



(11) **EP 4 575 089 A1**

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

- (43) Date of publication:
25.06.2025 Bulletin 2025/26

(21) Application number: **24863831.4**

(22) Date of filing: **29.07.2024**
- (51) International Patent Classification (IPC):
D21J 5/00 (2006.01) D21J 7/00 (2006.01)

(52) Cooperative Patent Classification (CPC):
D21H 17/00; D21H 21/16; D21J 3/00; D21J 5/00; D21J 7/00

(86) International application number:
PCT/JP2024/027030

(87) International publication number:
WO 2025/062833 (27.03.2025 Gazette 2025/13)

(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: GE KH MA MD TN (30) Priority: 19.09.2023 JP 2023151489 (71) Applicant: DAIKIN INDUSTRIES, LTD. Osaka-shi, Osaka 530-0001 (JP) (72) Inventors: • MATSUMOTO, Akane Osaka-Shi, Osaka 530-0001 (JP)	• AKUTA, Ryo Osaka-Shi, Osaka 530-0001 (JP) • SAKAMAKI, Tatsunori Osaka-Shi, Osaka 530-0001 (JP) • HIGASHI, Masahiro Osaka-Shi, Osaka 530-0001 (JP) • KISHIKAWA, Yosuke Osaka-Shi, Osaka 530-0001 (JP) (74) Representative: Hoffmann Eitle Patent- und Rechtsanwälte PartmbB Arabellastraße 30 81925 München (DE)
--	--

(54) **METHOD FOR MANUFACTURING PULP PRODUCT**

(57) Provide is a novel method for producing a pulp product to which liquid repellency is imparted by a method for producing a pulp product, comprising: a first heating of heating a pulp composition comprising pulp and a liquid repellent compound to a first heating temperature, thereby preparing a precursor product in which the liquid

repellent compound is adhered to the pulp; a first cooling of cooling the precursor product to a first cooling temperature, thereby preparing a cooled precursor product; and a second heating of heating the cooled precursor product to a second heating temperature, thereby preparing a pulp product.

EP 4 575 089 A1

Description

Technical Field

5 **[0001]** The present disclosure relates to a method for producing a pulp product.

Background Art

10 **[0002]** Patent Literature 1 discloses a method for producing a pulp mold product, comprising coating the surface with a coating agent immediately after pulp is formed, before or during vacuum suction from the back side of the pulp mold body, and discloses that this method can increase the effect of the coating agent (e.g., waterproofness, strength) and is economical.

Citation List

15

Patent Literature

[0003] Patent Literature 1: JP 2002-129499 A

20 Summary of Invention

Technical Problem

25 **[0004]** Patent literature 1 does not disclose or suggest multiple heating steps and a cooling step in the manufacturing process. Furthermore, Patent Literature 1 does not consider oil resistance of the product.

[0005] An object of the present disclosure is to provide a novel method for producing a pulp product to which liquid repellency is imparted.

Solution to Problem

30

[0006] : The present disclosure includes the following embodiments.

[Item 1]

35 **[0007]** A method for producing a pulp product, comprising:

40 a first heating of heating a pulp composition comprising pulp and a liquid repellent compound to a first heating temperature, thereby preparing a precursor product in which the liquid repellent compound is adhered to the pulp;
 a first cooling of cooling the precursor product to a first cooling temperature, thereby preparing a cooled precursor product; and
 a second heating of heating the cooled precursor product to a second heating temperature, thereby preparing a pulp product.

[Item 2]

45

[0008] The method for producing a pulp product according to item 1, wherein

50 the first heating temperature is 40°C or higher,
 the first cooling temperature is lower than 40°C, and
 the second heating temperature is 40°C or higher.

[Item 3]

55 **[0009]** The method for producing a pulp product according to item 1 or 2, wherein

 the first heating temperature is equal to or higher than the melting point of the liquid repellent compound, and
 the first cooling temperature is lower than the melting point of the liquid repellent compound.

[Item 4]

[0010] The method for producing a pulp product according to item 3, wherein the second heating temperature is at least 0.7 times the melting point of the liquid repellent compound.

[Item 5]

[0011] The method for producing a pulp product according to item 3, wherein the second heating temperature is equal to or higher than the first cooling temperature +30°C, and equal to or higher than the melting point of the liquid repellent compound -50°C.

[Item 6]

[0012] The method for producing a pulp product according to any one of items 1 to 5, wherein

the first heating temperature is equal to or higher than the melting point of the liquid repellent compound, the first cooling temperature is lower than 40°C, and the second heating temperature is equal to or higher than the melting point of the liquid repellent compound - 50°C, and equal to or lower than the melting point of the liquid repellent compound +100°C.

[Item 7]

[0013] The method for producing a pulp product according to any one of items 1 to 6, wherein

the pulp composition comprises a liquid medium, and in the first heating step, the liquid medium is removed to an amount of 10% by weight or less in the pulp composition.

[Item 8]

[0014] The method for producing a pulp product according to any one of items 1 to 7, wherein

the pulp composition is formed in the first heating step and the precursor product is a pulp mold.

[Item 9]

[0015] The method for producing a pulp product according to any one of items 1 to 8, wherein the liquid repellent compound has a biobased content of 30% or more.

[Item 10]

[0016] The method for producing a pulp product according to any one of items 1 to 9, wherein the liquid repellent compound has a hydrocarbon group having 6 or more and 40 or less carbon atoms.

[Item 11]

[0017] The method for producing a pulp product according to any one of items 1 to 10, wherein the liquid repellent compound is at least one selected from the group consisting of a fatty acid ester, a fatty acid amide, a linear hydrocarbon and a vinyl polymer.

[Item 12]

[0018] The method for producing a pulp product according to any one of items 1 to 11, wherein

the pulp composition comprises at least one repellent selected from the group consisting of a water-resistant agent, an oil-resistant agent, a water-repellent agent, an oil-repellent agent and an antifouling agent, and the repellent comprises the liquid repellent compound.

[Item 13]

[0019] The method for producing a pulp product according to item 12, wherein the repellent is at least one selected from the group consisting of a water-resistant agent and an oil-resistant agent.

[Item 14]

[0020] The method for producing a pulp product according to item 12 or 13, wherein the repellent comprises a dispersant and water.

[Item 15]

[0021] The method for producing a pulp product according to any one of items 1 to 14, wherein the pulp product is prepared by internally adding the liquid repellent compound.

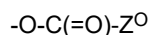
[Item 16]

[0022] The method for producing a pulp product according to any one of items 1 to 15, wherein the amount of the liquid repellent compound adhering to the pulp product is 3.0% by weight or less.

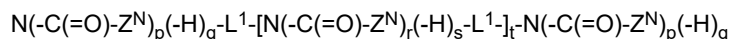
[Item 17]

[0023] The method for producing a pulp product according to any one of items 1 to 16, wherein

the liquid repellent compound is a modified body of polyol or a modified body of amine, the modified body of polyol is a compound formed by replacing a hydroxy group of polyglycerol having a degree of polymerization of 1 or more and 15 or less with a group represented by the following formula:



wherein Z^O is an alkyl group having 14 or more and 24 or less carbon atoms, the modified body of polyol has a hydroxy group substitution ratio of 50% or more, and the modified body of amine is a compound represented by the following formula:



wherein Z^N is independently at each occurrence an alkyl group having 14 or more and 24 or less carbon atoms,

L^1 is independently at each occurrence a divalent aliphatic hydrocarbon group having 2 to 20 carbon atoms or an aromatic hydrocarbon group,

p is independently at each occurrence an integer of 1 or more and 2 or less,

q is independently at each occurrence 0 or 1,

$p + q$ is 2 in each $N(-C(=O)-Z^N)_p(-H)_q$,

r is independently at each occurrence 0 or 1,

s is independently at each occurrence 0 or 1,

$r + s$ is 1 in each $N(-C(=O)-Z^N)_r(-H)_s$, and

t is an integer of 0 or more and 3 or less.

Advantageous Effect of Invention

[0024] According to the present disclosure, a pulp product to which liquid repellency is imparted can be produced.

Description of Embodiments

<Definition of Terms>

[0025] 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, halogen and the like at the end or in the molecular chain of a hydrocarbon group.

[0026] 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 hydrocarbon groups are not limited, but include C₁₋₂₀ hydrocarbon groups, such as an aliphatic hydrocarbon group and an aromatic hydrocarbon group. The above "aliphatic hydrocarbon group" may be either linear, branched, or cyclic, and may be either saturated or unsaturated. The hydrocarbon group may include one or more ring structures. In an explicit term, the hydrocarbon group may be substituted by one or more substituents.

[0027] Whether or not the phrases "independently at each occurrence", "independently with each other", "each independently" or similar expressions are explicitly described herein, unless otherwise described that they are exceptions, when a plurality of terms (symbols) that can occur in a chemical structure is defined, such definition is applied independently to each occurrence.

[0028] The chemical structures described herein should be understood not to encompass chemical structures that are recognized by those skilled in the art as being chemically impossible or extremely unstable.

<Method for producing pulp product>

[0029] The method for producing a pulp product of present disclosure comprises:

a first heating of heating a pulp composition comprising pulp and a liquid repellent compound to a first heating temperature, thereby preparing a precursor product in which the liquid repellent compound is adhered to the pulp;
a first cooling of cooling the precursor product to a first cooling temperature, thereby preparing a cooled precursor product; and
a second heating of heating the cooled precursor product to a second heating temperature, thereby preparing a pulp product.

[0030] In an embodiment of the present disclosure, a pulp product with good liquid repellency (in particular, oil resistance at high temperatures) can be produced. In an embodiment of the present disclosure, the amount of repellent to be used (especially a liquid repellent compound) can be reduced. It seems that the arrangement and rearrangement of the molecular structure (e.g., hydrocarbon groups in hydrocarbon repellent) of the liquid repellent compound attached to pulp contributes to the effect of the present disclosure.

{First heating step}

[0031] In the first heating step, a pulp composition comprising pulp and a liquid repellent compound is heated to the first heating temperature to prepare a precursor product with the liquid repellent compound adhering to the pulp. The pulp composition will be described in detail below.

[0032] In the first heating step, the liquid repellent compound, which is the active ingredient of repellent, adheres to the inside and/or surface of the pulp by heating. Herein, the adhesion may be physical adhesion or chemical adhesion, and for example, the liquid repellent compound may be physically or chemically modified (by reaction) onto a hydroxy group of the pulp.

[0033] When the pulp composition includes a liquid medium, the liquid medium included in the pulp composition may be removed from the pulp composition in the first heating step. In other words, drying may be performed in the first heating step. In the first heating step, the liquid medium may be removed to an amount of 20% by weight or less, 15% by weight or less, 10% by weight or less, 7.5% by weight or less, 5% by weight or less, 2.5% by weight or less, 1.0% by weight or less, 0.5% by weight or less, or 0.3% by weight or less in the pulp composition. The amount after the removal corresponds to the content of the liquid medium in the precursor product.

[0034] The first heating step may be performed with or without pressurizing the pulp composition. The pressure in pressurization may be 0.03 MPa or more, 0.05 MPa or more, 0.1 MPa or more, 0.2 MPa or more, 0.3 MPa or more, 0.5 MPa or more, or 1.0 MPa or more. The pressure in pressurization may be 10 MPa or less, 7.5 MPa or less, 5.0 MPa or less, 2.5 MPa or less, 1.0 MPa or less, 0.7 MPa or less, 0.5 MPa or less, or 0.3 MPa or less. Preferably the first heating step is performed while pressurizing at 0.1 to 1.0 MPa.

[0035] The pulp composition may be mold-formed in the first heating step. In other words, the precursor product may be a mold-formed body (pulp mold). An example of mold-forming is as follows:

(1) Preparation of pulp mold intermediate

[0036] A reticular body is arranged on a pulp mold molding mold made of metal with suction holes for slurry, and pulp slurry is placed therein. At that stage the liquid repellent compound may have been added to the pulp slurry. The pulp slurry is suctioned and dehydrated through the pulp mold molding mold and the reticular body to obtain a pulp mold intermediate.

(2) Drying of pulp mold intermediate

[0037] The resulting pulp mold intermediate is then dried by applying a predetermined pressure (e.g., 0.1 to 1 MPa) thereto from the tops and bottoms of male and female molding molds made of metal heated to a predetermined temperature (the first heating temperature, for example, of 60 to 250°C). This produces a mold-formed body (pulp mold) molded into a shape of a container.

[0038] The method of heating in the first heating step is not limited, and examples thereof include heat press, hot air drying and oven heating. Heat press is preferably used.

[0039] The first heating temperature may be 35°C or more, 40°C or more, 50°C or more, 60°C or more, 70°C or more, 80°C or more, 90°C or more, 100°C or more, 110°C or more, 120°C or more, 130°C or more, 140°C or more, 150°C or more, 160°C or more, 170°C or more, 180°C or more, 190°C or more, 200°C or more, 210°C or more, 220°C or more, 230°C or more, 240°C or more, 250°C or more, 260°C or more, 270°C or more, 280°C or more, 290°C or more, or 300°C or more, and is preferably 40°C or more, 80°C or more, 100°C or more, 120°C or more, or 150°C or more, and may be 500°C or less, 450°C or less, 400°C or less, 350°C or less, 300°C or less, 250°C or less, 200°C or less, 180°C or less, 160°C or less, 140°C or less, or 120°C or less, and is preferably 250°C or less or 200°C or less.

[0040] The first heating temperature may be a temperature at which the liquid medium in the pulp composition can be distilled off.

