(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 459 039 A1**

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

(43) Date of publication:
06.11.2024 Bulletin 2024/45

(21) Application number: **23752867.4**

(22) Date of filing: **07.02.2023**

(51) International Patent Classification (IPC):
D06M 15/277 *(2006.01)* ***D06M 15/295*** *(2006.01)*

(52) Cooperative Patent Classification (CPC):
D06M 15/277; D06M 15/295

(86) International application number:
PCT/JP2023/004006

(87) International publication number:
WO 2023/153403 (17.08.2023 Gazette 2023/33)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **09.02.2022 CN 202210121185**

(71) Applicant: **DAIKIN INDUSTRIES, LTD.**
Osaka-shi, Osaka 530-0001 (JP)

(72) Inventors:
- **MINAMI, Shinichi**
  Osaka-Shi, Osaka 530-0001 (JP)
- **NAKAMURA, Keisuke**
  Osaka-Shi, Osaka 530-0001 (JP)
- **ENOMOTO, Takashi**
  Changshu, Jiangsu 215522 (CN)
- **CHEN, Tao**
  Changshu, Jiangsu 215522 (CN)
- **HE, Zhaowei**
  Changshu, Jiangsu 215522 (CN)
- **ZHU, Wenxu**
  Changshu, Jiangsu 215522 (CN)

(74) Representative: **Hoffmann Eitle**
Patent- und Rechtsanwälte PartmbB
Arabellastraße 30
81925 München (DE)

(54) WATER- AND OIL-REPELLENT COMPOSITION FOR NONWOVEN FABRIC, AND NONWOVEN FABRIC PRODUCT

(57) A water- and oil-repellent composition for a nonwoven fabric, which comprises (1) a fluorine-containing water- and oil-repellent agent and (2) a sizing agent and is water-based, can impart good alcohol repellency, water pressure resistance, and antistatic properties to an object to be treated, such as a nonwoven fabric. The water- and oil-repellent composition for a nonwoven fabric does not contain a carbodiimide compound and may contain at least 20 wt% of water with respect to the water- and oil-repellent composition. The active ingredient of the sizing agent may include an alkylketene dimer and/or an alkenylketene dimer. The water- and oil-repellent composition may further contain an antistatic agent and a penetrant. A treated substrate is preferably a nonwoven fabric.

EP 4 459 039 A1

Description

Technical Field

[0001] The present disclosure relates to a water- and oil-repellent composition for a nonwoven fabric, and a nonwoven fabric product.

Background Art

[0002] Nonwoven fabrics are in use in various uses, particularly, in a medical use. Examples of main performances required for nonwoven fabrics, particularly, medical nonwoven fabrics include alcohol-repellency, water pressure resistance, and antistatic properties.

[0003] A fluorine-containing water- and oil-repellent agent imparts alcohol-repellency to nonwoven fabrics, and an antistatic agent is used in combination to prevent the charging of nonwoven fabrics. However, the antistatic agent impairs alcohol-repellency and water pressure resistance, and there is thus an object of satisfying antistatic properties together with alcohol-repellency and water pressure resistance. For example, in conventional fluorine-containing water- and oil-repellent agents, it is difficult to maintain the best balance of alcohol-repellency, water pressure resistance, and antistatic properties, and it is difficult to select a water- and oil-repellent agent that does not make water pressure resistance deteriorate on the occasion of the combined use of an antistatic agent.

[0004] Patent Literature 1 (JP 2021-75608 A) discloses a water-repellent composition containing an alkyl ketene dimer.

[0005] Patent Literature 2 (JP 1991-193972 A) discloses a water- and oil-repellent treatment agent for natural and recycled textile products containing a fluorine-containing water- and oil-repellent agent and a carbodiimide compound.

Citation List

Patent Literature

[0006]

Patent Literature 1: JP 2021-75608 A
Patent Literature 2: JP 1991-193972 A

Summary of Invention

Technical Problem

[0007] An object of the present disclosure is to provide a water- and oil-repellent composition that imparts good alcohol-repellency, water pressure resistance, and antistatic properties to a treatment target such as a nonwoven fabric.

Solution to Problem

[0008] The present disclosure provides a water- and oil-repellent composition containing a fluorine-containing water- and oil-repellent agent and a sizing agent.

[0009] Preferable aspects of the present disclosure are as follows.

Aspect 1:

[0010] A water- and oil-repellent composition for a nonwoven fabric that contains (1) a fluorine-containing water- and oil-repellent agent and (2) a sizing agent and is aqueous.

Aspect 2:

[0011] The water- and oil-repellent composition for a nonwoven fabric according to Aspect 1, wherein a carbodiimide compound is not contained, and the water- and oil-repellent composition contains 20% by weight or more of water, based on the water- and oil-repellent composition.

Aspect 3:

[0012] The water- and oil-repellent composition for a nonwoven fabric according to Aspect 1 or 2, wherein the fluorine-containing water- and oil-repellent agent contains a fluorine-containing polymer having a repeating unit formed from a monomer represented by the formula:

$$CH_2=C(-X^{11})-C(=O)-Y^{11}-Z^{11}-Rf$$

wherein X^{11} is a hydrogen atom, a monovalent organic group, or a halogen atom,

Y^{11} is -O- or -NH-,

Z^{11} is a direct bond or a divalent organic group, and Rf is a fluoroalkyl group having 1 to 20 carbon atoms.

Aspect 4:

[0013] The water- and oil-repellent composition for a nonwoven fabric according to any one of Aspects 1 to 3, wherein a sizing active ingredient in the sizing agent is at least one selected from the group consisting of an alkyl ketene dimer, an alkenyl ketene dimer, a wax, a vinyl alcohol polymer, a melamine/formalin polymer, a styrene/(meth)acrylic acid copolymer, a styrene/(meth)acrylic acid ester copolymer, a styrene/(meth)acrylic acid/(meth)acrylic acid ester copolymer, a styrene/maleic acid copolymer, an isobutylene/(meth)acrylic acid copolymer, a diisobutylene/maleic acid copolymer, a propylene/maleic acid copolymer, an ethylene/maleic acid copolymer, a poly(meth)acrylic homopolymer or copolymer, and a (meth)acrylic acid ester/acrylonitrile copolymer.

Aspect 5:

[0014] The water- and oil-repellent composition for a nonwoven fabric according to any one of Aspects 1 to 4, wherein the sizing active ingredient in the sizing agent contains an alkyl ketene dimer and/or an alkenyl ketene dimer.

Aspect 6:

[0015] The water- and oil-repellent composition for a nonwoven fabric according to any one of Aspects 1 to 5, wherein the sizing active ingredient in the sizing agent contains, in addition to the alkyl ketene dimer and/or the alkenyl ketene dimer, at least one selected from the group consisting of a wax, a vinyl alcohol polymer, a melamine/formalin polymer, a styrene/(meth)acrylic acid copolymer, a styrene/(meth)acrylic acid ester copolymer, a styrene/(meth)acrylic acid/(meth)acrylic acid ester copolymer, a styrene/maleic acid copolymer, an isobutylene/(meth)acrylic acid copolymer, a diisobutylene/maleic acid copolymer, a propylene/maleic acid copolymer, an ethylene/maleic acid copolymer, a poly(meth)acrylic homopolymer or copolymer, and a (meth)acrylic acid ester/acrylonitrile copolymer.

Aspect 7:

[0016] The water- and oil-repellent composition for a nonwoven fabric according to any one of Aspects 1 to 6, wherein the water- and oil-repellent composition contains at least one selected from an antistatic agent and a penetrating agent, or the water- and oil-repellent composition is used in combination with at least one selected from an antistatic agent and a penetrating agent. Aspect 8:

[0017] A water- and oil-repellent kit for a nonwoven fabric, comprising:

(1) a water- and oil-repellent agent; and
(2) a sizing agent.

Aspect 9:

[0018] A method for treating a nonwoven fabric, wherein a nonwoven fabric is treated with the water- and oil-repellent composition for a nonwoven fabric according to any one of Aspects 1 to 7 or the water- and oil-repellent kit for a nonwoven fabric according to Aspect 8.

Aspect 10:

[0019] A nonwoven fabric product to which a water- and oil-repellent polymer and the sizing active ingredient in the water- and oil-repellent composition for a nonwoven fabric according to any one of Aspects 1 to 7 or the water- and oil-repellent kit for a nonwoven fabric according to Aspect 8 are adhered.

Advantageous Effects of Invention

[0020] Good alcohol-repellency, antistatic properties, and water pressure resistance are imparted to a treatment target (particularly, a nonwoven fabric)

Description of Embodiments

[0021] A water- and oil-repellent composition contains a fluorine-containing water- and oil-repellent agent and a sizing agent.

[0022] The water- and oil-repellent composition is preferably aqueous. For example, the water- and oil-repellent composition is an aqueous dispersion. The water- and oil-repellent composition contains 20% by weight or more, 30% by weight or more, 50 to 99.9% by weight, or 60 to 99% by weight of water, based on the water- and oil-repellent composition in some embodiments.

[0023] Preferably, the water- and oil-repellent composition does not contain a carbodiimide compound.

<(1) Fluorine-containing water- and oil-repellent agent>

[0024] Preferably, the fluorine-containing water- and oil-repellent agent is an aqueous dispersion (aqueous emulsion) containing a fluorine-containing polymer (that is, a water- and oil-repellent polymer) and water. The fluorine-containing polymer is an active ingredient that imparts water-repellency and oil-repellency.

[0025] In the water- and oil-repellent composition, the weight ratio of the active ingredient (fluorine-containing polymer) of the water- and oil-repellent agent to the active ingredient (for example, an alkyl ketene dimer) of the sizing agent is 30:70 to 95:5, 55:45 to 90:10, 60:40 to 85:15, or 65:35 to 80:20 in some embodiments.

(A) Fluorine-containing polymer

[0026] The fluorine-containing polymer is a polymer having a repeating unit derived from a fluorine-containing monomer having a fluoroalkyl group.

[0027] The fluorine-containing polymer is

a homopolymer having a repeating unit derived from a fluorine-containing monomer having a fluoroalkyl group or a copolymer having a repeating unit derived from a fluorine-containing monomer having a fluoroalkyl group and a repeating unit derived from another copolymerizable polymerizable compound in some embodiments.

[0028] The fluorine-containing polymer is a random polymer in some embodiments or is a block copolymer in other embodiments.

[0029] In the present disclosure, the fluorine-containing polymer (A) consists of (A1) a repeating unit derived from a fluorine-containing monomer having a fluoroalkyl group in some embodiments, but preferably has at least one repeating unit selected from,
in addition to the repeating unit (A1),

(A2) a repeating unit derived from a long-chain hydrocarbon group-containing monomer,
(A3) a repeating unit derived from a non-crosslinkable monomer, and
(A4) a repeating unit derived from a crosslinkable monomer.

(A1) Fluorine-containing monomer

[0030] The fluorine-containing monomer is generally a polymerizable compound having a perfluoroalkyl group or a perfluoroalkenyl group and an acrylic acid group, a methacrylic acid group, or an α-substituted acrylic acid group.

