-, -X^2(-O-X^2-S(=O)$_2$-NR'-)$_3$-, -X^2(-O-X^2-NR'-)$_3$- - X^2(-O-X^2-NR'-S(=O)$_2$-)$_3$-, -X^2(-O-X^2-NR'-C(=O)-)$_3$-, -X^2(-O-X^2-NR'-C(=O)-O-)$_3$-, -X^2(-O-X^2-NR'-C(=O)-NR'-)$_3$-, -X^2(-O-X^2-NR'-X^2-)$_3$-, - X^2(-O-X^2-O-)$_3$-, -X^2(-O-X^2-O-C(=O)-)$_3$-, -X^2(-O-X^2-O-C(=O)-NR'-)$_3$-, -X^2(-O-X^2-C(=O) -O-)$_3$-, -X^2(-O-X^2-C(=O)-NR'-)$_3$-, -X^2(-O-X^2-O-X^2-)$_3$-, -X^2(-O-X^2-)$_3$-, -X^2(-NR'-)$_3$-, -X^2(-NR'-C(=O)-)$_3$-, -X^2(-NR'-C(=O)-O-)$_3$-, -X^2(-NR'-C(=O)-NR'-)$_3$-, -X^2(-NR'-X^2-S(=O)$_2$-NR'-)$_3$-, -X^2(-NR'-X^2-NR'-)$_3$-, -X^2(-NR'-X^2-NR'-S(=O)$_2$-)$_3$-, -X^2(-NR'-X^2-NR'-C(=O)-)$_3$-, -X^2(-NR'-X^2-NR'-C(=O)-O-)$_3$-, -X^2(-NR'-X^2-NR'-C(=O) - NR'-)$_3$-, -X^2(-NR'-X^2-NR'-X^2-)$_3$-, -X^2(-NR'-X^2-O-)$_3$-, -X^2(-NR'-X^2-O-C(=O)-)$_3$-, -X^2(-NR'-X^2-O-C(=O)-NR'-)$_3$-, -X^2(-NR'-X^2-O-X^2-)$_3$-, - X^2(-NR'-X^2-C(=O)-O-)$_3$-, -X^2(-NR'-X^2-C(=O)-NR'-)$_3$-, -X^2(-NR'-X^2-)$_3$--X^2(-C(=O)-)$_3$-, -X^2(-C(=O)-O-)$_3$-, -X^2(-C(=O)-NR'-)$_3$-, -X^2(-C(=O)-S-)$_3$-, -X^2(-SO_2-)$_3$-, -X^2(-SO_2NR'-)$_3$-, and -X^2(-C(OR')(R')(-))$_3$-.

[R]

[0076] R is a monovalent aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent. R may be cyclic, branched chain, or linear, and is preferably branched chain or linear and more preferably linear. R is preferably a saturated aliphatic hydrocarbon group (alkyl group) and optionally has a substituent.

[0077] The number of carbon atoms in R may be 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, or 18 or more, and is preferably 10 or more and more preferably 12 or more. The number of carbon atoms in R may be 40 or less, 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, or 10 or less, and is preferably 30 or less and more preferably 25 or less.

[Acrylic Polymer Type Liquid-Repellent Compound]

[0078] The liquid-repellent compound may be an acrylic polymer (acrylic polymer type liquid-repellent compound). The acrylic polymer type liquid-repellent compound contains the repeating unit derived from the following hydrocarbon-based monomer. Furthermore, it may contain repeating units derived from a crosslinkable monomer, a halogenated olefin monomer, and/or other monomers.

(Hydrocarbon-Based Monomer)

[0079] The acrylic polymer type liquid-repellent compound may be a polymer having a repeating unit derived from the hydrocarbon-based monomer represented by the following formula:

$$CH_2=C(-Q)-C(=O)-X-R_n$$

[wherein

Q is a hydrogen atom, a monovalent organic group, or a halogen atom;
X is a 1 + n valent group composed of one or more selected from the group consisting of

X^1 composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -S(=O)$_2$-, -NR'-, -C(OR')R'-, and -C(OR')(-)$_2$ (wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms), and

X^2 which is a hydrocarbon group having 1 to 40 carbon atoms; R is an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent; and

n is 1 or more and 3 or less.]. It is to be noted that the hydrocarbon-based monomer itself may be used as the liquid-repellent compound.

[0080] The explanations for X, R, and n are incorporated by the description in the {Liquid-Repellent Compound}.

[0081] In particular, in the acrylic polymer type liquid-repellent compound, X may be the group represented by the following formula:

$$-X^1- \text{ or } -X^1-X^2-X^1-$$

[wherein
X^1 is independently at each occurrence -O-, -NR'-, -C(=O)-NR'-, -NR'-C(=O)-, or -NR'-C(=O)-NR'- (wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms), and X^2 is a hydrocarbon group having 1 to 40 carbon atoms.].

[0082] Q is a hydrogen atom, a monovalent organic group, or a halogen atom. Examples of the monovalent organic groups include, for example, a cyano group, an aliphatic hydrocarbon group having 1 to 6 carbon atoms (for example, an alkyl group, an alkenyl group, etc.), and an aromatic group having 5 to 12 carbon atoms. Examples of the halogen atoms include, for example, fluorine, chlorine, bromine, and iodine. Q may be a hydrogen atom, a halogen atom, a methyl group, a cyano group, a substituted or unsubstituted benzyl group, or a substituted or unsubstituted phenyl group, and is, for example, a hydrogen atom, a methyl group, a chlorine atom, a bromine atom, an iodine atom, or a cyano group, preferably a hydrogen atom, a methyl group, or a chlorine atom, and particularly preferably a hydrogen atom or a methyl group.

[0083] From the viewpoint of liquid repellency, the hydrocarbon-based monomer may include a hydrocarbon-based monomer containing an amide group, a urea group, or a urethane group in **X.** The hydrocarbon-based monomer may be a combination of a hydrocarbon-based monomer having an amide group, a urea group, or a urethane group and a hydrocarbon-based monomer free of an amide group, a urea group, or a urethane group.

[0084] The hydrocarbon-based monomer may be an acyclic hydrocarbon group-containing monomer singly, but may also include a cyclic hydrocarbon group-containing monomer. The cyclic hydrocarbon group-containing monomer is a monomer having a cyclic hydrocarbon group, and may be a monomer having one ethylenically unsaturated double bond and a cyclic hydrocarbon group.

[0085] The cyclic hydrocarbon group-containing monomer preferably has a (meth)acrylic group as the ethylenically unsaturated double bond, and may have, for example, a (meth)acrylate group or a (meth)acrylamide group as the ethylenically unsaturated double bond.

[0086] The cyclic hydrocarbon group may be alicyclic or aromatic, and is preferably alicyclic. The cyclic hydrocarbon group may be saturated or unsaturated and is preferably saturated. The cyclic hydrocarbon group may be a monocyclic group, polycyclic group, or bridged ring group and is preferably the bridged ring group. The cyclic hydrocarbon group may have a chain group (for example, linear or branched chain hydrocarbon group).

[0087] The number of carbon atoms of the cyclic hydrocarbon group may be 4 or more, 6 or more, or 8 or more, and may be 30 or less, 26 or less, 22 or less, 18 or less, or 14 or less.

[0088] Specific examples of the cyclic hydrocarbon groups include a cyclohexyl group, t-butylcyclohexyl group, adamantyl group, 2-methyl-2-adamantyl group, 2-ethyl-2-adamantyl group, bornyl group, isobornyl group, norbornyl group, dicyclopentanyl group, dicyclopentenyl group, benzyl group, phenyl group, naphthyl group, 2-t-butylphenyl group, a residual group formed by removing one or more hydrogen atoms from any of these groups (for example, a cyclohexylene group, adamantylene group, phenylene group, and naphthylene group), and a group formed by substituting any of these groups.

[0089] Specific examples of the cyclic hydrocarbon group-containing monomers include, for example, cyclohexyl (meth)acrylate, t-butylcyclohexyl (meth)acrylate, benzyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentanyl (meth) acrylate, dicyclopentenyl (meth)acrylate, dicyclopentanyloxyethyl (meth)acrylate, tricyclopentanyl (meth)acrylate, adamantyl (meth)acrylate, 2-methyl-2-adamantyl (meth)acrylate, 2-ethyl-2-adamantyl (meth)acrylate, and compounds in which these acrylates are substituted with an acrylamide. These may be used singly or in combination of two or more thereof.

[0090] Specific examples of the hydrocarbon-based monomers are as follows. The compounds of the following chemical formulae are each an acrylic compound having a hydrogen atom at the α-position, but the α-position may be another Q, such as a methacrylic compound having a methyl group at the α-position or an α-chloroacrylic compound having a chlorine atom at the α-position.

$$CH_2=CHC(=O)OC_pH_{2p}NHC(=O)C_qH_{2q+1}$$

$CH_2=CHC(=O)OC_2H_4NHC(=O)C_{17}H_{35}$
$CH_2=CHC(=O)OC_2H_4NHC(=O)C_{15}H_{31}$
A mixture of $CH_2=CHC(=O)OC_2H_4NHC(=O)C_{17}H_{35}$ and $CH_2=CHC(=O)OC_2H_4NHC(=O)C_{15}H_{31}$
$CH_2=CHC(=O)OC_qH_{2q+1}$
$CH_2=CHC(=O)OC_{18}H_{37}$
$CH_2=CHC(=O)OC_{16}H_{33}$
$CH_2=CHC(=O)OC_2H_4OC(=O)NHC_qH_{2q+1}$
$CH_2=CHC(=O)OC_2H_4NHC(=O)OC_qH_{2q+1}$
$CH_2=CHC(=O)OC_2H_4NHC(=O)NHC_qH_{2q+1}$
$CH_2=CHC(=O)OC_4H_8OC(=O)\ NHC_qH_{2q+1}$
$CH_2=CHC(=O)OC_2H_4OC(=O)NHC_{18}H_{37}$
$CH_2=CHC(=O)OC_2H_4NHC(=O)OC_{18}H_{37}$
$CH_2=CHC(=O)NHC_pH_{2p}OC(=O)NHC_qH_{2q+1}$
$CH_2=CHC(=O)OC_pH_{2p-1}(NH(C=O)C_qH_{q+1})(NH(C=O)C_qH_{q+1})$
$CH_2=CHC(=O)OC_pH_{2p-1}\ (NH(C=O)C_{17}H_{35})(NH(C=O)C_{17}H_{35})$
$CH_2=CHC(=O)OC_pH_{2p-1}(O(C=O)NHC_qH_{q+1})(CH_2O(C=O)NHC_qH_{q+1})$
$CH_2=CHC(=O)OCH_2CH(O(C=O)NHC_{18}H_{37})(CH_2O(C=O)NHC_{18}H_{37})$
[In the above formula, p is 1 to 40 (for example, 1 to 6), and q is 6 to 40 (for example, 12 to 30).]

(Halogenated Olefin Monomer)

[0091] The acrylic polymer type liquid-repellent compound may have a repeating unit derived from a halogenated olefin monomer. The halogenated olefin monomer is preferably free of a fluorine atom. The halogenated olefin monomer is preferably an olefin having 2 to 20 carbon atoms, substituted with 1 to 10 chlorine atoms, bromine atoms or iodine atoms. The halogenated olefin monomer is preferably a chlorinated olefin having 2 to 20 carbon atoms and particularly an olefin having 2 to 5 carbon atoms and having 1 to 5 chlorine atoms. Preferred specific examples of the halogenated olefin monomers are vinyl halides, such as vinyl chloride, vinyl bromide, and vinyl iodide, and vinylidene halides, such as vinylidene dichloride, vinylidene dibromide, and vinylidene iodide. Vinyl chloride is preferred because it enhances water-repellency (in particular durability of water-repellency). The presence of a repeating unit derived from the halogenated olefin monomer enhances washing durability imparted by the acrylic polymer type liquid-repellent compound.

(Crosslinkable Monomer)

[0092] The acrylic polymer type liquid-repellent compound may have a repeating unit derived from a crosslinkable monomer. The crosslinkable monomer is a monomer capable of imparting crosslinkability to a polymer, and may have at least two selected from the group consisting of a reactive group and an olefinic carbon-carbon double bond. The crosslinkable monomer may be a compound having at least two ethylenically unsaturated double bonds, or a compound having at least one ethylenically unsaturated double bond and at least one reactive group.

[0093] The crosslinkable monomer preferably has a (meth)acrylic group as the ethylenically unsaturated double bond, and may have, for example, a (meth)acrylate group or a (meth)acrylamide group as the ethylenically unsaturated double bond.

[0094] Examples of the reactive groups include a hydroxyl group, an epoxy group, a chloromethyl group, a blocked isocyanate group, an amino group, a carboxyl group, a carbonyl group, an isocyanate group, etc.

[0095] Specific examples of the crosslinkable monomers include, for example, diacetone (meth)acrylamide, N-methylol (meth)acrylamide, hydroxyethyl (meth)acrylamide, glycidyl (meth)acrylate, hydroxymethyl (meth)acrylate, hydroxyethyl (meth)acrylate, 2,3-dihydroxypropyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, 2-acetoacetoxyethyl (meth)acrylate, butadiene, isoprene, chloroprene, vinyl monochloroacetate, vinyl methacrylate, glycidyl (meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, and neopentyl glycol di (meth)acrylate. These may be used singly or in combination of two or more thereof. These may be used singly or in combination of two or more thereof.

(Other Monomers)

[0096] The acrylic polymer type liquid-repellent compound may contain a repeating unit derived from other monomers other than the above-described monomers.

[0097] Specific examples of the other monomers include, for example, acrylonitrile, alkoxy polyalkylene glycol (meth) acrylate, dimethylaminoethyl (meth)acrylate, organosiloxane-containing (meth)acrylate, vinyl acetate, and a vinyl alkyl ether. The other monomers are not limited to these examples. These may be used singly or in combination of two or more

thereof.

(Composition and the Like)

[0098] The amount of repeating units derived from the hydrocarbon-based monomer may be 5% by weight or more, 15% by weight or more, 20% by weight or more, 25% by weight or more, 35% by weight or more, 45% by weight or more, 55% by weight or more, or 65% by weight or more, relative to the acrylic polymer type liquid-repellent compound. The amount of repeating units derived from the hydrocarbon-based monomer may be 98% by weight or less, 95% by weight or less, 90% by weight or less, 80% by weight or less, 70% by weight or less, or 60% by weight or less, relative to the acrylic polymer type liquid-repellent compound. Of the hydrocarbon-based monomers, the amount of the hydrocarbon-based monomer having an amide group, a urea group, or a urethane group may be 1% by weight or more, 3% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 50% by weight or more, or 75% by weight or more. Of the hydrocarbon-based monomers, the amount of the hydrocarbon-based monomer having an amide group, a urea group, or a urethane group may be 80% by weight or less, 60% by weight or less, 40% by weight or less, or 20% by weight or less. Of the hydrocarbon-based monomers, the amount of the cyclic hydrocarbon group-containing monomer may be 1% by weight or more, 3% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 50% by weight or more, or 75% by weight or more. Of the hydrocarbon-based monomers, the amount of the cyclic hydrocarbon group-containing monomer may be 80% by weight or less, 60% by weight or less, 40% by weight or less, or 20% by weight or less.

[0099] The amount of repeating units derived from the halogenated olefin monomer may be 3% by weight or more, 5% by weight or more, 10% by weight or more, 15% by weight or more, or 20% by weight or more, 25% by weight or more, or 35% by weight or more, relative to the acrylic polymer type liquid-repellent compound. The amount of repeating units derived from the halogenated olefin monomer may be 80% by weight or less, 70% by weight or less, 60% by weight or less, 50% by weight or less, 40% by weight or less, 30% by weight or less, 20% by weight or less, or 10% by weight or less, and is preferably 60% by weight or less, relative to the acrylic polymer type liquid-repellent compound.

[0100] The amount of repeating units derived from the cyclic hydrocarbon group-containing monomer may be 0.5% by weight or more, 1% by weight or more, 3% by weight or more, or 4% by weight or more, relative to the acrylic polymer type liquid-repellent compound. The amount of repeating units derived from the halogenated olefin monomer may be 30% by weight or less, 20% by weight or less, 15% by weight or less, 10% by weight or less, 7.5% by weight or less, or 5% by weight or less, relative to the acrylic polymer type liquid-repellent compound.

[0101] The amount of repeating units derived from the crosslinkable monomer may be 0.5% by weight or more, 1% by weight or more, 3% by weight or more, 5% by weight or more, 10% by weight or more, or 20% by weight or more, relative to the acrylic polymer type liquid-repellent compound. The amount of repeating units derived from the crosslinkable monomer may be 70% by weight or less, 60% by weight or less, 50% by weight or less, 40% by weight or less, 30% by weight or less, or 20% by weight or less, relative to the acrylic polymer type liquid-repellent compound.

[0102] The amount of repeating units derived from the other monomer may be 0.5% by weight or more, 1% by weight or more, 3% by weight or more, 5% by weight or more, 10% by weight or more, or 20% by weight or more, relative to the acrylic polymer type liquid-repellent compound. The amount of repeating units derived from the other monomer may be 70% by weight or less, 60% by weight or less, 50% by weight or less, 40% by weight or less, 30% by weight or less, or 20% by weight or less, relative to the acrylic polymer type liquid-repellent compound.

[0103] The weight-average molecular weight of the acrylic polymer type liquid-repellent compound may be 500 or more, 1,000 or more, 2,500 or more, 5,000 or more, 10,000 or more, 25,000 or more, or 50,000 or more, with 5,000 or more being preferred. The weight-average molecular weight of the acrylic polymer type liquid-repellent compound may be 1,000,000 or less, 500,000 or less, 250,000 or less, 100,000 or less, 50,000 or less, 25,000 or less, or 10,000 or less, with 100,000 or less being preferred.

(Polymerization Method)

[0104] The acrylic polymer type liquid-repellent compound can be produced by a known polymerization method, and the polymerization reaction conditions can be selected arbitrarily. Examples of such polymerization methods include solution polymerization, suspension polymerization, emulsion polymerization, and condensation polymerization.

[0105] In solution polymerization, a method for dissolving a monomer in an organic solvent in the presence of a polymerization initiator, and after nitrogen substitution, heating and stirring the mixture at a temperature in a range of 30 to 120°C for 1 to 10 hours, is employed. Examples of the polymerization initiators include, for example, azobisisobutyronitrile, benzoyl peroxide, di-t-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxypivalate, and diisopropyl peroxydicarbonate. The polymerization initiator is used in the range of 0.01 to 20 parts by weight, for example, 0.01 to 10 parts by weight, based on 100 parts by weight of the monomer.

[0106] The organic solvent is inactive to the monomers and dissolves them, and may be, for example, esters (for

example, esters having 2 to 40 carbon atoms, specifically, ethyl acetate and butyl acetate), ketones (for example, ketones having 2 to 40 carbon atoms, specifically, methyl ethyl ketone, diisobutyl ketone, and methyl isobutyl ketone), or alcohols (for example, alcohols having 1 to 40 carbon atoms, specifically, ethanol, butanol, and isopropyl alcohol). Specific examples of the organic solvents include, for example, acetone, chloroform, HCHC225, isopropyl alcohol, cyclohexane, benzene, toluene, xylene, petroleum ether, tetrahydrofuran, 1,4-dioxane, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, ethyl acetate, butyl acetate, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, tetrachlorodifluoroethane, and trichlorotrifluoroethane. The organic solvent is used in an amount of 10 to 3,000 parts by weight, for example, 50 to 2,000 parts by weight, based on 100 parts by weight of the total of the monomers.

[0107] In the emulsion polymerization, a method for emulsifying a monomer in water in the presence of a polymerization initiator and an emulsifier, and after nitrogen substitution, stirring the mixture in the range of 50 to 80°C for 1 to 20 hours to polymerize the monomer, is employed. The polymerization initiator for use is water-soluble initiators such as benzoyl peroxide, lauroyl peroxide, t-butyl perbenzoate, 1-hydroxycyclohexyl hydroperoxide, 3-carboxypropionyl peroxide, acetyl peroxide, azobisisobutylamidine dihydrochloride, sodium peroxide, potassium persulfate, and ammonium persulfate; as well as oil-soluble initiators such as azobisisobutyronitrile, benzoyl peroxide, di-t-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxypivalate, and diisopropyl peroxydicarbonate. The polymerization initiator is used in the range of 0.01 to 10 parts by weight, based on 100 parts by weight of the monomer.

[0108] In order to obtain an aqueous dispersion of polymer having excellent standing stability, it is desirable to micronize the monomer in water and then polymerize by using an emulsifying apparatus, such as a high-pressure homogenizer or an ultrasonic homogenizer which can apply intense crushing energy. Moreover, the emulsifying agent can be any of various types of anionic, cationic, and nonionic emulsifying agents, and is used in the range of 0.5 to 20 parts by weight, based on 100 parts by weight of the monomer. It is preferable to use an anionic and/or nonionic and/or cationic emulsifier. In a case in which a monomer is not completely compatible, a compatibilizer allowing the monomer to be sufficiently compatible, such as a water-soluble organic solvent or a low molecular weight monomer, is preferably added. The addition of the compatibilizer can improve emulsification properties and copolymerization properties.