[0041] The first heating temperature may be equal to or higher than the melting point of the liquid repellent compound -40°C, -30°C, -20°C, -10°C, $\pm 0^\circ\text{C}$ (melting point), +10°C, +20°C, +30°C, +40°C, +60°C, +80°C, +100°C, +120°C, +140°C, or +160°C, and is preferably equal to or higher than the melting point -10°C, $\pm 0^\circ\text{C}$ (melting point), or +10°C, and particularly preferably equal to or higher than the melting point $\pm 0^\circ\text{C}$ (melting point), and may be equal to or lower than the melting point of the liquid repellent compound +250°C, +200°C, +150°C, +100°C, +75°C, +50°C, +25°C, $\pm 0^\circ\text{C}$, -25°C, -50°C, or -75°C, and is preferably equal to or lower than the melting point +200°C, +150°C, +100°C, or +50°C.

[0042] The first heating temperature may be at least 0.5 times, 0.6 times, 0.7 times, 0.8 times, 0.9 times, 1.0 times, 1.1 times, 1.2 times, 1.5 times, 1.7 times, 2.0 times, or 2.5 times, and is preferably, at least 0.7 times, 1.0 times, or 1.2 times, and particularly preferably at least 1.0 times the melting point of the liquid repellent compound, and may be at most 4.0 times, 3.5 times, 3.0 times, 2.5 times, 2.0 times, 1.5 times, 1.2 times, or 1.0 times, and is preferably at least 3.0 times, or 2.0 times the melting point of the liquid repellent compound.

[0043] Heating in the first heating step may be performed in one or multiple stages, at least until the pulp composition reaches the first heating temperature. For example, when heating is performed in multiple stages (e.g., two stages), the heating temperature in the first stage may be 60°C or more, and is preferably 70°C or more and more preferably 80°C or more, and may be 250°C or less, and is preferably 200°C or less, more preferably 180°C or less, further preferably 150°C or less, and most preferably 100°C or less. The heating temperature in the second stage is preferably higher than the heating temperature in the first stage. The heating temperature in the second stage may be 60°C or more, and is preferably 80°C or more, more preferably 100°C or more, further preferably 120°C or more, even more preferably 140°C or more, still more preferably 160°C or more, and preferably 250°C or less, preferably 200°C or less, and is more preferably 180°C or less.

[0044] The time of keeping the first heating temperature is not limited, and may be 10 seconds or more, 30 seconds or more, 60 seconds or more, 90 seconds or more, or 120 seconds or more, and is preferably 30 seconds or more.

Furthermore, the time of keeping the first heating temperature may be preferably within 1 hour, 30 minutes, 10 minutes or 5 minutes from the viewpoint of productivity.

{First cooling step}

[0045] In the first cooling step, the precursor product prepared in the first heating step is cooled to the first cooling temperature to prepare a cooled precursor product.

[0046] The first cooling step may be performed with or without pressurizing (e.g., at 0.1 to 1 MPa) the precursor product. It is preferable that the precursor product is not pressurized. For example, when the precursor product is cooled, the precursor product may be cooled in the mold used in the previous step, or may be removed from the mold and then cooled. Preferably the precursor product is removed from the mold and then cooled.

[0047] The method of cooling in the first cooling step is not limited, and examples thereof include press cooling, heat release and air cooling.

[0048] The first cooling temperature may be -10°C or more, 0°C or more, 10°C or more, 20°C or more, 25°C or more,

30°C or more, 40°C or more, 50°C or more, 60°C or more, 70°C or more, 80°C or more, or 90°C or more, and may be 150°C or less, 125°C or less, 100°C or less, 90°C or less, 80°C or less, 70°C or less, 60°C or less, 50°C or less, 40°C or less (less than 40°C), 30°C or less, 25°C or less, 20°C or less, 15°C or less, or 10°C or less, and is preferably 50°C or less, 40°C or less (less than 40°C), 30°C or less, or 25°C or less.

[0049] The first cooling temperature may be in the range of room temperature (e.g., 10°C to 40°C, 15°C to 35°C, 20°C to 30°C).

[0050] The first cooling temperature may be equal to or higher than the melting point of the liquid repellent compound -200°C, -175°C, -150°C, -125°C, -100°C, -75°C, -50°C, -25°C, $\pm 0^\circ\text{C}$, +5°C, or +10°C, and is preferably equal to or higher than the melting point -150°C, -100°C, or -50°C, and equal to or lower than the melting point of the liquid repellent compound +25°C, +15°C, +5°C, $\pm 0^\circ\text{C}$, -5°C, -10°C, -15°C, -20°C, -25°C, -30°C, -35°C, -40°C, -50°C, -75°C, -100°C, -125°C, or -150°C, and is preferably equal to or lower than the melting point $\pm 0^\circ\text{C}$, -15°C, -30°C, -50°C, or -75°C.

[0051] The first cooling temperature may be at least 0.01 times, 0.03 times, 0.05 times, 0.1 times, 0.15 times, 0.20 times, 0.25 times, 0.3 times, 0.35 times, or 0.4 times the melting point of the liquid repellent compound, and at most 2.0 times, 1.75 times, 1.5 times, 1.25 times, 1.0 times (melting point), 0.9 times, 0.8 times, 0.7 times, 0.6 times, 0.5 times, 0.4 times, 0.3 times, 0.2 times, or 0.1 times the melting point of the liquid repellent compound.

[0052] The first cooling temperature may be equal to or higher than the first heating temperature -300°C, -275°C, -250°C, -225°C, -200°C, -175°C, -150°C, -125°C, -100°C, -75°C, -50°C, or -25°C, and equal to or lower than the first heating temperature -10°C, -30°C, -50°C, -75°C, -100°C, -125°C, -150°C, -175°C, -200°C, -225°C, or -250°C, and is preferably equal to or lower than the first heating temperature -75°C, or -150°C.

[0053] Cooling in the first cooling step may be performed in one or multiple stages, at least until the precursor product reaches the first cooling temperature.

[0054] The time of keeping the first cooling temperature is not limited, and is preferably 10 seconds or more, 30 seconds or more, or 1 minute or more, more preferably 5 minutes or more, further preferably 10 minutes or more, and may be 1 hour or more. Furthermore, the time of keeping the first cooling temperature may be preferably within 48 hours, within 24 hours, or within 12 hours from the viewpoint of productivity.

{Second heating step}

[0055] In the second heating step, the cooled precursor product is heated to the second heating temperature to prepare a pulp product.

[0056] The second heating step may be performed with or without pressurizing (e.g., at 0.1 to 1 MPa) the cooled precursor product. It is preferable that the cooled precursor product is not pressurized. For example, when the cooled precursor product is heated, the cooled precursor product may be heated in the mold used in the previous step, or may be removed from the mold and then heated. Preferably the cooled precursor product is removed from the mold and then heated.

[0057] The method of heating in the second heating step is not limited, and examples thereof include heat press, hot air drying and oven heating. Hot air drying and oven heating are preferably used.

[0058] The second heating temperature may be 35°C or more, 40°C or more, 50°C or more, 60°C or more, 70°C or more, 80°C or more, 90°C or more, 100°C or more, 110°C or more, 120°C or more, 130°C or more, 140°C or more, 150°C or more, 160°C or more, 170°C or more, 180°C or more, 190°C or more, 200°C or more, 210°C or more, 220°C or more, 230°C or more, 240°C or more, 250°C or more, 260°C or more, 270°C or more, 280°C or more, 290°C or more, or 300°C or more, and is preferably 40°C or more, 50°C or more, 60°C or more, 80°C or more, 100°C or more, 120°C or more, or 150°C or more, and may be 500°C or less, 450°C or less, 400°C or less, 350°C or less, 300°C or less, 250°C or less, 200°C or less, 180°C or less, 160°C or less, 140°C or less, 120°C or less, 100°C or less, 80°C or less, or 60°C or less, and is preferably 250°C or less, 200°C or less, 180°C or less, 150°C or less, 125°C or less, 100°C or less, or 80°C or less.

[0059] The second heating temperature may be equal to or higher than the melting point of the liquid repellent compound -100°C, -80°C, -60°C, -50°C, -40°C, -30°C, -20°C, -10°C, $\pm 0^\circ\text{C}$ (melting point), +10°C, +20°C, +30°C, +40°C, +60°C, +80°C, +100°C, +120°C, +140°C, or +160°C, and is preferably equal to or higher than the melting point -50°C, -30°C, or $\pm 0^\circ\text{C}$ (melting point), and may be equal to or lower than the melting point of the liquid repellent compound +200°C, +175°C, +150°C, +125°C, +100°C, +75°C, +50°C, +25°C, +10°C, $\pm 0^\circ\text{C}$ (melting point), -10°C, -25°C, -50°C, or -75°C, and is preferably equal to or lower than the melting point +75°C, +50°C, +10°C, $\pm 0^\circ\text{C}$ (melting point), or -10°C.

[0060] The second heating temperature may be at least 0.5 times, 0.6 times, 0.7 times, 0.8 times, 0.9 times, 1.0 times, 1.1 times, 1.2 times, 1.5 times, 1.7 times, 2.0 times, or 2.5 times, and is preferably 0.7 times, 0.8 times, 1.0 times, or 1.2 times, and particularly preferably 0.7 times the melting point of the liquid repellent compound, and may be at most 4.0 times, 3.5 times, 3.0 times, 2.5 times, 2.0 times, 1.5 times, 1.2 times, or 1.0 times, and is preferably 2.0 times, 1.5 times, or 1.2 times the melting point of the liquid repellent compound.

[0061] The second heating temperature may be equal to or higher than the first heating temperature -250°C, -200°C, -175°C, -150°C, -125°C, -100°C, -75°C, -50°C, -25°C, 0°C, +25°C, +50°C, +75°C, or +100°C, and equal to or lower than

the first heating temperature +100°C, +80°C, +60°C, +40°C, +20°C, 0°C, -20°C, -40°C, -60°C, -80°C, or -100°C.

[0062] The second heating temperature may be equal to or higher than the first heating temperature +10°C, +20°C, +30°C, +40°C, +50°C, +60°C, +70°C, +80°C, +90°C, +100°C, +110°C, +120°C, +130°C, +140°C, +150°C, +160°C, +170°C, or +180°C, and equal to or lower than the first heating temperature +300°C, +275°C, +250°C, +225°C, +200°C, +180°C, +160°C, +140°C, +120°C, +100°C, +80°C, +60°C, or +40°C.

[0063] Heating in the second heating step may be performed in one or multiple stages, at least until the cooled precursor product reaches the second heating temperature.

[0064] The time of keeping the second heating temperature is not limited, and is preferably 1 minute or more, more preferably 5 minutes or more, further preferably 10 minutes or more, and may be 1 hour or more. Furthermore, the time of keeping the second heating temperature is preferably within 48 hours, within 24 hours, or within 12 hours from the viewpoint of productivity.

[0065] A pulp product is obtained through the second heating step. The amount of the liquid repellent compound adhering to the pulp product after the second heating step is 0.1% by weight or more, 0.3% by weight or more, 0.5% by weight or more, 0.75% by weight or more, 1.0% by weight or more, 2.0% by weight or more, or 3.0% by weight or more, and may be 10% by weight or less, 7.5% by weight or less, 5.0% by weight or less, 4.0% by weight or less, 3.0% by weight or less, 2.0% by weight or less, 1.0% by weight or less, 0.75% by weight or less, or 0.5% by weight or less, and is preferably 3.0% by weight or less. According to the present disclosure, good liquid repellency can be achieved even when the amount of the liquid repellent compound is reduced.

{Step of preparing pulp composition}

[0066] The method for producing a pulp product of present disclosure may comprise obtaining a pulp composition by treating a pulp substrate with repellent.

[0067] As the method for treating a pulp substrate, an internal addition treatment method in which repellent is added to pulp before papermaking (e.g., pulp slurry), or an external addition treatment method in which repellent is applied to pulp after papermaking (e.g., a pulp product), can be employed.

[0068] Examples of internal addition include mixing and dipping, and internal addition may include adding a repellent to pulp slurry and mixing it with stirring.

[0069] Examples of external treatment methods include spraying and coating, and more specifically a pound-type two-roll size press, a gate roll type size press and a rod metering type size press.

[Pulp/ pulp substrate]

[0070] The pulp composition includes pulp, and the pulp has been treated with a repellent to give a pulp substrate. The pulp substrate may be in the form of pulp alone, pulp slurry, or a pulp product. Examples of pulp substrates include bleached or unbleached chemical pulp such as kraft pulp or sulfite pulp; bleached or unbleached high-yield pulp such as groundwood pulp, mechanical pulp, or thermomechanical pulp; pulp slurry including the above pulp; and a pulp product such as paper, a paper container and a paper molded body made of wastepaper pulp such as wastepaper of newspapers, magazines and cardboard, or deinked wastepaper. Specific examples of the paper products include, for example, a food packaging material, a food container, 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 rustproof 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, and molded paper (mold container).

[0071] The amount of pulp may be 0.1% 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, 30% by weight or more, 50% by weight or more, 75% by weight or more, or 90% by weight or more, and 99% by weight or less, 75% 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, 4% by weight or less, or 3% by weight or less in the pulp composition. Typically, when the pulp composition is prepared by internal addition, the amount of pulp is 30% by weight or less in the pulp composition; when the pulp composition is prepared by external addition, the amount of pulp is 75% by weight or more in the pulp composition.

[Liquid medium]

[0072] The pulp composition may comprise a liquid medium. The liquid medium may be water, an organic solvent, or a mixture of water and an organic solvent. The liquid medium is typically an aqueous medium, and in particular, water. The liquid medium may comprise a liquid medium derived from repellent.

[0073] The amount of the liquid medium may be 0.1% 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, 30% by weight or more, 50%

by weight or more, 75% by weight or more, 90% by weight or more, or 95% by weight or more, and 99% by weight or less, 75% 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, 4% by weight or less, or 3% by weight or less in the pulp composition. Typically, when the pulp composition is prepared by internal addition, the amount of the liquid medium is 50% by weight or more, and in particular 90% by weight or more in the pulp composition; when the pulp composition is prepared by external addition, the amount of the liquid medium is 30% by weight or less, and in particular, 10% by weight or less in the pulp composition.