[0031] Preferably, the fluorine-containing monomer (A1) is a compound (acrylate ester or acrylamide) represented by the formula:

$CH_2=C(-X^{11})-C(=O)-Y^{11}-Z^{11}-Rf$

wherein X^{11} is a hydrogen atom, a monovalent organic group, or a halogen atom,

Y^{11} is -O- or -NH-,

Z^{11} is a direct bond or a divalent organic group, and Rf is a fluoroalkyl group having 1 to 20 carbon atoms.

[0032] X^{11} is a hydrogen atom, a linear or branched alkyl group having 1 to 21 carbon atoms, a fluorine atom, a chlorine atom, a bromine atom, an iodine atom, a CFX^1X^2 group (provided that X^1 and X^2 are each a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom), a cyano group, a linear or branched fluoroalkyl group having 1 to 21 carbon atoms, a substituted or unsubstituted benzyl group, or a substituted or unsubstituted phenyl group in some embodiments. Specific examples of X^{11} are H, CH_3, Cl, Br, I, F, CN, and CF_3. X^{11} is preferably a hydrogen atom, a methyl group, or a chlorine atom and particularly preferably a methyl group.

[0033] Y^{11} is -O- or -NH-. Y^{11} is preferably -O-.

[0034] Z^{11} is a direct bond, a linear or branched aliphatic group having 1 to 20 carbon atoms (particularly, an alkylene group), for example, a group represented by the formula $-(CH_2)_x-$ (wherein x is 1 to 10), an aromatic group or a cycloaliphatic group having 6 to 18 carbon atoms, a group represented by the formula $-R^2(R^1)N-SO_2-$ or $-R^2(R^1)N-CO-$ (wherein R^1 is an alkyl group having 1 to 10 carbon atoms, and R^2 is a linear alkylene group or branched alkylene group having 1 to 10 carbon atoms), a group represented by the formula $-CH_2CH(OR^3)CH_2-(Ar-O)_p-$ (wherein R^3 is a hydrogen atom or an acyl group having 1 to 10 carbon atoms (for example, formyl, acetyl or the like), Ar is an arylene group having a substituent as necessary, and p represents 0 or 1), a group represented by the formula $-CH_2-Ar-(O)_q-$ (wherein Ar is an arylene group having a substituent as necessary, and q is 0 or 1), a $-(CH_2)_m-SO_2-(CH2)_n-$ group, or a $-(CH_2)_m-S-(CH_2)_n-$ group (provided that m is 1 to 10, and n is 0 to 10) in some embodiments.

[0035] Alternatively, Z^{11} is preferably an aliphatic group having 1 to 10 carbon atoms, an aromatic group or cycloaliphatic group having 6 to 18 carbon atoms, a $-CH_2CH_2N(R^1)SO_2-$ group (provided that R^1 is an alkyl group having 1 to 4 carbon atoms), a $-CH_2CH(OZ^1)CH_2-(Ph-O)_p-$ group (provided that Z^1 is a hydrogen atom or an acetyl group, Ph is a phenylene group, and p is 0 or 1), a $-(CH_2)_n-Ph-O-$group (provided that Ph is a phenylene group, and n is 0 to 10), a $-(CH_2)_m-SO_2-(CH_2)_n-$ group, or a $-(CH_2)_m-S-(CH_2)_n-$group (provided that m is 1 to 10, and n is 0 to 10). Preferably, the aliphatic group is an alkylene group (particularly, the number of carbon atoms is 1 to 4, for example, 1 or 2). The aromatic group or cycloaliphatic group is substituted in some embodiments and is not substituted in other embodiments. A S group or a SO_2 group directly bonds to an Rf group in some embodiments.

[0036] The Rf group is preferably a perfluoroalkyl group. Preferably, the number of carbon atoms of the Rf group is 1 to 12, for example, 1 to 6, particularly, 4 to 6, and especially 6. Examples of the Rf group are $-CF_3$, $-CF_2CF_3$, $-CF_2CF_2CF_3$, $-CF(CF_3)_2$, $-CF_2CF_2CF_2CF_3$, $-CF_2CF(CF_3)_2$, $-C(CF_3)_3$, $-(CF_2)_4CF_3$, $-(CF_2)_2CF(CF_3)_2$, $-CF_2C(CF_3)_3$, $-CF(CF_3)CF_2CF_2CF_3$, $-(CF_2)_5CF_3$, $-(CF_2)_3CF(CF_3)_2$, $-(CF_2)_4CF(CF_3)_2$, $-C_8F_{17}$, and the like.

[0037] As specific examples of the fluorine-containing monomer, for example, the following monomers can be exemplified, but the fluorine-containing monomer is not limited thereto.

$CH_2=C(-H)-C(=O)-O-(CH_2)_2-Rf$

$CH_2=C(-H)-C(=O)-O-C_6H_4-Rf$

$CH_2=C(-Cl)-C(=O)-O-(CH_2)_2-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_2N(-CH_3)\ SO_2-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_2N(-C_2H_5)\ SO_2-Rf$

$CH_2=C(-H)-C(=O)-O-CH_2CH(-OH)\ CH_2-Rf$

$CH_2=C(-H)-C(=O)-O-CH_2CH(-OCOCH_3)\ CH_2-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_2-S-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_2-S-(CH_2)_2-Rf$

$CH_2=C(-H)-C(=O)-O-(CH_2)_3-SO_2-Rf$

CH_2=C(-H)-C(=O)-O-$(CH_2)_2$-SO_2-$(CH_2)_2$-Rf

CH_2=C(-H)-C(=O)-NH-$(CH_2)_2$-Rf

CH_2=C($-CH_3$)-C(=O)-O-$(CH_2)_2$-S-Rf

CH_2=C($-CH_3$)-c(=O)-O-$(CH_2)_2$-S-$(CH_2)_2$-Rf

CH_2=C($-CH_3$)-C(=O)-O-$(CH_2)_3$-SO_2-Rf

CH_2=C($-CH_3$)-C(=O)-O-$(CH_2)_2$-SO_2-$(CH_2)_2$-Rf

CH_2=C($-CH_3$)-C(=O)-NH-$(CH_2)_2$-Rf

CH_2=C(-F)-C(=O)-O-$(CH_2)_2$-S-Rf

CH_2 =C(-F)-C(=O)-O-$(CH_2)_2$-S-$(CH_2)_2$-Rf

CH_2=C(-F)-C(=O)-O-$(CH_2)_2$-SO_2-Rf

CH_2=C(-F)-C(=O)-O-$(CH_2)_2$-SO_2-$(CH_2)_2$-Rf

CH_2=C(-F)-C(=)-NH-$(CH_2)_2$-Rf

CH_2=C(-Cl)-C(=O)-O-$(CH_2)_2$-S-Rf

CH_2=C(-Cl)-C(=O)-O-$(CH_2)_2$-S-$(CH_2)_2$-Rf

CH_2=C(-Cl)-C(=O)-O-$(CH_2)_2$-SO_2-Rf

CH_2=C(-Cl)-C(=O)-O-$(CH_2)_2$-SO_2-$(CH_2)_2$-Rf

CH_2=C(-Cl)-C(=O)-NH-$(CH_2)_2$-Rf

CH_2=C($-CF_3$)-C(=O)-O-$(CH_2)_2$-S-Rf

CH_2=C($-CF_3$)-C(=O)-O-$(CH_2)_2$-S-$(CH_2)_2$-Rf

CH_2=C($-CF_3$)-C(=O)-O-$(CH_2)_2$-SO_2-Rf

CH_2=C($-CF_3$)-C(=O)-O-$(CH_2)_2$-SO_2-$(CH_2)_2$-Rf

CH_2=C($-CF_3$)-C(=O)-NH-$(CH_2)_2$-Rf

CH_2=C($-CF_2H$)-C(=O)-O-$(CH_2)_2$-S-Rf

CH_2=C($-CF_2H$)-C(=O)-O-$(CH_2)_2$-S-$(CH_2)_2$-Rf

CH_2=C($-CF_2H$)-C(=O)-O-$(CH_2)_2$-SO_2-Rf

CH_2=C($-CF_2H$)-C(=O)-O-$(CH_2)_2$-SO_2-$(CH_2)_2$-Rf

CH_2=C($-CF_2H$)-C(=O)-NH-$(CH_2)_2$-Rf

CH_2=C(-CN)-C(=O)-O-$(CH_2)_2$-S-Rf

CH_2=C(-CN)-C(=O)-O-$(CH_2)_2$-S-$(CH_2)_2$-Rf

CH_2=C(-CN)-C(=O)-O-$(CH_2)_2$-SO_2-Rf

CH_2=C(-CN)-C(=O)-O-$(CH_2)_2$-SO_2-$(CH_2)_2$-Rf

CH_2=C(-CN)-C(=O)-NH-$(CH_2)_2$-Rf

CH_2=C(-CF_2CF_3)-C(=O)-O-$(CH_2)_2$-S-Rf

CH_2=C(-CF_2CF_3)-C(=O)-O-$(CH_2)_2$-S-$(CH_2)_2$-Rf

CH_2=C(-CF_2CF_3)-C(=O)-O-$(CH_2)_2$-SO_2-Rf

CH_2=C(-CF_2CF_3)-C(=O)-O-$(CH_2)_2$-SO_2-$(CH_2)_2$-Rf

CH_2=C(-CF_2CF_3)-C(=O)-NH-$(CH_2)_2$-Rf

CH_2=C(-F)-C(=O)-O-$(CH_2)_3$-S-Rf

CH_2=C(-F)-C(=O)-O-$(CH_2)_3$-S-$(CH_2)_2$-Rf

CH_2=C(-F)-C(=O)-O-$(CH_2)_3$-SO_2-Rf

CH_2=C(-F)-C(=O)-O-$(CH_2)_3$-SO_2-$(CH_2)_2$-Rf

CH_2=C(-F)-C(=O)-NH-$(CH_2)_3$-Rf

CH_2=C(-Cl)-C(=O)-O-$(CH_2)_3$-S-Rf

CH_2=C(-Cl)-C(=O)-O-$(CH_2)_3$-S-$(CH_2)_2$-Rf

CH_2=C(-Cl)-C(=O)-O-$(CH_2)_3$-SO_2-Rf

CH_2=C(-Cl)-C(=O)-O-$(CH_2)_3$-SO_2-$(CH_2)_2$-Rf

CH_2=C(-CF_3)-C(=O)-O-$(CH_2)_3$-S-Rf

CH_2=C(-CF_3)-C(=O)-O-$(CH_2)_3$-S-$(CH_2)_2$-Rf

CH_2=C(-CF_3)-C(=O)-O-$(CH_2)_3$-SO_2-Rf

CH_2=C(-CF_3)-C(=O)-O-$(CH_2)_3$-SO_2-$(CH_2)_2$-Rf

CH_2=C(-CF_2H)-C(=O)-O-$(CH_2)_3$-S-Rf

CH_2=C(-CF_2H)-C(=O)-O-$(CH_2)_3$-S-$(CH_2)_2$-Rf

CH_2=C(-CF_2H)-C(=O)-O-$(CH_2)_3$-SO_2-Rf

CH_2=C(-CF_2H)-C(=O)-O-$(CH_2)_3$-SO_2-$(CH_2)_2$-Rf

CH_2=C(-CN)-C(=O)-O-$(CH_2)_3$-S-Rf

CH_2=C(-CN)-C(=O)-O-$(CH_2)_3$-S-$(CH_2)_2$-Rf

CH_2=C(-CN)-C(=O)-O-$(CH_2)_3$-SO_2-Rf

CH_2=C(-CN)-C(=O)-O-$(CH_2)_3$-SO_2-$(CH_2)_2$-Rf

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_3-S-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_3-S-(CH_2)_2-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_3-SO_2-Rf$

$CH_2=C(-CF_2CF_3)-C(=O)-O-(CH_2)_2-SO_2-(CH_2)_2-Rf$

wherein Rf is a fluoroalkyl group having 1 to 20 carbon atoms.