[0109] The water-soluble organic solvent for use may be any of the organic solvents described above. Examples thereof include acetone, methyl ethyl ketone, ethyl acetate, propylene glycol, dipropylene glycol monomethyl ether, dipropylene glycol, tripropylene glycol, ethanol, etc., and each may be used in an amount of 1 to 50 parts by weight, for example 10 to 40 parts by weight, based on 100 parts by weight of water. Also, examples of the low molecular weight monomers include methyl methacrylate, glycidyl methacrylate, 2,2,2-trifluoroethyl methacrylate, and the like, and each may be used in an amount of 1 to 50 parts by weight, for example 10 to 40 parts by weight, based on 100 parts by weight of the total amount of monomers.

[0110] A chain transfer agent may be used in the polymerization. The molecular weight of the polymer can be changed according to the amount of the chain transfer agent used. Examples of the chain transfer agents include mercaptan group-containing compounds such as lauryl mercaptan, thioglycol, and thioglycerol (particularly, an alkyl mercaptan (for example, having 1 to 40 carbon atoms)), inorganic salts such as sodium hypophosphite and sodium hydrogen sulfite, and the like. The amount of the chain transfer agent used may be in the range of 0.01 to 10 part by weight, for example, 0.1 to 5 parts by weight, relative to 100 parts by weight of the total amount of the monomers.

[Base Material-Modified Liquid-Repellent Compound]

[0111] The liquid-repellent compound may be a liquid-repellent compound (base material-modified liquid-repellent compound) in which a base material is modified with a hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent.

[0112] The base material-modified liquid-repellent compound may be a compound in which one or more base material compounds selected from the group consisting of one or more compounds selected from a monosaccharide, a polysaccharide, an alcohol, a polyol, a carboxylic acid, and a polyvalent carboxylic acid, and derivatives thereof, are modified with the group represented by the following formula:

$$-X-R_n$$

[wherein

X is a direct bond or a 1 + n valent group;
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent; and
n is an integer of 1 or more and 3 or less.].

[0113] Examples of the base material compounds include, for example, one or more compounds selected from starch,

cellulose, curdlan, pullulan, carrageenan, guar gum, chitin, chitosan, locust bean gum, kappa carrageenan, iota carrageenan, isomaltodextrin, xanthan gum, gelatin gum, tamarind seed gum, cycloamylose, glucose, sucrose, mannitol, sorbitol, sorbitan, maltitol, stevioside, dextrin, cyclodextrin, glycerin, polyglycerin, and menthol, xylitol, sucralose, fructose, maltose, trehalose, lactosucrose, erythritol, vanillin, cholesterol, glucosamine, catechin, anthocyanin, quercetin, citric acid, malic acid, gluconic acid, alginic acid, butyric acid, lactic acid, tartaric acid, oxalic acid, malonic acid, succinic acid, fumaric acid, maleic acid, chlorogenic acid, aldonic acid, uronic acid, aldaric acid, phytic acid, and ascorbic acid, and derivatives thereof.

[0114] The base material compound may be polymers (for example, condensates or crosslinked products) of the compounds exemplified above. Examples of the suitable polymers include a glycerin polymer and citric acid polymer.

[0115] A condensation reaction or crosslinking reaction for obtaining a polymer is not limited, a known method for allowing polymerization to proceed at a functional group of the base material compound can be employed, and a publicly known catalyst, a dehydration condensing agent, a crosslinking agent, or the like may also be used. Examples of the catalysts, dehydration condensing agents, and crosslinking agents for use include acids such as p-toluenesulfonic acid, acetic acid, trifluoroacetic acid, hydrochloric acid, sulfuric acid, and fluoroboric acid; acid halides such as acetic acid chloride, propionic acid chloride, and benzoic acid chloride; bases such as sodium methoxide, potassium tert-butoxide, sodium hydride, potassium carbonate, cesium carbonate, triethylamine, and diisopropylamine, tetrabutylammonium bromide, sodium acetate, a Burgess reagent, condensing agents such as N,N'dicyclohexylcarbodiimide, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (WSC) or its hydrochloride salt, N,N'-carbonyldiimidazole, 1H-benzotriazol-1-yloxy-tris(dimethylamino)phosphonium hexafluorophosphate (BOP), O-(7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU), 2-chloro-1,3-dimethylimidazolium chloride, bromotripyrrolidinophosphonium hexafluorophosphate (PyBrop), diethyl phosphorocyanidate (diethyl phosphoryl cyanide; DEPC), diphenylphosphoryl azide (DPPA), and 4-(4,6-dimethoxy[1,3,5]triazin-2-yl)-4-methylmorpholinium chloride (DMTMM); a Lawesson's reagent, and the like.

[0116] The explanations for X, R, and n are incorporated by the description in the {Liquid-Repellent Compound}.

[0117] The base material compound may have a hydroxy group. In that case, the hydroxy group may form the group represented by the following formula:

-O-;

-O-C(=O)-;

-O-C(=O)-NR'-

or

-O-C=S-NR'-

[wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms.]
in the base material-modified liquid-repellent compound.

[0118] The base material compound may have a carboxyl group. In that case, the carboxyl group may form the group represented by the following formula:

-C(=O)-;

-C(=O)-O-;

-C(=O)-NR'-

or

-C(=O)-S-

[wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms.]
in the liquid-repellent compound.

[0119] The weight-average molecular weight of the base material compound may be 500 or more, 1,000 or more, 2,500 or more, 5,000 or more, 10,000 or more, 25,000 or more, 50,000 or more, 100,000 or more, or 250,000 or more. The weight-

average molecular weight of the acrylic polymer type liquid-repellent compound may be 1,000,000 or less, 750,000 or less, 500,000 or less, 250,000 or less, 100,000 or less, 50,000 or less, 25,000 or less, or 10,000 or less.

(Production Method of Base Material-Modified Liquid- Repellent Compound)

[0120] The method for modifying the base material compound with a hydrocarbon group having 6 to 40 carbon atoms and optionally having a substituent is not particularly limited. For example, methods such as a urethane bond-forming reaction, a urea bond-forming reaction, an ester bond-forming reaction, an amide bond-forming reaction, and an ether bond-forming reaction, can be used. In the bond-forming reaction, an acylating agent, a condensing agent, a catalyst, or the like is appropriately used.

[0121] As a method for modifying the base material compound with a hydrocarbon group having 6 to 40 carbon atoms and optionally having a substituent, the base material compound may be modified by reacting with a hydrocarbon group-containing reactant. The hydrocarbon group-containing reactant is a compound having a group capable of reacting with an aliphatic hydrocarbon group and a functional group of the base material compound.

[0122] Examples of the hydrocarbon group-containing reactants are as follows:

H_2N-R;

HO-R;

HO(O=)C-R;

G(O=)C-R;

RC(=O)OC(=O)R;

O=C=N-R;

S=C=N-R;

$(CH_2OCH)CH_2OR$;

and

G-R

[wherein, R is the aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, as defined above. G is a halogen atom (particularly F, Cl, Br, or I).].

· Urethane bond formation

[0123] The base material compound and the hydrocarbon group may be bonded via a urethane bond. The urethane bond may be formed, for example, by allowing a hydroxy group-containing base material compound to react with an aliphatic hydrocarbon-containing isocyanate. A tin catalyst or an amine may be used as a catalyst upon reaction. For example, the hydroxy group-containing base material compound is allowed to react with the aliphatic hydrocarbon group-containing isocyanate in an organic solvent for a certain period of time, which results in a reaction of the hydroxy group with the isocyanate group, yielding a base material-modified liquid-repellent compound in which the base material compound and the hydrocarbon group are bonded via a urethane bond.

· Urea bond formation

[0124] The base material compound and the hydrocarbon group may be bonded via a urea bond. The urea bond may be formed, for example, by allowing an amino group-containing base material compound to react with an aliphatic hydrocarbon group-containing isocyanate group (or, by allowing an isocyanate group-containing base material compound to react with an aliphatic hydrocarbon group-containing amine). A catalyst may be appropriately used upon reaction. For example, the amino group-containing base material compound is allowed to react with the aliphatic hydrocarbon-containing isocyanate in an organic solvent for a certain period of time, which results in a reaction of the amino group with the isocyanate group, yielding a base material-modified liquid-repellent compound in which the base material

compound and the hydrocarbon group are bonded via a urea bond.

· Ester bond formation

[0125] The base material compound and the hydrocarbon group may be bonded via an ester bond. The ester bond may be formed, for example, by allowing a hydroxy group-containing base material compound to react with an aliphatic hydrocarbon group-containing carboxylic acid (or, by allowing a carboxylic acid-containing base material compound to react with an aliphatic hydrocarbon group-containing alcohol). An acylation catalyst, a condensing agent, or the like may be used upon reaction. For example, the hydroxy group-containing base material compound is allowed to react with the aliphatic hydrocarbon group-containing carboxylic acid in an organic solvent for a certain period of time, which results in a reaction of the hydroxy group with the carboxylic acid, yielding a base material-modified liquid-repellent compound in which the base material compound and the hydrocarbon group are bonded via an ester bond.

· Amide bond formation

[0126] The base material compound and the hydrocarbon group may be bonded via an amide bond. The amide bond may be formed, for example, by allowing an amide group-containing base material compound to react with an aliphatic hydrocarbon group-containing carboxylic acid (or, by allowing a carboxylic acid-containing base material compound to react with an aliphatic hydrocarbon group-containing amine). An acylation catalyst, a condensing agent, or the like may be used upon reaction. For example, the amino group-containing base material compound is allowed to react with the aliphatic hydrocarbon group-containing carboxylic acid in an organic solvent for a certain period of time, which results in a reaction of the amino group with the carboxylic acid, yielding a base material-modified liquid-repellent compound in which the base material compound and the hydrocarbon group are bonded via an amide bond.

· Ether bond formation

[0127] The base material compound and the hydrocarbon group may be bonded via an ether bond. The ether bond may be formed, for example, by allowing a halogen-containing base material compound to react with an aliphatic hydrocarbon group-containing alcohol (or, by allowing a hydroxy group-containing base material compound to react with an aliphatic hydrocarbon group-containing halide). An acid catalyst, a base catalyst, or the like may be used upon reaction. For example, the halogen-containing base material compound is allowed to react with the aliphatic hydrocarbon group-containing alcohol by heating in an organic solvent in the presence of a catalyst, which results in serving the aliphatic hydrocarbon group-containing alcohol as a nucleating agent, yielding a base material-modified liquid-repellent compound in which the base material compound and the hydrocarbon group are bonded via an ether bond.

[Ring-Modified Liquid-Repellent Compound]

[0128] The liquid-repellent compound may be a liquid-repellent compound (ring-modified liquid-repellent compound) in which an aromatic ring or a nitrogen-containing heterocyclic ring is modified with an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent.

[0129] The ring-modified liquid-repellent compound may be the compound represented by the following formula:

$$A(\text{-}X\text{-}R_n)_m$$

[wherein

A is an m valent group obtained by removing m hydrogen atoms from an aromatic ring or a nitrogen-containing heterocyclic ring optionally having a substituent;
X is independently at each occurrence a direct bond or a 1 + n valent group;
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and to 40 or less carbon atoms and optionally having a substituent;
n is independently at each occurrence 1 or more and 3 or less; and
m is 1 or more and 6 or less.].

[0130] The explanations for X, R, and n are incorporated by the description in the {Liquid-Repellent Compound}.

[0131] A is an m valent group. m may be 1 or more, 2 or more, 3 or more, 4 or more, or 5 or more, and is preferably 2 or more. m may be 6 or less, 5 or less, 4 or less, 3 or less, or 2 or less, and is preferably 4 or less.

[0132] A is an m valent group obtained by removing m hydrogen atoms from an aromatic ring or a nitrogen-containing heterocyclic ring and optionally has a substituent. Examples of the aromatic rings include hydrocarbon aromatic rings such as a benzene ring, a naphthalene ring, an anthracene ring, and a phenanthrene ring; heteroaromatic rings such as a pyridine ring, a pyrimidine ring, a quinoline ring, a furan ring, a pyrrole ring, and a pyrazole ring; and the like. Examples of the nitrogen-containing heterocyclic rings include non-aromatic nitrogen-containing heterocyclic rings such as pyrrolidine, pyrazolidine, triazolidine, oxazolidine, isoxazolidine, thiazolidine, isothiazolidine, piperidine, piperazine, and morpholine; and aromatic nitrogen-containing heterocyclic rings such as a pyrrole ring, an imidazole ring, a pyrazole ring, an oxazole ring, an isoxazole ring, a thiazole ring, an isothiazole ring, a pyridine ring, a pyrazine ring, a pyrimidine ring, a pyridazine ring, a triazine ring, an oxazine ring, and a thiazine ring; and the like.

[0133] The aromatic ring or nitrogen-containing heterocyclic ring may have a substituent. Examples of the aromatic rings or nitrogen-containing heterocyclic rings, which optionally have a substituent include, but are not limited to, for example, one or more groups selected from a C_{1-6} alkyl group, a C_{2-6} alkenyl group, a C_{2-6} alkynyl group, a C_{3-10} cycloalkyl group, a C_{3-10} unsaturated cycloalkyl group, a 5 to 10 membered heterocyclyl group, a 5 to 10 membered unsaturated heterocyclyl group, a C_{6-10} aryl group, and a 5 to 10 membered heteroaryl group, which may be substituted with -OR', $-N(R')_2$, -COOR' (wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms), a halogen atom, or one or more halogen atoms.

[0134] The aromatic ring or nitrogen-containing heterocyclic ring may be a 4-membered ring, a 5-membered ring, a 6-membered ring, a 7-membered ring, or an 8-membered ring. The aromatic ring or nitrogen-containing heterocyclic ring may be a condensed polycyclic rings containing 2 to 5 (preferably 2 to 3) 4- to 8-membered rings.

[0135] The ring-modified liquid-repellent compound may be polymers (for example, condensates or crosslinked products) of the above-described ring-modified liquid-repellent compounds. In the polymer, polymerization may have proceeded via a substituent of A.

[0136] The condensation reaction or crosslinking reaction for obtaining a polymer is not limited, and a known method for proceeding polymerization at a functional group of A can be used, and a known catalyst, a dehydration condensing agent, a crosslinking agent, etc., may be used. Examples of the catalysts, dehydration condensing agents, and crosslinking agents for use include acids such as p-toluenesulfonic acid, acetic acid, trifluoroacetic acid, hydrochloric acid, sulfuric acid, and fluoroboric acid; acid halides such as acetic acid chloride, propionic acid chloride, and benzoic acid chloride; bases such as sodium methoxide, potassium tert-butoxide, sodium hydride, potassium carbonate, cesium carbonate, triethylamine, and diisopropylamine; condensing agents such as tetrabutylammonium bromide, sodium acetate, a Burgess reagent, N,N'-dicyclohexylcarbodiimide, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (WSC) or its hydrochloride salt, N,N'-carbonyldiimidazole, 1H-benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (BOP), O-(7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU), 2-chloro-1,3-dimethylimidazolium chloride, bromotripyrrolidinophosphonium hexafluorophosphate (PyBrop), diethyl phosphorocyanidate (diethyl phosphoryl cyanide; DEPC), diphenylphosphoryl azide (DPPA), and 4-(4,6-dimethoxy[1,3,5]triazin-2-yl)-4-methylmorpholinium chloride (DMTMM); a Lawesson's reagent, and the like.

[0137] In the ring-modified liquid-repellent compound, X may be the group represented by the following formula:

$$-X^1-$$

or

$$-X^1-X^2-X^1-$$

[wherein

X^1 is independently at each occurrence
a direct bond;
-O-;
-O-C(=O)-;
-O-C(=O)-O-;
-O-C(=O)-NR'-;
-NR'-;
-NR'-C(=O)-;
-NR'-C(=O)-O-;
-NR'-C(=O)-NR'-;
-C(=O)-;
-C(=O)-O-;
-C(=O)-NR'-;

-C(OR')R'- or
-C(OR') (-)$_2$
[R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms.]; and
X^2 is a hydrocarbon group having 1 to 40 carbon atoms.]. This can impart favorable liquid repellency to a substrate.

(Method for Producing Ring-Modified Liquid-Repellent Compound)

[0138] The method for modifying an aromatic ring or a nitrogen-containing heterocyclic ring with a hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent is not particularly limited. For example, methods such as a urethane bond-forming reaction, a urea bond-forming reaction, an ester bond-forming reaction, an amide bond-forming reaction, and an ether bond-forming reaction, can be used. In the bond-forming reaction, an acylating agent, a condensing agent, a catalyst, or the like is appropriately used.

[0139] As the method for modifying the aromatic ring or the nitrogen-containing heterocyclic ring with the hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, the aromatic ring or the nitrogen-containing heterocyclic ring may be modified by allowing the aromatic ring or the nitrogen-containing heterocyclic ring to react with a hydrocarbon group-containing reactant. The hydrocarbon group-containing reactant is a compound having an aliphatic hydrocarbon group and a group capable of reacting with a functional group that the aromatic ring or nitrogen-containing heterocyclic ring has.

[0140] Examples of the hydrocarbon group-containing reactants are as follows:

H_2N-R;

HO-R;

HO(O=)C-R;

G(O=)C-R;

RC (=O) OC(=O)R;

O=C=N-R;

S=C=N-R;

(CH_2OCH) CH_2OR;

and

G-R

[wherein, R is an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, as defined above. G is a halogen atom (particularly F, Cl, Br, or I).].

· Urethane bond formation

[0141] The aromatic ring or nitrogen-containing heterocyclic ring may be bonded to a hydrocarbon group via a urethane bond. The urethane bond may be formed, for example, by allowing a hydroxy group-containing aromatic ring or the nitrogen-containing heterocyclic ring to react with an aliphatic hydrocarbon-containing isocyanate. A tin catalyst or an amine may be used as a catalyst upon reaction. For example, the hydroxy group-containing aromatic ring or nitrogen-containing heterocyclic ring is allowed to react with the hydrocarbon group-containing isocyanate in an organic solvent for a certain period of time, which results in a reaction of the hydroxy group with the isocyanate group, yielding a ring-modified liquid-repellent compound in which the aromatic ring or nitrogen-containing heterocyclic ring is bonded to the hydrocarbon group via a urethane bond.

· Urea bond formation

[0142] The aromatic ring or nitrogen-containing heterocyclic ring may be bonded to a hydrocarbon group via a urea

bond. The urea bond may be formed, for example, by allowing an amino group-containing aromatic ring or the nitrogen-containing heterocyclic ring to react with a hydrocarbon group-containing isocyanate (alternatively, by allowing an isocyanate group-containing aromatic ring or the nitrogen-containing heterocyclic ring to react with a hydrocarbon group-containing amine). A catalyst may be appropriately utilized upon reaction. For example, the amino group-containing aromatic ring or nitrogen-containing heterocyclic ring is allowed to react with the aliphatic hydrocarbon-containing isocyanate in an organic solvent for a certain period of time, which results in a reaction of the amino group with the isocyanate group, yielding a ring-modified liquid-repellent compound in which the aromatic ring or nitrogen-containing heterocyclic ring is bonded to the hydrocarbon group via a urea bond.

· Ester bond formation

[0143] The aromatic ring or nitrogen-containing heterocyclic ring may be bonded to a hydrocarbon group via an ester bond. The ester bond may be formed, for example, by allowing a hydroxy group-containing aromatic ring or the nitrogen-containing heterocyclic ring to react with a hydrocarbon group-containing carboxylic acid (alternatively, by allowing a carboxylic acidcontaining aromatic ring or the nitrogen-containing heterocyclic ring to react with a hydrocarbon group-containing alcohol). Upon reaction, an acylation catalyst, a condensing agent, or the like may be used. For example, the hydroxy group-containing aromatic ring or nitrogen-containing heterocyclic ring is allowed to react with the hydrocarbon group-containing carboxylic acid in an organic solvent for a certain period of time, which results in a reaction of the hydroxy group with the carboxylic acid, yielding a ring-modified liquid-repellent compound in which the aromatic ring or nitrogen-containing heterocyclic ring is bonded to the hydrocarbon group via an ester bond.

· Amide bond formation

[0144] The aromatic ring or nitrogen-containing heterocyclic ring may be bonded to a hydrocarbon group via an amide bond. The amide bond may be formed, for example, by allowing an amino group-containing aromatic ring or the nitrogen-containing heterocyclic ring to react with a hydrocarbon group-containing carboxylic acid (alternatively, by allowing an carboxylic acid-containing aromatic ring or the nitrogen-containing heterocyclic ring to react with a hydrocarbon group-containing amine). Upon reaction, an acylation catalyst, a condensing agent, or the like may be used. For example, the amino group-containing aromatic ring or nitrogen-containing heterocyclic ring is allowed to react with the hydrocarbon group-containing carboxylic acid in an organic solvent for a certain period of time to result in a reaction of the amino group with the carboxylic acid, yielding a ring-modified liquid-repellent compound in which the aromatic ring or nitrogen-containing heterocyclic ring is bonded to the hydrocarbon group via an amide bond.