[Repellent]

[0074] The repellent includes a liquid repellent compound. The repellent will be separately described in <Repellent> below. The amount of the repellent added to the pulp substrate may be adjusted to achieve the desired amount of the liquid repellent compound.

[0075] The amount of the liquid repellent compound may be 0.1 parts by weight or more, 0.3 parts by weight or more, 0.5 parts by weight or more, 0.75 parts by weight or more, 1.0 part by weight or more, 2.0 parts by weight or more, or 3.0 parts by weight or more, and 10 parts by weight or less, 7.5 parts by weight or less, 5.0 parts by weight or less, 4.0 parts by weight or less, 3.0 parts by weight or less, 2.0 parts by weight or less, 1.0 part by weight or less, 0.75 parts by weight or less, or 0.5 parts by weight or less, and is preferably 5.0 parts by weight or less, and more preferably 3.0 parts by weight or less based on 100 parts by weight of the pulp.

[0076] The amount of the liquid repellent compound which is a fatty acid ester may be 0.1 parts by weight or more, - 0.3 parts by weight or more, 0.5 parts by weight or more, 0.75 parts by weight or more, 1.0 part by weight or more, 2.0 parts by weight or more, or 3.0 parts by weight or more, and may be 10 parts by weight or less, 7.5 parts by weight or less, 5.0 parts by weight or less, 4.0 parts by weight or less, 3.0 parts by weight or less, 2.0 parts by weight or less, 1.0 part by weight or less, 0.75 parts by weight or less, or 0.5 parts by weight or less, and is preferably 5.0 parts by weight or less, more preferably 3.0 parts by weight or less based on 100 parts by weight of the pulp.

[0077] The amount of the liquid repellent compound which is a fatty acid amide may be 0.1 parts by weight or more, 0.3 parts by weight or more, 0.5 parts by weight or more, 0.75 parts by weight or more, 1.0 part by weight or more, 2.0 parts by weight or more, or 3.0 parts by weight or more, and may be 10 parts by weight or less, 7.5 parts by weight or less, 5.0 parts by weight or less, 4.0 parts by weight or less, 3.0 parts by weight or less, 2.0 parts by weight or less, 1.0 part by weight or less, 0.75 parts by weight or less, or 0.5 parts by weight or less, and is preferably 3.0 parts by weight or less, more preferably 2.0 parts by weight or less, and further preferably 1.0 part by weight or less based on 100 parts by weight of the pulp.

[0078] The amount of the liquid repellent compound which is a linear hydrocarbon may be 0.1 parts by weight or more, 0.3 parts by weight or more, 0.5 parts by weight or more, 0.75 parts by weight or more, 1.0 part by weight or more, 2.0 parts by weight or more, or 3.0 parts by weight or more, and may be 10 parts by weight or less, 7.5 parts by weight or less, 5.0 parts by weight or less, 4.0 parts by weight or less, 3.0 parts by weight or less, 2.0 parts by weight or less, 1.0 part by weight or less, 0.75 parts by weight or less, or 0.5 parts by weight or less, and is preferably 5.0 parts by weight or less, and more preferably 3.0 parts by weight or less based on 100 parts by weight of the pulp.

[0079] The amount of the liquid repellent compound which is a modified body of amine may be 0.1 parts by weight or more, 0.3 parts by weight or more, 0.5 parts by weight or more, 0.75 parts by weight or more, 1.0 part by weight or more, 2.0 parts by weight or more, or 3.0 parts by weight or more, and may be 10 parts by weight or less, 7.5 parts by weight or less, 5.0 parts by weight or less, 4.0 parts by weight or less, 3.0 parts by weight or less, 2.0 parts by weight or less, 1.0 part by weight or less, 0.75 parts by weight or less, or 0.5 parts by weight or less, and is preferably 5.0 parts by weight or less, and more preferably 3.0 parts by weight or less based on 100 parts by weight of the pulp.

[0080] The amount of the liquid repellent compound which is a modified body of polyol may be 0.1 parts by weight or more, 0.3 parts by weight or more, 0.5 parts by weight or more, 0.75 parts by weight or more, 1.0 part by weight or more, 2.0 parts by weight or more, or 3.0 parts by weight or more, and may be 10 parts by weight or less, 7.5 parts by weight or less, 5.0 parts by weight or less, 4.0 parts by weight or less, 3.0 parts by weight or less, 2.0 parts by weight or less, 1.0 part by weight or less, 0.75 parts by weight or less, or 0.5 parts by weight or less, and is preferably 5.0 parts by weight or less, and more preferably 3 parts by weight or less based on 100 parts by weight of the pulp.

[0081] The amount of the liquid repellent compound which is a modified body of polycarboxylic acid may be 0.1 parts by weight or more, 0.3 parts by weight or more, 0.5 parts by weight or more, 0.75 parts by weight or more, 1.0 part by weight or more, 2.0 parts by weight or more, or 3.0 parts by weight or more, and may be 10 parts by weight or less, 7.5 parts by weight or less, 5.0 parts by weight or less, 4.0 parts by weight or less, 3.0 parts by weight or less, 2.0 parts by weight or less, 1.0 part by weight or less, 0.75 parts by weight or less, or 0.5 parts by weight or less, and is preferably 5.0 parts by weight or less, more preferably 3.0 parts by weight or less based on 100 parts by weight of the pulp.

[0082] The amount of the liquid repellent compound which is a vinyl polymer may be 0.1 parts by weight or more, 0.3 parts by weight or more, 0.5 parts by weight or more, 0.75 parts by weight or more, 1.0 part by weight or more, 2.0 parts by weight or more, or 3.0 parts by weight or more, and may be 10 parts by weight or less, 7.5 parts by weight or less, 5.0 parts by weight or less, 4.0 parts by weight or less, 3.0 parts by weight or less, 2.0 parts by weight or less, 1.0 part by weight or

less, 0.75 parts by weight or less, or 0.5 parts by weight or less, and is preferably 5.0 parts by weight or less, more preferably 3.0 parts by weight or less, and further preferably 2.0 parts by weight or less based on 100 parts by weight of the pulp.

[0083] In the external addition treatment, the amount of the liquid repellent compound contained in the coating layer may be 0.01 g/m² or more, 0.03 g/m² or more, 0.05 g/m² or more, 0.1 g/m² or more, 0.3 g/m² or more, 0.5 g/m² or more, or 1.0 g/m² or more, and 5.0 g/m² or less, 4.0 g/m² or less, 3.0 g/m² or less, 2.0 g/m² or less, 1.0 g/m² or less, 0.5 g/m² or less, 0.3 g/m² or less, or 0.1 g/m² or less.

[Additive]

[0084] The pulp composition may also include an additive used for producing a pulp product in addition to the pulp and the repellent (liquid repellent compound), such as a sizing agent (for example, a cationic sizing agent, an anionic sizing agent, and a rosin-based sizing agent (for example, an acidic rosin-based sizing agent and a neutral rosin-based sizing agent)), a paper strengthening agent, an agglomerating agent, a fixing agent, a yield improver, a dye, a fluorescent dye, a slime control agent, and an antifoaming agent. Specific examples of additives include an alkyl ketene dimer, an alkenyl succinic anhydride, a styrenic polymer (styrene/maleic acid polymer, styrene/acrylic acid-based polymer), a urea-formaldehyde polymer, a polyethyleneimine, a melamine-formaldehyde polymer, starch, modified starch, carboxymethyl cellulose, a polyamidoamine-epichlorohydrin polymer, a polyacrylamide-based polymer, a polyamine-based polymer, a polydiallyldimethylammonium chloride, an alkylamine epichlorohydrin condensate, a condensate of alkylene dichloride and polyalkylene polyamine, a dicyandiamide formalin condensate, a dimethyldiallylammonium chloride polymer, and an olefin/maleic anhydride polymer. While the pulp composition includes a component derived from a repellent, the respective components contained in the repellent may be added to the pulp composition as an additive.

[0085] The additive may be nonionic, cationic, anionic or amphoteric. The additive may have an ionic charge density of -10,000 to 10,000 $\mu\text{eq/g}$, preferably -4,000 to 8,000 $\mu\text{eq/g}$, and more preferably -1,000 to 7,000 $\mu\text{eq/g}$. In the case of a paper substrate containing a cationic additive for pulp, the repellent may be anionic. In the case of a paper substrate containing an anionic additive, the repellent may be cationic.

[0086] The amount of the above additive 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, and 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, respectively, based on 100 parts by weight of the pulp.

{Other steps}

[0087] The method for producing a pulp product of the present disclosure may comprise other steps. For example, the method may or may not comprise a step of controlling humidity and/or temperature of the pulp product after the second heating. For example, when a pulp mold product is subjected to humidity and temperature control, the pulp mold product after the second heating may be placed in a constant temperature constant humidity bath adjusted to 10°C or more and a humidity of 20% or more, and stored for 30 minutes or more. The controlled temperature is preferably 15°C or more and 30°C or less, and the controlled humidity is 20% or more and less than 60%, which are not limited.

<Repellent>

[0088] The repellent in present disclosure adheres to a substrate (in particular, a pulp substrate) and imparts liquid-repellency, for example, water resistance, oil resistance, water-repellency, oil-repellency and/or antifouling properties to the substrate, and may function as a water-resistant agent, an oil-resistant agent, a water-repellent agent, an oil-repellent agent and an antifouling agent. The repellent in the present disclosure includes a liquid repellent compound. The liquid repellent compound itself may be used as a repellent, or may be combined with other components described below and used as a repellent.

[0089] The repellent of the present disclosure may not include one 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 of the present disclosure can impart liquid-repellency to a substrate without these fluorine compounds.

[0090] The volume abundance ratio of particles with a size of 100 μm or larger in the repellent of the present disclosure may be 0.1% or more, 0.3% or more, 0.5% or more, 1% or more, 1.5% or more, 3% or more, 4% or more, 5% or more, or 10% or more, and may be 50% or less, 30% or less, 20% or less, 15% or less, 10% or less, 5% or less, 3% or less, or 1.5% or less, as measured by laser diffraction scattering. The method for setting the volume abundance ratio of particles with a size of 1 μm or larger as measured by laser diffraction scattering to the above range is not limited, and for example, particles in the raw material and/or dispersion may be formed into fine particles using a pulverizer or a homogenizer.

[0091] The repellent in the present disclosure may have a median diameter as measured by laser diffraction scattering of 0.1 μm or more, 1 μm or more, 3 μm or more, 5 μm or more, 10 μm or more, 15 μm or more, 30 μm or more, or 50 μm or more, and 300 μm or less, 200 μm or less, 100 μm or less, 50 μm or less, 30 μm or less, 20 μm or less, 10 μm or less, 5 μm or less, or 1 μm or less. In the present disclosure, the volume median diameter refers to the median diameter (D50) in a volume-based particle size distribution by laser diffraction scattering.

{Liquid repellent compound}

[0092] The liquid repellent compound in the present disclosure adheres to a substrate (in particular, a pulp substrate) and imparts liquid repellency such as water resistance, oil resistance, water-repellency, oil-repellency and/or antifouling properties to the substrate.

[Characteristics]

[0093] The possible characteristics of the liquid repellent compound will be described below. These characteristics may vary depending on the type of the compound.

[0094] The liquid repellent compound may have a HD (n-hexadecane) contact angle of 10° or more, 20° or more, 25° or more, 30° or more, 35° or more, 40° or more, 45° or more, 50° or more, 55° or more, 60° or more, or 65° or more, and is preferably 25° or more, more preferably 30° or more, and may have a HD (n-hexadecane) contact angle of 100° or less, 90° or less, or 75° or less. A HD contact angle of the liquid repellent compound of the lower limit or more can impart good liquid-repellency (in particular oil-repellency) to a substrate. The HD contact angle is a static contact angle of the liquid repellent compound to a spin-coated film, which is obtained by dropping 2 μL of HD on a spin-coated film and measuring the contact angle one second after the droplet reaches the film.

[0095] The liquid repellent compound may have a water contact angle of 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, and 160° or less, 140° or less, 130° or less, 120° or less, 110° or less, 100° or less or 90° or less. A water contact angle of the liquid repellent compound of the lower limit or more can impart good liquid-repellency (in particular water-repellency) to a substrate. The water contact angle is a static contact angle of a liquid repellent compound to a spin-coated film, which is obtained by dropping 2 μL of water on a spin-coated film and measuring the contact angle one second after the droplet reaches the film.

[0096] The liquid repellent compound is preferably a biobased compound with carbon of biobased origin. A biobased content is measured in accordance with ASTM D6866. The biobased content may be 20% or more, preferably 30% or more, more preferably 50% or more, even more preferably 60% or more, still more preferably 70% or more, and most preferably 80% or more or 90% or more, and for example, 100%. A high biobased content means that the amount of use of fossil resource materials, which are typically petroleum, is small, and a higher biobased content of the liquid repellent compound is preferred from that point of view.

[0097] The liquid repellent compound has a biodegradation as of the 180th day of preferably 5% or more. A higher biodegradation is preferred because of small environmental load. The liquid repellent compound may have a biodegradation as of the 180th day of, for example, 10% or more, 20% or more, 30% or more, 50% or more, 60% or more, 70% or more, 80% or more, or 90% or more, and preferably 30% or more, more preferably 50% or more, further preferably 70% or more, and most preferably 80% or more. The liquid repellent compound has a biodegradation as of the 60th day of preferably 5% or more. A higher biodegradation is preferred because of small environmental load. The liquid repellent compound may have a biodegradation as of the 60th day of, for example, 10% or more, 15% or more, 20% or more, 25% or more, 30% or more, 35% or more, 40% or more, or 45% or more, and preferably 10% or more, and more preferably 30% or more. This biodegradation refers to the biodegradation specified in JIS K 6953-1 and ASTM D6400.