[0038] The fluorine-containing monomer is one monomer or a combination of two or more monomers in some embodiments.

[0039] Examples of the combination of two or more fluorine-containing monomers include

a combination of a monomer 1 in which X^{11} is a hydrogen atom and a monomer 2 in which X^{11} is a methyl group, a combination of a monomer 1 in which X^{11} is a hydrogen atom and a monomer 2 in which X^{11} is a chlorine atom, and a combination of a monomer 1 in which X^{11} is a methyl group and a monomer 2 in which X^{11} is a halogen atom. In the combinations, the mole ratio of the monomer 1 to the monomer 2 is 10:90 to 90:10 or 30:70 to 70:30 in some embodiments.

(A2) Long-chain hydrocarbon group-containing monomer

[0040] The long-chain hydrocarbon group-containing monomer does not have any fluoroalkyl groups. Alternatively, the long-chain hydrocarbon group-containing monomer does not have any fluorine atoms.

[0041] The long-chain hydrocarbon group is a saturated or unsaturated group. Preferably, the long-chain hydrocarbon group is a saturated hydrocarbon group, particularly, an alkyl group.

[0042] Preferably, the long-chain hydrocarbon group is a linear or branched hydrocarbon group having 7 to 40 carbon atoms. The number of carbon atoms of the linear or branched hydrocarbon group is 10 to 40, 12 to 40, or 18 to 40 in some embodiments. The number of carbon atoms of the linear or branched hydrocarbon group is preferably 12 to 40, more preferably 12 to 30, particularly 18 to 28, and especially 18 to 22 (or 18 to 24) and is generally preferably a saturated aliphatic hydrocarbon group, particularly, an alkyl group. The long-chain hydrocarbon group is particularly preferably a stearyl group, an icosyl group, or a behenyl group.

[0043] Preferably, the long-chain hydrocarbon group-containing monomer is a monomer represented by the formula: $CH_2=C(-X)-C(=O)-Y-R_n$

wherein X is a hydrogen atom, a monovalent organic group, or a halogen atom,
Y is a di- to tetravalent linking group having at least one group selected from -O- and -NH-,
R is a hydrocarbon group having 7 to 40 carbon atoms, and n is an integer of 1 to 3.

[0044] X is a hydrogen atom, a methyl group, a halogen other than a fluorine atom, a substituted or unsubstituted benzyl group, or a substituted or unsubstituted phenyl group in some embodiments. Examples of X are a hydrogen atom, a methyl group, a chlorine atom, a bromine atom, an iodine atom, and a cyano group. Preferably, X is a hydrogen atom, a methyl group, or a chlorine atom.

[0045] Y is a di- to tetravalent group. Y is preferably a divalent group.

[0046] Preferably, Y is a group (provided that the group is other than a hydrocarbon group) composed of at least one or more selected from a hydrocarbon group having 1 carbon atom, $-C_6H_6-$, -O-, -C(=O)-, $-S(C=O)_2-$ or -NH-. Examples of the hydrocarbon group having 1 carbon atom include $-CH_2-$, -CH=, or -C=.

[0047] Examples of Y are -Y'-, -Y'-C(=O)-, -C(=O)-Y'-, -Y'-C(=O)-Y'-, -Y'-C(=O)-Y'-, -Y'-R'-, -Y'-R'-Y'-, -Y'-R'--Y'-C(=O)-, -Y'-R'-C(=O)-Y'-, -Y'-R'-Y'-C(=O)-Y'-, or -Y'-R'-Y'-R'-

wherein Y' is a direct bond, -O- or -NH-, and
R' is $-(CH_2)_m-$ (m is an integer of 1 to 5) or $-C_6H_6-$(phenylene group).

[0048] Specific examples of Y include -O-, -NH-, -O-C(=O)-, -C(=O)-NH-, -NH-C(=O)-, -O-C(=O)-NH-, -NH-C(=O)-O-, -NH-C(=O)-NH-, $-O-C_6H_6-$, $-O-(CH_2)_m-O-$, $-NH-(CH_2)_m-NH-$, $-O-(CH_2)_m-NH-$, $-NH-(CH_2)_m-O-$, $-O-(CH_2)_m-O-C(=O)-$, $-O-(CH_2)_m-C(=O)-O-$, $-NH-(CH_2)_m-O-C(=O)-$, $-NH-(CH_2)_m-C(=O)-O-$, $-O-(CH_2)_m-O-C(=O)-NH-$, $-O-(CH_2)_m-NH-C(=O)-O-$, $-O-(CH_2)_m-C(=O)-NH-$, $-O-(CH_2)_m-NH-C(=O)-$, $-O-(CH_2)_m-NH-C(=O)-NH-$, $-O-(CH_2)_m-O-C_6H_6-$, $-NH-(CH_2)_m-O-C(=O)-NH-$, $-NH-(CH_2)_m-NH-C(=O)-O-$, $-NH-(CH_2)_m-C(=O)-NH-$, $-NH-(CH_2)_m-NH-C(=O)-$, $-NH-(CH2)_m-NH-C(=O)-NH-$, $-NH-(CH_2)_m-O-C_6H_6-$, $-NH-(CH_2)_m-NH-C_6H_6-$, wherein m is an integer of 1 to 5, and is

particularly 2 or 4.

[0049] Y is more preferably -O-, -NH-, -O-$(CH_2)_m$-O-C(=O)-, - O-$(CH_2)_m$-NH-C(=O)-, -O-$(CH_2)_m$-O-C(=O)-NH-, -O-$(CH_2)_m$-NH-C(=O)-O-, or -O-$(CH_2)_m$-NH-C(=O)-NH-,
wherein m is an integer of 1 to 5, particularly, 2 or 4. Y is particularly preferably -O-$(CH_2)_m$-NH-C(=O)-.

[0050] Y is particularly preferably -O-, -NH-, -O-$(CH_2)_m$-NH-C(=O)-, -O-$(CH_2)_m$-O-C(=O)-NH-, -O-$(CH_2)_m$-NH-C(=O)-O-, or - O-$(CH_2)_m$-NH-C(=O)-NH-,
wherein m is an integer of 1 to 5, particularly, 2 or 4.

[0051] R is preferably a linear or branched hydrocarbon group. In some embodiments, the hydrocarbon group is particularly a linear hydrocarbon group. Preferably, the hydrocarbon group is an aliphatic hydrocarbon group, particularly a saturated aliphatic hydrocarbon group, and especially an alkyl group. Preferably, the number of carbon atoms of the hydrocarbon group is 12 to 30, for example, 16 to 26, and particularly 18 to 22.

[0052] n is an integer of 1 to 3, and is preferably 1.

[0053] When Y has a tetravalent hydrocarbon group having 1 carbon atom, n = 3 is preferable. When Y has a trivalent hydrocarbon group having 1 carbon atom, n = 2 is preferable. When Y has neither of trivalent and tetravalent hydrocarbon groups having 1 carbon atom, n = 1.

[0054] Examples of the long-chain hydrocarbon group-containing monomer (A2) include

(a1) an acrylic monomer in which C(=O)-O- or C(=O)-NH- is directly bonded to a hydrocarbon group having 7 to 40 carbon atoms, and
(a2) an acrylic monomer in which C(=O)-O- or C(=O)-NH- is not directly bonded to a hydrocarbon group having 7 to 40 carbon atoms.

[0055] The acrylic monomer (a2) is a compound different from the acrylic monomer (a1).

[0056] The acrylic monomer (a2) is (meth)acrylate or (meth)acrylamide having an amide group, urethane group, or urea group (that does not directly bond to C(=O)-O- or C(=O)-NH-, but directly bonds to a hydrocarbon group having 7 to 40 carbon atoms) in some embodiments. A nitrogen-containing monomer is preferably an acrylate having an amide group that does not directly bond to C(=O)-O- or C(=O)-NH-, but directly bonds to a hydrocarbon group having 7 to 40 carbon atoms.

(a1) Acrylic monomer

[0057] The acrylic monomer (a1) is preferably a compound represented by the formula:

$$CH_2=C(-X^1)-C(=O)-Y^1-R^1$$

wherein X^1 is a hydrogen atom, a monovalent organic group, or a halogen atom,
Y^1 is -O- or -NH-, and
R^1 is a hydrocarbon group having 7 to 40 carbon atoms.

[0058] The acrylic monomer (a1) is a long-chain acrylate ester monomer wherein Y^1 is -O- or a long-chain acrylamide monomer wherein Y^1 is -NH-.

[0059] In some embodiments, X^1 is a hydrogen atom, a methyl group, a halogen other than a fluorine atom, a substituted or unsubstituted benzyl group, or a substituted or unsubstituted phenyl group. Examples of X^1 include a hydrogen atom, a methyl group, a chlorine atom, a bromine atom, an iodine atom, and a cyano group. X^1 is preferably a hydrogen atom, a methyl group, or a chlorine atom.

[0060] Y^1 is -O- or -NH-.

[0061] R is preferably a linear or branched hydrocarbon group. In some embodiments, the hydrocarbon group is particularly a linear hydrocarbon group. Preferably, the hydrocarbon group is an aliphatic hydrocarbon group, particularly a saturated aliphatic hydrocarbon group, and especially an alkyl group. In some embodiments, the number of carbon atoms of the hydrocarbon group is 7 to 30 or 12 to 30, for example, 16 to 26, and particularly 18 to 22 (or 18 to 24) .

[0062] Specific examples of the long-chain acrylate ester monomer include nonyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, icosyl (meth)acrylate, behenyl (meth)acrylate, stearyl α chloroacrylate, icosyl α chloroacrylate, and behenyl α chloroacrylate.

[0063] Specific examples of the long-chain acrylamide monomer are nonyl (meth)acrylamide, lauryl (meth)acrylamide, stearyl (meth)acrylamide, icosyl (meth)acrylamide, and behenyl (meth)acrylamide.

[0064] The presence of the long-chain acrylate ester monomer or the long-chain acrylamide monomer makes water-repellency, oil-repellency, and texture that the fluorine-containing monomer imparts high.

(a2) Acrylic monomer

[0065] The acrylic monomer (a2) is a (meth)acrylate or a (meth)acrylamide having a di- to tetravalent linking group having at least one group selected from -O- and -NH-between C(=O)-O- or C(=O)-NH- and a hydrocarbon group having 7 to 40 carbon atoms in some embodiments.