· Ether bond formation

[0145] The aromatic ring or nitrogen-containing heterocyclic ring may be bonded to a hydrocarbon group via an ether bond. The ether bond may be formed, for example, by allowing a halogen-containing aromatic ring or the nitrogen-containing heterocyclic ring to react with a hydrocarbon group-containing alcohol (alternatively, by allowing a hydroxy group-containing aromatic ring or the nitrogen-containing heterocyclic ring to react with a hydrocarbon group-containing halide). Upon reaction, an acid catalyst, a base catalyst, or the like may be used. For example, the halogen-containing aromatic ring or nitrogen-containing heterocyclic ring is allowed to react with the hydrocarbon group-containing alcohol by heating in an organic solvent in the presence of a catalyst, which results in serving the hydrocarbon group-containing alcohol as a nucleating agent, yielding a ring-modified liquid-repellent compound in which the aromatic ring or nitrogen-containing heterocyclic ring is bonded to the hydrocarbon group via an ether bond.

[Isocyanate-Based Liquid-Repellent Compound]

[0146] The liquid-repellent compound may be a liquid-repellent compound that is a reaction product of an isocyanate group-containing compound and an isocyanate-reactive compound (isocyanate-based liquid-repellent compound) and preferably may also be an isocyanate-based liquid-repellent compound having a hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent.

[0147] Examples of the isocyanate group-containing compounds that are to be raw materials for the isocyanate-based liquid-repellent compounds include higher functional isocyanates, including an isocyanate, a diisocyanate, a triisocyanate, and a polymeric isocyanate. These may be aliphatic (including alicyclic) and cyclic (including aromatic). Examples of the diisocyanates include 4,4'-methylenediphenylene diisocyanate (MDI), 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, o-, m-, and p-xylylene diisocyanate, 4,4'-diisocyanatodiphenyl ether, 3,3'-dichloro-4,4'-diisocyanatodiphenylmethane, 4,4'-diphenyl diisocyanate, 4,4'-diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dimethyl-4,4'-diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanatodiphenyl, 1,3-diisocyanatobenzene,

1,2-naphthylene diisocyanate, 4-chloro-1,2-naphthylene diisocyanate, 1,3-naphthylene diisocyanate, and 1,8-dinitro-2,7-naphthylene diisocyanate, alicyclic diisocyanates such as 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, aliphatic diisocyanates such as 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, and 1,2-ethylene diisocyanate, and cyclic diisocyanates such as isophorone diisocyanate (IPDI) and dicyclohexylmethane-4,4'-diisocyanate. Examples of the triisocyanates include an aliphatic triisocyanate such as 1,3,6-hexamethylene triisocyanate, and an aromatic triisocyanate such as tri-(4-isocyanatophenyl)-methane. An example of the polymeric isocyanate includes polymethylene polyphenylisocyanate (PAPI).

[0148] The isocyanate-reactive compound is a compound containing an isocyanate-reactive group, examples of which include, for example, monofunctional, difunctional, and polyfunctional alcohols, thiols, and amines. Examples of the isocyanate-reactive compounds include linear or branched long chain alkanols such as alkanols such as methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, t-butyl alcohol, n-amyl alcohol, t-amyl alcohol, 2-ethylhexanol, glycidol, (iso) stearyl alcohol, and behenyl alcohol, and an alkyl alcohol having C6 to C40 alkyl chains; and alcohols containing poly (oxyalkylene) groups such as a methyl or ethyl ether of polyethylene glycol and a hydroxy-terminated methyl or ethyl ether of a random or block copolymer of ethylene oxide and/or propylene oxide with a polysiloxane (for example, polydimethylsiloxane) group-containing alcohol. Further examples include diols, triols, and polyols such as 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol, 4,4'-isopropylidenediphenol (bisphenol A), glycerol, pentaerythritol, and dipentaerythritol, polycaprolactone diol, a fatty acid dimer diol, as well as poly(oxy)alkylene diols having an oxyalkylene group having 2 to 4 carbon atoms, such as $-OCH_2CH_2-$, $-O(CH_2)_4-$, $-OCH_2CH_2CH_2-$, $-OCH(CH_3)CH_2-$, and $-OCH(CH_3)CH(CH_3)-$ (the oxyalkylene unit in the above poly(oxyalkylene) may be the same as in polypropylene glycol or may be present as a mixture), as well as ester diols such as glycerol monostearate and a polysiloxane-containing diol (for example, a polydimethylsiloxane-containing diol). Examples of the isocyanate-reactive compounds include amino-containing compounds such as octadecylamine, di(octadecyl)amine, and 1,6-hexamethylenediamine, amino-terminated polyethylene oxide or propylene oxide or copolymers thereof, amino-terminated methyl or ethyl ethers of polyethylene oxide or polypropylene oxide or copolymers thereof, and an amino-terminated polysiloxane, such as polydimethylsiloxane.

[0149] In the isocyanate-based compound, the isocyanate-reactive compound preferably has, in addition to the isocyanate-reactive group, a hydrocarbon group having 6 or more and 40 or less carbon atoms (particularly an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms (corresponding to the above R) and optionally having a substituent.

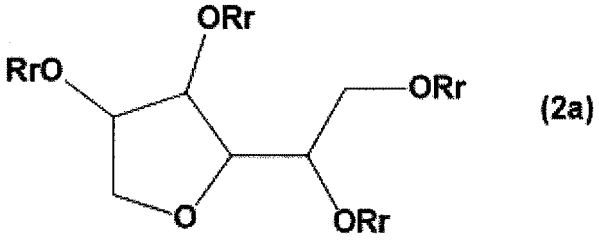
[0150] The isocyanate-based compound may be a polymer in which an isocyanate and the isocyanate-reactive compound have been reacted successively.

[0151] The isocyanate-based liquid-repellent compound may be a compound represented by the following formula:

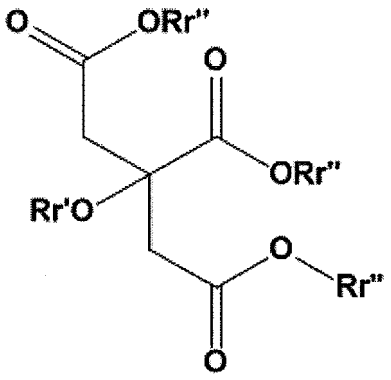
$$L(-X-R_n)$$

[wherein

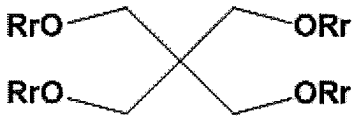
L is an m valent urethane/amide backbone that is a reaction product of (a) one or more isocyanate group-containing compounds selected from the group consisting of an isocyanate, a diisocyanate, and a polyisocyanate, and
(b) one or more isocyanate-reactive compounds selected from the group consisting of compounds
represented by the following general formulae (2a), (2b), and (2c),
X is independently at each occurrence a direct bond or a 1 + n valent group;
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent;
n is independently at each occurrence 1 or more and 3 or less; and
m is 1 or more and 6 or less.]
and



(2a)



(2b)



(2c)

[In the general formulae (2a) and (2c):

Rr is independently at each occurrence -H, -*, -C(O)-*, - $(CH_2CH_2O)_p(CH(CH_3)CH_2O)_qH$, - $(CH_2CH_2O)_p(CH(CH_3)CH_2O)_q$-*, or - $(CH_2CH_2O)_p(CH(CH_3)CH_2O)_qC(O)$-*;
p is independently at each occurrence 0 to 20;
q is independently at each occurrence 0 to 20;
p+q is greater than 0;
and the symbol * is a bond of L;
provided that when the isocyanate-reactive compound is represented by the general formula (2a) or (2c), at least one of Rr is -H or -$(CH_2CH_2O)_p(CH(CH_3)CH_2O)_qH$, and at least one of another Rr is -*, -C(O)-*, - $(CH_2CH_2O)_p(CH(CH_3)CH_2O)_q$-*, or - $(CH_2CH_2O)_p(CH(CH_3)CH_2O)_qC(O)$-*;
in the general formula (2b):

Rr' is independently at each occurrence -H, -*, -C(O)-*, - $(CH_2CH_2O)_{p'}(CH(CH_3)CH_2O)_{q'}H$, -$(CH_2CH_2O)_{p'}(CH(CH_3)CH_2O)_{q'}$-*, or - $(CH_2CH_2O)_{p'}(CH(CH_3)CH_2O)_{q'}C(O)$-*;
Rr'' is independently at each occurrence -H, -*, - $(CH_2CH_2O)_{p'}(CH(CH_3)CH_2O)_{q'}H$, - $(CH_2CH_2O)_{p'}(CH(CH_3)CH_2O)_{q'}$-*, or - $(CH_2CH_2O)_{p'}(CH(CH_3)CH_2O)_{q'}C(O)$-*;
P' is independently at each occurrence 0 to 20;
q' is independently at each occurrence 0 to 20;
p' + q' is greater than 0;
and the symbol * is a bond of L
with the proviso that when the isocyanate-reactive compound is represented by the general formula (2b), at least one of Rr' and Rr'' is -H or - $(CH_2CH_2O)_{p'}(CH(CH_3)CH_2O)_{q'}H$, and at least one of another Rr' and Rr'' is -*, -C(O)-*, - $(CH_2CH_2O)_{p'}(CH(CH_3)CH_2O)_{q'}$-*' or - $(CH_2CH_2O)_{p'}(CH(CH_3)CH_2O)_{q'}C(O)$-*.].

[0152] It is to be noted that p, q, p', and q' are each an integer of 0 to 20 in the case of only one isocyanate-based liquid-repellent compound, but can be denoted as an average value thereof in the case of an aggregate of a plurality of isocyanate-based liquid-repellent compounds.

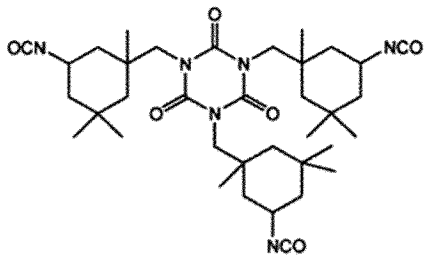
[0153] In this case, L in the isocyanate-based liquid-repellent compound is a urethane backbone prepared by a process including allowing the isocyanate group-containing compound (a) to react with the isocyanate-reactive compound (b), and such a urethane/amide backbone can usually be polyvalent, but is not limited thereto. When the isocyanate-reactive compound (b) is represented by the general formula (2a) or (2c), it has at least one -OH group, and when represented by general formula (2b), it has at least one -OH group or -COOH group. Therefore, by allowing the isocyanate group-containing compound (a) to react with the isocyanate-reactive compound (b), a reaction product in which they are bonded by a urethane bond or an amide bond, can be obtained. Such reactions are known and may be carried out under any suitable conditions.

[0154] In such an isocyanate-based liquid-repellent compound, **-X-**R_n is bonded to each of m bonds (denoted by the symbol *) present in a moiety derived from the isocyanate-reactive compound (b) (X is bonded to a bond of L). The "-X-R_n" moiety is bonded to a bond (denoted by the symbol *) present in the isocyanate-reactive compound (b) before a reaction. The isocyanate-reactive compound (b) may be one or a mixture of arbitrary two or more selected from the group consisting

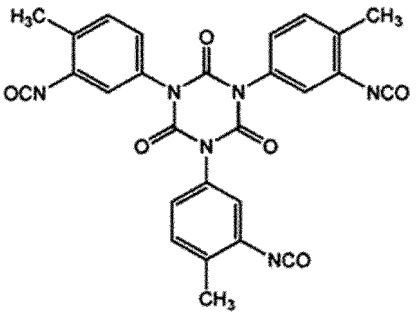
of the compounds represented by general formulae (2a), (2b) and (2c), and among these, the compound represented by the general formula (2a) is preferred.

[0155] The isocyanate group-containing compound (a) may be one or a mixture of arbitrary two or more selected from the group consisting of an isocyanate, a diisocyanates and a polyisocyanate. When the isocyanate group-containing compound (a) is a diisocyanate and/or a polyisocyanate, and the isocyanate-reactive compound (b) has a total of two or more -OH groups and/or -COOH groups, a reaction product obtained from them may be a polymer in some cases, but is not limited thereto.

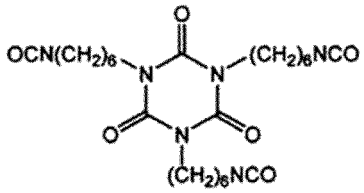
[0156] The isocyanate, diisocyanate, and polyisocyanate are each preferably one or more selected from the group consisting of compounds represented by the following formulae (3a) to (3h).



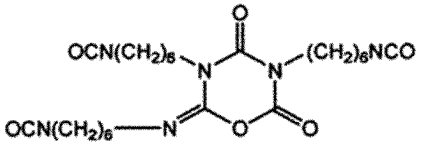
··· (3a)



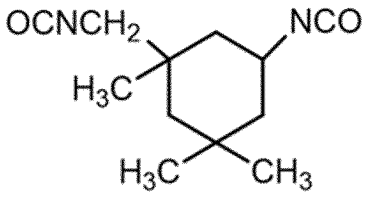
··· (3b)



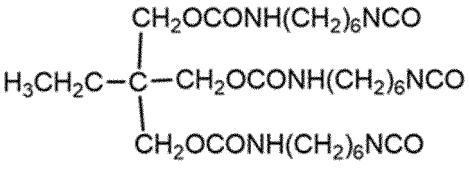
··· (3c)



··· (3d)



· · · (3e)



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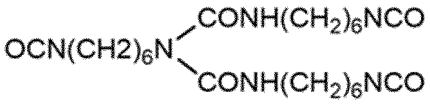
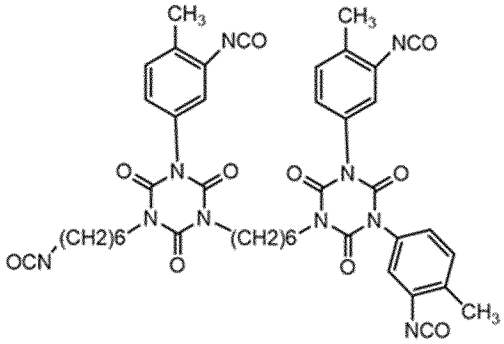


· · · (3g)



· · · (3h)

[0157] Examples of the isocyanate-based liquid-repellent compounds include, for example, those described in JP2022-33218A (WO 2016/049278), JP6987847B (WO 2018/031534), and WO 2021/251302.

[Polysiloxane Group-Containing Liquid-Repellent Compound]

[0158] The liquid-repellent compound may be a liquid-repellent compound having a polysiloxane group (polysiloxane group-containing liquid-repellent compound). The polysiloxane group can impart liquid repellency to a substrate, similar to the aliphatic hydrocarbon group (R) having 6 or more and 40 or less carbon atoms and optionally having a substituent, in the other liquid-repellent compounds described above.

[0159] The polysiloxane group may be represented by the following formula:

$$-[-Si(Rs^1)_2-O-]_a-$$

[wherein

Rs^1 is independently at each occurrence a hydrocarbon group or reactive group having 1 to 40 carbon atoms, and a is 5 or more and 10,000 or less.].

[0160] Rs^1 is a hydrocarbon group having 1 to 40 carbon atoms or a reactive group.

[0161] Examples of the hydrocarbon group having 1 to 40 carbon atoms include hydrocarbon groups having 1 to 5 carbon atoms such as a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group (particularly an aliphatic hydrocarbon group, particularly an alkyl group), and a hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent.

[0162] The hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent may be an aromatic hydrocarbon group or an aliphatic hydrocarbon group, preferably the aliphatic hydrocarbon group, and particularly preferably a saturated aliphatic hydrocarbon group (alkyl group). The hydrocarbon group may be cyclic, linear, or a branched chain, and is preferably linear. The number of carbon atoms in the hydrocarbon group may be 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, or 18 or more, and is preferably 10 or more and more preferably 12 or more. The number of carbon atoms in the hydrocarbon group may be 40 or less, 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, or 10 or less, and is preferably 30 or less and more preferably 25 or less. It is to be noted that the hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, used herein may correspond to R described above, the explanation is incorporated by the description of the above-described hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent.

[0163] Examples of the reactive groups are groups having functional groups (for example, a hydroxy group, an amino group, a mercapto group, an epoxy group, a carboxyl group, a halogen-substituted alkyl group, a vinyl group, a (meth) acrylate group, a (meth)acrylamide group, a hydrogen atom directly bonded to a silicon atom, and the like). These functional groups may be directly bonded to a silicon atom, or may be bonded to an organic group directly bonded to the silicon atom. The organic group may be a hydrocarbon group, for example, an alkylene group or a divalent aromatic group. The hydrocarbon group may have 2 or more and 12 or less carbon atoms, and the alkylene group preferably has 2 or more and 10 or less carbon atoms. The divalent aromatic group preferably has 6 or more and 12 or less carbon atoms.

[0164] a may be 5 or more, 10 or more, 30 or more, 50 or more, 100 or more, 500 or more, 1,000 or more, 2,000 or more,

or 3,000 or more. a may be 10,000 or less, 7,500 or less, 5,000 or less, 3,000 or less, 1,500 or less, 1,000 or less, 500 or less, 300 or less, 100 or less, or 50 or less.

[0165] The amount of the hydrocarbon group having 1 to 40 carbon atoms may be 20 mol% or more, 40 mol% or more, 60 mol% or more, or 80 mol% or more, based on the total Rs^1. The amount of the hydrocarbon group having 1 to 40 carbon atoms may be 100 mol% or less, 90 mol% or less, 80 mol% or less, or 70 mol% or less, based on the total Rs^1.

[0166] The amount of reactive group (for example, the amount of - OH, -COOH, or $-NR'_2$) may be 5 mol% or more, 10 mol% or more, 20 mol% or more, or 30 mol% or more, relative to the total of Rs^1. The amount of reactive group (for example, the amount of -OH, - COOH, or $-NR'_2$) may be 50 mol % or less, 40 mol % or less, 30 mol % or less, or 20 mol % or less, relative to the total Rs^1.

[0167] In the polysiloxane group-containing liquid-repellent compound, the polysiloxane group may be present in a main chain, mother nucleus, or side chain. For example, when a polysiloxane group is present in the side chain of the polysiloxane group-containing liquid-repellent compound, the polysiloxane-containing liquid-repellent compound may be a compound in which the aliphatic hydrocarbon group (R) having 6 or more and 40 or less carbon atoms and optionally having a substituent in the other liquid-repellent compounds described above (for example, the acrylic polymer type liquid-repellent compound, the base material-modified liquid-repellent compound, and the isocyanate-based liquid-repellent compound) is partially or totally replaced with a polysiloxane group.

[0168] The polysiloxane group may be present in the main chain or mother nucleus of the polysiloxane group-containing liquid-repellent compound.

[0169] The polysiloxane group-containing liquid-repellent compound may be free of a structure other than a polysiloxane, and the polysiloxane group-containing liquid-repellent compound may be represented by the following formula:

$$(Rs^2)_3Si\text{-}O\text{-}[\text{-}Si(Rs^1)_2\text{-}O\text{-}]_a\text{-}Si(Rs^2)_3$$

[wherein

Rs^1 and a are as described above,
Rs^2 is independently at each occurrence a hydrocarbon group having 1 to 40 carbon atoms, an alkoxy group having 1 to 40 carbon atoms, or a reactive group.].

[0170] The polysiloxane group may be present in the side chain of the polysiloxane group-containing liquid-repellent compound (for example, a side chain of an acrylic polymer type liquid-repellent compound). The side chain is a partial structure other than the main chain or mother nucleus of a compound, and may be, for example, an end structure. When the polysiloxane group is present in the side chain, the polysiloxane group may be represented by the following formula:

$$\text{-}[\text{-}Si(Rs^1)_2\text{-}O\text{-}]_a\text{-}Si(Rs^2)_3$$

[wherein

Rs^1 and a are as described above,
and Rs^2 is independently at each occurrence a hydrocarbon group having 1 to 40 carbon atoms, an alkoxy group having 1 to 40 carbon atoms, or a reactive group.].

[0171] Rs^2 may be a hydrocarbon group having 1 to 40 carbon atoms or an alkoxy group having 1 to 40 carbon atoms. The hydrocarbon group having 1 to 40 carbon atoms in Rs^2 is preferably an aliphatic hydrocarbon group, preferably an alkyl group, and preferably has 1 to 5 carbon atoms. The number or carbon atoms of the alkoxy group having 1 to 40 carbon atoms in Rs^2 is preferably 1 to 5, 1 to 3, or 1 or 2. When Rs^2 is a reactive group, examples of the reactive group may be the same as those of Rs^1.

[0172] The polysiloxane group-containing liquid-repellent compound can be synthesized by a conventionally known method. For example, the polysiloxane group-containing liquid-repellent compound having a hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, can be obtained by modifying SiH in methylhydrogensilicone or a copolymer of dimethylsiloxane and methylhydrogensiloxane with an α-olefin by a hydrosilylation reaction using a catalyst such as a compound such as platinum or palladium, if necessary. Also, the polysiloxane group-containing liquid-repellent compound may be obtained by polymerizing an acrylic monomer containing a polysiloxane group, or by allowing a reactive group of a polysiloxane to react with a mother nucleus compound.

[Amine Modified Product]

[0173] The liquid-repellent compound may be an amine modified product.

[0174] The molecular weight of the amine modified product may be 200 or more, 300 or more, 350 or more, 400 or more, 500 or more, 550 or more, or 750 or more. The molecular weight of the amine modified product may be 3,000 or less, 2,500 or less, 2,000 or less, 1,500 or less, 1,000 or less, 900 or less, 800 or less, 750 or less, or 500 or less.