[0098] The liquid repellent compound may have a melting point of 30°C or more, 40°C or more, 60°C or more, 80°C or more, 100°C or more, or 120°C or more, and is preferably 40°C or more, and may have a melting point of 250°C or less, 225°C or less, 200°C or less, 150°C or less, 130°C or less, 120°C or less, 110°C or less, 100°C or less, 80°C or less, or 50°C or less.

[Structure]

[0099] The liquid repellent compound in the present disclosure may not have 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 without including these fluorine-containing groups to a substrate.

[0100] The liquid repellent compound may be a compound having a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or a monovalent polysiloxane group. The liquid repellent

compound may have a hydrocarbon group having 6 or more and 40 or less carbon atoms (e.g., an alkyl group) from the viewpoint of liquid repellency.

(Monovalent hydrocarbon group optionally having a substituent)

[0101] The liquid repellent compound may have a monovalent hydrocarbon group optionally having a substituent.

[0102] The hydrocarbon group may be a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms. The hydrocarbon group may be an aromatic hydrocarbon group or an aliphatic hydrocarbon group, and is preferably an aliphatic hydrocarbon group, and in particular a saturated aliphatic hydrocarbon group (an alkyl group). The hydrocarbon group may be branched, cyclic or linear, and preferably linear.

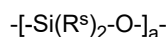
[0103] The hydrocarbon group may have 1 or more, 3 or more, 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, 18 or more, 20 or more, or 22 or more, preferably 6 or more, 10 or more, 12 or more, or 16 or more carbon atoms, and 40 or less, 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, or 10 or less, preferably 30 or less, 25 or less, or 20 or less carbon atoms.

[0104] The hydrocarbon group may have a substituent, but is preferably non-substituted. Examples of substituents include -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 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may or may not have active hydrogen. The number of substituents 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 atom relative to the carbon atom and the heteroatom may be 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and preferably 75 mol% or more, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, or 80 mol% or less. The hydrocarbon group may have 1 to 3 (for example, 1) -OR' (in particular, -OH) as a substituent (for example at a site other than the end).

(Monovalent polysiloxane group)

[0105] The liquid repellent compound may have a monovalent polysiloxane group. A (monovalent) polysiloxane group can impart liquid-repellency to the substrate as the (monovalent) hydrocarbon group does.

[0106] The polysiloxane group may also be represented by the following formula:



[wherein R^s is independently at each occurrence a hydrocarbon group having 1 to 40 carbon atoms or a reactive group, and a is an integer of 5 or more and 10,000 or less].

[0107] R^s is a hydrocarbon group having 1 to 40 carbon atoms or a reactive group.

[0108] Examples of hydrocarbon groups having 1 to 40 carbon atoms include a hydrocarbon group having 1 to 5 carbon atoms and a hydrocarbon group having 6 to 40 carbon atoms.

[0109] Examples of hydrocarbon groups having 1 to 5 carbon atoms include a hydrocarbon group having 1 to 5 carbon atoms such as a methyl group, an ethyl group, a propyl group, a butyl group and a pentyl group (in particular an aliphatic hydrocarbon group, in particular an alkyl group, for example, a methyl group or an ethyl group, and in particular a methyl group).

[0110] The hydrocarbon group having 6 to 40 carbon atoms may be an aromatic hydrocarbon group or an aliphatic hydrocarbon group, and is preferably an aliphatic hydrocarbon group, and in particular a saturated aliphatic hydrocarbon group (an alkyl group). The hydrocarbon group may be cyclic, linear or branched, and preferably linear. The hydrocarbon group may have 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, 18 or more, preferably 10 or more, more preferably 12 or more carbon atoms, and 40 or less, 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, or 10 or less, preferably 30 or less, and more preferably 25 or less carbon atoms.

[0111] Examples of reactive groups include a group having a functional group (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)acrylic group, a (meth)acryloyloxy group, a (meth)acrylamide group, and a hydrogen atom directly bonded to a silicon atom). These functional groups may be directly bonded to a silicon atom, or may be bonded to an organic group directly bonded to a silicon atom. The organic group may be a hydrocarbon group, and for example, an alkylene group or a divalent aromatic group. The hydrocarbon group may have 2 or more and 12 or less carbon atoms. An alkylene group having 2 or more and 10 or less carbon atoms is preferred. A divalent aromatic group having 6 or more and 12 or less carbon atoms is preferred. The reactive group may be a group selected from the group consisting of a hydroxy group, an epoxy ring, a carboxyl group, a (meth)acrylic group and an amino group, and for example, may be at least one selected from the group consisting of an epoxy ring, a hydroxy group, a (meth)acrylic group and a carboxyl group.

[0112] a is 3 or more, 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, and preferably 10 or more, and 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, 200 or less, 100 or less, or 50 or less, and preferably 500 or less.

[0113] In the polysiloxane group, the amount of R^s , which is a hydrocarbon group having 1 to 5 carbon atoms, may be 20 mol% or more, 40 mol% or more, 60 mol% or more, or 80 mol% or more, and preferably 50 mol% or more, and 100 mol% or less, 90 mol% or less, 80 mol% or less, or 70 mol% or less relative to the total amount of R^s . For example, 50 mol% or more of the total amount of the R^s group may be a methyl group or an ethyl group, and in particular, a methyl group.

[0114] In the polysiloxane group, the amount of R^s , which is a hydrocarbon group having 6 to 40 carbon atoms, may be 3 mol% or more, 10 mol% or more, 20 mol% or more, or 30 mol% or more, and 100 mol% or less, 90 mol% or less, 80 mol% or less, or 70 mol% or less relative to the total amount of R^s .

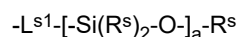
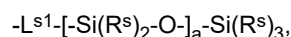
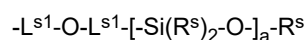
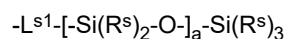
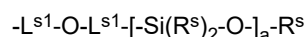
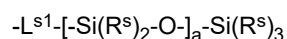
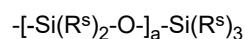
[0115] In the polysiloxane group, the amount of R^s , which is a reactive group, may be 5 mol% or more, 10 mol% or more, 20 mol% or more, or 30 mol% or more relative to the total amount of R^s , and 50 mol% or less, 40 mol% or less, 30 mol% or less, or 20 mol% or less relative to the total amount of R^s .

[0116] The R^s group may be introduced randomly or in block, and preferably randomly.

[0117] The end structure of the polysiloxane group is not limited, and may be $-OR^s$, $-Si(R^s)_3$ and the like. R^s in the end structure may have one or more reactive groups. Examples of reactive groups are as described above, and may be at least one selected from the group consisting of an epoxy ring, a hydroxy group, a (meth)acrylic group and a carboxyl group.

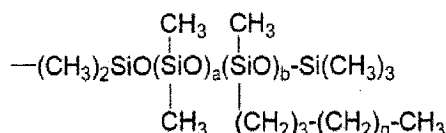
[0118] The polysiloxane group may have a linker. The matrix compound and the polysiloxane group may be linked by a linker, and examples of linkers are not limited, and include a hydrocarbon group having 1 to 40 (for example, 1 to 20) carbon atoms optionally disconnected via an oxygen atom, and may be, for example, a (poly)oxyalkylene group having 1 to 40 (for example 1 to 20) carbon atoms.

[0119] Examples of polysiloxane groups include



[wherein R^s is independently at each occurrence a hydrocarbon group having 1 to 40 carbon atoms or a reactive group, R^s at the end has one or more reactive groups,

methyl groups account for 50 mol% or more of the total amount of the R^s group,
 L^{s1} is a hydrocarbon group having 1 to 20 carbon atoms, and
 a is 5 or more and 10,000 or less], and



[wherein a is an integer of 0 to 150, b is an integer of 1 to 150, (a + b) is 5 to 200 and n is an integer of 0 to 36].

[Examples of liquid repellent compound]

[0120] Examples of liquid repellent compounds include a compound having a hydrocarbon group having 6 or more and 40 or less hydrocarbon group. Examples of hydrocarbon groups and preferred ranges are as described above.

[0121] Examples of liquid repellent compounds include at least one compound selected from the group consisting of a fatty acid ester, a fatty acid amide, a linear hydrocarbon and a vinyl polymer. Examples of fatty acid esters and fatty acid amides may include a compound corresponding to the modified body of amine, the modified body of polyol and the modified body of polycarboxylic acid described below. Examples of linear hydrocarbons include wax (e.g., paraffin wax, microcrystalline wax, Fischer Tropsch wax and polyolefin wax (polyethylene wax)).

[0122] Examples of liquid repellent compounds include at least one selected from a modified body of amine, a modified body of polyol, a modified body of polycarboxylic acid and a vinyl polymer (described in detail below).

[0123] The liquid repellent compound may include an ester group, an amide group, a urethane group, a urea group, an imide group, a thioamide group, a thiourethane group, a thiourea group, a thioimide group, a sulfone amide group, a sulfone urea group, a sulfone urethane group or a sulfone imide group (e.g., an ester group, an amide group, a urethane group, a urea group, an imide group). For example, the liquid repellent compound may include $-C(=O)-O-$, $-O-C(=O)-$, $-C(=O)-NR'-$, $-O-C(=O)-NR'-$, $-NR'-C(=O)-$, $-NR'-C(=O)-NR'-$ or $-SO_2NR'-$ wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms. The liquid repellent compound may be a compound in which a raw material compound and a modifying group (in particular the above monovalent hydrocarbon group optionally having a substituent) are bonded through at least one of the above groups. The liquid repellent compound may include an amide structure. Inclusion of at least the amide structure in the liquid repellent compound may improve liquid repellency. Herein the amide structure may be an amide structure in the broad sense, and may be selected from the amide structure in an amide (acid amide) group, a urethane group, a urea group, an imide group, a thioamide group, a thiourethane group, a thiourea group, a thioimide group, a sulfone amide group, a sulfone urethane group, a sulfone urea group and a sulfone imide group. The amide structure may be selected from the group consisting of $-(C=O)N(-)_2$, $-(C=S)N(-)_2$ and $-S(=O)_2N(-)_2$ (each group may be left-right inverted). In this regard, of the bonds possessed by N in the amide structure, at least one may be bonded to a hydrogen atom. The amide structure is preferably $-(C=O)N(-)_2$, and may be an amide structure in a group selected from the group consisting of an amide group, a urethane group, a urea group and an imide group.

[Amount of liquid-repellent compound]

[0124] The amount of the liquid-repellent compound may be 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, 30% by weight or more, and 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 in the repellent. The liquid repellent compound alone may be used as a repellent.

{Modified body of amine}

[0125] The modified body of amine will be described as an example of the liquid repellent compound. A modified body of amine is a compound prepared by chemically modifying an amine compound so that the amine compound exhibits liquid repellency.

[0126] The modified body of amine according to the present disclosure is highly dispersible in liquid medium due to its structure, and thus the repellent of the present disclosure can have stable properties. Repellents using a polymer compound as an active ingredient tend to have a wide molecular weight distribution and contain relatively large amounts of impurity components. On the other hand, the molecular weight of the modified body of amine can be reduced and the molecular weight distribution of the modified body of amine can be narrowed (monodisperse), and this can lead to better performance.

[Structure]

[0127] The modified body of amine has a molecular weight of 200 or more, 300 or more, 350 or more, 400 or more, 500 or more, 550 or more, or 750 or more, and 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.

[0128] In some embodiments, the modified body of amine according to the present disclosure does not have an active hydrogen-containing group. Examples of active hydrogen-containing groups include an amino group (an amino group not adjacent to a carbonyl group, e.g., a primary or secondary amino group), a hydroxy group and a carboxyl group. In some embodiments, the modified body of amine according to the present disclosure does not have a primary or secondary amino group which is not adjacent to a carbonyl group.

[0129] The modified body of amine according to the present disclosure may be polyamide having a plurality of amide structures, and for example, may be a polyamide in which amine (a raw material amine compound, for example, polyamine) is modified with a plurality of modifying group (e.g., Z^N described below) through an amide structure. Here, amide may have an amide structure included in a urethane group, a urea group, imide and the like.

[0130] The modified body of amine may be a compound in which amine (a raw material amine compound) is modified with a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent, or a monovalent polysiloxane group.

[0131] In the modified body of amine, one or more of amino groups in amine are replaced with a modifying group. The

modifying group is preferably a monovalent hydrocarbon group optionally having a substituent, or a monovalent polysiloxane group. The modified body of amine may have a structure in which amine is modified by an alkyl group having 6 or more and 40 or less carbon atoms from the viewpoint of the improvement in liquid-repellency.

[0132] Details of the monovalent hydrocarbon group optionally having a substituent and the monovalent polysiloxane group are as described in the above (Monovalent hydrocarbon group optionally having a substituent) and (Monovalent polysiloxane group).

(Amine backbone)

[0133] The modified body of amine according to the present disclosure has an amine backbone. The amine backbone has one or more amino groups which have a predetermined number of bonds (valence), obtained by removing a predetermined number of atoms or atomic groups (e.g., 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, which is included in an amide group, a urethane group, a urea group, imide and the like.

The amine backbone may be an aliphatic group or an aromatic group having one or more amino groups, and this does not exclude the presence of a heteroatom other than nitrogen.

[0134] The amine backbone may have a molecular weight of 30 or more, 50 or more, 100 or more, 200 or more, 300 or more, 400 or more, or 500 or more, and 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.

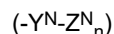
[0135] The amine backbone may have 1 or more, 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, or 18 or more and 100 or less, 80 or less, 60 or less, 40 or less, 30 or less, 20 or less, 10 or less, or 5 or less, and preferably 50 or less, and particularly preferably 30 or less carbon atoms.

[0136] The amine backbone has one or more amino groups. The amino group is a mono to trivalent amino group and is one or more groups selected from the group consisting of $-NH_2$, $-NH-$ and $-N(-)_2$. The amine backbone may have 1 or more, 2 or more, 3 or more, 4 or more, 5 or more, or 6 or more, and preferably 2 or more, and 12 or less, 10 or less, 8 or less, 6 or less, 4 or less, 3 or less, 2 or less, or 1 amino group.