[0066] The acrylic monomer (a2) is preferable a compound represented by the formula:

$$CH_2=C(-X^2)-C(=O)-Y^2-Z^1(-Z^2-R^2)_p$$

wherein X^2 is a hydrogen atom, a monovalent organic group, or a halogen atom,

Y^2 is -O- or -NH-,
Z^1 is a direct bond or a divalent or trivalent hydrocarbon group having 1 to 5 carbon atoms,
Z^2 is each independently a di- to tetravalent linking group having at least one group selected from a direct bond, -O-, and -NH-,
R^2 is each independently a hydrocarbon group having 7 to 40 carbon atoms, and
p is 1 or 2.

[0067] The acrylic monomer (a2) is a long-chain acrylate ester monomer wherein Y^2 is -O- or a long-chain acrylamide monomer wherein Y^2 is -NH-.

[0068] In some embodiments, X^2 is a hydrogen atom, a methyl group, a halogen other than a fluorine atom, a substituted or unsubstituted benzyl group, or a substituted or unsubstituted phenyl group. Examples of X^2 include a hydrogen atom, a methyl group, a chlorine atom, a bromine atom, an iodine atom, and a cyano group. The less rigid the main chain of the obtained polymer, the less likely it is to inhibit the crystallinity of a side chain, and thus X^2 is preferably a hydrogen atom, a methyl group, or a chlorine atom, more preferably a hydrogen atom or a methyl group, and particularly preferably a hydrogen atom.

[0069] Y^2 is -O- or -NH-.

[0070] Z^1 is a direct bond or a divalent or trivalent hydrocarbon group having 1 to 5 carbon atoms (particularly, an alkyl group), and optionally has a branched structure. Preferably, the number of carbon atoms of Z^1 is 2 to 4, and particularly 2. Specific examples of Z^1 include a direct bond, $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2CH_2-$, as divalent groups, $-CH_2CH=$, $-CH_2(CH-)CH_2-$, $-CH_2CH_2CH=$, $-CH_2CH_2CH_2CH_2CH=$, $-CH_2CH_2(CH-)CH_2-$, and $-CH_2CH_2CH_2CH=$ (trivalent groups) having a branched structure. Preferably, Z^1 is not a direct bond.

[0071] Specific examples of Z^2 include a direct bond, -O-, - NH-, -O-C(=O)-, -C(=O)-O-, -C(=O)-NH-, -NH-C(=O)-, $-NH-S(=O)_2-$, $-S(=O)_2-NH-$, -O-C(=O)-NH-, -NH-C(=O)-O-, -NH-C(=O)-NH-, $-O-C_6H_6-$, $-O-(CH_2)$m-O-, $-NH-(CH_2)_m-NH-$, $-O-(CH_2)_m-NH-$, $-NH-(CH_2)_m-O-$, $-O-(CH_2)_m-O-C(=O)-$, $-O-(CH_2)_m-C(=O)-O-$, $-NH-(CH_2)_m-O-C(=O)-$, $-NH-(CH_2)_m-C(=O)-O-$, $-O-(CH_2)_m-O-C(=O)-NH-$, $-O-(CH_2)_m-NH-C(=O)-O-$, $-O-(CH_2)_m-C(=O)-NH-$, $-O-(CH_2)_m-NH-C(=O)-$, $-O-(CH_2)_m-NH-C(=O)-NH-$, $-O-(CH_2)_m-O-C_6H_6-$, $-NH-(CH_2)_m-O-C(=O)-NH-$, $-NH-(CH_2)_m-NH-C(=O)-O-$, $-NH-(CH_2)_m-C(=O)-NH-$, $-NH-(CH_2)_m-NH-C(=O)-$, $-NH-(CH_2)$m-NH-C(=O)-NH-, $-NH-(CH_2)_m-O-C_6H_6-$, or $-NH-(CH_2)_m-NH-C_6H_6-$, wherein k is 0 or 1, m is an integer of 1 to 5, and is particularly 2 or 4.

[0072] Z^2 is particularly preferably $-(O)_k-$, -NH-, $-(O)_k-(CH_2)_m-O-C(=O)-$, $-(O)_k-(CH_2)_m-NH-C(=O)-$, $-(O)_k-(CH_2)_m-O-C(=O)-NH-$,$-(O)_k-(CH_2)_m-NH-C(=O)-O-$, or $-(O)_k-(CH_2)_m-NH-C(=O)-NH-$,
wherein k is 0 or 1, m is an integer of 1 to 5 and particularly 2 or 4.

[0073] Z^1 and Z^2 are not direct bonds at the same time.

[0074] R^2 is preferably a linear or branched hydrocarbon group. In some embodiments, the hydrocarbon group is particularly a linear hydrocarbon group. Preferably, the hydrocarbon group is an aliphatic hydrocarbon group, particularly a saturated aliphatic hydrocarbon group, and especially an alkyl group. Preferably, the number of carbon atoms of the hydrocarbon group is 12 to 30, for example, 16 to 26, and particularly 18 to 22 (or 18 to 24).

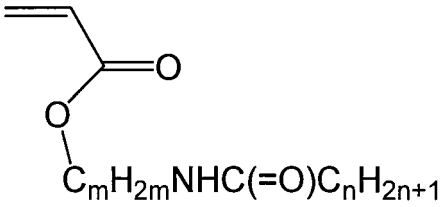
[0075] Preferably, the acrylic monomer (a2) is $CH_2=C(-X^2)-C(=O)-O-(CH_2)_m-NH-C(=O)-R^2$, $CH_2=C(-X^2)-C(=O)-O-R^2$, or a combination thereof (here, X^2, m, and R^2 are the same meanings as described above). The acrylic monomer (a2) is particularly preferably $CH_2=C(-X^2)-C(=O)-O-(CH_2)_m-NH-C(=O)-R^2$.

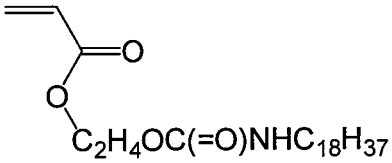
[0076] The acrylic monomer (a2) can be produced by reacting hydroxyalkyl (meth)acrylate or hydroxyalkyl (meth)acrylamide with a long-chain alkyl isocyanate. Examples of the long-chain alkyl isocyanate include lauryl isocyanate, myristyl isocyanate, cetyl isocyanate, stearyl isocyanate, oleyl isocyanate, and behenyl isocyanate.

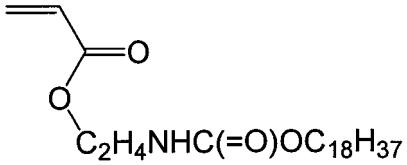
[0077] Alternatively, the acrylic monomer (A2) can also be produced by reacting a (meth)acrylate having an isocyanate group in a side chain, for example, 2-methacryloyloxyethyl isocyanate, with a long-chain alkylamine or a long-chain alkyl alcohol. Examples of the long-chain alkylamine include laurylamine, myristylamine, cetylamine, stearylamine, oleylamine, and behenylamine. Examples of the long-chain alkyl alcohol include lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl

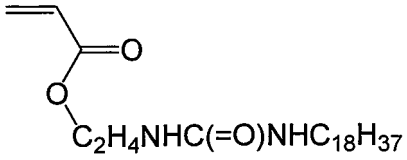
isocyanate, oleyl alcohol, and behenyl alcohol.

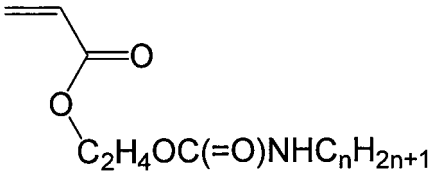
[0078] Specific examples of the acrylic monomer (a2) are as follows. The compound having the following chemical formula is an acrylate having a hydrogen atom at the α-position, and in some embodiments, specific examples are a methacrylate having a methyl group at the α-position and an acrylate having a chlorine atom at the α-position.

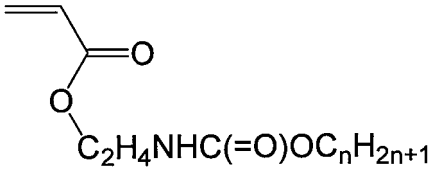


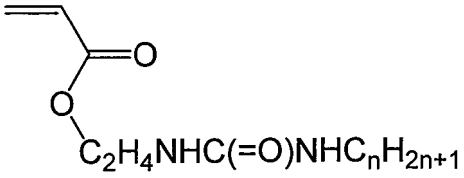


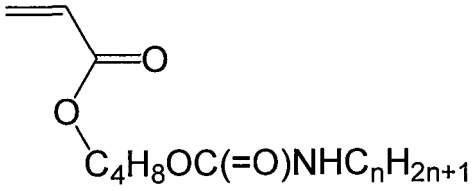


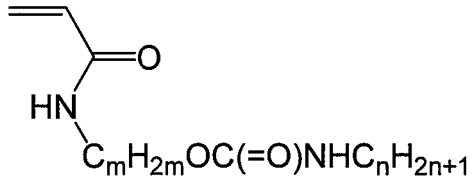


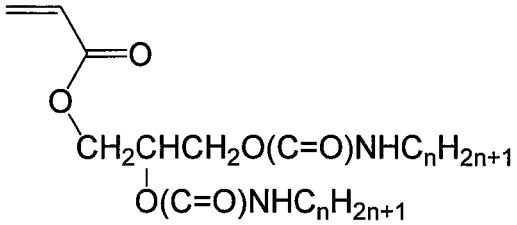












wherein m is an integer of 1 to 5, and n is an integer of 7 to 40, and
a methacrylate having a methyl group at the α-position and an acrylate having a chlorine atom at the α-position in the above chemical formulae.

[0079] Typical specific examples of the acrylic monomer (a2) include palmitic acid amidoethyl (meth)acrylate, stearic acid amidoethyl (meth)acrylate, behenic acid amidoethyl (meth)acrylate, and myristic acid amidoethyl (meth)acrylate.

[0080] The acrylic monomer (a2) is particularly preferably an amide group-containing monomer represented by the formula:

$$R^{22}\text{-}C(=O)\text{-}NH\text{-}R^{23}\text{-}O\text{-}R^{21}$$

wherein R^{21} is an organic residue having an ethylenically unsaturated polymerizable group,
R^{22} is a hydrocarbon group having 7 to 40 carbon atoms, and
R^{23} is a hydrocarbon group having 1 to 5 carbon atoms.

[0081] An example of the amide group-containing monomer is carboxylic acid amide alkyl (meth)acrylate.

[0082] Specific examples of the amide group-containing monomer include palmitic acid amidoethyl (meth)acrylate, stearic acid amidoethyl (meth)acrylate, behenic acid amidoethyl (meth)acrylate, myristic acid amidoethyl (meth)acrylate, lauric acid amidoethyl (meth)acrylate, isostearic acid ethyl amido (meth)acrylate, oleic acid ethyl amido (meth)acrylate, tert-butylcyclohexylcaproic acid amidoethyl (meth)acrylate, adamantanecarboxylic acid ethyl amido (meth)acrylate, naphthalenecarboxylic acid amidoethyl (meth)acrylate, anthracenecarboxylic acid amidoethyl (meth)acrylate, palmitic acid amidopropyl (meth)acrylate, stearic acid amidopropyl (meth)acrylate, palmitic acid amidoethyl vinyl ether, stearic acid amidoethyl vinyl ether, palmitic acid amidoethyl allyl ether, stearic acid amidoethyl allyl ether, and mixtures thereof.