[0175] The amine modified product in the present disclosure may be free of an active hydrogen-containing group. Examples of the active hydrogen-containing group include an amino group (an amino group not adjacent to a carbonyl group, for example, the primary or secondary amino group), a hydroxy group, and a carboxyl group. In particular, the amine modified product in the present disclosure may be free of the primary or secondary amino group that is not adjacent to a carbonyl group.

[0176] The amine modified product may be a compound having:

an amine backbone; and
one or more aliphatic hydrocarbon-containing groups represented by the following formula:

$$-X^N-R_n$$

[wherein
X^N is a direct bond or a 1+ n valent group,
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, and
n is an integer of 1 or more and 3 or less.],
wherein at least one of the aliphatic hydrocarbon-containing groups is bonded to a nitrogen atom of the amine backbone.

(Amine Backbone)

[0177] The amine modified product in the present disclosure has an amine backbone. The amine backbone has one or more amino groups with a predetermined number of bond (valence), which is obtained by removing the predetermined number of atom or atomic group (for example, hydrogen) from an amine compound. The amino group in the amine backbone refers to a group selected from the group consisting of $-NH_2$, -NH-, and $-N(-)_2$, and also includes an amino group adjacent to a carbonyl group contained in an amide group, a urethane group, a urea group, an imide group, or the like. It is to be noted that the amine backbone may be an aliphatic group or an aromatic group, having one or more amino groups, and does not exclude the presence of a heteroatom other than nitrogen.

[0178] The molecular weight of the amine backbone may be 30 or more, 50 or more, 100 or more, 200 or more, 300 or more, 400 or more, or 500 or more. The molecular weight of the amine backbone may be 2,800 or less, 2,500 or less, 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, 600 or less, 450 or less, 300 or less, or 250 or less.

[0179] The number of carbon atoms in the amine backbone may be 1 or more, 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, or 18 or more. The number of carbon atoms in the amine backbone may be 100 or less, 80 or less, 60 or less, 40 or less, 30 or less, 20 or less, 10 or less, or 5 or less, and is preferably 50 or less and particularly 30 or less.

[0180] The amine backbone has one or more amino groups. The amino group is a monovalent to trivalent amino group and is one or more groups selected from the group consisting of $-NH_2$, -NH-, and $-N(-)_2$. The number of amino group that the amine backbone has may be 1 or more, 2 or more, 3 or more, 4 or more, 5 or more, or 6 or more, and is preferably 2 or more. The number of amino group that the amine backbone has may be 12 or less, 10 or less, 8 or less, 6 or less, 4 or less, 3 or less, 2 or less, or 1.

[0181] The amine backbone has a hydrocarbon group (aliphatic hydrocarbon group or aromatic hydrocarbon group). The hydrocarbon group may be cyclic, a branched chain, or linear. The hydrocarbon group may be saturated or unsaturated (for example, saturated). Herein, the hydrocarbon group may be interrupted by an oxygen atom and/or a sulfur atom, or may be composed only of a carbon atom, a nitrogen atom, and a hydrogen atom. For example, the hydrocarbon group may also be a hydrocarbon group (for example, a chain saturated aliphatic hydrocarbon group or an aromatic hydrocarbon group having one or two hydrocarbon aromatic rings) optionally interrupted by an oxygen atom and/or a sulfur atom, or for example, a general hydrocarbon group (for example, a chain saturated aliphatic hydrocarbon group or an aromatic hydrocarbon group having one or two hydrocarbon aromatic rings). When the hydrocarbon group is interrupted by an oxygen atom and/or a sulfur atom, it will have a structure of an ether, thioether, polyether, or polythioether. The number of hydrocarbon group that the amine backbone has may be 1 or more, 2 or more, 3 or more, 4 or more, 5 or more, or 6 or more. The number of hydrocarbon group that the amine backbone has may be 12 or less, 10 or less, 8 or less, 6 or less, 4 or less, 3 or less, 2 or less, or 1.

[0182] The amine backbone may be composed of a monovalent to trivalent amino group and a chain saturated aliphatic hydrocarbon group or aromatic hydrocarbon group optionally interrupted by an oxygen atom and/or a sulfur atom.

[0183] A molar ratio of carbon atoms to nitrogen atoms (C/N ratio) in the amine backbone may be 1 or more, 2 or more, 2.5 or more, 3 or more, 3.5 or more, or 4 or more. The molar ratio of carbon atoms to nitrogen atoms (C/N ratio) in the amine backbone may be 8 or less, 7 or less, 6 or less, 5 or less, 4 or less, 3.5 or less, 3 or less, 2.5 or less, or 2 or less, and is preferably 6 or less or 4 or less.

· Raw Material Amine Compound

[0184] Examples of the raw material amine compound that is a precursor of the amine backbone include alkylamines such as methylamine, ethylamine, propylamine, butylamine, and dibutylamine; alkylenediamines such as ethylenediamine, propylenediamine, butylenediamine, pentanediamine, hexamethylenediamine, cyclohexanediamine, and methylenebiscyclohexylamine; polyalkylenepolyamines such as diethylenetriamine, triethylenetetramine, tris(2-aminoethyl) amine, tetraethylenepentamine, pentaethylenehexamine, dipropylenetriamine, tripropylenetetramine, tris(2-aminopropyl)amine, tetrapropylenepentamine, pentapropylenehexamine, iminobispropylamine, dibutylenetriamine, bis(2-aminoethoxy)ethane, bis(2-aminoethyl)ether, bis[2-(2-aminoethoxy)ethyl]ether, bis[2-(3-aminoprotoxy)ethyl] ether, spermine, and spermidine; oxygen- or sulfur-containing aliphatic amines such as 1-aminopropanediol, 2-amino-1,3-propanediol, 3-amino-1,2-propanediol, polyoxypropylenediamine, and polyoxyethylenediamine; aromatic monoamines such as aniline, 1-or 2-naphthylamine, 1-, 2-, or 9-aminoanthracene, 9-aminophenanthracene, and 2-, 3-, or 4-aminobiphenyl; monocyclic aromatic polyamines such as o-, m-, or p-phenylenediamine, o-, m-, or p-xylylenediamine, diaminotoluene, and 2,3-, 2,4-, or 2,5-tolylenediamine; polycyclic aromatic polyamines such as diaminobiphenyl, bisaminophenoxyphenylpropane, diaminodiphenyl ether, diaminodiphenyl sulfide, diaminodiphenyl sulfone, diaminobenzophenone, diaminodiphenylmethane, diaminophenylpropane, diaminophenylhexafluoropropane, diaminophenyl phenyl ethane,bisaminophenoxybenzene, bisaminobenzoylbenzene, bisaminodimethylbenzylbenzene, aminophenoxybiphenyl, aminophenoxyphenyl ketone, bisaminoditrifluoromethylbenzylbenzene, aminophenoxyphenyl sulfone, aminophenoxyphenyl ether, aminophenoxyphenyl propane, bis(aminophenoxybenzoyl)benzene, bis(aminophenoxy-α,a-dimethylbenzyl) benzene, bis[(aminoaryloxy)benzoyl]diphenyl ether, bis(amino-α,α-dimethylbenzylphenoxy)benzophenone, aminophenoxyphenyl sulfide, bis[amino-α,α-dimethylbenzylphenoxy]diphenyl sulfone, 4,4'-bis[aminophenoxyphenoxy]diphenyl sulfone, diaminodiaryloxybenzophenone, diaminoaryloxybenzophenone, 3,3'-dimethoxy-4,4'-diaminobiphenyl, 4,4'-diaminotriphenylmethane, 3,3'-dimethyl-4,4'-diaminobiphenyl, 4,4'-methylenebisaniline, 4,4'-oxydianiline, 1,3-bis(4-aminophenoxy)benzene, 4,4'-diaminodiphenyl ether, and 4,4'-bis(aminophenyl)amine; oxygen-or sulfur-containing polycyclic aromatic polyamines such as 2,2'-bis[4-(4-aminophenoxy)phenyl]propane, 1,3-bis(4-aminophenoxy)benzene, 1,3-bis(3-aminophenoxy)benzene, 3,4'-diaminodiphenyl ether, and 4,4'-diaminodiphenyl sulfide; and hydroxy group-containing polyamines such as 2-hydroxyethylethylenediamine, 2-hydroxyethylpropylenediamine, di-2-hydroxyethylethylenediamine, di-2-hydroxyethylpropylenediamine, 2-hydroxypropylethylenediamine, and di-2-hydroxypropylethylenediamine.

(Aliphatic Hydrocarbon-Containing Group)

[0185] The amine modified product in the present disclosure has one or more aliphatic hydrocarbon-containing groups represented by the following formula:

$$-X^N-R_n$$

[wherein

X^N is a direct bond or a 1+ n valent group,
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, and
n is an integer of 1 or more and 3 or less.].

[0186] The number of aliphatic hydrocarbon-containing group that the amine modified product has may be 1 or more, 2 or more, 3 or more, 4 or more, 5 or more, or 6 or more, and is preferably 2 or more. The number of aliphatic hydrocarbon-containing group in the amine modified product may be 12 or less, 10 or less, 8 or less, 6 or less, 4 or less, 3 or less, 2 or less, or 1.

[0187] At least one aliphatic hydrocarbon-containing group in the amine modified product is bonded to a nitrogen atom of the amine backbone. The proportion of the number of aliphatic hydrocarbon-containing groups bonded to the nitrogen atom of the amine backbone based on the number of all the aliphatic hydrocarbon-containing groups in the amine modified product may be 10% or more, 30% or more, 60% or more, 80% or more, or 100%. The proportion of the number of aliphatic hydrocarbon-containing groups bonded to the nitrogen atom of the amine backbone based on the number of all the aliphatic hydrocarbon-containing groups in the amine modified product may be 75% or less, 50% or less, or 25% or less.

The aliphatic hydrocarbon-containing group not bonded to a nitrogen atom of the amine backbone is bonded to other group (for example, a hydrocarbon group) of the amine backbone.

.X^N

[0188] X^N is a direct bond or a 1 + n valent group and preferably a 1 + n valent group. X^N functions as a linker connecting the amine backbone and n Rs.

[0189] n is the number of R bonded to X^N, and may be an integer of 1 or more and 3 or less. n may be 1 or more, 2 or more, or 3 or more. n may be 3 or less, 2 or less, or 1 or less, for example, 2 or less.

[0190] X^N may be an aliphatic group (unsaturated aliphatic group or saturated aliphatic group) or an aromatic group.

[0191] The molecular weight of X^N may be 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, 500 or more, or 750 or more. The molecular weight of X^N may be 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, 500 or less, or 300 or less.

[0192] X^N may have a carbonyl group. X^N may have one or more selected from the group consisting of an amide group, a urea group, a urethane group, and an imide, or X^N may form one or more selected from the group consisting of an amide group, a urea group, a urethane group, and an imide together with an amino group in the amine backbone. Examples of such an amide group, a urea group, a urethane group, and an imide include

-O-C(=O)-NR'-;

-NR'-C(=O)-;

-NR'-C(=O)-O-;

-NR'-C(=O)-NR'-;

-C(=O)-NR'-;

-C(=O)-NR'-C(=O)- [wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms.]. X^N is preferably bonded to a nitrogen atom in the amine backbone via a -(C=O)- group.

[0193] X^N may be a 1 + n valent group composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -C(=NR')-, -S-, $-S(=O)_2-$, -NR'-, -C(OR')R'-, $-C(OR')(-)_2$, $-N(-)_2$, a divalent to tetravalent aliphatic hydrocarbon group having 1 to 20 carbon atoms, a divalent to tetravalent hydrocarbon aromatic ring, and a divalent to tetravalent heterocyclic ring
[wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms.].

[0194] X^N may be a 1 + n valent group composed of one or more selected from the group consisting of

X^{N1} composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -C(=NR')-, -S-, $-S(=O)_2-$, -NR'-, -C(OR')R'-, $-C(OR')(-)_2$, and $-N(-)_2$ (wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms), and
X^{N2} composed of one or more selected from the group consisting of a divalent to tetravalent aliphatic hydrocarbon group having 1 to 20 carbon atoms, a divalent to tetravalent hydrocarbon aromatic ring, and a divalent to tetravalent heterocyclic ring. It is to be noted that the left hand side of the group described herein as X^N is bonded to an amine backbone and the right hand side of the group is bonded to R.

X^{N1}

[0195] X^{N1} is a non-hydrocarbon linker.

[0196] X^{N1} is a direct bond or a divalent or higher valent group. A valence of X^{N1} may be 2 to 4, 2 to 3, or 2. X^{N1} is not preferably a direct bond singly.

[0197] A molecular weight of X^{N1} may be 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, or 500 or more. A molecular weight of X^{N1} may be 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, or 500 or less.

[0198] X^{N1} is composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -C(=NR')-, -S-, $-S(=O)_2-$, -NR'-, -C(OR')R'-, $-C(OR')(-)_2$, and $-N(-)_2$ (wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms). Examples of X^{N1} include, for example,

a direct bond;

-O-;
-O-C(=O)-;
-O-C(=O)-O-;
-O-C(=O)-NR'-;
-NR'-;
-NR'-C(=O)-;
-NR'-C(=O)-O-;
-NR'-C(=O)-NR'-;
-C(=O)-;
-C(=O)-O-;
-C(=O)-NR'-;
-C(=O)-NR'-C(=O)-;
-C(=NR')-;
-S-;
$-SO_2-$;
$-SO_2NR'-$;
-C(OR')R'-;
$-C(OR')(-)_2$;
$-N(-)_2$;
[wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms.]. It is to be noted that when X^{N1} is bonded to a nitrogen atom of the amine backbone, the nitrogen atom is regarded as a moiety of the amine backbone (amino group).

X^{N2}

[0199] X^{N2} is a hydrocarbon or aromatic linker.

[0200] X^{N2} may be a hydrocarbon group or a non-hydrocarbon group (including a heteroatom). X^{N2} may be aliphatic or aromatic, and is preferably aliphatic. X^{N2} may be a linear, branched chain, or cyclic. X^{N2} is preferably a chain.

[0201] X^{N2} is a divalent or higher valent group. A valence of X^{N2} may be, for example, 2 to 4, 2 to 3, or 2.

[0202] The number of carbon atoms in X^{N2} may be 1 or more, 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, or 18 or **more.** The number of carbon atoms in X^{N2} may be 40 or less, 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, 10 or less, or 5 or **less.**

[0203] X^{N2} is composed of one or more selected from the group consisting of a divalent to tetravalent aliphatic hydrocarbon group having 1 to 20 carbon atoms, a divalent to tetravalent hydrocarbon aromatic ring, and a divalent to tetravalent heterocyclic **ring.**

[0204] The divalent to tetravalent aliphatic hydrocarbon group having 1 to 20 carbon atoms may be a cyclic, branched chain, or linear hydrocarbon group and is preferably a chain hydrocarbon group (particularly a linear hydrocarbon group). The divalent to tetravalent aliphatic hydrocarbon group having 1 to 20 carbon atoms may be a saturated or unsaturated (for example, saturated) aliphatic hydrocarbon group. The number of carbon atoms in the aliphatic hydrocarbon group having 1 to 20 carbon atoms may be 1 or more, 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, or 10 or more. The number of carbon atoms in the aliphatic hydrocarbon group having 1 to 20 carbon atoms may be 15 or less, 10 or less, or 5 or **less.**

[0205] Examples of the divalent to tetravalent hydrocarbon aromatic ring include groups obtained by removing 2 to 4 hydrogen atoms from hydrocarbon aromatic rings such as benzene, naphthalene, anthracene, phenanthrene, tetracene (naphthacene), pentacene, pyrene, and coronene. The number of ring constituting atom of the hydrocarbon aromatic ring is 3 to 20, 4 to 16, or 5 to 12 and preferably 5 to 12. The hydrocarbon aromatic ring may have a substituent, and examples thereof include an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, $-N(R')_2$ (wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms), a hydroxyl group, a carboxyl group, or a halogen atom. A valence of the hydrocarbon aromatic ring may be 2 or more, 3 or more, or 4, and may be 4 or less, 3 or less, or 2.

[0206] The divalent to tetravalent heterocyclic ring may be an aliphatic group or an aromatic group. Examples of the divalent to tetravalent heterocyclic rings include groups obtained by removing 2 to 4 hydrogen atoms from pyridine, pyrazine, pyrimidine, pyridazine, triazine, quinoline, isoquinoline, quinazoline, cinnoline, phthalazine, quinoxaline, pyrrole, indole, furan, benzofuran, thiophene, benzothiophene, pyrazole, imidazole, benzimidazole, triazole, oxazole, benzoxazole, thiazole, benzothiazole, isothiazole, benzisothiazole, pyrrolidine, piperidine, piperazine, imidazolidine, thiazoline, and the like. The number of ring constituting atom of the heterocyclic ring is 3 to 20, 4 to 16, or 5 to 12 and preferably 5 to 12. The heterocyclic ring may have a substituent, and examples thereof include an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, $-N(R')_2$ (wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms), a hydroxyl group, a carboxyl group, a halogen atom, or the like. A valence of the heterocyclic ring may be 2 or more, 3 or more, or 4, and may be 4 or less, 3 or less, or 2.

[0207] Examples of X^{N2} include, for example,

- Ali-
- Cy-
- $Ali(-)_2$
- $Cy(-)_2$
- Ali-Cy-
- Cy-Ali-
- Cy-Ali-Cy-
- Ali-Cy-Ali-

[wherein Ali is an aliphatic hydrocarbon group having 1 to 20 carbon atoms, and Cy is a hydrocarbon aromatic ring or a heterocyclic ring.].

[0208] Specific examples of X^{N2} include, for example,

$-(CH_2)_p-$ wherein p is 1 to 20, for example 1 to 10;
a linear hydrocarbon group having 1 to 40 carbon atoms, for example 1 to 10 unsaturated bonds;
a hydrocarbon group with a branched structure, having 1 to 40 carbon atoms, for example 1 to 10 carbon atoms;
$-(CH_2)_q$-Cy-$(CH_2)_r-$ wherein q and r are each independently 0 to 20, for example 1 to 10, and Cy is a hydrocarbon aromatic ring or a heterocyclic ring.

Example of X^N

[0209] Examples of X^N will be described. It is to be noted that in the following, R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms.

[0210] Examples of X^N include, in the case of X^N being divalent, for example, $-X^{N1}-$, $-X^{N1}-X^{N2}-$, $-X^{N1}-X^{N2}-X^{N1}-$, $-X^{N1}-X^{N2}-X^{N1}-X^{N2}-$, $-X^{N2}-$, $-X^{N2}-X^{N1}-$, $-X^{N2}-X^{N1}-X^{N2}-$, and $-X^{N2}-X^{N1}-X^{N2}-X^{N1}-$.

[0211] Examples of X^N include, in the case of X^N being trivalent, for example, $-X^{N1}(-)_2$, $-X^{N1}-X^{N2}(-)_2$, $-X^{N1}-(X^{N2}-)_2$, $-X^{N1}-X^{N2}-X^{N1}(-)_2$, $-X^{N1}-X^{N2}(-X^{N1}-)_2$, $-X^{N1}-(X^{N2}-X^{N1}-)_2$, $-X^{N1}-X^{N2}-X^{N1}-X^{N2}(-)_2$, $-X^{N1}-X^{N2}-X^{N1}-X^{N2}-)_2$, $-X^{N1}-X^{N2}-(X^{N1}-X^{N2}-)_2$, and $-X^{N1}-(X^{N2}-X^{N1}-X^{N2}-)_2$; $-X^{N2}(-)_2$, $-X^{N2}-X^{N1}(-)_2$, $-X^{N2}-(X^{N1}-)_2$, $-X^{N2}-X^{N1}-X^{N2}(-)_2$, $-X^{N2}-X^{N1}(-X^{N2}-)_2$, $-X^{N2}-(X^{N1}-X^{N2}-)_2$, $-X^{N2}-X^{N1}-X^{N2}-X^{N1}(-)_2$, $-X^{N2}-X^{N1}-X^{N2}(X^{N1}-)_2$, $-X^{N2}-X^{N1}-(X^{N2}-X^{N1}-)_2$, and $-X^{N2}-(X^{N1}-X^{N2}-X^{N1}-)_2$.

[0212] Examples of X^N include, in the case of X^N being tetravalent, for example, $-X^{N1}(-)_3$, $-X^{N1}-X^{N2}(-)_3$, $-X^{N1}-(X^{N2}-)_3$, $-X^{N1}-X^{N2}-X^{N1}(-)_3$, $-X^{N1}-X^{N2}(-X^{N1}-)_3$, $-X^{N1}-(X^{N2}-X^{N1}-)_3$, $-X^{N1}-X^{N2}-X^{N1}-X^{N2}(-)_3$, $-X^{N1}-X^{N2}-X^{N1}-(X^{N2}-)_3$, $-X^{N1}-X^{N2}-(X^{N1}-X^{N2}-)_3$, and $-X^{N1}-(X^{N2}-X^{N1}-X^{N2}-)_3$; $-X^{N2}(-)_3$, $-X^{N2}-X^{N1}(-)_3$, $-X^{N2}-(X^{N1}-)_3$, $-X^{N2}-X^{N1}-X^{N2}(-)_3$, $-X^{N2}-X^{N1}(-X^{N2}-)_3$, $-X^{N2}-(X^{N1}-X^{N2}-)_3$, $-X^{N2}-X^{N1}-X^{N2}-X^{N1}(-)_3$, $-X^{N2}-X^{N1}-X^{N2}-(X^{N1}-)_3$, $-X^{N2}-X^{N1}-(X^{N2}-X^{N1}-)_3$, and $-X^{N2}-(X^{N1}-X^{N2}-X^{N1}-)_3$.