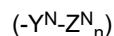
[0137] The amine backbone has a hydrocarbon group (an aliphatic hydrocarbon group or an aromatic hydrocarbon group). The hydrocarbon group may be cyclic, branched or linear. The hydrocarbon group may be saturated or unsaturated (for example, saturated). In this case, the hydrocarbon group may be interrupted by an oxygen atom and/or sulfur atom, and may be composed of only a carbon atom, a nitrogen atom and a hydrogen atom. The hydrocarbon group may be a hydrocarbon group optionally interrupted by an oxygen atom and/or a sulfur atom (e.g., a chain saturated aliphatic hydrocarbon group or an aromatic hydrocarbon group having 1 or 2 hydrocarbon aromatic rings), a usual hydrocarbon group (e.g., a chain saturated aliphatic hydrocarbon group or an aromatic hydrocarbon group having 1 or 2 hydrocarbon aromatic rings). When the hydrocarbon group is interrupted by an oxygen atom and/or a sulfur atom, the amine backbone has an ether, thioether, polyether or polythioether structure. The amine backbone may have 1 or more, 2 or more, 3 or more, 4 or more, 5 or more, or 6 or more, and 12 or less, 10 or less, 8 or less, 6 or less, 4 or less, 3 or less, 2 or less, or 1 carbon atom.

[0138] The amine backbone may be composed of mono 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.

[0139] The molar ratio between the carbon atom and the nitrogen atom (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, and 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 preferably 6 or less or 4 or less.



[0140] The modified body of amine according to the present disclosure has one or more groups represented by the following formula:



[wherein Y^N is a direct bond or a $1+n$ valent group,

Z^N is a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or a monovalent polysiloxane group, and

n is an integer of 1 or more and 3 or less], and

at least one $-Y^N-Z^N_n$ is bonded to the nitrogen atom of the amine backbone.

[0141] The modified body of amine may have 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, and may have 12 or less, 10 or less, 8 or less, 6 or less, 4 or less, 3 or less, 2 or less, or 1 $-Y^N-Z^N_n$.

[0142] At least one $-Y^N-Z^N_n$ in the modified body of amine is bonded to the nitrogen atom of the amine backbone. The proportion of the number of $-Y^N-Z^N_n$ bonded to the nitrogen atom of the amine backbone to the total number of $-Y^N-Z^N_n$ in the modified body of amine may be 10% or more, 30% or more, 60% or more, 80% or more, or 100%, and 75% or less, 50% or less, or 25% or less. $-Y^N-Z^N_n$ not bonded to the nitrogen atom of the amine backbone is bonded to another group (e.g., a hydrocarbon group) of the amine backbone.

(Y^N)

[0143] Y^N is a direct bond or a $1+n$ valent group, and preferably a $1+n$ valent group. Y^N functions as a linker connecting the amine backbone and n Z^N groups.

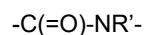
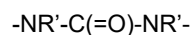
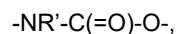
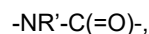
[0144] n is the number of Z^N bonded to Y^N , and may be an integer of 1 or more and 3 or less. n may be 1 or more, 2 or more, or 3 or more, and 3 or less, 2 or less, or 1 or less, and for example, 2 or less.

[0145] Y^N may be an aliphatic group (unsaturated aliphatic group or saturated aliphatic group) or an aromatic group.

[0146] Y^N may have a molecular weight of 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, 500 or more, or 750 or more, and 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, 500 or less, or 300 or less.

[0147] Y^N may have a carbonyl group. Y^N may have one or more selected from the group consisting of an amide group, a urea group, a urethane group and an imide group. Alternatively, Y^N may form one or more selected from the group consisting of an amide group, a urea group, a urethane group and an imide with the amino group in the amine backbone.

Examples of the amide group, urea group, urethane group and imide group include: $-O-C(=O)-NR'$,



[wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 30 (e.g., 1 to 20, 1 to 10, or 1 to 4) carbon atoms]. Y^N is preferably bonded to a nitrogen atom in the amine backbone through a $-(C=O)-$ group.

[0148] Y^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 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms.

[0149] Y^N may be a $1+n$ valent group composed of one or more selected from the group consisting of Y^{N1} and Y^{N2} ,

[0150] Y^{N1} may be a group composed of one or more selected from the group consisting of a direct bond, $-O-$, $-C(=O)-$, $-C(=NR')$, $-S-$, $-S(=O)_2-$, $-C(=S)-$, $-NR'$, $-C(OR')R'$, $-C(OR')(-)_2$ and $-N(-)_2$ (wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms),

[0151] Y^{N2} may be a group 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. In the present description, the left side of the group represented by Y^N is bonded to the amine backbone and the right side thereof is bonded to Z^N .

◦ Y^{N1}

Y^{N1} is a non-hydrocarbon linker

[0152] Y^{N1} is a direct bond or a divalent or higher valent group. Y^{N1} may have a valence of 2 to 4, 2 or 3, or 2. It is preferable that Y^{N1} is not limited to direct bond.

[0153] Y^{N1} may have a molecular weight of 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, or 500 or more, and 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, or 500 or less.

[0154] Y^{N1} may be composed of one or more selected from the group consisting of a direct bond, $-O-$, $-C(=O)-$, $-C(=NR')$, $-S-$, $-S(=O)_2-$, $-C(=S)-$, $-NR'$, $-C(OR')R'$, $-C(OR')(-)_2$, $-N(-)_2$ (wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms). Examples of Y^{N1} include:

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-,

-SO₂-,

-SO₂NR'-,

-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 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms]. When Y^{N1} is bonded to the nitrogen atom of the amine backbone, the nitrogen atom is regarded as a part of the amine backbone (an amino group).

o Y^{N2}

Y^{N2} is a hydrocarbon optionally having a substituent, a hydrocarbon aromatic ring optionally having a substituent or a heterocyclic linker optionally having a substituent.

[0155] Y^{N2} may be a hydrocarbon group or a non-hydrocarbon group (including a heteroatom). Y^{N2} may be aliphatic or aromatic. Y^{N2} may be linear, branched or cyclic.

[0156] Y^{N2} is a divalent or higher valent group. Y^{N2} may have a valence of, for example, 2 to 4, 2 or 3, or 2.

[0157] Y^{N2} may have 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 carbon atoms, and 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 carbon atoms.

[0158] Y^{N2} is composed of one or more selected from the group consisting of a divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms and optionally having a substituent, a divalent to tetravalent hydrocarbon aromatic ring optionally having a substituent, and a divalent to tetravalent heterocyclic ring optionally having a substituent.

[0159] The divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms may be a cyclic, branched or linear hydrocarbon group. The divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms may be a

saturated or unsaturated (e.g., saturated) aliphatic hydrocarbon group. The aliphatic hydrocarbon group having 1 to 40 carbon atoms may have 1 or more, 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, or 10 or more carbon atoms, and 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, 10 or less, or 5 or less carbon atoms. The aliphatic hydrocarbon group may have a valence of 2 or more, 3 or more, or 4, and 4 or less, 3 or less, or 2.

[0160] The aliphatic hydrocarbon group may have a substituent. Examples of substituents include -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 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may or may not have active hydrogen. The substituent may have or be free of active hydrogen. The number of substituents may be 6 or less, 5 or less, 4 or less, 3 or less, 2 or less, 1 or less, or 0. In the aliphatic hydrocarbon group having a substituent, the amount of carbon atom relative to the amount of carbon atom and heteroatom may be 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and preferably 75 mol% or more, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, or 80 mol% or less.

[0161] 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 atoms 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 valence of 2 or more, 3 or more, or 4, and may be 4 or less, 3 or less, or 2.

[0162] The hydrocarbon aromatic ring may have a substituent. Examples of substituents include -R', -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 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may have or be free of active hydrogen. The number of substituents 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 aromatic ring having a substituent, the amount of carbon atom relative to the amount of carbon atom and heteroatom may be 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and preferably 75 mol% or more, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, or 80 mol% or less.

[0163] 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. 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.

[0164] The heterocyclic ring may have a substituent. Examples of substituents include -R', -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 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may or may not have active hydrogen. The number of substituents may be 6 or less, 5 or less, 4 or less, 3 or less, 2 or less, 1 or less, or 0. In the heterocyclic ring having a substituent, the amount of carbon atom relative to the carbon atom and the heteroatom may be 60 mol% or more, 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and for example 65 mol% or more, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, 80 mol% or less, or 70 mol% or less.

[0165] Examples of Y^{N2} include

-Ali-

-Cy-

-Ali(-)₂

-Cy(-)₂

(-)₂Ali-

(-)₂Cy-

(-)₂Ali(-)₂

(-)₂Cy(-)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].

[0166] Specific examples of Y^{N2} include:

-(CH₂)_p- (p is 1 to 40, 1 to 20, or 1 to 10),

a linear hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms and having an unsaturated bond,

a branched hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms, and

-(CH₂)_q-Cy-(CH₂)_r- (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).

· Examples of Y^N

[0167] Examples of Y^N will be described. In the following, R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms.

[0168] When Y^N is divalent, examples of Y^N include -Y^{N1}-, -Y^{N1}-Y^{N2}-, -Y^{N1}-Y^{N2}-Y^{N1}-, -Y^{N1}-Y^{N2}-Y^{N1}-Y^{N2}-, -Y^{N2}-, -Y^{N2}-Y^{N1}-, -Y^{N2}-Y^{N1}-Y^{N2}- and -Y^{N2}-Y^{N1}-Y^{N2}-Y^{N1}-.

[0169] When Y^N is trivalent, examples of Y^N include -Y^{N1}(-)₂-, -Y^{N1}-Y^{N2}(-)₂-, -Y^{N1}-(Y^{N2}-)₂-, -Y^{N1}-Y^{N2}-Y^{N1}(-)₂-, -Y^{N1}-Y^{N2}(-Y^{N1}-)₂-, -Y^{N1}-(Y^{N2}-Y^{N1}-)₂-, -Y^{N1}-Y^{N2}-Y^{N1}-Y^{N2}(-)₂-, -Y^{N1}-Y^{N2}-Y^{N1}-(Y^{N2}-)₂-, -Y^{N1}-Y^{N2}-(Y^{N1}-Y^{N2}-)₂-, -Y^{N1}-(Y^{N2}-Y^{N1}-Y^{N2}-)₂-, -Y^{N2}(-)₂-, -Y^{N2}-Y^{N1}(-)₂-, -Y^{N2}-(Y^{N1}-)₂-, -Y^{N2}-Y^{N1}-Y^{N2}(-)₂-, -Y^{N2}-Y^{N1}-(Y^{N2}-)₂-, -Y^{N2}-(Y^{N1}-Y^{N2}-)₂-, -Y^{N2}-Y^{N1}-Y^{N2}-Y^{N1}(-)₂-, -Y^{N2}-Y^{N1}-Y^{N2}-(Y^{N1}-)₂-, -Y^{N2}-Y^{N1}-(Y^{N2}-Y^{N1}-)₂-, and -Y^{N2}-(Y^{N1}-Y^{N2}-Y^{N1}-)₂.

[0170] When Y^N is tetravalent, examples of Y^N include -Y^{N1}(-)₃-, -Y^{N1}-Y^{N2}(-)₃-, -Y^{N1}-(Y^{N2}-)₃-, -Y^{N1}-Y^{N2}-Y^{N1}(-)₃-, -Y^{N1}-Y^{N2}(-Y^{N1}-)₃-, -Y^{N1}-(Y^{N2}-Y^{N1}-)₃-, -Y^{N1}-Y^{N2}-Y^{N1}-Y^{N2}(-)₃-, -Y^{N1}-Y^{N2}-Y^{N1}-(Y^{N2}-)₃-, -Y^{N1}-Y^{N2}-(Y^{N1}-Y^{N2}-)₃-, -Y^{N1}-(Y^{N2}-Y^{N1}-Y^{N2}-)₃-, -Y^{N2}(-)₃-, -Y^{N2}-Y^{N1}(-)₃-, -Y^{N2}-(Y^{N1}-)₃-, -Y^{N2}-Y^{N1}-Y^{N2}(-)₃-, -Y^{N2}-Y^{N1}-(Y^{N2}-)₃-, -Y^{N2}-(Y^{N1}-Y^{N2}-)₃-, -Y^{N2}-Y^{N1}-Y^{N2}-Y^{N1}(-)₃-, -Y^{N2}-Y^{N1}-Y^{N2}-(Y^{N1}-)₃-, -Y^{N2}-Y^{N1}-(Y^{N2}-Y^{N1}-)₃-, and -Y^{N2}-(Y^{N1}-Y^{N2}-Y^{N1}-)₃.

[0171] Preferred examples of Y^N include -Y^{N1}-, -Y^{N1}-Y^{N2}-, -Y^{N1}-Y^{N2}-Y^{N1}-, -Y^{N1}-Y^{N2}(-)₂-, -Y^{N2}-, -Y^{N2}-Y^{N1}-, -Y^{N2}-Y^{N1}-Y^{N2}-, -Y^{N2}-Y^{N1}(-)₂-. It is preferable that in the modified body of amine, there is -(C=O)- at the end of the amine backbone in one or more Y^N , and one or more Y^N is bonded to the nitrogen atom in the amine backbone.

Y^N is preferably -Y^{N1}-, -Y^{N1}-Y^{N2}-, -Y^{N1}-Y^{N2}-Y^{N1}-, -Y^{N1}-Y^{N2}(-)₂-,

-Y^{N2}-, -Y^{N2}-Y^{N1}-, -Y^{N2}-Y^{N1}-Y^{N2}-, -Y^{N2}-Y^{N1}(-)₂-,

[wherein Y^{N1} is independently at each occurrence

a direct bond, -O-,

-O-C(=O)-,

-O-C(=O)-O-,

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

-NR'-,

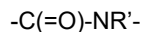
-NR'-C(=O)-,

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

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

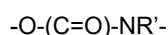
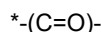
-C(=O)-,

-C(=O)-O-



(wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms), and
 Y^{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 or a divalent triazole group)]. By this, excellent liquid-repellency is imparted to substrates.