[0083] The amide group-containing monomer is preferably stearic acid amidoethyl (meth)acrylate. The amide group-containing monomer is a mixture containing stearic acid amidoethyl (meth)acrylate in some embodiments. In the mixture containing stearic acid amidoethyl (meth)acrylate, the amount of the stearic acid amidoethyl (meth)acrylate is, for example, 55 to 99% by weight, preferably 60 to 85% by wight, and further preferably 65 to 80% by weight, based on the weight of the amide group-containing monomer in some embodiments. The residual monomer is, for example, palmitic acid amidoethyl (meth)acrylate in some embodiments.

(A3) Non-crosslinkable monomer

[0084] The non-crosslinkable monomer (A3) is a monomer other than the long-chain hydrocarbon group-containing

monomer (A2). The non-crosslinkable monomer (A3) is a monomer not containing any fluorine atoms. The non-crosslinkable monomer (A3) does not have any crosslinkable functional group. Unlike a crosslinkable monomer (A4), the non-crosslinkable monomer (A3) is not crosslinkable. The non-crosslinkable monomer (A3) is preferably a monomer having an ethylenically unsaturated carbon-carbon double bond. The non-crosslinkable monomer (A3) is preferably a vinyl monomer not containing fluorine. The non-crosslinkable monomer (A3) is generally a compound having one ethylenically unsaturated carbon-carbon double bond.

[0085] A preferable non-crosslinkable monomer (A3) is a compound represented by the formula:

$$CH_2=CA\text{-}T$$

wherein A is a hydrogen atom, a methyl group, or a halogen atom other than a fluorine atom (for example, a chlorine atom, a bromine atom, or an iodine atom), and
T is a chain or cyclic organic group having a hydrogen atom, a chain or cyclic hydrocarbon group, or an ester bond (and also an oxyalkylene group depending on the case).

[0086] Examples of the chain or cyclic hydrocarbon group (for example, having 1 to 40 carbon atoms) are a linear or branched aliphatic hydrocarbon group having 1 to 40 carbon atoms, a cycloaliphatic group having 4 to 40 carbon atoms, an aromatic hydrocarbon group having 6 to 40 carbon atoms, and an aromatic-aliphatic hydrocarbon group having 7 to 40 carbon atoms.

[0087] Examples of the chain or cyclic organic group having an ester bond (and having 1 to 300 or 1 to 41 carbon atoms) are -C(=O)-O-Q or -O-C(=O)-Q (here, Q is a linear or branched aliphatic hydrocarbon group having 1 to 40 carbon atoms, a cycloaliphatic group having 4 to 40 carbon atoms, an aromatic hydrocarbon group having 6 to 40 carbon atoms, or an aromatic-aliphatic hydrocarbon having 7 to 40 carbon atoms in some embodiments, is one or a plurality (for example, 2 to 300) of alkylene glycol groups (having 2 to 4 carbon atoms, particularly, 2 or 3) in other embodiments, or has the glycol group in some embodiments).

[0088] Preferable examples of the non-crosslinkable monomer (A3) include, for example, ethylene, vinyl acetate, acrylonitrile, styrene, polyethylene glycol (meth)acrylate, polypropylene glycol (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acrylate, and vinyl alkyl ether. The non-crosslinkable monomer (A3) is not limited to these examples.

[0089] The non-crosslinkable monomer (A3) is a (meth)acrylate ester having an alkyl group in some embodiments. The number of carbon atoms of the alkyl group is 1 to 17, 1 to 10, 1 to 6, or 1 to 4 in some embodiments. For example, the non-crosslinkable monomer (A3) is an acrylate represented by the general formula in some embodiments:

$$CH_2=CA^1COOA^2$$

wherein A^1 is a hydrogen atom, a methyl group, or a halogen atom other than a fluorine atom (for example, a chlorine atom, a bromine atom, or an iodine atom), and
A^2 is an alkyl group represented by C_nH_{2n+1} (n = 1 to 17 or 1 to 6).

[0090] The fluorine-containing polymer does not have any repeating unit derived from a (meth)acrylate ester having an alkyl group having 1 to 17 carbon atoms in some embodiments.

[0091] The non-crosslinkable monomer (A3) is a (meth)acrylate monomer having a cyclic hydrocarbon group in some embodiments. The (meth)acrylate monomer having a cyclic hydrocarbon group is a compound having a (preferably monovalent) cyclic hydrocarbon group and a monovalent (meth)acrylate group. The monovalent cyclic hydrocarbon group and the monovalent (meth)acrylate group directly bond to each other. Examples of the cyclic hydrocarbon group include a saturated or unsaturated monocyclic group, a polycyclic group, a bridged ring group, and the like. The cyclic hydrocarbon group is preferably saturated. The number of carbon atoms of the cyclic hydrocarbon group is preferably 4 to 20. Examples of the cyclic hydrocarbon group include a cycloaliphatic group having 4 to 20, particularly, 5 to 12 carbon atoms, an aromatic group having 6 to 20 carbon atoms, and an aromatic-aliphatic group having 7 to 20 carbon atoms. The number of carbon atoms of the cyclic hydrocarbon group is particularly preferably 15 or less, for example, 10 or less. Preferably, the carbon atoms in the cyclic hydrocarbon group directly bond to an ester group in the (meth)acrylate group. The cyclic hydrocarbon group is preferably a saturated cycloaliphatic group.

[0092] Specific examples of the cyclic hydrocarbon group include a cyclohexyl group, a t-butylcyclohexyl group, an isobornyl group, a dicyclopentanyl group, a dicyclopentenyl group, and an adamantyl group. The acrylate group is preferably an acrylate group or a methacrylate group, and particularly preferably a methacrylate group. Specific examples of the monomer having a cyclic hydrocarbon group include 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.

[0093] The non-crosslinkable monomer (A3) is a halogenated olefin in some embodiments. In some embodiments, the halogenated olefin is a halogenated olefin having 2 to 20 carbon atoms substituted with 1 to 10 chlorine atoms, bromine atoms, or iodine atoms. Preferably, the halogenated olefin is 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. Preferable specific examples of the halogenated olefin include a vinyl halide such as vinyl chloride, vinyl bromide, or vinyl iodide, and a vinylidene halide such as vinylidene chloride, vinylidene bromide, or vinylidene iodide.

(A4) Crosslinkable monomer

[0094] The fluorine-containing polymer has a repeating unit derived from a crosslinkable monomer (A4) in some embodiments. The crosslinkable monomer (A4) is a monomer not containing any fluorine atoms. The crosslinkable monomer (A4) is a compound that has at least two reactive groups and/or ethylenically unsaturated carbon-carbon double bonds and does not have fluorine in some embodiments. The crosslinkable monomer (A4) is a compound having at least two ethylenically unsaturated carbon-carbon double bonds or a compound having at least one ethylenically unsaturated carbon-carbon double bond and at least one reactive group in some embodiments. Examples of the reactive group include a hydroxyl group, an epoxy group, a chloromethyl group, a blocked isocyanate group, an amino group, a carboxyl group, and the like.

[0095] As the crosslinkable monomer (A4), for example, diacetone acrylamide, (meth)acrylamide, N-methylol acrylamide, hydroxymethyl (meth)acrylate, hydroxyethyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, 2-acetoacetoxyethyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, butadiene, isoprene, chloroprene, glycidyl (meth)acrylate, and the like are exemplified, but the crosslinkable monomer (A4) is not limited thereto.

[0096] Copolymerization of the non-crosslinkable monomer (A3) and/or the crosslinkable monomer (A4) makes it possible to improve various properties such as water- and oil-repellency or antifouling properties, the cleaning durability or washing durability of these performances, solubility in solvents, hardness, and feeling as necessary.

[0097] The monomer is polymerized in the presence of at least one compound selected from the group consisting of a blocked isocyanate compound and an organopolysiloxane compound in some embodiments. The amount of the blocked isocyanate compound (or the organopolysiloxane compound) is 0 to 100 parts by weight, for example, 1 to 50 parts by weight, based on 100 parts by weight of the monomer in some embodiments.

[0098] A polymer having a blocked isocyanate group can be obtained by polymerizing a monomer in the presence of the blocked isocyanate compound. The blocked isocyanate compound is an isocyanate that has been blocked by at least one blocking agent. Examples of the blocking agent include oximes, phenols, alcohols, mercaptans, amides, imides, imidazoles, ureas, amines, imines, pyrazoles, and active methylene compounds. Other examples of the blocking agent include pyridinols, thiophenols, diketones, and esters. The blocked isocyanate compound is also modified by a compound having a hydrophilic group in some embodiments.

[0099] In some embodiments, the amount of the fluorine-containing monomer (A1) is 30 to 100% by weight, preferably 32 to 98% by weight, for example, 35 to 95% by weight, particularly, 40 to 90% by weight, based on the fluorine-containing polymer.

[0100] In the fluorine-containing polymer, based on 100 parts by weight of the fluorine-containing monomer (A1),

the amount of the long-chain hydrocarbon group-containing monomer (A2) is 1,000 parts by weight or less, for example, 0.1 to 300 parts by weight, particularly, 1 to 200 parts by weight,
the amount of the non-crosslinkable monomer (A3) is 1,000 parts by weight or less, for example, 0.1 to 300 parts by weight, particularly, 1 to 200 parts by weight, and
the amount of the crosslinkable monomer (A4) is 50 parts by weight or less, for example, 30 parts by weight or less, particularly, 0.1 to 20 parts by weight.

[0101] Alternatively, based on the fluorine-containing polymer,

the amount of the fluorine-containing monomer (A1) is 30 to 90% by weight, for example, 35 to 80% by weight, particularly, 40 to 70% by weight,
the amount of the long-chain hydrocarbon group-containing monomer (A2) is 1 to 60% by weight, for example, 5 to 50% by weight, particularly, 10 to 40% by weight,
the amount of the non-crosslinkable monomer (A3) is 1 to 60% by weight, for example, 5 to 50% by weight, particularly, 10 to 40% by weight, and

the amount of the crosslinkable monomer (A4) is 30 parts by weight or less, for example, 0.1 to 20% by weight, particularly, 1 to 10% by weight.

[0102] The number average molecular weight (Mn) of the fluorine-containing polymer is generally 1,000 to 1,000,000, for example, 2,000 to 500,000, and particularly 3,000 to 200,000 in some embodiments. The number average molecular weight (Mn) of the fluorine-containing polymer is generally measured by GPC (gel permeation chromatography).

[0103] The water- and oil-repellent agent and the fluorine-containing polymer can be used singly or in combination of two or more.

[0104] The water- and oil-repellent agent preferably contains a surfactant when the water- and oil-repellent agent is an aqueous emulsion. The surfactant is at least one selected from a nonionic surfactant, a cationic surfactant, an anion surfactant, and an amphoteric surfactant in some embodiments.