[0213] Preferred examples of X^N include, for example, $-X^{N1}-$, $-X^{N1}-X^{N2}-$, $-X^{N1}-X^{N2}-X^{N1}-$, $-X^{N1}-X^{N2}(-)_2$, $-X^{N2}-$, $-X^{N2}-X^{N1}-$, $-X^{N2}-X^{N1}-X^{N2}-$ and $-X^{N2}-X^{N1}(-)_2$. In the amine modified product, it is preferred that one or more X^N are each a -(C=O)- group at an end on the amine backbone side and is bonded to a nitrogen atom in the amine backbone.

[0214] X^N is preferably a group represented by

$-X^{N1}-$, $-X^{N1}-X^{N2}-$, $-X^{N1}-X^{N2}-X^{N1}-$, $-X^{N1}-X^{N2}(-)_2$,

$-X^{N2}-$, $-X^{N2}-X^{N1}-$, $-X^{N2}-X^{N1}-X^{N2}-$, or $-X^{N2}-X^{N1}(-)_2$

[wherein

X^{N1} is independently at each occurrence
a direct bond;
-O-;
-O-C(=O)-;
-O-C(=O)-O-;
-O-C(=O)-NR'-;
-NR'-;
$-NR^{I}$-C(=O)-;
-NR'-C(=O)-O-;
-NR'-C(=O)-NR'-;

-C(=O)-;
-C(=O)-O-; or
-C(=O)-NR'-;
-C(=O)-NR'-C(=O)-
(wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms), and X^{N2} is a divalent to tetravalent aliphatic hydrocarbon group having 1 to 10 carbon atoms, or a divalent aromatic group (for example, a divalent phenyl group and a divalent triazole group).]. This can impart favorable liquid repellency to a substrate.

[0215] Further specific examples of X^N include, for example,

*-(C=O)-

-O-(C=O)-NR'-

[wherein * means bonding to a nitrogen atom of the amine backbone, and
R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms.].

· R

[0216] R is an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent. R is a branched chain or a linear chain and is more preferably linear. R may be saturated or unsaturated. R is preferably a saturated aliphatic hydrocarbon group (alkyl group).

[0217] The number of carbon atoms of R may be 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, or 18 or more, and is preferably 10 or more and more preferably 12 or more. The number of carbon atoms of R may be 40 or less, 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, or 10 or less, and is preferably 30 or less and more preferably 25 or less.

[0218] The hydrocarbon group may have a substituent, but is preferably unsubstituted. Examples of the substituents include, for example, -OR', $-N(R')_2$, -COOR', and a halogen atom (wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms). The substituent may have or be free of active hydrogen. The number of substituent may be 6 or less, 5 or less, 4 or less, 3 or less, 2 or less, 1 or less, or 0. In a hydrocarbon group having a substituent, the amount of carbon atoms relative to the amount of carbon atoms and heteroatoms may be 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and is preferably 75 mol% or more. In the hydrocarbon group having a substituent, the amount of carbon atoms relative to the amount of carbon atoms and heteroatoms may be 95 mol% or less, 90 mol% or less, 85 mol% or less, or 80 mol% or less. For example, the hydrocarbon group may have 1 to 3 (for example, 1) -OR' (particularly -OH) as substituents (for example, other than an end) .

(Examples of Amine Modified Product)

· Amine Modified Product Example 1

[0219] Examples of the amine modified product include a compound (amine modified product example 1) represented by the following formula:

$$N(-X^N-R_n)_p(-H)_q-L^1-[N(-X^N-R_n)_r(-H)_s-L^1-]_t-N(-X^N-R_n)_p(-H)_q$$

[wherein

X^N is independently at each occurrence a direct bond or a 1 + n valent group;
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent;
L^1 is independently at each occurrence a divalent aliphatic hydrocarbon group having 2 to 20 carbon atoms or aromatic hydrocarbon group optionally interrupted by an oxygen atom and/or a sulfur atom;
n is independently at each occurrence an integer of 1 or more and 3 or less;
p is independently at each occurrence an integer of 0 or more and 2 or less;
q is independently at each occurrence an integer of 0 or more and 2 or less;
p + q is 2 in each $N(-X^N-R_n)_p(-H)_q$;

r is independently at each occurrence 0 or 1;
s is independently at each occurrence 0 or 1;
r + s is 1 in each $N(-X^N-R_n)_r(-H)_s$;
the sum of all p and all r is 1 or more; and
t is an integer of 0 or more and 10 or less.].

[0220] In amine modified product example 1, the details of X^N, R, and n are incorporated by the above described.

[0221] In the amine modified product example 1, L^1 is a divalent aliphatic hydrocarbon group having 2 to 20 carbon atoms or an aromatic hydrocarbon group, optionally interrupted by an oxygen atom and/or a sulfur atom, and may be a cyclic, branched chain, or linear hydrocarbon group, and is preferably a chain hydrocarbon group or an aromatic hydrocarbon. L^1 may incorporate the hydrocarbon group described in [Amine Backbone] for use, wherein the hydrocarbon group may be interrupted by an oxygen atom and/or a sulfur atom, or L^1 may be composed only of a carbon atom, a nitrogen atom, and a hydrogen atom. L^1 may be, for example, a saturated or unsaturated (for example, saturated) aliphatic hydrocarbon group or an aromatic hydrocarbon group having 1 to 2 hydrocarbon aromatic rings. L^1 is preferably a cyclic group having both a ring (for example, an aromatic ring) and a chain structure (for example, a linear structure, ether oxygen, or thioether sulfur), and specific examples of L^1 include, for example, a 1,3-phenylenebisalkylene group, a 1,4-phenylenebisalkylene group, a diphenyletherdiyl group, and a diphenylthioetherdiyl group. The number of carbon atoms in L^1 may be 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, 10 or more, or 12 or more. The number of carbon atoms in L^1 may be 20 or less, 18 or less, 16 or less, 14 or less, 12 or less, 10 or less, 8 or less, 6 or less, 4 or less, or 3 or less.

[0222] In the amine modified product example 1, p is independently at each occurrence an integer of 0 or more and 2 or less, q is independently at each occurrence an integer of 0 or more and 2 or less, and p + q is 2 in each $N(-X^N-R_n)_p(-H)_q$. Preferably, p may be independently at each occurrence 1 or more, and for example, it is 2.

[0223] In the amine modified product example 1, r is independently at each occurrence 0 or 1, s is independently at each occurrence 0 or 1, and r + s is 1 in each $N(-X^N-R_n)_r(-H)_s$. Preferably, p may be independently at each occurrence 1 or more, and for example, it is 2.

[0224] The sum of all p and all r is 1 or more, i.e., the amine modified product example 1 has one or more $-X^N-R_n$. The sum of all p and all r may be 1 or more, 3 or more, 5 or more, 7 or more, 9 or more, or 12 or more (the sum of all q and all s may be 0). The sum of all p and all r may be 14 or less, 12 or less, 10 or less, 8 or less, 6 or less, or 4 or less.

[0225] In the amine modified product example 1, t is an integer of 0 or more and 10 or less. t may be 0 or more, 1 or more, 2 or more, 4 or more, or 6 or more, and is preferably 0 or more or 2 or more. t may be 8 or less, 6 or less, 4 or less, or 3 or less.

· Amine modified product example 2

[0226] Examples of another amine modified product include a compound (amine modified product example 2) represented by the following formula:

$$N(-X^N-R_n)_p(-H)_q-L^2(-X^N-R_n)_u$$

[wherein

X^N is independently at each occurrence a direct bond or a 1 + n valent group;
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent;
L^2 is a 1+ u valent aliphatic hydrocarbon group having 2 to 20 carbon atoms or aromatic hydrocarbon group optionally interrupted by an oxygen atom and/or a sulfur atom;
n is independently at each occurrence an integer of 1 or more and 3 or less;
p is an integer of 0 or more and 2 or less;
q is an integer of 0 or more and 2 or less;
p + q is 2;
u is an integer of 1 or more and 3 or less; and
the sum of p and u is 1 or more.

[0227] In the amine modified product example 2, the details of X^N, R, and n are incorporated by the above described.

[0228] In the amine modified product example 2, L^2 is a 1 + u valent aliphatic hydrocarbon group having 2 to 20 carbon atoms or an aromatic hydrocarbon group, optionally interrupted by an oxygen atom and/or a sulfur atom, and may be a cyclic, branched chain, or linear hydrocarbon group, and is preferably a chain hydrocarbon group or an aromatic hydrocarbon. L^2 may incorporate the hydrocarbon group described in [Amine Backbone] for use, wherein the hydrocarbon group may be interrupted by an oxygen atom and/or a sulfur atom, and L^2 may be composed only of a carbon atom, a

nitrogen atom, and a hydrogen atom. L^2 may be, for example, a saturated or unsaturated (for example, saturated) aliphatic hydrocarbon group or an aromatic hydrocarbon group having 1 to 2 hydrocarbon aromatic rings. L^2 is preferably a cyclic group having both a ring (for example, an aromatic ring) and a chain structure (for example, a linear structure, ether oxygen, or thioether sulfur), and specific examples of L^2 include, for example, a 1,3-phenylenebisalkylene group, a 1,4-phenylenebisalkylene group, a diphenyletherdiyl group, and a diphenylthioetherdiyl group. The number of carbon atoms in L^2 may be 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, 10 or more, or 12 or more. The number of carbon atoms in L^2 may be 20 or less, 18 or less, 16 or less, 14 or less, 12 or less, 10 or less, 8 or less, 6 or less, 4 or less, or 3 or less.

[0229] In the amine modified product example 2, p is an integer of 0 or more and 2 or less, q is an integer of 0 or more and 2 or less, and p + q is 2. Preferably, p may be 1 or more, and for example it is 2.

[0230] In the amine modified product example 2, u is an integer of 1 or more and 3 or less. u is 1, 2, or 3, for example, 2 or 3.

[0231] In the amine modified product example 2, the sum of p and u is 1 or more, i.e., the amine modified product example 2 has one or more $-X^N-R_n$. The sum of all p and u may be 1 or more, 2 or more, 3 or more, 4 or more, or 5 or more (the sum of all q may be 0). The sum of p and u may be 5 or less, 4 or less, 3 or less, or 2 or less.

[0232] The amine modified product may also be synthetic wax derived from animal or vegetable oil and fat. The synthetic wax may be obtained by condensing a fatty acid derived from animal or vegetable oil and fat and an aliphatic amine or an amine containing an aromatic group. Examples of the synthetic waxes include aliphatic fatty acid amide compounds such as a hydroxy fatty acid amide compound, a palmitic acid amide compound, an octadecanoic acid amide compound, a stearic acid amide compound, an arachidic acid amide compound, a behenic acid amide compound, a lignoceric acid amide compound, an oleic acid amide compound, a linoleic acid amide compound, an α-linolenic acid amide compound, a γ-linolenic acid amide compound, an arachidonic acid amide compound, an icosapentaenoic acid amide compound, and a docosahexaenoic acid amide compound.

(Method for Producing Amine Modified Product)

[0233] The method for producing the amine modified product is not limited, but examples thereof include, for example, a method for reacting various amines with a R group-containing carboxylic acid in the presence of a condensing agent, if necessary to synthesize the amine modified products; and a method for reacting various amines with a R group-containing acid chloride of carboxylic acid, acid anhydride, isocyanate, or the like, to synthesize the amine modified products. The condensing agent may be known condensing agents such as DCC, EDCI, CDI, BOP, COMU, DMT-MM, DPPA, and Py-Bop.

[Amount of Liquid-Repellent Compound]

[0234] The amount of the liquid-repellent compound may be, in a treatment agent, 0.01% by weight or more, 0.5% by weight or more, 1% by weight or more, 3% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, or 30% by weight or more. The amount of the liquid-repellent compound may be, in the treatment agent, 60% by weight or less, 50% by weight or less, 40% by weight or less, 30% by weight or less, 20% by weight or less, 10% by weight or less, 5% by weight or less, or 3% by weight or less.

{Supercritical Carbon Dioxide}

[0235] The repellent in the present disclosure may contain supercritical carbon dioxide. Supercritical carbon dioxide refers to carbon dioxide that is placed under temperature and pressure that exceed the critical temperature (31.1°C) and critical pressure (7.38 MPa). The supercritical carbon dioxide in the repellent functions as a treatment medium, and a repellent containing supercritical carbon dioxide is used as a treatment agent for treating a fiber substrate. Supercritical carbon dioxide is in a fluid state that cannot be said to belong to either a gas phase or a liquid phase, and has excellent solubility for various components and flowability of facilitating penetration into details of textile products, making it possible for the repellent (treatment agent) in the present disclosure to effectively impart liquid repellency to textile products.

{Liquid Medium}

[0236] The repellent in the present disclosure may contain a liquid medium. The liquid medium may be water, an organic solvent, or a mixture of water and an organic solvent. Since the repellent in the present disclosure uses supercritical carbon dioxide as a treatment medium, the amount of liquid medium in the repellent may be small, or the repellent may be free of a liquid medium.

[0237] Examples of the organic solvents include esters (for example, esters having 2 to 40 carbon atoms, specifically ethyl acetate and butyl acetate), ketones (for example, ketones having 2 to 40 carbon atoms, specifically methyl ethyl

ketone and diisobutyl ketone), alcohols (for example, alcohols having 1 to 40 carbon atoms, specifically isopropyl alcohol), aromatic solvents (for example, toluene and xylene), petroleum-based solvents (for example, alkanes having 5 to 10 carbon atoms, specifically, naphtha and kerosene). The organic solvent is preferably a water-soluble organic solvent. The water-soluble organic solvent may contain compounds having at least one hydroxy group (for example, an alcohol, a polyhydric alcohol such as a glycol-based solvent, and an ether form (for example, a monoether form) of polyhydric alcohol). These may be used singly or in combination of two or more thereof.

[Amount of Liquid Medium]

[0238] The amount of liquid medium may be 0.1 parts by weight or more, 0.5 parts by weight or more, 1 part by weight or more, 3 parts by weight or more, 5 parts by weight or more, 10 parts by weight or more, 20 parts by weight or more, 30 parts by weight or more, 40 parts by weight or more, or 50 parts by weight or more, relative to 1 part by weight (or 10 parts by weight, or 100 parts by weight) of the liquid-repellent compound. The amount of liquid medium may be 200 parts by weight or less, 175 parts by weight or less, 150 parts by weight or less, 125 parts by weight or less, 100 parts by weight or less, 80 parts by weight or less, 60 parts by weight or less, 40 parts by weight or less, 20 parts by weight or less, 10 parts by weight or less, 5 parts by weight or less, 3 parts by weight or less, 1 part by weight or less, 0.5 parts by weight or less, 0.1 parts by weight or less, or 0, and is preferably 40 parts by weight or less and more preferably 10 parts by weight or less, relative to 1 part by weight (or 10 parts by weight, or 100 parts by weight) of the liquid-repellent compound.

[0239] The amount of the liquid medium in the treatment agent may be 0.000001 mol/L or more, 0.000003 mol/L or more, 0.000005 mol/L or more, or 0.00001 mol/L or more. The amount of the liquid medium in the treatment agent may be 0.001 mol/L or less, 0.0005 mol/L or less, 0.0001 mol/L or less, 0.00005 mol/L or less, 0.00001 mol/L or less, or 0, and is preferably 0.0001 mol/L or less.

[0240] The amount of water may be 0.1 parts by weight or more, 0.5 parts by weight or more, 1 part by weight or more, 3 parts by weight or more, 5 parts by weight or more, 10 parts by weight or more, 20 parts by weight or more, 30 parts by weight or more, 40 parts by weight or more, or 50 parts by weight or more, relative to 1 part by weight (or 10 parts by weight, or 100 parts by weight) of the liquid-repellent compound. The amount of organic solvent may be 200 parts by weight or less, 175 parts by weight or less, 150 parts by weight or less, 125 parts by weight or less, 100 parts by weight or less, 80 parts by weight or less, 60 parts by weight or less, 40 parts by weight or less, 20 parts by weight or less, 10 parts by weight or less, 5 parts by weight or less, 3 parts by weight or less, 1 part by weight or less, 0.5 parts by weight or less, **0.1** parts by weight or less, or 0, and is preferably 40 parts by weight or less and more preferably 10 parts by weight or less, based on 1 part by weight (or 10 parts by weight, or 100 parts by weight) of the liquid-repellent compound.

[0241] The amount of water in a treatment agent may be 0.000001 mol/L or more, 0.000003 mol/L or more, 0.000005 mol/L or more, or 0.00001 mol/L or more. The amount of water in the treatment agent may be 0.001 mol/L or less, 0.0005 mol/L or less, 0.0001 mol/L or less, 0.00005 mol/L or less, 0.00001 mol/L or less, or 0, and is preferably 0.0001 mol/L or less.

[0242] The amount of organic solvent may be 1 part by weight or more, 3 parts by weight or more, 5 parts by weight or more, 10 parts by weight or more, 20 parts by weight or more, 30 parts by weight or more, 40 parts by weight or more, or 50 parts by weight or more, based on 1 part by weight (or 10 parts by weight, or 100 parts by weight) of the liquid-repellent compound. The amount of organic solvent may be 200 parts by weight or less, 175 parts by weight or less, 150 parts by weight or less, 125 parts by weight or less, 100 parts by weight or less, 80 parts by weight or less, 60 parts by weight or less, 40 parts by weight or less, 20 parts by weight or less, 10 parts by weight or less, 5 parts by weight or less, 3 parts by weight or less, or 0, and is preferably 40 parts by weight or less and more preferably 10 parts by weight or less, based on 1 part by weight (or 10 parts by weight, or 100 parts by weight) of the liquid- repellent compound.

[0243] The amount of organic solvent in a treatment agent may be 0.000001 mol/L or more, 0.000003 mol/L or more, 0.000005 mol/L or more, or 0.00001 mol/L or more. The amount of organic solvent in the treatment agent may be 0.001 mol/L or less, 0.0005 mol/L or less, 0.0001 mol/L or less, 0.00005 mol/L or less, 0.00001 mol/L or less, or 0, and is preferably 0.0001 mol/L or less.

{Surfactant}

[0244] The repellent may contain a surfactant. The surfactant may contain one or more surfactants selected from a nonionic surfactant, a cationic surfactant, an anionic surfactant, and an amphoteric surfactant. Since the repellent in the present disclosure uses supercritical carbon dioxide as a treatment medium, components can be effectively dispersed, so that the amount of surfactant in the repellent may be small, or the repellent may be free of a surfactant.

[Nonionic Surfactant]

[0245] Examples of the nonionic surfactants include an ether, an ester, an ester ether, an alkanolamide, a polyhydric

alcohol and an amine oxide.

[0246] The ether is, for example, a compound having an oxyalkylene group (preferably a polyoxyethylene group).

[0247] The ester is, for example, an ester of an alcohol and a fatty acid. The alcohol is, for example, an alcohol which is monohydric to hexahydric (particularly dihydric to pentahydric) and has 1 to 50 carbon atoms (particularly 10 to 30 carbon atoms) (for example, an aliphatic alcohol). Examples of the fatty acids are saturated or unsaturated fatty acids having 2 to 50 carbon atoms, particularly 5 to 30 carbon atoms.

[0248] The ester ether is, for example, a compound in which an alkylene oxide (particularly ethylene oxide) is added to an ester of an alcohol and a fatty acid. The alcohol is, for example, an alcohol which is monohydric to hexahydric (particularly dihydric to pentahydric) and has 1 to 50 carbon atoms (particularly 3 to 30 carbon atoms) (for example, an aliphatic alcohol). Examples of the fatty acids are saturated or unsaturated fatty acids having 2 to 50 carbon atoms, particularly 5 to 30 carbon atoms.

[0249] The alkanolamide is formed of for example, a fatty acid and an alkanolamine. The alkanolamide may be a monoalkanolamide or a dialkanolamide. Examples of the fatty acids are saturated or unsaturated fatty acids having 2 to 50 carbon atoms, particularly 5 to 30 carbon atoms. The alkanolamine may be an alkanol with 1 to 3 amino groups and 1 to 5 hydroxyl groups, having 2 to 50, particularly 5 to 30 carbon atoms.

[0250] The polyhydric alcohol may be, for example, a dihydric to pentahydric alcohol having 10 to 30 carbon atoms.

[0251] The amine oxide may be an oxide (for example, having 5 to 50 carbon atoms) of an amine (secondary amine or preferably tertiary amine).

[0252] The nonionic surfactant is preferably a nonionic surfactant having an oxyalkylene group (preferably a polyoxyethylene group). The alkylene group in the oxyalkylene group preferably has 2 to 10 carbon atoms. The number of oxyalkylene groups in the molecule of the nonionic surfactant is generally preferably 2 to 100.