[0172] Specific examples of Y^N also include:



[wherein * means a bond to a nitrogen atom in the amine backbone,
 R' is a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms.]

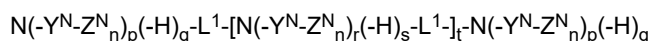
(Z^N)

[0173] Z^N is a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or a monovalent polysiloxane group. The same explanation in the above (Monovalent hydrocarbon group optionally having a substituent) and (Monovalent polysiloxane group) applies.

[Examples of modified body of amine]

(Example 1 of modified body of amine)

[0174] An example of the modified body of amine is (Example 1 of modified body of amine), which is a compound represented by the following formula:



[wherein Y^N is independently at each occurrence a direct bond or a 1+n valent group,

Z^N is independently at each occurrence a linear or branched monovalent hydrocarbon group having 6 or more and 40 or less carbon atoms and optionally having a substituent,

L¹ is independently at each occurrence a divalent aliphatic hydrocarbon group having 2 to 20 carbon atoms or an aromatic hydrocarbon group which are 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(-Y^N-Z^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(-Y^N-Z^N)_p(-H)_q,

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].

[0175] In Example 1 of the modified body of amine, the details of Y^N, Z^N and n are as described above.

[0176] In Example 1 of the modified body of amine, L¹ is a divalent aliphatic hydrocarbon group having 2 to 20 carbon atoms or an aromatic hydrocarbon group which are optionally interrupted by an oxygen atom and/or a sulfur atom, and may be a cyclic, branched or linear hydrocarbon group, and is preferably a chain hydrocarbon group or an aromatic hydrocarbon. L¹ may be the hydrocarbon group described in the above [Amine backbone]. The hydrocarbon group may be interrupted by an oxygen atom and/or sulfur atom, may be composed of only a carbon atom, a nitrogen atom and hydrogen atom. L¹ may be, for example, a saturated or unsaturated (e.g., saturated) aliphatic hydrocarbon group or an

aromatic hydrocarbon group with 1 or 2 hydrocarbon aromatic rings. L^1 is preferably a cyclic group having both a ring (e.g., an aromatic ring) and a chain structure (e.g., a linear structure, ether oxygen, or thioether sulfur). Specific examples thereof include 1,3-phenylenebisalkylene group, 1,4-phenylenebisalkylene group, diphenyl ether diyl group, diphenyl thioether diyl group. L^1 has 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, 10 or more, or 12 or more, and 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 carbon atoms.

[0177] In Example 1 of the modified body of amine, 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 $N(-Y^N-Z^N_n)_p(-H)_q$. Preferably p is independently at each occurrence an integer of 1 or more and for example, 2.

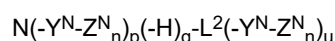
[0178] In Example 1 of the modified body of amine, r is independently at each occurrence 0 or 1, s is independently at each occurrence 0 or 1, and $r + s$ is 1 in each $N(-Y^N-Z^N_n)_r(-H)_s$. Preferably p is independently at each occurrence an integer of 1 or more and for example, 2.

[0179] The sum of all p and all r is 1 or more, which means that Example 1 of the modified body of amine has one or more $-Y^N-Z^N_n$. 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, 12 or more (the sum of all q and s may be 0), 14 or less, 12 or less, 10 or less, 8 or less, 6 or less, or 4 or less.

[0180] In Example 1 of the modified body of amine, 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 and t may be 8 or less, 6 or less, 4 or less, 3 or less, 2 or less, or 1 or less, and for example 0 or 1.

[Example 2 of modified body of amine]

[0181] Another example of the modified body of amine is (Example 2 of modified body of amine), which is a compound represented by the formula:



[wherein Y^N is independently at each occurrence a direct bond or a 1+n valent group,

Z^N is independently at each occurrence a linear or branched monovalent 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 an aromatic hydrocarbon group which are 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].

[0182] In Example 2 of the modified body of amine, the details of Y^N , Z^N_n and n are as described above.

[0183] In Example 2 of the modified body of amine, L^2 is a 1+u valent aliphatic hydrocarbon group having 2 to 20 carbon atoms or an aromatic hydrocarbon group which are optionally interrupted by an oxygen atom and/or a sulfur atom, and may be a cyclic, branched or linear hydrocarbon group, and is preferably a chain hydrocarbon group or an aromatic hydrocarbon. L^2 may be the hydrocarbon group described in the above [Amine backbone]. The hydrocarbon group may be interrupted by an oxygen atom and/or sulfur atom, may be composed of only a carbon atom, a nitrogen atom and hydrogen atom. L^2 may be, for example, a saturated or unsaturated (e.g., saturated) aliphatic hydrocarbon group or an aromatic hydrocarbon group with 1 or 2 hydrocarbon aromatic rings. L^2 is preferably a cyclic group having both a ring (e.g., an aromatic ring) and a chain structure (e.g., a linear structure, ether oxygen, or thioether sulfur). Specific examples thereof include 1,3-phenylenebisalkylene group, 1,4-phenylenebisalkylene group, diphenyl ether diyl group, diphenyl thioether diyl group. L^2 has 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, 10 or more, or 12 or more, and 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 carbon atoms.

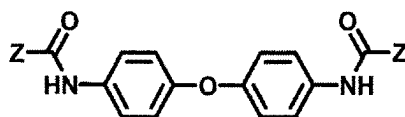
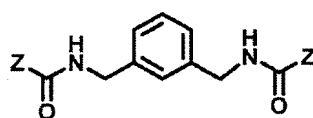
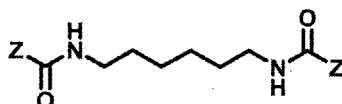
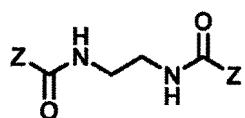
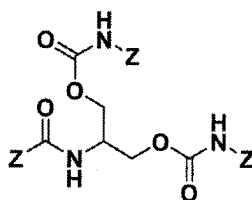
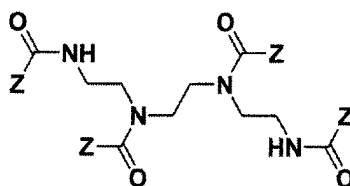
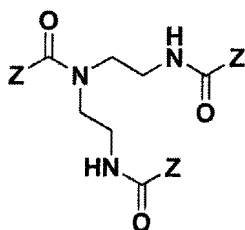
[0184] In Example 2 of the modified body of amine, p is an integer of 0 or more and 2 or less, q is an integer of 0 or more and 2 or less, and $p + q$ is 2. p may be preferably 1 or more and for example, 2.

[0185] In Example 2 of the modified body of amine, u is an integer of 1 or more and 3 or less. u is 1, 2 or 3, and for example 2 or 3.

[0186] In Example 2 of the modified body of amine, the sum of p and u is 1 or more, which means that Example 2 of the modified body of amine has one or more $-Y^N-Z^N_n$. The sum of all p and all 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), and may be 5 or less, 4 or less, 3 or less, or 2 or less.

(Specific Examples)

[0187] Specific examples of modified bodies of amine include the compounds represented by the following formula. In the following formula, the details of Y^N , Z^N and n are as described above.



[0188] The modified body of amine may be a synthesized wax derived from animal or vegetable oil and fat. The synthesized wax may also be prepared by condensing fatty acid derived from animal or vegetable oil and fat and aliphatic amine or amine containing aromatic. Examples of synthetic wax include a fatty acid amide compound such as a hydroxy fatty acid amide compound, a palmitamide 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, γ -linolenic acid amide compound, an arachidonic acid amide compound, an icosapentaenoic acid amide compound and a docosahexaenoic acid amide compound.

[Production Method]

[0189] The method for producing the modified body of amine is not limited, and examples thereof include a method in which a modified body of amine is synthesized by allowing various types of amines (raw material amines) to react with a Z^N group-containing carboxylic acid in the presence of a condensing agent, if necessary, and a method in which a modified body of amine is synthesized by allowing amines to react with Z^N group-containing carboxylic acid chloride, acid anhydride, isocyanate or the like. A known condensing agent may be used, and examples thereof include DCC, EDCI, CDI, BOP, COMU, DMT-MM, DPPA and Py-Bop.

(Amine (raw material amine))

[0190] Examples of amine (raw material amine), which is a precursor of amine backbone, include those capable of forming amine backbone, such as alkylamine such as methylamine, ethylamine, propylamine, butylamine and dibutylamine; alkylenediamine such as ethylenediamine, propylenediamine, butylenediamine, pentanediamine, hexamethylenediamine, cyclohexanediamine and methylenebiscyclohexylamine; polyalkylenepolyamine such as diethylenetriamine, triethylenetetramine, tris (2-aminoethyl) amine, tetraethylenepentamine, pentaethylenhexamine, dipropylene-triamine, tripropylenetetramine, tris (2-aminopropyl) amine, tetrapropylene-pentamine, pentapropylenehexamine, imino-bispropylamine, dibutylenetriamine, bis(2-aminoethoxy) ethane, bis(2-aminoethyl) ether, bis [2-(2-aminoethoxy)ethyl] ether, bis[2-(3-aminopropoxy)ethyl] ether, spermine and spermidine; oxygen or sulfur-containing aliphatic amine such as 1-aminopropanediol, 2-amino-1,3-propanediol, 3-amino-1,2-propanediol, polyoxypropylenediamine and polyoxyethylenediamine; aromatic monoamine such as aniline, 1- or 2-naphthylamine, 1-, 2-, or 9-aminoanthracene, 9-aminophenanthracene and 2-, 3- or 4-aminobiphenyl; monocyclic aromatic polyamine such as o-, m- or p-phenylene diamine, o-, m- or p-xylylenediamine, diaminotoluene and 2,3-, 2,4- or 2,5-tolylenediamine; polycyclic aromatic polyamine such as diamino-biphenyl, bisaminophenoxyphenylpropane, diaminodiphenyl ether, diaminodiphenyl sulfide, diaminodiphenylsulfone, diaminobenzophenone, diaminodiphenylmethane, diaminophenylpropane, diaminophenyl hexafluoropropane, diaminophenylphenylethane, bisaminophenoxybenzene, bisaminobenzoyl benzene, bisaminodimethylbenzyl benzene, aminophenoxybiphenyl, aminophenoxyphenyl ketone, bisaminoditrifluoromethylbenzyl benzene, aminophenoxyphenyl sulfone, aminophenoxyphenyl ether, aminophenoxyphenyl propane, bis(aminophenoxybenzoyl) benzene, bis(aminophenoxy- α,α -dimethylbenzyl) benzene, bis[(aminophenoxy)benzoyl] diphenylether, bis (amino- α,α -dimethylbenzylphenoxy) benzophenone, aminophenoxyphenyl sulfide, bis [amino- α,α -dimethylbenzylphenoxy]diphenyl sulfone, 4,4'-bis[aminophenoxyphenoxy]diphenyl sulfone, diaminodiarloxybenzophenone, diaminophenoxybenzophenone, 3,3'-dimethoxy-4,4'-diaminobiphenyl, 4,4'-diaminotriphenyl methane, 3,3'-dimethyl-4,4'-diaminobiphenyl, 4,4'-methylenebis-aniline, 4,4'-oxydianiline, 1,3-bis(4-aminophenoxy)benzene, 4,4'-diaminodiphenylether and 4,4'-bis(aminophenyl)amine; oxygen or sulfur-containing polycyclic aromatic polyamine 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'-diaminodiphenylsulfide; and hydroxyl group-containing polyamine such as 2-hydroxyethylethylenediamine, 2-hydroxyethylpropylenediamine, di-2-hydroxyethylethylenediamine, di-2-hydroxyethylpropylenediamine, 2-hydroxypropylethylenediamine and di-2-hydroxypropylethylenediamine. Polyamine may also be a polymer of a polymerizable compound such as allylamine.

{Modified body of polyol}

[0191] The modified body of polyol will be described as an example of the liquid repellent compound. A modified body of polyol is a compound prepared by chemically modifying polyol so that the polyol exhibits liquid repellency.

[Structure]

[0192] The modified body of polyol may be a polymer having a degree of polymerization of 1 or more. The modified body of polyol may have a degree of polymerization of 2 or more, 3 or more, 5 or more, 6 or more, preferably 7 or more, more preferably 8 or more, and further preferably 9 or more from the viewpoint of the improvement in the liquid-repellency. The modified body of polyol may have a degree of polymerization of 100 or less, preferably 50 or less, more preferably 30 or less, further preferably 15 or less from the viewpoint of the improvement in handling properties of the repellent. The degree of polymerization means the repeating number of monomer units constituting the polymer.

[0193] The degree of polymerization in the present disclosure means an average degree of polymerization. The average degree of polymerization in the present disclosure is measured under the following conditions.

[0194] When the modified body of polyol in the present disclosure is a modified body of polyglycerol obtained by modifying polyglycerol, the degree of polymerization of the modified body of polyol means the average degree of polymerization of the polyglycerol. The average degree of polymerization of polyglycerol refers to an average degree

of polymerization (n) calculated from the hydroxyl number determined by the end group analysis. More specifically, the average degree of polymerization and the average molecular weight are calculated from the following (Formula 1) and (Formula 2).

$$\text{(Formula 1) Average molecular weight} = 74n + 18$$

$$\text{Hydroxyl number} = 56110 (n+2) / \text{average molecular weight} \quad \text{(Formula 2)}$$

[0195] The hydroxyl number in the above (Formula 2) indicates the number of hydroxyl groups in polyglycerol. The hydroxyl number is calculated from the amount of potassium hydroxide necessary for neutralizing acetic acid used for acetylation of free hydroxyl groups contained in 1 g of polyglycerol, which is determined according to The JOCS Standard Methods for the Analysis of Fats, Oils and Related Materials (I), 2003, edited by Japan Oil Chemists' Society. The hydroxyl number of polyglycerol, which is the raw material, is actually measured by the above Standard Methods for the Analysis of Fats, Oils and Related Materials, and the average degree of polymerization and the average molecular weight of polyglycerol may be calculated by the above relational expression.