[0105] Examples of the nonionic surfactant include ethers, esters, ester ethers, alkanolamides, polyvalent alcohols, amine oxides, and polyoxyalkylene (particularly, ethylene)-added compounds thereof.

[0106] Examples of the cationic surfactant include amines, amine salts, quaternary ammonium salts, imidazolines, and imidazolinium salts.

[0107] Examples of the anionic surfactant include fatty acid salts, sulfonates, and sulfate ester salts.

[0108] Examples of the amphoteric surfactant include alanines, imidazolinium betaines, amido betaines, acetic acid betaines, and the like.

[0109] The amount of the surfactant is 0.1 to 50 parts by weight, for example, 1 to 20 parts by weight, based on 100 parts by weight of the fluorine-containing polymer (or the total of the monomers) in some embodiments.

[0110] The fluorine-containing polymer can be produced by any of the usual polymerization methods, and the conditions of the polymerization reaction can be arbitrarily selected. Examples of such a polymerization method include solution polymerization, suspension polymerization, and emulsion polymerization. The fluorine-containing polymer is preferably produced by emulsion polymerization or solution polymerization.

[0111] The water- and oil-repellent agent preferably forms the dispersion of the fluorine-containing polymer by emulsion polymerization. Preferably, the water- and oil-repellent agent is an aqueous dispersion, in more detail, an aqueous dispersion in which the particles of the fluorine-containing polymer are dispersed in an aqueous medium.

[0112] After the fluorine-containing polymer is produced by polymerization, the fluorine-containing polymer is preferably added to water (or an aqueous medium) and dispersed in water.

[0113] In some embodiments, water (or the aqueous medium) is added after the fluorine-containing polymer is produced by polymerization. For example, in some embodiments, after a monomer is polymerized in the presence of an organic solvent to produce the fluorine-containing polymer, water is added to the polymer mixture, and the fluorine-containing polymer is dispersed in water by distilling the organic solvent away. The organic solvent is not distilled away in other embodiments. The surfactant is added before polymerization or after polymerization in some embodiments or is not added in other embodiments. Even when the surfactant is not added, a good aqueous dispersion can be obtained.

<(2) Sizing agent>

[0114] The sizing agent is a sizing agent that is generally used for paper. The sizing agent has a function of suppressing the permeability of liquid such as ink into paper and preventing bleed-through or smudge.

[0115] The sizing agent is preferably an agent that is used as an internally-added sizing agent or an externally-added sizing agent, for example, as an externally-added sizing agent (that is, a front side sizing agent) in the production of paper.

[0116] The sizing agent preferably contains an active ingredient (ingredient that suppresses the permeability of liquid) of the sizing agent and water. In the present specification, the active ingredient of the sizing agent will be referred to as "sizing active ingredient" in some cases.

[0117] The sizing active ingredient is not limited, but examples thereof include

ketene dimers such as an alkyl ketene dimer and an alkenyl ketene dimer;
alkyl succinic anhydrides, alkenyl succinic anhydrides; waxes;
vinyl alcohol polymers such as polyvinyl alcohol and modified polyvinyl alcohol;
melamine/formalin polymers;
styrene polymers such as a styrene/(meth)acrylic acid copolymer, a styrene/(meth)acrylic acid ester copolymer, a styrene/(meth)acrylic acid/(meth)acrylic acid ester copolymer, and a styrene/maleic acid copolymers;
olefin polymers such as an isobutylene/(meth)acrylic acid copolymer, a diisobutylene/maleic acid copolymer, a propylene/maleic acid copolymer, and an ethylene/maleic acid copolymer;
poly(meth)acrylic homopolymers, and copolymers, for example, a (meth)acrylic acid ester/acrylonitrile copolymer.

[0118] In the alkyl ketene dimer and the alkenyl ketene dimer, the number of carbon atoms of the alkyl group and the

alkenyl group is 3 to 40, 4 to 36, or 4 to 24, for example, 12 to 24 in some embodiments.

[0119] Examples of the waxes include paraffin wax, microcrystalline wax, Fischer-Tropsch wax, polyethylene wax, animal and vegetable wax, mineral wax, and the like. Examples thereof include normal alkanes. The number of carbon atoms of the wax is 20 to 60, for example, 25 to 45 in some embodiments. The molecular weight of the wax is 150 to 1,000 or 300 to 700 in some embodiments.

[0120] In the (meth)acrylic acid ester, an alcohol residue is preferably a hydrocarbon alcohol (particularly, an aliphatic hydrocarbon alcohol such as a saturated aliphatic hydrocarbon alcohol or a saturated alicyclic alcohol) (the number of carbon atoms of the hydrocarbon group is 1 to 40 or 3 to 30). A copolymer of two or more (meth)acrylic acid alkyl esters having different alkyl chain lengths or a copolymer of (meth)acrylic acid alkyl ester and a crosslinking group, for example, (meth)acrylic acid ester containing a -OH group and/or a-COOH group is preferable.

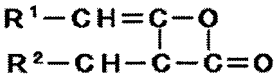
[0121] In the present specification, (meth)acrylic acid means acrylic acid and methacrylic acid.

[0122] Preferable sizing agents are an alkyl ketene dimer, an alkenyl ketene dimer, a wax, a styrene polymer such as a styrene/(meth)acrylic acid copolymer, a styrene/acrylic acid ester copolymer, a styrene/(meth)acrylic acid/(meth)acrylic acid ester copolymer, and a styrene/maleic acid copolymer, an isobutylene/acrylic acid copolymer, a diisobutylene/maleic acid copolymer, a propylene/maleic acid copolymer, and an ethylene/maleic acid copolymer.

[0123] More preferable sizing agents are an alkyl ketene dimer, an alkenyl ketene dimer, an alkyl ketene dimer, a styrene polymer, a styrene copolymer, and mixtures thereof.

[0124] The alkyl ketene dimer and the alkenyl ketene dimer are particularly preferable since the alcohol resistance becomes higher. In the present specification, the alkyl ketene dimer and the alkenyl ketene dimer will be expressed as "AKD" in some cases.

[0125] The alkyl ketene dimer and the alkenyl ketene dimer are compounds represented by the formula in some embodiments:



wherein R^1 and R^2 are the same as or different from each other in some embodiments, and each represent an alkyl group or alkenyl group having 4 to 24 carbon atoms.

[0126] The sizing agent can be used singly or in combination of two or more.

[0127] The sizing agent contains, in addition to the alkyl ketene dimer and/or the alkenyl ketene dimer, the above other active ingredient such as the wax in some embodiments. In the combination of the alkyl ketene dimer and/or the alkenyl ketene dimer, and the other active ingredient, the weight ratio of the alkyl ketene dimer and the alkenyl ketene dimer to the other active ingredient is 10:90 to 90:10 or 30:70 to 70:30 in some embodiments.

[0128] The sizing agent is preferably an aqueous solution or an aqueous dispersion (aqueous liquid).

[0129] The aqueous dispersion of the sizing agent can be produced, for example, by dispersing the sizing agent in water in the presence of a surfactant.

[0130] When the sizing agent is an aqueous emulsion, the sizing agent preferably contains a surfactant. The surfactant is at least one selected from a nonionic surfactant, a cationic surfactant, an anion surfactant, and an amphoteric surfactant in some embodiments. Examples of the nonionic surfactant, the cationic surfactant, the anion surfactant, and the amphoteric surfactant are the same examples as described in the fluorine-containing polymer. The amount of the surfactant is 0.1 to 50 parts by weight, for example, 1 to 20 parts by weight, based on 100 parts by weight of the sizing active ingredient in some embodiments.

[0131] When the sizing agent is referred to as cationic or amphoteric (for example, a cationic dispersion), generally, the surfactant is cationic or amphoteric in some embodiments.

<Water- and oil-repellent kit>

[0132] A water- and oil-repellent kit has a water- and oil-repellent agent (1) and a sizing agent (2). The water- and oil-repellent kit means a combination of the water- and oil-repellent agent (1) and the sizing agent (2).

[0133] The water- and oil-repellent agent (1) generally contains a fluorine-containing polymer and a liquid medium. The sizing agent (2) generally contains a sizing active ingredient and a liquid medium.

[0134] In one aspect, there is no need to form a water- and oil-repellent composition in advance by mixing the water- and oil-repellent agent (1) and the sizing agent (2). For example, the water- and oil-repellent agent (1) and the sizing agent (2) are separately prepared and added to a treatment liquid in some embodiments.

<Water- and oil-repellent composition>

[0135] The water- and oil-repellent composition is preferably in the form of a dispersion, a solution, an emulsion, or an aerosol. The water- and oil-repellent composition preferably contains, in addition to a fluorine-containing copolymer and a sizing active ingredient, a medium (particularly, a liquid medium, for example, an organic solvent and/or water). In the water- and oil-repellent agent, the concentrations of the fluorine-containing polymer and the sizing active ingredient are, for example, 0.01 to 50% by weight in some embodiments.

[0136] The liquid medium that the water- and oil-repellent composition (or the water- and oil-repellent agent or the sizing agent) contains is preferably an aqueous medium. In the present specification, "aqueous medium" means a medium consisting of water only and a medium also containing an organic solvent (the amount of the organic solvent is 80 parts by weight or less, for example, 0.1 to 50 parts by weight, particularly, 5 to 30 parts by weight, based on 100 parts by weight of water) in addition to water.

[0137] The water- and oil-repellent composition can be applied to a treatment target (substrate) by an arbitrary appropriate method, for example, the substrate can be treated with the water- and oil-repellent composition. In other words, a method for treating the substrate including treatment with the water- and oil-repellent composition is provided. In the present disclosure, "treatment" means applying the water- and oil-repellent agent or a treatment agent containing the water- and oil-repellent agent to the treatment target by dipping, spraying, coating, or the like. The treatment causes the fluorine-containing polymer, which is an active ingredient of the treatment agent, to penetrate into the treatment target and/or adhere to the surface of the treatment target. In general, the treatment method of the present disclosure can make the treatment target be water- and oil-repellent (or water-repellent/hydrophobic and oil-repellent/lipophobic) and alcohol-repellent.

[0138] Typically, a method involving dispersing the water- and oil-repellent composition (or the water- and oil-repellent agent and the sizing agent) in water, diluting the resulting dispersion to give a treatment liquid, adhering the treatment liquid to the treatment target by a known method such as immersion coating, spray coating, or foam coating, and drying the same can be adopted. In addition, in some embodiments, if necessary, the water- and oil-repellent composition is used and applied to the treatment target together with a suitable cross-linking agent for curing. Further, the water- and oil-repellent composition can also be used in combination with an antistatic agent, a penetrating agent, an insect repellent, a softening agent, an antibacterial agent, a flame retarder, a coating material fixing agent, a wrinkle-resistant agent, and the like. In some embodiments, the concentrations of the fluorine-containing polymer and the sizing active ingredient in the treatment liquid at the time of being contacted with the treatment target are 0.01 to 10% by weight (particularly, in the case of dip coating), for example, 0.05 to 10% by weight.