[0253] The nonionic surfactant is selected from the group consisting of an ether, an ester, an ester ether, an alkanolamide, a polyhydric alcohol, or an amine oxide, and is preferably a nonionic surfactant having an oxyalkylene group.

[0254] The nonionic surfactant may be, for example, an alkylene oxide adduct of a linear and/or branched aliphatic (saturated and/or unsaturated) group, a polyalkylene glycol ester of a linear and/or branched fatty acid (saturated and/or unsaturated), a polyoxyethylene (POE)/polyoxypropylene (POP) copolymer (random copolymer or block copolymer), an alkylene oxide adduct of acetylene glycol. Among them, the nonionic surfactant is preferably a surfactant such that the structures of the alkylene oxide addition moiety and polyalkylene glycol moiety are polyoxyethylene (POE) or polyoxypropylene (POP) or POE/POP copolymer (which may be a random copolymer or block copolymer, for example.).

[0255] The nonionic surfactants preferably has a structure free of an aromatic group due to environmental issues (biodegradability, environmental hormones, and the like).

[0256] The nonionic surfactant may be a compound represented by the formula:

$$R^1O\text{-}(CH_2CH_2O)_p\text{-}(R^2O)_q\text{-}R^3$$

[wherein R^1 is an alkyl group having 1 to 22 carbon atoms, an alkenyl group or an acyl group, having 2 to 22 carbon atoms,
R^2 is each independently the same or different and is an alkylene group having 3 or more carbon atoms (for example, 3 to 10),
R^3 is a hydrogen atom, an alkyl group having 1 to 22 carbon atoms, or an alkenyl group having 2 to 22 carbon atoms,
p is a numeral of 2 or more,
q is 0 or a numeral of 1 or more.].

[0257] R^1 preferably has 8 to 20 carbon atoms, particularly 10 to 18 carbon atoms. Preferred specific examples of R^1 include a lauryl group, a tridecyl group, and an oleyl group.

[0258] R^2 is, for example, a propylene group and a butylene group.

[0259] In the nonionic surfactant, for example, p may be a numeral of 3 or more (for example, 5 to 200) and q may be a numeral of 2 or more (for example, 5 to 200). Namely, $-(R^2O)_q-$ may form, for example, a polyoxyalkylene chain.

[0260] The nonionic surfactant may be, for example, a polyoxyethylene alkylene alkyl ether comprising a hydrophilic polyoxyethylene chain and a hydrophobic oxyalkylene chain (particularly a polyoxyalkylene chain) in the center. The hydrophobic oxyalkylene chain includes, for example, an oxypropylene chain, an oxybutylene chain, and a styrene chain. The oxypropylene chain is preferred among them.

[0261] Specific examples of the nonionic surfactants include a condensation product of ethylene oxide with hexylphenol, isooctatylphenol, hexadecanol, oleic acid, an alkane (C_{12} - C_{16}) thiol, a sorbitan mono fatty acid (C_7 - C_{19}), an alkyl (C_{12} -C_{18}) amine, or the like.

[0262] The proportion of the polyoxyethylene block can be 5 to 80% by weight, for example, 30 to 75% by weight, particularly 40 to 70% by weight, based on a molecular weight of the nonionic surfactant (copolymer).

[0263] The average molecular weight of the nonionic surfactant is generally 300 to 5,000, for example, 500 to 3,000.

[0264] The nonionic surfactant may be a mixture of a compound with an HLB (hydrophilic-hydrophobic balance) of less than 15 (particularly 5 or less) and a compound with an HLB of 15 or more. An example of a compound with an HLB of less than 15 is a sorbitan fatty acid ester. An example of a compound with an HLB of 15 or more is a polyoxyethylene alkyl ether. A weight ratio of the compound with an HLB of less than 15 to the compound with an HLB of 15 or more may be 90: 10 to 20: 80, for example, 85: 15 to 55: 45.

[0265] For example, the nonionic surfactant may be used singly or in admixture of two or more.

[Cationic Surfactant]

[0266] The cationic surfactant is preferably a compound free of an amide group.

[0267] The cationic surfactant may be an amine salt, quaternary ammonium salt, or oxyethylene-added ammonium salt. Specific examples of the cationic surfactants are not limited, but include amine salt-type surfactants such as an alkylamine salt, aminoalcohol fatty acid derivative, polyamine fatty acid derivative, and imidazoline; quaternary ammonium salt-type surfactants such as an alkyltrimethylammonium salt, dialkyldimethylammonium salt, alkyldimethylbenzylammonium salt, pyridinium salt, alkylisoquinolinium salt, benzalkonium chloride, and benzethonium chloride.

[0268] Preferred examples of the cationic surfactant are a compound represented by the formula:

$$R^{21}\text{-}N^{+}(\text{-}R^{22})(\text{-}R^{23})(\text{-}R^{24})X^{-}$$

[wherein R^{21}, R^{22}, R^{23}, R^{24} are each a hydrocarbon group having 1 to 40 carbon atoms, and
X is an anionic group.].

[0269] Specific examples of R^{21}, R^{22}, R^{23}, R^{24} are alkyl groups (for example, a methyl group, a butyl group, a stearyl group, and a palmityl group). Specific examples of X are halogen (for example, chlorine) and acids (hydrochloric acid and acetic acid).

[0270] The cationic surfactant is particularly preferably a monoalkyltrimethylammonium salt (with an alkyl having 4 to 40 carbon atoms).

[0271] The cationic surfactant is preferably an ammonium salt. The cationic surfactant may be, for example, an ammonium salt represented by the formula:

$$R^{1}{}_{p}\text{-}N^{+}R^{2}{}_{q}X^{-}$$

[wherein R^1 is a C12 or more (for example C_{12} to C_{50}) linear and/or branched aliphatic (saturated and/or unsaturated) group,
R^2 is H or a C1 to C4 alkyl group, a benzyl group, a polyoxyethylene group (the number of oxyethylene group is, for example, 1 (particularly 2, especially 3) to 50),
and is particularly preferably CH_3 and C_2H_5,
X is a halogen atom (for example) and a C_1 to C_4 fatty acid base, p is 1 or 2, q is 2 or 3, and p + q=4.]. The number of carbon atoms of R^1 may be 12 to 50, for example, 12 to 30.

[0272] Specific examples of the cationic surfactants include dodecyltrimethylammonium acetate, trimethyltetradecylammonium chloride, hexadecyltrimethylammonium bromide, trimethyloctadecylammonium chloride, (dodecylmethylbenzyl)trimethylammonium chloride, benzyldodecyldimethylammonium chloride, methyldodecyl di(hydropolyoxyethylene) ammonium chloride, benzyldodecyl di(hydropolyoxyethylene) ammonium chloride, and N-[2-(diethylamino)ethyl] oleamide hydrochloride.

[Anionic Surfactant]

[0273] Examples of the anionic surfactant include an alkyl ether sulfate, an alkyl sulfate, an alkenyl ether sulfate, an alkenyl sulfate, an olefin sulfonate, an alkanesulfonate, a saturated or unsaturated fatty acid salt, an alkyl or alkenyl ether carbonate, an α-sulfone fatty acid salt, a N-acylamino acid surfactant, a phosphate mono- or diester surfactant, and a sulfosuccinic acid ester.

[Ampholytic Surfactant]

[0274] Examples of the amphoteric surfactants include, for example, alanines, imidazolinium betaines, amidobetaines, and acetic acid betaine, and specific examples of the amphoteric surfactants include, for example, lauryl betaine, stearyl

betaine, lauryl carboxymethyl hydroxyethyl imidazolinium betaine, lauryl dimethylamino acetic acid betaine, and fatty acid amidopropyldimethylaminoacetic acid betaine.

[0275] The surfactant may be one type or in combination of two or more of nonionic surfactants, cationic surfactants, and amphoteric surfactants, respectively.

[Amount of Surfactant]

[0276] The amount of surfactant may be 0.01 parts by weight or more, 0.1 parts by weight or more, 1 part by weight or more, 3 parts by weight or more, 5 parts by weight or more, 10 parts by weight or more, 15 parts by weight or more, 20 parts by weight or more, 50 parts by weight or more, 100 parts by weight or more, 200 parts by weight or more, or 300 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound. The amount of surfactant may be 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 75 parts by weight or less, 50 parts by weight or less, 30 parts by weight or less, 20 parts by weight or less, 10 parts by weight or less, 5 parts by weight or less, 3 parts by weight or less, 1 part by weight or less, 0.5 parts by weight or less, 0.3 parts by weight or less, 0.1 parts by weight or less, or 0, and is preferably 10 parts by weight or less and more preferably 1 part by weight or less, relative to 100 parts by weight of the liquid-repellent compound.

{Silicone}

[0277] The repellent in the present disclosure may include silicone (polyorganosiloxane). Containing the silicone enables providing favorable texture and durability in addition to favorable liquid repellency.

[0278] As the silicone, a known silicone can be used, and examples of the silicone include a polydimethylsiloxane and modified silicones (for example, amino-modified silicone, epoxy-modified silicone, carboxy-modified silicone, and methylhydrogen silicone). For example, the silicone may be silicone wax having waxy properties. These may be used singly or in combination of two or more thereof.

[0279] A weight-average molecular weight of the silicone may be 300 or more, 1,000 or more, 10,000 or more, or 50,000 or more. A weight-average molecular weight of the silicone may be 500,000 or less, 2,500,000 or less, 100,000 or less, or 50,000 or less.

[Amount of Silicone]

[0280] The amount of silicone may be 0.1 parts by weight or more, 1 part by weight or more, 3 parts by weight or more, 5 parts by weight or more, 10 parts by weight or more, 15 parts by weight or more, 20 parts by weight or more, 50 parts by weight or more, 100 parts by weight or more, 200 parts by weight or more, or 300 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound. The amount of silicone may be 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 75 parts by weight or less, 50 parts by weight or less, 40 parts by weight or less, 30 parts by weight or less, 20 parts by weight or less, 10 parts by weight or less, or 5 parts by weight or less, relative to 100 parts by weight of the liquid-repellent compound.

{Wax}

[0281] The repellent in the present disclosure may include wax. Containing the wax can impart favorable liquid repellency to a substrate.

[0282] Examples of the wax include paraffin wax, microcrystalline wax, Fischer-Tropsch wax, polyolefin wax (for example, polyethylene wax and polypropylene wax), oxidized polyolefin wax, silicone wax, animal and vegetable wax, and mineral wax. The paraffin wax is preferred. Specific examples of compounds constituting the wax include normal alkanes (for example, tricosane, tetracosane, pentacosane, hexacosane, heptacosane, octacosane, nonacosane, triacontane, hentriacontane, dotriacontane, tritriacontane, tetratriacontane, pentatriacontane, and hexatriacontane), normal alkenes (for example, 1-eicosene, 1-docosene, 1-tricosene, 1-tetracosene, 1-pentacosene, 1-hexacosene, 1-heptacosene, 1-octacosene, nonacosane, triacontane, hentriacontane, dotriacontane, tritriacontane, tetratriacontane, pentatriacontane, and hexatriacontane). The number of carbon atom in the compound constituting the wax is preferably 20 to 60, for example 25 to 45. A molecular weight of the wax may be 200 to 2,000, for example, 250 to 1,500 or 300 to 1,000. These may be used singly or in combination of two or more thereof.

[0283] A melting point of the wax may be 50°C or higher, 55°C or higher, 60°C or higher, 65°C or higher, or 70°C or higher, and is preferably 55°C or higher and more preferably 60°C or higher. The melting point of wax is measured in accordance with JIS K 2235-1991.

[Amount of Wax]

[0284] The amount of wax may be 0.1 parts by weight or more, 1 part by weight or more, 3 parts by weight or more, 5 parts by weight or more, 10 parts by weight or more, 15 parts by weight or more, 20 parts by weight or more, 50 parts by weight or more, 100 parts by weight or more, 200 parts by weight or more, or 300 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound. The amount of wax may be 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 75 parts by weight or less, 50 parts by weight or less, 40 parts by weight or less, 30 parts by weight or less, 20 parts by weight or less, 10 parts by weight or less, or 5 parts by weight or less, relative to 100 parts by weight of the liquid-repellent compound.

{Organic Acid}

[0285] The repellent may contain an organic acid. As the organic acid, a known organic acid can be used. Examples of the organic acid preferably include, for example, a carboxylic acid, a sulfonic acid, and a sulfinic acid, with the carboxylic acid being particularly preferred. Examples of the carboxylic acid include, for example, formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, succinic acid, glutaric acid, adipic acid, malic acid, and citric acid, with the formic acid or acetic acid being particularly preferred. In the present disclosure, one type of organic acid may be used, or two or more thereof may be combined for use. For example, formic acid and acetic acid may be combined for use.

[Amount of Organic Acid]

[0286] The amount of organic acid may be 0.1 parts by weight or more, 1 part by weight or more, 3 parts by weight or more, 5 parts by weight or more, 10 parts by weight or more, 15 parts by weight or more, 20 parts by weight or more, 50 parts by weight or more, 100 parts by weight or more, 200 parts by weight or more, or 300 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound. The amount of organic acid may be 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 75 parts by weight or less, 50 parts by weight or less, 40 parts by weight or less, 30 parts by weight or less, 20 parts by weight or less, 10 parts by weight or less, or 5 parts by weight or less, relative to 100 parts by weight of the liquid-repellent compound. The amount of organic acid may be adjusted so that a pH of the repellent is 3 to 10, for example 5 to 9, particularly 6 to 8. For example, the repellent may be acidic (pH of 7 or less, for example 6 or less).

{Curing Agent}

[0287] The repellent may contain a curing agent (active hydrogen-reactive compound or active hydrogen-containing compound).

[0288] The curing agent (cross-linking agent) in the repellent can effectively cure the liquid-repellent compound. The curing agent may be an active hydrogen-reactive compound or an active hydrogen-containing compound which reacts with an active hydrogen or an active hydrogen-reactive group of the liquid-repellent compound. Examples of the active hydrogen-reactive compound include an isocyanate compound, epoxy compound, chloromethyl group-containing compound, carboxyl group-containing compound, and hydrazide compound. Examples of the active hydrogen-containing compound include a hydroxyl group-containing compound, an amino group-containing compound and a carboxyl group-containing compound, a ketone group-containing compound, a hydrazide compound, and a melamine compound.

[0289] The curing agent may contain an isocyanate compound. The isocyanate compound may be a polyisocyanate compound. The polyisocyanate compound is a compound having two or more isocyanate groups in one molecule. The polyisocyanate compound serves as a cross-linking agent. Examples of the polyisocyanate compound include, for example, an aliphatic polyisocyanate, an alicyclic polyisocyanate, an araliphatic polyisocyanate, an aromatic polyisocyanate, and derivatives of these polyisocyanates. The isocyanate compound may be a blocked isocyanate compound (for example, a blocked polyisocyanate compound). The blocked isocyanate compound is a compound in which an isocyanate group of an isocyanate compound is masked with a blocking agent to inhibit reaction.

[0290] Examples of the aliphatic polyisocyanates are aliphatic triisocyanates such as trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, pentamethylene diisocyanate, 1,2-propylene diisocyanate, 1,2-butylene diisocyanate, 2,3-butylene diisocyanate, 1,3-butylene diisocyanate, 2,4,4- or 2,2,4-trimethylhexamethylene diisocyanate, an aliphatic diisocyanate of 2,6-diisocyanatomethylcaproate, and aliphatic triisocyanates such as lysine ester triisocyanate, 1,4,8-triisocyanateoctane, 1,6,11-triisocyanatoundecane, 1,8-diisocyanato-4-isocyanatomethyloctane, 1,3,6-triisocyanatohexane, 2,5,7-trimethyl-1,8-diisocyanato-5-isocyanatomethyloctane. These may be used singly or in combination of two or more thereof.

[0291] Examples of the alicyclic polyisocyanates include, for example, an alicyclic diisocyanate and an alicyclic triisocyanate. Specific examples of the alicyclic polyisocyanate include 1,3-cyclopentene diisocyanate, 3-isocyanato-

methyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate), and 1,3,5-triisocyanatocyclohexane. These may be used singly or in combination of two or more thereof.

[0292] Examples of the aromatic-aliphatic polyisocyanate include an aromatic-aliphatic diisocyanate and aromatic-aliphatic triisocyanate. Specific examples of the araliphatic polyisocyanate include 1,3- or 1,4-xylylene diisocyanate or a mixture thereof, 1,3- or 1,4-bis(1-isocyanato-1-methylethyl)benzene (tetramethyl xylylene diisocyanate) or a mixture thereof, and 1,3,5-triisocyanatomethylbenzene. These may be used singly or in combination of two or more thereof.

[0293] Examples of the aromatic polyisocyanates include an aromatic diisocyanate, aromatic triisocyanate, and aromatic tetraisocyanate. Specific examples of the aromatic polyisocyanate include, for example, m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 1,5-naphthalene diisocyanate, 2,4'- or 4,4'-diphenylmethane diisocyanate, or a mixture thereof, 2,4- or 2,6-tolylene diisocyanate or a mixture thereof, triphenylmethane-4,4'4"-triisocyanate, and 4,4'-diphenylmethane-2,2',5,5'-tetraisocyanate. These may be used singly or in combination of two or more thereof.

[0294] Examples of the derivative of the polyisocyanate include various derivatives such as a dimer, trimer, biuret, allophanate, carbodiimide, urethodione, urethoimine, isocyanurate, and iminooxadiazinedione of the aforementioned polyisocyanate compounds. These may be used singly or in combination of two or more thereof.

[0295] These polyisocyanates can be used singly or in combination of two or more thereof.

[0296] As the polyisocyanate compound, a blocked polyisocyanate compound (blocked isocyanate), which is a compound obtained by blocking isocyanate groups of the polyisocyanate compound with a blocking agent, is preferably used. The blocked polyisocyanate compound is preferably used because it is relatively stable even in solution and can be used in the same solution as solution of the repellent.

[0297] The blocking agent is an agent that blocks free isocyanate groups. The blocked polyisocyanate compound, for example, can be heated 100°C or higher, for example, 130°C or higher to regenerate isocyanate groups, facilitating a reaction with hydroxyl groups. Examples of the blocking agent include, for example, a phenolic compound, lactam-based compound, aliphatic alcohol-based compound, and oxime-based compound. The polyisocyanate compound may be used singly or in combination of two or more thereof.

[0298] The epoxy compound is a compound having an epoxy group. Examples of the epoxy compound include epoxy compounds having a polyoxyalkylene group, such as a polyglycerol polyglycidyl ether and a polypropylene glycol diglycidyl ether; as well as a sorbitol polyglycidyl ether.

[0299] The chloromethyl group-containing compound is a compound having a chloromethyl group. Examples of the chloromethyl group-containing compound include, for example, a chloromethyl polystyrene.

[0300] The carboxyl group-containing compound is a compound having a carboxyl group. Examples of the carboxyl group-containing compound include, for example, a (poly)acrylic acid, and a (poly)methacrylic acid.

[0301] Specific examples of the ketone group-containing compound include, for example, a (poly)diacetone acrylamide, and diacetone alcohol.

[0302] Specific examples of the hydrazide compound include, for example, hydrazine, a carbohydrazide, and adipic acid hydrazide.

[0303] Specific examples of the melamine compound include, for example, a melamine resin and a methyl etherified melamine resin.

[Amount of Curing Agent]

[0304] The amount of curing agent may be 0.1 parts by weight or more, 1 part by weight or more, 3 parts by weight or more, 5 parts by weight or more, 10 parts by weight or more, 15 parts by weight or more, 20 parts by weight or more, 50 parts by weight or more, 100 parts by weight or more, 200 parts by weight or more, or 300 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound. The amount of curing agent may be 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 75 parts by weight or less, 50 parts by weight or less, 40 parts by weight or less, 30 parts by weight or less, 20 parts by weight or less, 10 parts by weight or less, or 5 parts by weight or less, relative to 100 parts by weight of the liquid-repellent compound.

{Other Component}

[0305] The repellent may contain a component other than the aforementioned components. Examples of the other components include, for example, water- and/or oil-repellent agents, an anti-slip agent, an antistatic agent, an antiseptic agent, an ultraviolet absorber, an antibacterial agent, a deodorant, and a fragrance. These may be used singly or in combination of two or more thereof. In addition to the above components, as other components, for example, a texture modifier, a softening agent, an antibacterial agent, a flame retardant, a coating material fixing agent, a wrinkle-resistant agent, a drying rate adjuster, a cross-linking agent, a film formation agent, a compatibilizer, an antifreezing agent, a viscosity adjuster, an ultraviolet absorber, an antioxidant, a pH adjuster, an insect repellent, an antifoaming agent, an anti-

shrinkage agent, a laundry wrinkle-resistant agent, a shape retention agent, a drape retention agent, an ironing improving agent, a brightening agent, a whitening agent, fabric softening clay, a migration-proofing agent such as polyvinylpyrrolidone, a polymer dispersant, a soil release agent, a scum dispersant, a fluorescent brightening agent such as 4,4-bis(2-sulfostyryl)biphenyl disodium (Tinopal CBS-X manufactured by Ciba Specialty Chemicals Plc), a dye fixing agent, an anti-color fading agent such as 1,4-bis(3-aminopropyl)piperazine, a stain removing agents, enzymes such as cellulase, amylase, protease, lipase, and keratinase as fiber surface modifiers, a foam inhibitor, silk protein powder that can impart texture and functions of silk such as moisture absorption and release properties, surface modifiers and emulsified dispersions, thereof and specifically K-50, K-30, K-10, A-705, S-702, L-710, FP series (Idemitsu Petrochemical Co., Ltd.), hydrolyzed silk liquid (Jomo), SILKGEN G Soluble S (ICHIMARU PHARCOS Co., Ltd.), an antifouling agent, for example, a nonionic polymer compound composed of alkylene terephthalate and/or alkylene isophthalate units and polyoxyalkylene units, for example, FR627 manufactured by GOO CHEMICAL CO., LTD. and SRC-1 manufactured by Clariant (Japan) K. K, can be compounded. These may be used singly or in combination of two or more thereof.