[0196] When the modified body of polyol in the present disclosure is a modified body of polyvinyl alcohol obtained by modifying polyvinyl alcohol, the degree of polymerization of the modified body of polyol means the average degree of polymerization of the polyvinyl alcohol. The average degree of polymerization of polyvinyl alcohol may be measured according to JIS K 6726, Testing Methods for Polyvinyl Alcohol.

[0197] When the modified body of polyol in the present disclosure is a modified body of polysaccharide obtained by modifying polysaccharide, the degree of polymerization of the modified body of polyol means the average degree of polymerization of the polysaccharide. The average degree of polymerization of polysaccharide may be analyzed as follows. The degree of polymerization refers to the number of monosaccharide units in polysaccharide (fructose and glucose units), and the average degree of polymerization means the maximum of the peaks in the results of analysis obtained by a common analytical method such as HPLC, GC or HPAEC as described below. The average degree of polymerization may be measured by using ULTRON PS-80N made by Shinwa Chemical Industries Ltd. (8 × 300 mm) (solvent: water, flow rate: 0.5 ml/ minute, temperature: 50°C) or TSK-GEL G30000 PWXL made by Tosoh Corporation (7.8 × 300 mm) (solvent: water, flow rate: 0.5 ml/ minute, temperature: 50°C) as the column, and a differential refractometer as the detector.

[0198] The modified body of polyol may be a low molecular weight compound (having a weight average molecular weight of less than 1,500, less than 1,000 or 500 or less) and/or a high molecular weight compound. The modified body of polyol may have a weight average molecular weight of 100 or more, 200 or more, 300 or more, 400 or more, 500 or more, 1,000 or more, 3,000 or more, 5,000 or more, 10,000 or more, 30,000 or more, 100,000 or more, 300,000 or more, or 500,000 or more, and may have a weight average molecular weight of 1,000,000 or less, 750,000 or less, 500,000 or less, 300,000 or less, 100,000 or less, 75,000 or less, 50,000 or less, 30,000 or less, 10,000 or less, 9,000 or less, 8,000 or less, 7,000 or less, 6,000 or less, 5,000 or less, 3,000 or less, 2,000 or less, 1,000 or less, or 500 or less.

[0199] The hydroxy group substitution ratio of the modified body of polyol may be 1% or more, 3% or more, 5% or more, 10% or more, 20% or more, 30% or more, 40% or more, 50% or more, 60% or more, 70% or more, 80% or more, 90% or more, or 100%, preferably 10% or more, for example, 30% or more, 40% or more, 50% or more, 60% or more, 70% or more, particularly 50% or more, and for example, 80% or more, and 100% or less, 95% or less, 85% or less, 75% or less, 65% or less, 55% or less, 45% or less, 35% or less, 25% or less, 15% or less, and for example, 95% or less. The "substitution ratio" means the proportion (mol%) of modified hydroxy groups out of the hydroxy groups derived from polyol, and may mean the proportion (mol%) of hydroxy groups modified by a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent, or with a monovalent polysiloxane group.

[0200] The residual ratio of hydroxyl groups in the modified body of polyol may be 1% or more, 3% or more, 5% or more, 10% or more, 20% or more, 30% or more, 40% or more, 50% or more, 60% or more, 70% or more, 80% or more, or 90% or more, and for example, is 5% or more, and may be 100% or less, 95% or less, 85% or less, 75% or less, 65% or less, 55% or less, 45% or less, 35% or less, 25% or less, 15% or less, or 5% or less, and for example, 50% or less, 30% or less, or 10% or less. In this regard, the "residual ratio" means the proportion (mol%) of hydroxyl groups without modification, out of the hydroxy groups derived from the polyol.

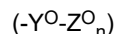
[0201] The number of modifying groups that the modified body of polyol has may be 2 or more, 5 or more, 7 or more, 8 or more, 9 or more, 10 or more, 12 or more, 15 or more, 30 or more, or 50 or more, and 1,000 or less, 750 or less, 500 or less, 300 or less, 100 or less, 50 or less, 30 or less, or 20 or less. In this regard, the modifying group is preferably a monovalent hydrocarbon group optionally having a substituent, or a monovalent polysiloxane group.

[0202] The modifying group equivalent of the modified body of polyol may be 150 or more, 250 or more, 350 or more, 450 or more, 550 or more, 650 or more, 750 or more, or 1,000 or more, and 2,500 or less, 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, 500 or less, or 400 or less. The modifying group equivalent is obtained by dividing the weight average

molecular weight of modified body of polyol by the number of modifying groups. In this regard, the modifying group is preferably a monovalent hydrocarbon group optionally having a substituent, or a monovalent polysiloxane group.

[0203] In the modified body of polyol, one or more of hydroxy groups in polyol are modified by a modifying group. The modifying group is preferably a monovalent hydrocarbon group optionally having a substituent, or a monovalent polysiloxane group. The modified body of polyol may have a structure in which polyol is modified by an alkyl group having 6 or more and 40 or less carbon atoms from the viewpoint of the improvement in liquid-repellency.

[0204] Details of the monovalent hydrocarbon group optionally having a substituent and the monovalent polysiloxane group are as described in the above (Monovalent hydrocarbon group optionally having a substituent) and (Monovalent polysiloxane group).



[0205] In the modified body of polyol in the present disclosure, one or more hydroxy groups in polyol are optionally substituted by a group represented by the following formula:



[wherein Y^O is a 1+n valent group composed of one or more selected from the group consisting of Y^{O1} and Y^{O2} ,

Y^{O1} is a group composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -C(=NR')-, -S-, -S(=O)₂-, -C(=S)-, -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 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms),

Y^{O2} is a group composed of one or more selected from the group consisting of a divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms and optionally having a substituent, a divalent to tetravalent hydrocarbon aromatic ring optionally having a substituent, and a divalent to tetravalent heterocyclic ring optionally having a substituent,

Z^O is a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or a monovalent polysiloxane group, and

n is an integer of 1 or more and 3 or less].

(Y^O)

[0206]

Y^O is a 1+n valent group composed of one or more selected from the group consisting of Y^{O1} and Y^{O2} ,

Y^{O1} is a group composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -C(=NR')-, -S-, -S(=O)₂-, -C(=S)-, -NR'-, -C(OR')R'-, -C(OR')(-)₂ and -N(-)₂ (wherein R' is independently at each occurrence a hydrogen atom or hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms),

Y^{O2} is a group composed of one or more selected from the group consisting of a divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms and optionally having a substituent, a divalent to tetravalent hydrocarbon aromatic ring optionally having a substituent, and a divalent to tetravalent heterocyclic ring optionally having a substituent.

[0207] n is the number of Z^O bonded to Y^O , 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, and 3 or less, 2 or less, or 1 or less, and for example, 2 or less.

[0208] Y^O may have a molecular weight of 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, 500 or more, or 750 or more, and 3,000 or less, 2,500 or less, 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, 500 or less, 300 or less, 200 or less, 100 or less, or 50 or less.

[0209] Y^O may include at least an amide group, a urethane group, a urea group, an imide group, a thioamide group, a thiourethane group, a thiourea group, a thioimide group, a sulfone amide group, a sulfone urea group, a sulfone urethane group, or a sulfone imide group. For example, Y^O may include -C(=O)-NR'-, -C(=S)-NR'-, -O-C(=O)-NR'-, -NR'-C(=O)-, -NR'-C(=O)-NR'- or -SO₂NR'-. Inclusion of these groups in Y^O may improve liquid repellency.

◦ Y^{O1}

Y^{O1} is a non-hydrocarbon linker.

[0210] Y^{O1} is a direct bond or a divalent or higher valent group. Y^{O1} may have a valence of 2 to 4, 2 or 3, or 2. It is preferable that Y^{O1} is not limited to direct bond.

[0211] Y^{O1} may have a molecular weight of 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, or 500 or more, and 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, or 500 or less.

[0212] Y^{O1} may be 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 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms).

[0213] Examples of Y^{O1} include:

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'-,

-SO₂-,

-SO₂NR'-,

-C(OR')R'-,

and

-C(OR')(-)₂

(wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms).

[0214] Y^{O1} may include at least an amide group, a urethane group, a urea group, an imide group, a thioamide group, a thiourethane group, a thiourea group, a thioimide group, a sulfone amide group, a sulfone urea group, a sulfone urethane group, or a sulfone imide group. For example, Y^{O2} may include -C(=O)-NR'-, -O-C(=O)-NR'-, -NR'-C(=O)-, -NR'-C(=O)-NR'- or -SO₂NR'-. Inclusion of these groups in Y^{O1} may improve liquid repellency.

[0215]

◦ Y^{O2}

Y^{O2} is a hydrocarbon optionally having a substituent, a hydrocarbon aromatic ring optionally having a substituent or a heterocyclic linker optionally having a substituent.

[0216] Y^{O2} may be a hydrocarbon group or a non-hydrocarbon group (including a heteroatom). Y^{O2} may be aliphatic or aromatic. Y^{O2} may be linear, branched or cyclic.

[0217] Y^{O2} is a divalent or higher valent group. Y^{O2} may have a valence of, for example, 2 to 4, 2 or 3, or 2.

[0218] Y^{O2} may have 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 carbon atoms, and 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 carbon atoms.

[0219] Y^{O2} is composed of one or more selected from the group consisting of a divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms and optionally having a substituent, a divalent to tetravalent hydrocarbon aromatic ring optionally having a substituent, and a divalent to tetravalent heterocyclic ring optionally having a substituent.

[0220] The divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms may be a cyclic, branched or linear hydrocarbon group. The divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms may be a saturated or unsaturated (e.g., saturated) aliphatic hydrocarbon group. The aliphatic hydrocarbon group having 1 to 40 carbon atoms may have 1 or more, 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, or 10 or more carbon atoms, and 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, 10 or less, or 5 or less carbon atoms. The aliphatic hydrocarbon group may have a valence of 2 or more, 3 or more, or 4, and 4 or less, 3 or less, or 2.

[0221] The aliphatic hydrocarbon group may have a substituent. Examples of substituents include -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 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may have or be free of active hydrogen. The number of substituents may be 6 or less, 5 or less, 4 or less, 3 or less, 2 or less, 1 or less, or 0. In the aliphatic hydrocarbon group having a substituent, the amount of carbon atom relative to the amount of carbon atom and heteroatom may be 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and preferably 75 mol% or more, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, or 80 mol% or less.

[0222] 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 valence of 2 or more, 3 or more, or 4, and 4 or less, 3 or less, or 2.

[0223] The hydrocarbon aromatic ring may have a substituent. Examples of substituents include -R', -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 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may have or be free of active hydrogen. The number of substituents 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 aromatic ring having a substituent, the amount of carbon atom relative to the carbon atom and the heteroatom 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, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, or 80 mol% or less.

[0224] 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. 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.

[0225] The heterocyclic ring may have a substituent. Examples of substituents include -R', -OR', -N(R')₂, -COOR' and a halogen atom (wherein R' is independently at each occurrence a hydrogen atom or hydrocarbon group having 1 to 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may or may not have active hydrogen. The number of substituents may be 6 or less, 5 or less, 4 or less, 3 or less, 2 or less, 1 or less, or 0. In the heterocyclic ring having a substituent, the amount of carbon atom relative to the carbon atom and the heteroatom may be 60 mol% or more, 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and is for example 65 mol% or more, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, 80 mol% or less, or 70 mol% or less.

[0226] Examples of Y^{O2} include

-Ali-

-Cy-

-Ali(-)₂

-Cy(-)₂

(-)₂Ali-

(-)₂Cy-

$(-)_2\text{Ali}(-)_2$ $(-)_2\text{Cy}(-)_2$

-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].

[0227] Specific examples of Y^{O2} include:

 $-(CH_2)_p-$ (p is 1 to 40, 1 to 20, or 1 to 10),

a linear hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms and having an unsaturated bond, a branched hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms, and

-(CH₂)_q-Cy-(CH₂)_r- (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 Y^0)

[0228] Examples of Y^o will be described. In the following, R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms.

[0229] When Y⁰ is divalent, examples of Y⁰ include -Y⁰1-, -Y⁰1-Y⁰2-, -Y⁰1-Y⁰2-Y⁰1-, -Y⁰1-Y⁰2-Y⁰1-Y⁰2-, -Y⁰2-, -Y⁰2-Y⁰1-, -Y⁰2-Y⁰1-Y⁰2- and -Y⁰2-Y⁰1-Y⁰2-Y⁰1-

[0230] When Y^O is trivalent, examples of Y^O include -Y^O1(-)₂, -Y^O1.Y^O2(-)₂, -Y^O1.(Y^O2-)₂, -Y^O1.Y^O2.Y^O1(-)₂, -Y^O1.Y^O2
(-Y^O1-)₂, -Y^O1.(Y^O2.Y^O1-)₂, -Y^O1.Y^O2.Y^O1.Y^O2(-)₂, -Y^O1.Y^O2.Y^O1.(Y^O2-)₂, -Y^O1.Y^O2.(Y^O1.Y^O2-)₂, -Y^O1.(Y^O2.Y^O1.Y^O2-)₂;
-Y^O2(-)₂, -Y^O2.Y^O1(-)₂, -Y^O2.(Y^O1-)₂, -Y^O2.Y^O1.Y^O2(-)₂, -Y^O2.Y^O1.(Y^O2-)₂, -Y^O2.(Y^O1.Y^O2-)₂, -Y^O2.Y^O1.Y^O2.Y^O1(-)₂,
-Y^O2.Y^O1.Y^O2.(Y^O1-)₂, -Y^O2.Y^O1.(Y^O2.Y^O1-)₂, and -Y^O2.(Y^O1.Y^O2.Y^O1-)₂.