[0139] Preferably, the water- and oil-repellent composition contains an antistatic agent and/or a penetrating agent, or the water- and oil-repellent composition is used in combination with an antistatic agent and/or a penetrating agent.

[0140] The present disclosure imparts a significant effect when an antistatic agent is used. That is, good antistatic properties can be obtained while holding good alcohol-repellency and water pressure resistance.

[0141] Examples of the antistatic agent include an anionic surfactant, a nonionic surfactant, a cationic surfactant, and an amphoteric surfactant. Specifically, examples of the anionic surfactant include phosphoric acid ester-based compounds, for example, ZELEC TY (manufactured by Stepan Company) as a butyl phosphate metal salt. Examples of the nonionic surfactant include polyoxyethylene-based compounds, examples of the cationic surfactant include alkyl ammonium chloride, and examples of the amphoteric surfactant include amide alkyl betaine-based compounds. The antistatic agent is used singly or in combination of two or more in some embodiments.

[0142] The amount of the antistatic agent is 0.01 to 1.0% by weight or 0.1 to 0.5% by weight in a hydrophobic substrate treatment agent composition (100% by weight) in some embodiments. Alternatively, the amount of the antistatic agent is 1 to 1,000 parts by weight or 10 to 500 parts by weight, based on 100 parts by weight of the fluorine-containing polymer in some embodiments.

[0143] The penetrating agent can penetrate the water- and oil-repellent composition into a hydrophobic substrate. Examples of the penetrating agent include an alcohol, an anionic surfactant, a nonionic surfactant, a cationic surfactant, an amphoteric surfactant, and the like. Specific examples of the penetrating agent include alcohols having an alkyl group having 1 to 10 carbon atoms, polyoxyethylene alkyl ether, nonionic emulsifier emulsified dispersions of n-hexanol or n-decanol. The penetrating agent can be used singly or in combination of two or more.

[0144] The amount of the penetrating agent is 0.01 to 1.0% by weight or 0.1 to 0.5% by weight in the hydrophobic substrate treatment agent composition (100% by weight) in some embodiments. Alternatively, the amount of the penetrating agent is 1 to 1,000 parts by weight or 10 to 500 parts by weight, based on 100 parts by weight of the fluorine-containing polymer in some embodiments.

[0145] The treatment target (substrate) that is treated with the water- and oil-repellent composition is preferably a fiber base material. A textile product can be obtained by treating the fiber base material with the water- and oil-repellent composition.

[0146] When the treatment target is a fiber base material, the water- and oil-repellent composition can be applied to

the fiber base material using a treatment liquid containing the water- and oil-repellent composition according to an arbitrary appropriate method to treat the fiber base material with a liquid.

[0147] The water- and oil-repellent composition (the water- and oil-repellent agent and the sizing agent) is applied to the inside of the substrate in some embodiments, but the water- and oil-repellent composition is preferably applied to the surface of the substrate. The amount of each of the fluorine-containing polymer and the sizing active ingredient adhering to the substrate surface (per surface) is 0.001 g/m^2 to 10 g/m^2 or 0.01 g/m^2 to 1 g/m^2 (solid content amount) in some embodiments.

[0148] The fiber base material can be an arbitrary form of a fiber, a thread, a fabric, or the like, and typically a fabric. Typically, a textile product imparted with water- and oil-repellency and alcohol-repellency can be obtained by dipping the fiber base material in a treatment liquid prepared by dispersing and diluting the water- and oil-repellent composition in an aqueous medium, then, extracting the fiber base material (for example, a fabric) from the treatment liquid, pressing the fiber base material with a roll or the like (for example, between rolls) to remove the surplus treatment liquid, and drying the fiber base material to leave the active ingredient of the water- and oil-repellent composition in the fiber base material. The water- and oil-repellent composition has high processing stability, allows emulsion particles to be stably maintained even when a mechanical impact (or shear force) is applied to the treatment liquid due to the fiber base material entering the treatment liquid during such a treatment, and can effectively prevent the adhesion of a lump of the polymer (fluorine-containing polymer) to the roll or the like or the adhesion of the fiber base material. Such an effect is particularly significant when the number of carbon atoms of the fluoroalkyl group of the fluorine-containing polymer is 6 or less.

[0149] Alternatively, the water- and oil-repellent composition is applied to the fiber base material by a cleaning method in some embodiments, and is applied to the fiber base material in, for example, washing application, a dry cleaning method, or the like.

[0150] The fiber base material is typically a form of a fabric (which can also be referred to as cloth), which includes a textile, a knitted fabric, and a nonwoven fabric (for example, a medical nonwoven fabric), a fabric in the form of clothing, and a carpet. The fiber base material is also a different form, for example, a fiber, a yarn, or an intermediate textile product (for example, a sliver or a roving) in some embodiments. The fiber base material is preferably a nonwoven fabric, particularly, a medical nonwoven fabric.

[0151] The material of the fiber base material can be various examples and is an arbitrary fiber material including natural fibers and chemical fibers in some embodiments. Examples of the natural fibers include vegetable fibers such as cotton and hemp, animal fibers such as wool and silk, and mineral fibers such as asbestos, and animal or vegetable natural fibers can be preferably used. The chemical fibers include purified fibers such as lyocell, recycled fibers such as rayon (including viscose rayon or the like), semi-synthetic fibers such as acetate, synthetic fibers such as a polyamide-based synthetic fiber (nylon, aramid or the like), a polyvinyl alcohol-based synthetic fiber, a polyvinyl chloride-based synthetic fiber, a polyester-based synthetic fiber, a polyacrylonitrile-based synthetic fiber, a polyolefin-based synthetic fiber (including polyethylene, polypropylene, or the like), a polyether ester-based synthetic fiber, and a polyurethane-based synthetic fiber, and inorganic fibers such as a glass fiber and a carbon fiber, and the purified fibers, the semi-synthetic fibers, and the synthetic fibers are preferably used. In some embodiments, the material of the fiber base material is a mixture of two or more selected from the group consisting of the fiber materials exemplified herein (which is, for example, a mixture of an arbitrary natural fiber and an arbitrary synthetic fiber in some embodiments or is a form of a mixed fiber, a composite fiber, a blended yarn, a mixed yarn, or the like in other embodiments).

[0152] The water- and oil-repellent composition can impart water- and oil-repellency and alcohol-repellency to any of hydrophilic fiber materials and hydrophobic fiber materials. Examples of the hydrophilic fiber materials include cellulose-based materials (cotton, rayon, and the like). Examples of the hydrophobic fiber materials include polyolefin-based materials (polyethylene, polypropylene, polyethylene-blended materials, and the like), polyvinyl chloride-based materials, polyamide-based materials (nylon and the like), polyester-based materials, and polystyrene-based materials.

[0153] Particularly, the water- and oil-repellent composition can be applied to a fiber base material of a nonwoven fabric to produce a textile product for which high alcohol-repellency is required, for example, a nonwoven fabric product such as a medical nonwoven fabric that can be used for a medical gown, a surgical gown, or the like, but where to apply is not limited thereto. The medical nonwoven fabric is typically a nonwoven fabric composed of a hydrophobic fiber material in some embodiments, or is, for example, a polypropylene (PP) nonwoven fabric, a polyethylene terephthalate (PET) nonwoven fabric, a composite nonwoven fabric of polypropylene and polyethylene, a polyethylene nonwoven fabric, or the like in other embodiments.

[0154] Alternatively, in some embodiments, the fiber base material is leather. In order to make leather hydrophobic and lipophobic, the water- and oil-repellent composition is optionally applied to the leather from an aqueous solution or an aqueous emulsion at various stages of leather processing, for example, during the wetting processing of the leather or during the finishing of the leather.

[0155] Alternatively, in some embodiments, the fiber base material is paper. The fiber base material is optionally applied to preformed paper or applied to paper at various stages of papermaking, for example, during the drying of the

paper.

[0156] Although the embodiments have been described above, it will be understood that various modifications of the embodiments and details are possible without departing from the purpose and scope of the claims.

Examples

[0157] Hereinafter, the present disclosure will be specifically described with reference to Examples, but the present disclosure is not limited to these Examples. "Parts" or "%" are "parts by weight" or "% by weight" unless otherwise specified.

[0158] The test methods used below are as follows.

[Alcohol-repellency]

[0159] A water- and oil-repellent agent was diluted with pure water, and a medical agent such as a sizing agent was added thereto to prepare a treatment liquid (1,000 g). In the present test, as a fabric (fiber base material) to be treated, a polypropylene nonwoven fabric (45 g/m^2) was used. 1 polypropylene nonwoven fabric (45 g/m^2) (510 mm $\times$ 205 mm) was dipped into this treatment liquid, passed through between mangle rolls, and treated with a pin tenter at 120°C for 2 minutes. Regarding the obtained test fabric (treated fabric), the alcohol-repellency was evaluated. Specifically, the test fabric was tested and evaluated as follows according to AATCC test method 193-2007.

[0160] The treated fabric was stored in a constant temperature and humidity machine at a temperature of 21°C and a humidity of 50% for 4 hours or longer. Test liquids (isopropyl alcohol (IPA), water, and a mixture thereof, shown in Table 1) were also used after being stored at a temperature of 21°C. The test was performed in a constant temperature and humidity chamber at a temperature of 21°C and a humidity of 50%. 5 droplets (50 μL/droplet) of the test liquid were quietly dropped onto the test fabric with a micropipette and left to stand for 30 seconds, and when 4 or 5 liquid droplets remained on the test fabric, the test liquid was considered to be pass. The alcohol-repellency was evaluated as 12 classes of fail, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 ranging from poor waterrepellency to a good level with the largest isopropyl alcohol (IPA) content (% by volume) of the passed test liquid considered as the score. High class numbers indicate high alcohol-repellency.

[Table 1]

	Formulation (% by volume)	
Class	Isopropyl alcohol	Water
10	100	0
9	90	10
8	80	20
7	70	30
6	60	40
5	50	50
4	40	60
3	30	70
2	20	80
1	10	90
0	0	100
Fail	When isopropyl alcohol/water falls short of 0/100	

[Water pressure resistance]

[0161] A pressure at which a three-point water drip passed through or a pressure at which an evaluation sample ruptured under a condition of a pressure increase rate of 60 mbar/minute was defined as the water pressure resistance according to Worldwide Strategic Partners (hereinafter, referred to as WSP) 80.1.

[Surface resistivity]

[0162] A load voltage (100 V) was applied to the evaluation sample according to WSP40.1, and the surface electrical resistivity after 30 seconds was measured.

[0163] Substances used in the Examples and Comparative Examples are as follows.