[Antistatic Agent]

[0306] Examples of the antistatic agent include, for example, cationic antistatic agents having cationic functional groups such as a quaternary ammonium salt, a pyridinium salt, and primary, secondary, and tertiary amino groups; anionic antistatic agents having anionic functional groups such as a sulfonate salt and a sulfate ester salt, a phosphonate and a phosphate ester salt; amphoteric antistatic agents such as an alkyl betaine and a derivative thereof, imidazoline and a derivative thereof, and alanine and a derivative thereof; and nonionic antistatic agents such an amino alcohol and a derivative thereof, glycerin and a derivative thereof, and a polyethylene glycol and a derivative thereof. For example, an ion conductive polymer obtained by polymerizing or copolymerizing a monomer having an ion conductive group of the cationic, anionic, or amphoteric antistatic agent, may be used. These may be used singly or in combination of two or more thereof.

[Antiseptic Agent]

[0307] The antiseptic agent may be used mainly to enhance antisepsis power and bactericidal power to maintain antiseptic during long-term storage. Examples of the antiseptic agent include isothiazolone-based organosulfur compounds, benzisothiazolone-based organosulfur compounds, benzoic acids, and 2-bromo-2-nitro-1,3-propanediol.

[Ultraviolet Absorber]

[0308] The ultraviolet absorber is an agent that has a protection effect against ultraviolet rays, and is a component that absorbs ultraviolet rays, converts them into infrared rays, visible rays, and the like, and emits them. Examples of the ultraviolet absorber include aminobenzoic acid derivatives, salicylic acid derivatives, silicic acid derivatives, benzophenone derivatives, azole-based compounds, and 4-t-butyl-4'-methoxybenzoylmethane.

[Antibacterial Agent]

[0309] The antibacterial agent is a component that exhibits the effect of inhibiting bacteria from growing on fibers and further exhibits the effect of inhibiting generation of unpleasant odors derived from decomposition products of microorganisms. Examples of the antibacterial agents include, for example, cationic antibacterial agents such as a quaternary ammonium salt, bis-(2-pyridylthio-1-oxide) zinc, a polyhexamethylene biguanidine hydrochloride salt, 8-oxyquinoline, and a polylysine.

[Deodorant]

[0310] Examples of the deodorant include cluster dextrin, methyl-β-cyclodextrin, 2-hydroxypropyl-β-cyclodextrin, monoacetyl-β-cyclodextrin, acylamidopropyl dimethylamine oxide, and an aminocarboxylic acid-based metal complex (the zinc complex of trisodium methylglycine diacetate described in WO2012/090580).

[Amount of Other Component]

[0311] Each amount or the total amount of the other components may be 0.1 parts by weight or more, 1 part by weight or more, 3 parts by weight or more, 5 parts by weight or more, 10 parts by weight or more, 15 parts by weight or more, 20 parts by weight or more, 50 parts by weight or more, 100 parts by weight or more, 200 parts by weight or more, or 300 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound. Each amount or the total amount of the

other components may be 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 75 parts by weight or less, 50 parts by weight or less, 40 parts by weight or less, 30 parts by weight or less, 20 parts by weight or less, 10 parts by weight or less, or 5 parts by weight or less, relative to 100 parts by weight of the liquid-repellent compound.

<Method for Producing Liquid-Repellent Fiber>

[0312] The method for producing a liquid-repellent fiber in the present disclosure includes a fiber treatment of treating a fiber substrate with a repellent containing a liquid-repellent compound using supercritical carbon dioxide as a treatment medium.

The repellent (treatment agent) used to treat the fiber substrate contains a liquid-repellent compound and supercritical carbon dioxide. The treatment allows the liquid-repellent compound, which is an active ingredient of the repellent to penetrate into the substrate and/or adheres to a surface of the substrate.

[0313] If necessary, the repellent of the present disclosure can be further combined for use with various additives such as water- and/or oil-repellent agents, an anti-slip agent, an antistatic agent, a texture modifier, a softening agent, an antibacterial agent, a flame retarder, a coating material fixing agent, a wrinkle-resistant agent, a drying rate adjuster, a cross-linking agent, a film formation agent, a compatibilizer, an antifreezing agent, a viscosity modifier, an ultraviolet absorber, an antioxidant, a pH adjuster, an insect repellent, and an antifoaming agent. Examples of the various additives may be the same as those explained in the section "Other Component" in the water-repellent composition described above. A concentration of the repellent in a treatment agent brought into contact with a substrate may be appropriately changed depending on its use, and may be 0.01 to 10% by weight, for example 0.05 to 5% by weight.

[0314] In the method for producing a liquid-repellent fiber of the present disclosure, a treatment temperature in a treatment container is set to 31.1°C or higher (preferably 40°C or higher), which is the critical temperature of carbon dioxide, and treatment pressure is set to 7.38 MPa or higher (preferably 10 MPa or higher), which is the critical pressure of carbon dioxide, and using supercritical carbon dioxide as a treatment medium, a fiber substrate placed in the treatment tank is treated with a repellent containing the liquid-repellent compound.

[0315] The treatment temperature may be 31.1°C or higher, 40°C or higher, 50°C or higher, 60°C or higher, 70°C or higher, 80°C or higher, or 100°C or higher. The treatment temperature may be 200°C or lower, 150°C or lower, 120°C or lower, 100°C or lower, 80°C or lower, or 60°C or lower. The treatment temperature may vary depending on the type of repellent used, the treatment conditions, desired physical properties, and the like.

[0316] The treatment pressure may be 7.38 MPa or more, 8 MPa or more, 10 MPa or more, 15 MPa or more, 20 MPa or more, or 25 MPa or more. The treatment pressure may be 100 MPa or less, 75 MPa or less, 50 MPa or less, 30 MPa or less, 25 MPa or less, or 20 MPa or less. The treatment pressure may vary depending on the type of repellent used, the treatment conditions, desired physical properties, and the like.

[0317] The treatment time may be 10 seconds or more, 1 minute or more, 3 minutes or more, 5 minutes or more, 10 minutes or more, 20 minutes or more, or 30 minutes or more. A treatment time may be 300 minutes or less, 240 minutes or less, 180 minutes or less, 120 minutes or less, 60 minutes or less, 30 minutes or less, 15 minutes or less, or 5 minutes or less. The treatment pressure may vary depending on the type of repellent used, the treatment conditions, desired physical properties, and the like.

{Fiber Substrate}

[0318] Examples of the fiber substrates include animal and vegetable natural fibers such as cotton, linen, wool, and silk, synthetic fibers such as a polyamide, a polyester, a polyvinyl alcohol, a polyacrylonitrile, a polyvinyl chloride, and a polypropylene, and semi-synthetic fibers such as rayon and acetate, inorganic fibers such as a glass fiber, a carbon fiber, and an asbestos fiber, or blended fibers thereof. Textile products include a woven fabric, a knitted fabric, and a nonwoven fabric, fabric in the form of clothing form and carpets, and a fiber, yarn and intermediate fiber product (for example, a sliver or a crude yarn) in a state of before being formed into fabric, may undergo treatment. Examples of suitable fiber substrates in the present disclosure include polyester or polyester mixed fibers.

[0319] As the fiber substrate, a paper product may be used. Examples of the paper product include papers made of bleached or unbleached chemical pulps such as kraft pulp or sulfite pulp, bleached or unbleached high-yield pulp such as groundwood pulp, mechanical pulp, or thermomechanical pulp, paper made from wastepaper pulp such as wastepaper of newspapers, magazines, cardboards, and deinked wastepaper, a container made of paper, and a molded product made of paper. Specific examples of the paper products include, for example, packaging paper, gypsum liner board base paper, coated base paper, medium-quality paper, a general liner and core, neutral pure white roll paper, a neutral liner, a rust-proof liner and metal pasted paper, kraft paper, neutral printing writing paper, neutral coated base paper, neutral PPC paper, neutral thermal paper, neutral pressure-sensitive base paper, neutral inkjet paper and neutral information paper, molded paper (molded container), and the like.

{Pretreatment of Textile Product}

[0320] The textile product may be pretreated before being treated with the repellent of the present disclosure. Pretreatment of the textile product enables imparting excellent fastness to a textile product after treated with the repellent.

[0321] Examples of the pretreatment of textile product include, for example, cationization treatment such as reaction with a reactive quaternary ammonium salt, anionization treatment such as sulfonation, carboxylation, and phosphorylation, acetylation treatment after the anionization treatment, benzoylation treatment, carboxymethylation treatment, grafting treatment, tannin acid treatment, and polymer coating treatment.

[0322] A method for pretreating the textile product is not limited, but the textile product can be pretreated by a conventionally known method. The method for pretreating the textile product may be a method for dispersing a pretreatment liquid in an organic solvent or water, if necessary, to dilute the pretreatment liquid and adhering it to a surface of the textile product and drying the liquid by a known method such as dip coating, spray coating, or foam coating, may be employed. The pH, temperature, etc. of the pretreatment liquid may be adjusted according to an extent of treatment desired. As an example of the method for pretreating a textile product, a method for pretreating a textile product with a hydrocarbon-based water-repellent agent will be described in detail.

[0323] The pretreatment of a textile product may involve a step of imparting to a fiber with one or more functional groups (hereinafter may be referred to as "specific functional groups") selected from the group consisting of the monovalent group represented by $-SO_3M^1$ (wherein M^1 represents a monovalent cation) or the monovalent group represented by $-COOM^2$ (wherein M^2 represents a monovalent cation), and the monovalent group represented by $-O-P(O)(OX^1)(OX^2)$ (wherein X^1 and X^2 each independently represent a hydrogen atom or an alkyl group having 1 to 22 carbon atoms).

[0324] Examples of M^1 include H, K, Na, or an ammonium ion which may have a substituent. Examples of M^2 include H, K, Na, or an ammonium ion which may have a substituent. When X^1 or X^2 is an alkyl group, it is preferably an alkyl group having 1 to 22 carbon atoms and more preferably an alkyl group having 4 to 12 carbon atoms.

[0325] A fiber containing the above specific functional group (hereinafter sometimes referred to as the "functional group-containing fiber") can be prepared, for example, by the following method.

(i) A compound having the above specific functional group is allowed to adhere to a fiber material. The adhesion of the compound may be in a condition such that a portion of the compound and a portion of the fibers are chemically bonded as long as the above specific functional groups remain in a sufficient amount.

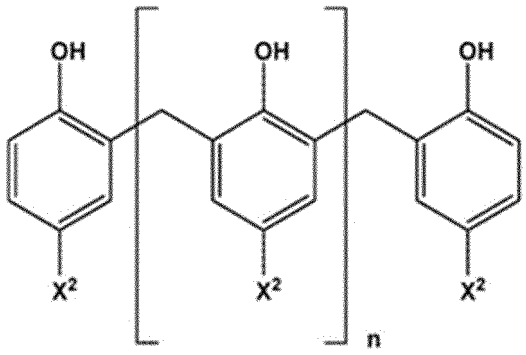
(ii) As a material forming the fiber, a fiber into which the above specific functional group is directly introduced is used.

[0326] In the case of (i), for example, a functional group-containing fiber can be obtained by treating the fiber material with a pretreatment liquid containing one or more compounds having the above specific functional group, namely, by the step of introducing the functional group.

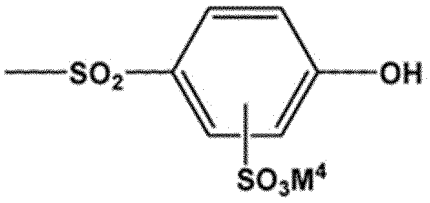
[0327] Materials used for the fiber material, are not particularly limited, and examples thereof include natural fibers such as cotton, linen, silk, and wool, semi-synthetic fibers such as rayon and acetate, synthetic fibers such as a polyamide (nylon, etc.), a polyester, a polyurethane, and a polypropylene, composite fibers thereof, blended fibers, and the like. A form of the fiber material may be any form such as a fiber (tow, sliver, etc.), a yarn, a knitted fabric (including an interknitted fabric), a woven fabric (including an interwoven fabric), or a nonwoven fabric.

[0328] In the present embodiment, from the viewpoint of improving water-repellency of the obtained textile product, a fiber material containing a polyamide and a polyester as raw materials, is preferably used, and in particular, nylon such as nylon 6, or nylon 6,6, a polyester such as a polyethylene terephthalate (PET), a polytrimethyl terephthalate, or polylactic acid, and blended fibers containing these, are preferably used.

[0329] A phenolic polymer can be used as the compound having $-SO_3M^1$ described above. Examples of such a phenolic polymer include that containing one or more compounds represented by the following general formula:



[wherein X^2 represents $-SO_3M^3$ (wherein M^3 represents a monovalent cation), or a group represented by the following general formula, and n is an integer of 20 to 3,000.]



[wherein M^4 represents a monovalent cation.].

[0330] Examples of M^3 includes H, K, Na or an ammonium ion which may have a substituent.

[0331] Examples of M^4 includes H, K, Na or an ammonium ion which may have a substituent.

[0332] The compounds represented by the general formula above may be, for example, formalin condensates of phenol sulfonic acid and formalin condensates of sulfonated bisphenol S.

[0333] Examples of the compound having $-COOM^2$ above include a polycarboxylic acid-based polymer.

[0334] As the polycarboxylic acid-based polymer, for example, a polymer synthesized by a conventionally known radical polymerization method using acrylic acid, methacrylic acid, maleic acid, or the like as a monomer, or a commercially available polymer, can be used.

[0335] A method for producing the polycarboxylic acid-based polymers may include, for example, adding a radical polymerization initiator to an aqueous solution of the aforementioned monomer and/or salt thereof and heating and reacting the mixture at 30 to 150°C for 2 to 5 hours. At this time, an aqueous solution of the above monomer and/or salt thereof may be added with aqueous solvents such as alcohols such as methanol, ethanol, and isopropyl alcohol, and acetone. Examples of the radical polymerization initiator include persulfates such as potassium persulfate, sodium persulfate, and ammonium persulfate, redox polymerization initiators in combination of the persulfate and sodium bisulfite or the like, hydrogen peroxide, and a water-soluble azo-based polymerization initiator. These radical polymerization initiators may be used singly or in combination of two or more thereof. Furthermore, a chain transfer agent (for example, octyl thioglycolate) may be added upon radical polymerization for the purpose of adjusting the degree of polymerization.

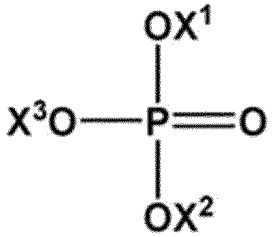
[0336] In addition to the aforementioned monomers, a copolymerizable monomer can be used for radical polymerization. Examples of the copolymerizable monomer include vinyl-based monomers such as ethylene, vinyl chloride, and vinyl acetate, an acrylamide, acrylates, and methacrylates. The acrylates and methacrylates preferably have a hydrocarbon group having 1 to 3 carbon atoms, which may have a substituent such as a hydroxyl group. Examples of such acrylates or methacrylates include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, propyl acrylate, propyl methacrylate, and the like. These copolymerizable monomers may be used singly or in combination of two or more thereof.

[0337] A carboxyl group in the polycarboxylic acid-based polymer may be free or may be neutralized with an alkali metal, an amine-based compound, or the like. Examples of the alkali metal include sodium, potassium, lithium, and the like, and examples of the amine-based compound include ammonia, monoethanolamine, diethanolamine, triethanolamine, and the like.

[0338] The weight-average molecular weight of the polycarboxylic acid-based polymer is preferably 1,000 to 20,000 and more preferably from 3,000 to 15,000, from the viewpoint of favorable water-repellency of the resulting textile product.

[0339] As the polycarboxylic acid-based polymer, commercially available products such as "Neocrystal 770" (trade name, manufactured by NICCA CHEMICAL CO., LTD.) and "Ceropol PC-300" (trade name, manufactured by Sanyo Chemical Industries, Ltd.) can be used.

[0340] Examples of the compound having $-O-P(O)(OX^1)(OX^2)$ as described above include phosphoric acid ester compounds represented by the following general formula:



[wherein X^1 or X^2 is the same as defined above, and X^3 represents an alkyl group having 1 to 22 carbon atoms.].

[0341] As the aforementioned phosphoric acid ester compound, phosphoric acid monoesters, diesters and triesters,

and mixtures thereof can be used in which the alkyl ester moiety is an alkyl group having 1 to 22 carbon atoms.

[0342] In view of favorable water-repellency of the textile products to be obtained, lauryl phosphoric acid ester and decyl phosphoric acid ester are preferably used.

[0343] As the phosphoric acid ester compound, for example, a commercially available product such as "Phosphanol ML-200" (trade name, manufactured by TOHO Chemical Industry Co., Ltd.) can be used.

[0344] A pretreatment liquid containing one or more of the compounds having the aforementioned specific functional group can be, for example, an aqueous solution of the compound described above. The pretreatment liquid may also contain an acid, alkali, surfactant, chelating agent, and the others.

[0345] Examples of the method for treating a fiber material with the above pretreatment liquid include padding treatment, dip treatment, spray treatment, and coating treatment. Examples of padding treatment include the method involving using the padding apparatus as described on pages 396 to 397 of Seni Sensyoku Kako Jiten (in Japanese; Fiber-dyeing process dictionary) (published by THE NIKKAN KOGYO SHIMBUN, LTD., 1963) and pages 256 to 260 of Irozome Kagaku (in Japanese; dyeing chemistry) III (published by Jikkyo Shuppan Co., Ltd., 1975). Examples of the coating treatment include the method involving using a coating machine as described on pages 473 to 477 of Sensyoku Shiage Kiki Soran (in Japanese; Comprehensive guide to dyeing and finishing machines) (published by Fiber Japan CO., LTD., 1981). Examples of the dip treatment include the method involving using a batch type dyeing machine as described in pages 196 to 247 of Sensyoku Shiage Kiki Soran (in Japanese) (published by Fiber Japan Co., LTD., 1981), and for example, a jet dyeing machine, air flow dyeing machine, drum dyeing machine, wince dyeing machine, washer dyeing machine, and cheese dyeing machine can be used. Examples of the spray treatment includes a method involving using an air spray that nebulizes and sprays a treatment liquid by compressed air, or an air spray by hydraulic pressure nebulization system. In this case, the concentration of the treatment liquid and treatment conditions of heat treatment after application can be adjusted appropriately, taking into consideration various conditions such as their purposes and performance. Moreover, in a case in which the pretreatment liquid contains water, it is preferably dried to remove water after the pretreatment liquid has been allowed to adhere to the fiber material. The drying method are not limited, and either a dry heat method or a wet heat method may be employed. Drying temperatures are also not limited, and for example, drying may be carried out at room temperature to 200°C for 10 seconds to several days. Heat treatment at a temperature of 100 to 180°C for about 10 seconds to 5 minutes may be carried out after the drying, as necessary.

[0346] In a case in which a fiber material is such that it is to be dyed, treatment with the pretreatment liquid may be carried out before dyeing or in the same bath as in dyeing, but in the case of carrying out reduction soaping, a compound with the above specified functional group (for example, a phenolic polymer compound or the like) adsorbed in the process may fall off, and therefore the treatment with the pretreatment liquid is preferably carried out after the reduction soaping after dyeing.

[0347] The treatment temperature in the dip treatment can be 60 to 130°C. The treatment time can be 5 to 60 minutes.

[0348] The step of introducing a functional group by the pretreatment liquid is preferably carried out so that the amount of compound having the above specified functional group adhered is 1.0 to 7.0 parts by weight relative to 100 parts by weight of a fiber material. Within this range, both durable water-repellency and texture can be achieved at a high level.

[0349] The pH of the pretreatment liquid is preferably adjusted to 3 to 5. The pH adjustment can be carried out by using a pH adjuster such as acetic acid or malic acid.

[0350] A salt can be used in combination with the pretreatment liquid to adsorb the compound having the aforementioned specific functional group effectively onto the fiber material by a salting effect. Examples of the salts that can be used include sodium chloride, sodium carbonate, ammonium sulfate, and sodium sulfate.

[0351] In the step of introducing the functional group by the pretreatment liquid, an excess amount of the compound having the aforementioned specific functional group, which has been given by the treatment, is preferably removed. Examples of the removal method include washing with water. Sufficient removal can avoid inhibition of development of water-repellency in the subsequent water-repellent treatment, and additionally, the textile product to be obtained has the favorable texture. The resulting functional group-containing fiber is preferably fully dried prior to contact with a hydrocarbon-based water-repellent.