Fluorine-containing water- and oil-repellent agent A: Production Example 1
Fluorine-containing water- and oil-repellent agent B: Production Example 2
PERGLUTIN K 175 EP: BK Giulini GmbH, polymer solution with high cationic charge density, acrylate copolymer
PERGLUTIN K 485: BK Giulini GmbH, cationic polymer dispersion, styrene-acrylate copolymer
AD1602: Seiko PMC Corporation, cationic, alkyl ketene dimer
AD1606: Seiko PMC Corporation, weakly cationic, alkyl ketene dimer
Basoplast 265D: BASF SE, cationic dispersion, styrene-Butylacrylate copolymer
Basoplast 2023LC: BASF SE, standard dispersion, AKD FennoSize S A466: Kemira Oyj, amphoteric surface sizing agent
Hydrores 166M: Kemira Oyj, alkylketendimer wax aqueous dispersion

Production Example 1

[0164] 61 g of $F(CF_2)_6CH_2CH_2OCOC(CH_3)=CH_2$, 11 g of isononyl methacrylate, 1 g of lauryl acrylate, 160 g of pure water, 25 g of a water-soluble glycol-based solvent, and 9.5 g of polyoxyethylene alkyl ether were put into a 500 mL autoclave and emulsification-dispersed with ultrasonic waves under stirring at 60°C for 15 minutes. After nitrogen substitution was performed in a flask, 25 g of vinyl chloride was injected and loaded into the flask, 0.4 g of an azo group-containing water-soluble initiator was added thereto, and the components were reacted at 60°C for 20 hours to obtain an aqueous dispersion (fluorine-containing water- and oil-repellent agent A) of a polymer. The composition of monomers in the polymer almost matched the prepared composition of the monomers.

Production Example 2

[0165] 65.1 g of CF_3CF_2-$(CF_2CF_2)_n$-$CH_2CH_2OCOC(Cl)=CH2$ (n=2.0), 65.1 g of CF_3CF_2-$(CF2CF2)_n$-$CH_2CH_2OCOCH=CH_2$ (n=2.0), 30.9 g of stearyl acrylate, 400 g of pure water, 56 g of a water-soluble glycol-based solvent, 1.56 g of alkyldimethylammonium chloride, and 16.1 g of polyoxyethylene alkyl ether were put into a 1,000 mL autoclave and emulsification-dispersed with ultrasonic waves under stirring at 60°C for 15 minutes. After nitrogen substitution was performed in a flask, 61.2 g of vinyl chloride was injected and loaded into the flask, 0.4 g of an azo group-containing water-soluble initiator was added thereto, and the components were reacted at 60°C for 20 hours to obtain an aqueous dispersion (fluorine-containing water- and oil-repellent agent B) of a polymer. The composition of monomers in the polymer almost matched the prepared composition of the monomers.

Example 1

[0166] After the fluorine-containing water- and oil-repellent agent A was diluted with pure water, a sizing agent, an antistatic agent, and a penetrating agent were added to prepare a treatment liquid (1,000 g) containing 0.8% of the fluorine-containing water- and oil-repellent agent A, 0.33% of the sizing agent, 0.3% of the antistatic agent, and 0.6% of the penetrating agent. As a fabric (fiber base material) to be treated, a polypropylene nonwoven fabric (45 g/m^2) was used. 1 polypropylene nonwoven fabric (45 g/m^2) (510 mm $\times$ 205 mm) was dipped into this treatment liquid, passed through between the mangle rolls, and treated with the pin tenter at 120°C for 2 minutes. The alcohol-repellency, the water pressure resistance, and the surface resistivity were measured. The results are shown in Table 2.

Examples 2 to 18

[0167] The same procedure as in Example 1 was repeated except that a medical agent shown in Table 2 was used. Results are shown in Table 2.

Comparative Examples 1 to 4

[0168] The same procedure as in Example 1 was repeated except that a medical agent shown in Table 2 was used. Results are shown in Table 2.

[Discussion of results]

[0169] Comparison between Examples 1 to 18 where the sizing agent was added and Comparative Examples 1 and 2 where the sizing agent was not added shows that the water pressure resistance was improved by the addition of the sizing agent. On the other hand, in Comparative Example 3 where carbodiimide was added to Example 1, the water pressure resistance improvement effect became weak. In addition, in Comparative Example 4 where alkenyl succinic anhydride was added, the water pressure resistance did not improve. While there is no intention to combine the results with theory, it is estimated that even the effect of the sizing agent that improves the water pressure resistance is low in highly hydrophilic formulations.

[Table 2]

		Example																	Co. Ex.			
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	1	2	3	4
Fluorine-based water- and oil-repellent agent	Fluorine-based water- and oil-repellent agent A (%)	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8											0.8		0.8	0.8
	Fluorine-based water- and oil-repellent agent B (%)									0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8		0.8		
Sizing agent	PERGLUTIN K 175EP (%)	0.33								0.33												0.33	
	PERGLUTIN K 485 (%)		0.33								0.33												
	AD1602 (%)			0.33								0.33											
	AD1606 (%)				0.33								0.33										
	Basoplast 265D (%)					0.33								0.33									
	Basoplast 2023LC (%)						0.33								0.33			0.18	0.50				
	FennoSize S A466 (%)							0.33								0.33							
	Hydrores 166M (%)								0.33								0.33						
	Carbodiimide																				0.08		
	Alkenyl succinic anhydride																						0.33
Antistatic agent	ZELEC TY (%)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Penetrating agent	n-Hexanol (%)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Performance evaluation	Alcohol-repellency	8	8	8	8	8	8	8	8	9	9	9	9	9	9	9	9	9	8	8	9	8	8
	Water pressure resistance (mbar)	58	57	60	61	58	62	62	62	58	58	61	62	58	62	62	62	57	64	48	48	50	46
	Surface Resistivity(GΩ)	<10²	<10²	<10²	<10²	<10²	<10²	<10²	<10²	<10²	<10³	<10²	<10²	<10²	<10²	<10²	<10²	<10²	<10²	<10²	<10²	<10²	<10²

Industrial Applicability

[0170] The water- and oil-repellent composition of the present disclosure is useful in a fiber base material, particularly, a nonwoven fabric such as a medical nonwoven fabric.

Claims

1. A water- and oil-repellent composition for a nonwoven fabric, comprising (1) a fluorine-containing water- and oil-repellent agent and (2) a sizing agent, and being aqueous.

2. The water- and oil-repellent composition for a nonwoven fabric according to claim 1, wherein a carbodiimide compound is not contained, and the water- and oil-repellent composition contains 20% by weight or more of water, based on the water- and oil-repellent composition.

3. The water- and oil-repellent composition for a nonwoven fabric according to claim 1 or 2, wherein the fluorine-containing water- and oil-repellent agent contains a fluorine-containing polymer having a repeating unit formed from a monomer represented by the formula:

$$CH_2=C(-X^{11})-C(=O)-Y^{11}-Z^{11}-Rf$$

wherein X^{11} is a hydrogen atom, a monovalent organic group, or a halogen atom,

Y^{11} is -O- or -NH-,

Z^{11} is a direct bond or a divalent organic group, and Rf is a fluoroalkyl group having 1 to 20 carbon atoms.

4. The water- and oil-repellent composition for a nonwoven fabric according to any one of claims 1 to 3, wherein a sizing active ingredient in the sizing agent is at least one selected from the group consisting of an alkyl ketene dimer, an alkenyl ketene dimer, a wax, a vinyl alcohol polymer, a melamine/formalin polymer, a styrene/(meth)acrylic acid copolymer, a styrene/(meth)acrylic acid ester copolymer, a styrene/(meth)acrylic acid/(meth)acrylic acid ester copolymer, a styrene/maleic acid copolymer, an isobutylene/(meth)acrylic acid copolymer, a diisobutylene/maleic acid copolymer, a propylene/maleic acid copolymer, an ethylene/maleic acid copolymer, a poly(meth)acrylic homopolymer or copolymer, and a (meth)acrylic acid ester/acrylonitrile copolymer.

5. The water- and oil-repellent composition for a nonwoven fabric according to any one of claims 1 to 4, wherein the sizing active ingredient in the sizing agent contains an alkyl ketene dimer and/or an alkenyl ketene dimer.

6. The water- and oil-repellent composition for a nonwoven fabric according to any one of claims 1 to 5, wherein the sizing active ingredient in the sizing agent contains, in addition to the alkyl ketene dimer and/or the alkenyl ketene dimer,
at least one selected from the group consisting of a wax, a vinyl alcohol polymer, a melamine/formalin polymer, a styrene/(meth)acrylic acid copolymer, a styrene/(meth)acrylic acid ester copolymer, a styrene/(meth)acrylic acid/(meth)acrylic acid ester copolymer, a styrene/maleic acid copolymer, an isobutylene/(meth)acrylic acid copolymer, a diisobutylene/maleic acid copolymer, a propylene/maleic acid copolymer, an ethylene/maleic acid copolymer, a poly(meth)acrylic homopolymer or copolymer, and a (meth)acrylic acid ester/acrylonitrile copolymer.

7. The water- and oil-repellent composition for a nonwoven fabric according to any one of claims 1 to 6, wherein the water- and oil-repellent composition contains at least one selected from an antistatic agent and a penetrating agent, or the water- and oil-repellent composition is used in combination with at least one selected from an antistatic agent and a penetrating agent.

8. A water- and oil-repellent kit for a nonwoven fabric, comprising:

(1) a water- and oil-repellent agent; and
(2) a sizing agent.

9. A method for treating a nonwoven fabric, wherein a nonwoven fabric is treated with the water- and oil-repellent composition for a nonwoven fabric according to any one of claims 1 to 7 or the water- and oil-repellent kit for a nonwoven fabric according to claim 8.

10. A nonwoven fabric product to which a water- and oil-repellent polymer and the sizing active ingredient in the water- and oil-repellent composition for a nonwoven fabric according to any one of claims 1 to 7 or the water- and oil-repellent kit for a nonwoven fabric according to claim 8 are adhered.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/004006

A. CLASSIFICATION OF SUBJECT MATTER

D06M 15/277(2006.01)i; ***D06M 15/295***(2006.01)i
FI: D06M15/277; D06M15/295

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)

D06M13/00-15/715

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 2014-221456 A (HOKUETSU KISHU PAPER CO., LTD.) 27 November 2014 (2014-11-27) claims, paragraphs [0016]-[0020], examples 2-7	1-10
X	JP 2005-288282 A (POWDERTECH CO., LTD.) 20 October 2005 (2005-10-20) claims, paragraphs [0027], [0028], [0049], example 1	1-4, 7-10
A		5-6
X	JP 7-292573 A (HIGASHI KAGAKU KK) 07 November 1995 (1995-11-07) claims, examples	1-3, 7-10
A		4-6
A	JP 2020-153057 A (UNITIKA TRADING CO., LTD.) 24 September 2020 (2020-09-24) paragraphs [0025]-[0030]	1-10
A	JP 6-57659 A (BAYER KK) 01 March 1994 (1994-03-01) paragraphs [0007]-[0014]	1-10

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

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

Date of the actual completion of the international search	Date of mailing of the international search report
17 April 2023	**25 April 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.

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/004006

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2014-221456 A	27 November 2014	(Family: none)	
JP 2005-288282 A	20 October 2005	(Family: none)	
JP 7-292573 A	07 November 1995	(Family: none)	
JP 2020-153057 A	24 September 2020	(Family: none)	
JP 6-57659 A	01 March 1994	(Family: none)	

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

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- JP 2021075608 A **[0004] [0006]**
- JP 3193972 A **[0005] [0006]**