[0352] Examples of (ii) the fiber in which the aforementioned specific functional group has been introduced directly into the material forming the fiber include a cation-dyeable polyester (CD-PET).

[0353] In view of favorable water-repellency of the textile products to be obtained, the functional group-containing fiber preferably has a zeta potential of its surface of -100 to -0.1 mV and more preferably -50 to -1 mV. The zeta potential of the fiber surface can be measured, for example, using a zeta potential and particle size measurement system, ELSZ-1000ZS (manufactured by Otsuka Electronics Co., Ltd.).

[0354] Embodiments have been described above, but it will be understood that various modifications can be made to embodiments and details without departing from the spirit and the scope of the claims.

Examples

[0355] The present disclosure will be described in more detail below by way to Examples, but the present disclosure is not limited to these Examples.

<Test Method>

[0356] The test procedures are as follows.

[Water Contact Angle]

[0357] A silicon wafer was coated with a solution of a liquid-repellent compound with a solid concentration of 1.0% to obtain a smooth spin-coated film. 2 μL of water was dropped onto the spin-coated film, and a contact angle one second after the drop was taken as the water contact angle of the liquid-repellent compound.

[Adhesion Rate]

[0358] A fiber substrate was weighed before and after treatment, the weight before treatment was subtracted from the weight after treatment, and the weight difference was divided by the weight before treatment to calculate the amount adhered.

[Water-Repellency Performance]

[0359] One droplet of water is placed on a treated liquid-repellent fiber, and the treated fiber is evaluated based on whether the water droplet spread or not. In the case of the water droplets not spreading out, it is evaluated as "O"; and in the case of the water droplets spreading out, it is evaluated as "X."

<Compound 1>

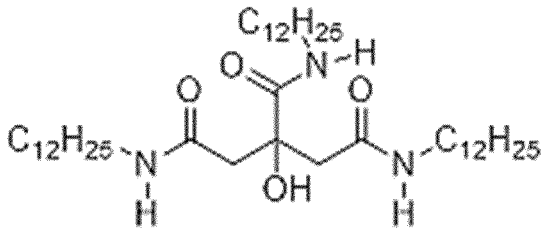
[0360] Octadecyl acrylate (manufactured by FUJIFILM Wako Pure Chemical Corporation) was used.

<Compound 2>

[0361] A polyglycerol fatty acid ester (TS-3S manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.) was used.

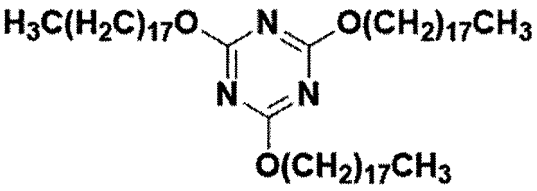
<Synthesis of Compound 3>

[0362] A reaction vessel equipped with a reflux condenser and a Dean-Stark trap was added with 2.8 g of citric acid, and 9.5 g of dodecylamine and heated to 70°C followed by addition of 20 ml of toluene. The obtained mixture was heated and stirred at 135°C for 64 hours. The reaction vessel was cooled to room temperature and added with an additional 20 ml of toluene, and the mixture was cleaned with acetone and ethanol in this order, yielding the Compound 3 shown below.



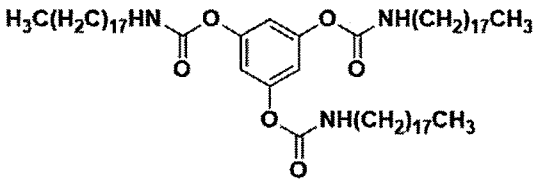
<Synthesis of Compound 4>

[0363] 4.69 g of stearyl alcohol was dissolved in 80.0 mL of dehydrated tetrahydrofuran, then 0.69 g of sodium hydride was added, and the mixture was stirred at room temperature for 1 hour. After 1 hour, 1.0 g of cyanuric acid chloride was added, and the mixture was heated and stirred overnight at an oil bath temperature of 66°C. Next morning, the mixture was neutralized with 3N hydrochloric acid and then filtered. The resulting solid was washed with water, cleaned with methanol and diethyl ether to obtain 3.32 g of the Compound 4 shown below.



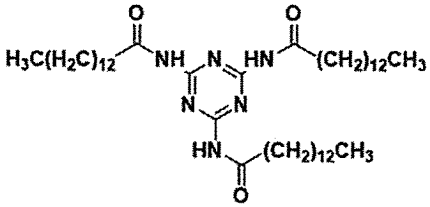
<Synthesis of Compound 5>

[0364] 0.5 g of phloroglucinol was dissolved in 20.0 mL of dehydrated tetrahydrofuran, then 3.75 g of octadecyl isocyanate, 1.71 mL of triethylamine, and 3 droplets of dibutyltin dilaurate were added in this order, and the mixture was heated and stirred overnight at an oil bath temperature of 60°C. Next morning, the mixture was cooled and then filtered. The obtained solid was cleaned with acetone, methanol, and dichloromethane to obtain 3.27 g of the Compound 5 shown below.



<Synthesis of Compound 6>

[0365] A flask was fed with 0.82 g of melamine and 10 g of myristic anhydride, and the mixture was heated and stirred at an oil bath temperature of 200°C for 1 hour. After 1 hour, the flask was cooled to room temperature, and the obtained solid was cleaned with acetone and diethyl ether to obtain 4.33 g of the compound shown below.



[0366] The water contact angles of Compounds 1 to 6 were measured.

<Example 1>

[0367] A polyethylene terephthalate fabric (basis weight 88 g/m^2, 70 denier, and gray) was cut and weighed (approximately 1 g). 40 mg of the Compound 1 was supported on a glass filter. A 10-mL treatment container was placed with the polyethylene terephthalate fabric and the Compound 1- supported glass filter and set in a supercritical carbon dioxide treatment apparatus. Then, the container was injected with supercritical carbon dioxide at pressure of 25 MPa and treated at a temperature of 120°C for 30 minutes. After a predetermined time, the supercritical carbon dioxide was discharged to obtain liquid-repellent fibers. The adhesion rate of the repellent to the fabric in this case was calculated to be 0.65% by weight.

<Example 2>

[0368] Liquid-repellent fibers were obtained by the same treatment as in Example 1, except that the Compound 2 was used instead of the Compound 1. The adhesion rate of the repellent to the fabric was calculated to be 0.87% by weight.

<Example 3>

[0369] Liquid-repellent fibers were obtained by the same treatment as in Example 1, except that the Compound 3 was used instead of the Compound 1. The adhesion rate of the repellent to the fabric was calculated to be 0.73% by weight.

<Example 4>

[0370] Liquid-repellent fibers were obtained by the same treatment as in Example 1, except that the Compound 4 was used instead of the Compound 1. The adhesion rate of the repellent to the fabric was calculated to be 0.62% by weight.

<Example 5>

[0371] Liquid-repellent fibers were obtained by the same treatment as in Example 1, except that the Compound 5 was used instead of the Compound 1. The adhesion rate of the repellent to the fabric was calculated to be 0.28% by weight.

<Example 6>

[0372] Liquid-repellent fibers were obtained by the same treatment as in Example 1, except that the Compound 6 was used instead of the Compound 1. The adhesion rate of the repellent to the fabric was calculated to be 0.27% by weight.

<Comparative Example 1>

[0373] An evaluation was performed on an untreated fiber substrate.

[0374] Water-repellency evaluations were performed on the fiber substrates of Examples 1 to 5 and Comparative Example 1.

[0375] The test results are summarized in the table below.

	Repellent	Water-contact angle /°	Adhesion rate /% by weight	Water-repellency performance
Example 1	Compound 1	39	0.65	O
Example 2	Compound 2	66	0.87	O
Example 3	Compound 3	75	0.73	O
Example 4	Compound 4	82	0.62	O
Example 5	Compound 5	87	0.28	O
Example 6	Compound 6	108	0.27	O
Comparative Example 1	-	-	-	X

Claims

1. A method for producing a liquid-repellent fiber, comprising a fiber treatment of treating a fiber substrate with a repellent containing a liquid-repellent compound using supercritical carbon dioxide as a treatment medium.

2. The method for producing a liquid-repellent fiber according to claim 1, wherein a water contact angle of the liquid-repellent compound is 35° or more.

3. The method for producing a liquid-repellent fiber according to claim 1 or 2, wherein the liquid-repellent compound has a group represented by the following formula:

$$-X-R_n$$

wherein

X is a direct bond or a 1 + n valent group,
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, or a polysiloxane group, and
n is 1 or more and 3 or less.

4. The method for producing a liquid-repellent fiber according to claim 3, wherein R is an aliphatic hydrocarbon group

having 6 or more and 40 or less carbon atoms and optionally having a substituent, and R has 12 or more carbon atoms.

5. The method for producing a liquid-repellent fiber according to claim 3 or 4, wherein X is a 1 + n valent group composed of one or more selected from the group consisting of

X^1 composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, $-S(=O)_2-$, -NR'-, -C(OR')R'-, and $-C(OR')(-)_2$, wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms, and
X^2 which is a hydrocarbon group having 1 to 40 carbon atoms.

6. The method for producing a liquid-repellent fiber according to any one of claims 3 to 5, wherein X is a group represented by

$$-X^1-$$

or

$$-X^1-X^2-X^1-$$

wherein

X^1 is independently at each occurrence
a direct bond;
-O-;
-O-C(=O)-;
-O-C(=O)-O-;
-O-C(=O)-NR'-;
-NR'-;
-NR'-C(=O)-;
-NR'-C(=O)-O-;
-NR'-C(=O)-NR'-;
-C(=O)-;
-C(=O)-O-;
-C(=O)-NR'-;
$-SO_2-$;
$-SO_2NR'-$;
-C(OR')R'- or
$-C(OR')(-)_2$
wherein
R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms; and
X^2 is a hydrocarbon group having 1 to 40 carbon atoms.

7. The method for producing a liquid-repellent fiber according to any one of claims 1 to 6, wherein the liquid-repellent compound has a repeating unit derived from a compound represented by the following formula:

$$CH_2=C(-Q)-C(=O)-X-R_n$$

wherein

Q is a hydrogen atom, a monovalent organic group, or a halogen atom;
X is a 1 + n valent group composed of one or more selected from the group consisting of

X^1 composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, $-S(=O)_2-$, -NR'-, - C(OR')R'-, and $-C(OR')(-)_2$, wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms, and
X^2 which is a hydrocarbon group having 1 to 40 carbon atoms; R is an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent; and

n is 1 to 3.

8. The method for producing a liquid-repellent fiber according to claim 7, wherein X is a group represented by the following formula:

$$-X^1- \text{ or } -X^1-X^2-X^1-$$

wherein
X^1 is independently at each occurrence -O-, -NR'-, -C(=O)-NR'-, -NR'-C(=O)-, or -NR'-C(=O)-NR'-, wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms; and X^2 is a hydrocarbon group having 1 to 40 carbon atoms.

9. The method for producing a liquid-repellent fiber according to any one of claims 1 to 6, wherein the liquid-repellent compound is a compound in which one or more base material compounds selected from the group consisting of a monosaccharide, a polysaccharide, an alcohol, a polyol, a carboxylic acid, a polyvalent carboxylic acid, and derivatives thereof are modified with a group represented by the following formula:

$$-X-R_n$$

wherein

X is a direct bond or a 1 + n valent group,
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent, and
n is an integer of 1 to 3.

10. The method for producing a liquid-repellent fiber according to claim 9, wherein the base material compound is one or more selected from the group consisting of starch, cellulose, curdlan, pullulan, carrageenan, guar gum, chitin, chitosan, locust bean gum, kappa-carrageenan, iota carrageenan, isomaltodextrin, xanthan gum, gellan gum, tamarind seed gum, cycloamylose, glucose, sucrose, mannitol, sorbitol, sorbitan, maltitol, stevioside, dextrin, cyclodextrin, glycerin, polyglycerin, menthol, xylitol, sucralose, fructose, maltose, trehalose, lactosucrose, erythritol, vanillin, cholesterol, glucosamine, catechin, anthocyanin, quercetin, citric acid, malic acid, gluconic acid, alginic acid, butyric acid, lactic acid, tartaric acid, oxalic acid, malonic acid, succinic acid, fumaric acid, maleic acid, chlorogenic acid, aldonic acid, uronic acid, aldaric acid, phytic acid, ascorbic acid, and derivatives thereof.

11. The method for producing a liquid-repellent fiber according to claim 9 or 10, wherein the base material compound is a glycerin polymer or a citric acid polymer.

12. The method for producing a liquid-repellent fiber according to any one of claims 9 to 11, wherein the base material compound has a hydroxy group, and
the hydroxy group forms a group represented by the following formula:

$$-O-;$$

$$-O-C(=O)-;$$

$$-O-C(=O)-NR'-$$

or

$$-O-C=S-NR'-$$

wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms,
in the liquid-repellent compound.

13. The method for producing a liquid-repellent fiber according to any one of claims 9 to 12, wherein the base material

compound has a carboxyl group, and
the carboxyl group forms a group represented by the following formula:

-C(=O)-;

-C(=O)-O-;

-C(=O)-NR'-

or

-C(=O)-S-

wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms,
in the liquid-repellent compound.

14. The method for producing a liquid-repellent fiber according to any one of claims 1 to 6, wherein the liquid-repellent compound is a compound represented by the following formula:

$$A(-X-R_n)_m$$

wherein

A is an m valent group obtained by removing m hydrogen atoms from an aromatic ring or a nitrogen-containing heterocyclic ring optionally having a substituent;
X is independently at each occurrence a direct bond or a 1 + n valent group;
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent;
n is independently at each occurrence 1 or more and 3 or less; and
m is 1 or more and 6 or less.

15. The method for producing a liquid-repellent fiber according to any one of claims 1 to 6, wherein the liquid-repellent compound is a compound obtained by polymerizing a compound represented by the following formula:

$$A(-X-R_n)_m$$

wherein

A is an m valent group obtained by removing m hydrogen atoms from an aromatic ring or a nitrogen-containing heterocyclic ring optionally having a substituent;
X is independently at each occurrence a direct bond or a 1 + n valent group;
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent;
n is independently at each occurrence 1 or more and 3 or less; and
m is 1 or more and 6 or less,
via a substituent of A.

16. The method for producing a liquid-repellent fiber according to claim 14 or 15, wherein X is a group represented by the following formula:

$$-X^1-$$

or

$$-X^1-X^2-X^1-$$

wherein

X^1 is independently at each occurrence
a direct bond;
-O-;
-O-C(=O)-;
-O-C(=O)-O-;
-O-C(=O)-NR'-;
-NR'-;
-NR'-C(=O)-;
-NR'-C(=O)-O-;
-NR'-C(=O)-NR'-;
-C(=O)-;
-C(=O)-O-;
-C(=O)-NR'-;
-C(OR')R'- or
$-C(OR')(-)_2$
wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 4 carbon atoms, and
X^2 is a hydrocarbon group having 1 to 40 carbon atoms.

17. The method for producing a liquid-repellent fiber according to any one of claims 1 to 6, wherein the liquid-repellent compound is a reaction product of an isocyanate group-containing compound and an isocyanate-reactive compound.

18. The method for producing a liquid-repellent fiber according to any one of claims 1 to 6, wherein the liquid-repellent compound has a polysiloxane group.

19. The method for producing a liquid-repellent fiber according to claim 18, wherein the liquid-repellent compound has the polysiloxane group in a side chain.

20. The method for producing a liquid-repellent fiber according to any one of the claims 1 to 6, wherein the liquid-repellent compound is an amine modified product having:

an amine backbone; and
one or more aliphatic hydrocarbon-containing groups represented by the following formula:

$$-X^N-R_n$$

wherein
X^N is a direct bond or a 1 + n valent group,
R is independently at each occurrence an aliphatic hydrocarbon group having 6 or more and to 40 or less carbon atoms and optionally having a substituent, and
n is an integer of 1 or more and 3 or less,
wherein at least one of the aliphatic hydrocarbon-containing groups is bonded to a nitrogen atom of the amine backbone.

21. The repellent according to claim 20, wherein the amine backbone is composed of a monovalent to trivalent amino group and a chain saturated aliphatic hydrocarbon group or aromatic hydrocarbon group optionally interrupted by an oxygen atom and/or a sulfur atom.

22. The method for producing a liquid-repellent fiber according to any one of claims 1 to 21, wherein the fiber is a polyester or polyester blended fiber.

23. The method for producing a liquid-repellent fiber according to any one of claims 1 to 22, wherein a water concentration in a treatment agent for treating the fiber substrate is 0.001 mol/L or less.

24. A composition comprising the liquid-repellent compound defined in any one of claims 1 to 21 and supercritical carbon dioxide.

25. A repellent comprising the liquid-repellent compound defined in any one of claims 1 to 21 and supercritical carbon dioxide.

26. A fiber subjected to water-repellent treatment with a composition or repellent comprising the liquid-repellent compound defined in any one of claims 1 to 21.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/033331

A. CLASSIFICATION OF SUBJECT MATTER

D06M 23/00(2006.01)i; ***C09K 3/18***(2006.01)i; ***D06M 13/224***(2006.01)i; ***D06M 13/425***(2006.01)i; ***D06M 15/263***(2006.01)i; ***D06M 15/643***(2006.01)i
FI: D06M23/00 Z; C09K3/18 101; D06M13/224; D06M13/425; D06M15/263; D06M15/643

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)

D06M10/00-16/00; D06M19/00-23/18; C09K3/18

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 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2000-220074 A (TORAY IND INC) 08 August 2000 (2000-08-08) claims 1-3, 6-8, paragraph [0010], examples 1, 2	1-3, 5-6, 18, 22-26
Y	claims 1-3, 6-8, paragraph [0010], examples 1, 2	9-17, 19-21
X	JP 2002-511907 A (MICELL TECHNOLOGIES) 16 April 2002 (2002-04-16) claims 1, 3, 5, 6, 9, 11, p. 7, lines 11-14, p. 12, lines 6-14, p. 13, lines 5-9, examples 22, 26	1-8, 18, 22-26
Y	claims 1, 3, 5, 6, 9, 11, p. 7, lines 11-14, p. 12, lines 6-14, p. 13, lines 5-9, examples 22, 26	9-17, 19-21
Y	JP 2021-155492 A (TAIYO KAGAKU KK) 07 October 2021 (2021-10-07) claims 1, 4, paragraph [0004]	9-13
Y	JP 2021-075609 A (ARAKAWA CHEM IND) 20 May 2021 (2021-05-20) claims 1, 2, 7, 8, paragraphs [0002]-[0007]	9-13
Y	JP 52-005400 A (ALLIED CHEMICAL CORPORATION) 17 January 1977 (1977-01-17) claims 1, 2, p. 4, upper left column, lines 5-9	14, 16

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

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"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
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"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	Date of mailing of the international search report
08 November 2023	**28 November 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/033331

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2017-504730 A (RUDOLF GMBH) 09 February 2017 (2017-02-09) claims 1, 24, paragraphs [0001]-[0005], [0020]	15-16
Y	JP 2022-33218 A (THE CHEMOURS COMPANY FC, LLC) 28 February 2022 (2022-02-28) claim 9, paragraphs [0006]-[0007]	17
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Y	WO 2019/026593 A1 (DAIKIN INDUSTRIES, LTD.) 07 February 2019 (2019-02-07) claims 1, 12, paragraphs [0002], [0005]	20-21
A	JP 2018-122250 A (AIST) 09 August 2018 (2018-08-09)	1-26
A	US 2002/0108183 A1 (SMITH, Carl Brent) 15 August 2002 (2002-08-15)	1-26

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/033331

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2000-220074 A	08 August 2000	(Family: none)	
JP 2002-511907 A	16 April 2002	US 6165559 A claims 1, 2, column 2, lines 54-59, examples 22, 26 WO 1998/054397 A1 EP 986667 A1	
JP 2021-155492 A	07 October 2021	(Family: none)	
JP 2021-075609 A	20 May 2021	CN 112779772 A KR 10-2021-0055609 A	
JP 52-005400 A	17 January 1977	US 4209610 A claims 1, 2, column 2, lines 3-7	
WO 01/44209 A1	21 June 2001	US 6391948 B1	
JP 2017-504730 A	09 February 2017	US 2017/0022657 A1 claims 1, 24, paragraphs [0001]-[0005], [0020] EP 3074437 A1 KR 10-2016-0091947 A CN 105980427 A	
JP 2022-33218 A	28 February 2022	US 2015/0361300 A1 claims 1, 16, paragraphs [0002], [0005] EP 3155164 A1 KR 10-2017-0066453 A CN 107278221 A	
JP 2017-222967 A	21 December 2017	(Family: none)	
WO 2019/026593 A1	07 February 2019	US 2020/0239613 A1 claims 1, 12, paragraphs [0002], [0011] EP 3663376 A1 KR 10-2020-0023436 A CN 111032816 A	
JP 2018-122250 A	09 August 2018	(Family: none)	
US 2002/0108183 A1	15 August 2002	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2004076190 A **[0004]**
- JP 2022033218 A **[0157]**
- WO 2016049278 A **[0157]**
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- Sensyoku Shiage Kiki Soran. Fiber Japan Co., 1981, 196-247 **[0345]**