[0231] When Y^O is tetravalent, examples of Y^O include $-Y^O1(-)_3$, $-Y^O1-Y^O2(-)_3$, $-Y^O1-(Y^O2-)_3$, $-Y^O1-Y^O2-Y^O1(-)_3$, $-Y^O1-Y^O2(-Y^O1-)_3$, $-Y^O1-(Y^O2-Y^O1-)_3$, $-Y^O1-Y^O2-Y^O1-Y^O2(-)_3$, $-Y^O1-Y^O2-Y^O1-(Y^O2-)_3$, $-Y^O1-Y^O2-(Y^O1-Y^O2-)_3$, $-Y^O1-(Y^O2-Y^O1-Y^O2-)_3$;

$$\begin{aligned} & -Y_{02}(-)_3, -Y_{02}\cdot Y_{01}(-)_3, -Y_{02}\cdot(Y_{01})_3, -Y_{02}\cdot Y_{01}\cdot Y_{02}(-)_3, -Y_{02}\cdot Y_{01}(-Y_{02})_3, -Y_{02}\cdot(Y_{01}\cdot Y_{02})_3, -Y_{02}\cdot Y_{01}\cdot Y_{02}\cdot Y_{01}(-)_3, \\ & -Y_{02}\cdot Y_{01}\cdot Y_{02}\cdot(Y_{01})_3, -Y_{02}\cdot Y_{01}\cdot(Y_{02}\cdot Y_{01})_3, \text{ and } -Y_{02}\cdot(Y_{01}\cdot Y_{02}\cdot Y_{01})_3. \end{aligned}$$

[0232] Preferred examples of Y^O include $-Y^{O1-}$, $-Y^{O1-}Y^{O2-}$, $-Y^{O1-}Y^{O2-}Y^{O1-}$, $-Y^{O1-}Y^{O2-}(-)_2$, $-Y^{O2-}$, $-Y^{O2-}Y^{O1-}$, $-Y^{O2-}Y^{O1-}Y^{O2-}$, $-Y^{O2-}Y^{O1-}(-)_2$.

(Preferred example of Y^0)

[0233] Y^O is preferably

-O-Y^{O11}-

or

$$-\text{O}-\text{Y}^{\text{O11}}-\text{Y}^{\text{O21}}-\text{Y}^{\text{O12}}-$$

[wherein, independently at each occurrence,

Y^{O11} is a direct bond, -C(=O)-, -C(=O)-NR'- or -C(=S)-NR'-,

Y^{O21} is a hydrocarbon group having 1 to 40 carbon atoms, and

Y^{O12} is -O-, -O-C(=O)-, -O-C(=O)-O-, -C(=O)-NR'-, -O-C(=O)-NR'-, -NR'-, -NR'-C(=O)-, -NR'-C(=O)-O-, -NR'-C(=O)-NR'-, -C(=O)-, -C(=O)-O-, -C(=O)-NR'-, -SO₂-, -SO₂NR'-, -C(OR')R', or -C(OR')(-)₂].

[00234] Y^{O11} is a non-hydrocarbon linker, and is a direct bond or divalent or higher valent group.

[0235] Y^{O11} may have a molecular weight of 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, or 500 or more, and 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, or 500 or less.

[0236] Y^{O11} is a direct bond, $-C(=O)-$, $-C(=O)-NR'-$ or $-C(=S)-NR'-$.

[0237] Y^{O21} is a divalent hydrocarbon linker, and may be a hydrocarbon group having 1 to 40 carbon atoms.

[0238] Y^{O21} may have 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, and 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 carbon atoms.

[0239] The hydrocarbon group having 1 to 40 carbon atoms may be cyclic, branched or linear, and may be a saturated or unsaturated (e.g., saturated) aliphatic hydrocarbon group.

[0240] Specific examples Y^{O21} include:

$-(CH_2)_p-$ (p is 1 to 40, 1 to 20, or 1 to 10),

a linear hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms and having an unsaturated bond,

a branched hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms, and

$-(CH_2)_q-Cy-(CH_2)_r-$ (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).

[0241] Y^{O12} may be $-O-$, $-O-C(=O)-$, $-O-C(=O)-O-$, $-O-C(=O)-NR'-$, $-NR'-$, $-NR'-C(=O)-$, $-NR'-C(=O)-O-$, $-NR'-C(=O)-NR'-$, $-C(=O)-$, $-C(=O)-O-$, $-C(=O)-NR'-$, $-SO_2-$, $-SO_2NR'-$, $-C(OR')R'-$ or $-C(OR')(-)_2$.

[0242] Y^{O12} may include at least an amide group, a urethane group, a urea group, an imide group, a thioamide group, a thiourethane group, a thiourea group, a thioimide group, a sulfone amide group, a sulfone urea group, a sulfone urethane group, or a sulfone imide group. For example, Y^{O12} may be $-C(=O)-NR'-$, $-O-C(=O)-NR'-$, $-NR'-C(=O)-$, $-NR'-C(=O)-NR'-$ or $-SO_2NR'-$. Inclusion of these groups in Y^{O12} may improve liquid repellency.

(Z^O)

[0243] Z^O is a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or a monovalent polysiloxane group. The same explanation in the above a monovalent hydrocarbon group optionally having a substituent and the monovalent polysiloxane group applies.

[Other modifying groups]

[0244] The hydroxy group of polyol may be substituted by a modifying group other than $-Y^O-Z^O_n$. Examples of modifying groups include an anionic group and/ or a cationic group.

[0245] Examples of anionic groups include a monomer having a carboxyl group, a sulfonic acid group or a phosphoric acid group.

[0246] Examples of salts of the anionic group include alkaline metal salt, alkaline earth metal salt, or an ammonium salt such as methyl ammonium salt, ethanol ammonium salt and triethanol ammonium salt.

[0247] Examples of cationic groups include an amino group, which is preferably a tertiary amino group and a quaternary amino group. It is preferable that in the tertiary amino group, two groups bonded to a nitrogen atom, which are the same or different, are an aliphatic group having 1 to 5 carbon atoms (in particular alkyl group), an aromatic group having 6 to 20 carbon atoms (an aryl group), or an aromatic aliphatic group having 7 to 25 carbon atoms (in particular an aralkyl group, e.g., a benzyl group ($C_6H_5-CH_2-$)). It is preferable that in the quaternary amino group, three groups bonded to a nitrogen atom, which are the same or different, are an aliphatic group having 1 to 5 carbon atoms (in particular alkyl group), an aromatic group having 6 to 20 carbon atoms (an aryl group), or an aromatic aliphatic group having 7 to 25 carbon atoms (in particular an aralkyl group, e.g., benzyl group ($C_6H_5-CH_2-$)). In the tertiary amino group and the quaternary amino group, the last group bonded to the nitrogen atom may have a carbon-carbon double bond. The cationic group may be in the form of salt.

[0248] The cationic group in the form of salt is a salt with an acid (an organic acid or an inorganic acid). An organic acid such as a carboxylic acid having 1 to 20 carbon atoms (in particular, a monocarboxylic acid such as acetic acid, propionic acid, butyric acid and stearic acid) are preferred.

[Production Method]

[0249] The modified body of polyol may be produced by reacting a modifying agent including a modifying group (or a precursor structure of the modifying group) with the hydroxy group of polyol.

(Polyol)

[0250] Polyol has two or more hydroxy groups and is a raw material of the modified body of polyol. Polyol has two or more hydroxy groups in the molecule. Polyol may be aliphatic or aromatic, and is preferably aliphatic.

[0251] Polyol may have an ether bond. Preferably polyol may have two or more ether bonds. More specifically, polyol is preferably a compound having two or more hydroxy groups and two or more ether bonds. In other words, polyol is preferably polyether having two or more hydroxy groups.

[0252] When polyol is a polymer, polyol may have a hydroxy group and an ether bond in the repeating structure of the monomer unit.

[0253] Polyol may be a low molecular weight compound (having a weight average molecular weight of, for example, less than 1,000 or 500 or less) and/or a high molecular weight compound. Polyol has a weight average molecular weight of 50 or more, 100 or more, 300 or more, 500 or more, 1,000 or more, 3,000 or more, 5,000 or more, 10,000 or more, 30,000 or more, 100,000 or more, 300,000 or more, or 500,000 or more, and 1,000,000 or less, 750,000 or less, 500,000 or less, 300,000 or less, 100,000 or less, 75,000 or less, 50,000 or less, 30,000 or less, 10,000 or less, 5,000 or less, 3,000 or less, 2,000 or less, 1,000 or less, or 500 or less.

[0254] Polyol may have 2 or more, 5 or more, 7 or more, 10 or more, 15 or more, 30 or more, 50 or more, or 100 or more hydroxy groups, and 3,000 or less, 1,000 or less, 750 or less, 500 or less, 300 or less, 100 or less, 50 or less, 30 or less, or 20 or less hydroxy groups.

[0255] The hydroxy group equivalent of polyol may be 20 or more, 40 or more, 60 or more, 80 or more, 100 or more, 120 or more, or 150 or more, and 1,000 or less, 800 or less, 600 or less, 400 or less, 200 or less, 100 or less, or 75 or less. Dividing the weight average molecular weight of polyol by the number of hydroxyl groups gives the hydroxy group equivalent of polyol.

[0256] Polyol may be a natural product. The natural product may be a high molecular weight natural product, a low molecular weight natural product, or a derivative thereof. The above natural product also includes a compound converted from microorganisms. Examples of polyol include a monosaccharide, an oligosaccharide, a polysaccharide, a sugar alcohol (reducing sugar), a hydroxy acid, an amino acid, vitamin, flavonol, hydroxyhydrocarbon, a polymer of a hydroxy group-containing compound, polyether polyol, polymer polyol, polyester polyol and other polyols.

[0257] Examples of monosaccharides include glucose, fructose, galactose and xylose.

[0258] Examples of oligosaccharides include sucrose, cycloamylose, cyclodextrin, maltose, trehalose, lactose and sucralose.

[0259] Examples of sugar alcohols (reducing sugar) include sorbitol, maltitol, erythritol, isomalt, lactitol, mannitol, xylitol, sorbitan and lactitol.

[0260] Examples of polysaccharides include starch, cellulose, curdlan, pullulan, alginic acid, carrageenan, guar gum, chitin, chitosan, locust bean gum, kappa-carrageenan, iota-carrageenan, isomaltodextrin, gellan gum and tamarind seed gum.

[0261] Examples of hydroxy acids include ascorbic acid, kojic acid, quinic acid, chlorogenic acid and gluconic acid.

[0262] Examples of amino acids include glucosamine.

[0263] Examples of vitamins include ascorbic acid and inositol.

[0264] Examples of flavonols include catechin, quercetin and anthocyanin.

[0265] Examples of hydroxyhydrocarbons include ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, neopentyl glycol, trimethylene glycol, glycerol, trimethylolpropane and trimethylolethane. The hydroxyhydrocarbon are a hydrocarbon having a hydroxy group, and may be aliphatic or aromatic, and is preferably aliphatic. The term "hydroxyhydrocarbon" may also mean a hydroxyhydrocarbon other than the compounds included in a different group, such as polysaccharide (other hydroxyhydrocarbons).

[0266] Examples of polymers of a hydroxy group-containing compound include polyglycerol, polyvinyl alcohol, hydroxyethyl (meth)acrylate polymer, hydroxypropyl (meth)acrylate polymer and hydroxybutyl (meth)acrylate polymer.

[0267] Polyether polyol may be a compound obtained by addition polymerization of alkylene oxide onto an initiator. Examples of initiators include a bifunctional or higher functional compound having a hydroxyl group. Examples of initiators include propylene glycol, polypropylene glycol, ethylene glycol, polyethylene glycol, glycerol, polyglycerol, trimethylolpropane, triethanolamine, pentaerythritol, ethylenediamine, aromatic diamine, diethylenetriamine, sorbitol and sucrose. Alkylene oxide include ethylene oxide and propylene oxide. The polyether polyol, which is obtained by addition polymerization of alkylene oxide onto the initiator, is also referred to as polyoxyalkylene polyol, or an oxyalkylene derivative of polyol. Typical examples of polyether polyol include polyoxypropylene triol obtained by addition polymerization of propylene oxide onto glycerol and polyoxypropylene polyglyceryl ether obtained by addition polymerization of propylene oxide onto polyglycerol.

[0268] An example of polymer polyol is a compound obtained by polymerizing at least a moiety of polyether polyol in the polyether polyol with an ethylenically unsaturated monomer. Examples of ethylenically unsaturated monomers include acrylonitrile and styrene.

[0269] An example of polyester polyol may be a compound obtained by dehydration condensation of a difunctional or higher functional compound having a carboxyl group and a difunctional or higher functional compound having a hydroxyl group. Examples of difunctional or higher functional compounds having a carboxyl group include terephthalic acid, isophthalic acid, phthalic acid, methylphthalic acid, trimellitic acid, pyromellitic acid, adipic acid, sebacic acid, succinic acid, maleic acid, fumaric acid, tetrahydrophthalic acid, methyltetrahydrophthalic acid, hexahydrophthalic acid and an acid anhydride thereof. Examples of difunctional or higher functional compounds having a hydroxyl group include ethylene glycol, propylene glycol, propanediol, neopentyl glycol, glycerol, trimethylolethane, trimethylolpropane, pentaerythritol and a polymer thereof.

(Modifying agent)

[0270] The modifying agent is preferably a compound which is reactive to polyol and comprises the above monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or monovalent polysiloxane group.

[0271] Examples of modifying agents are as follows:

Acid halide	$G(O)C-Z^O$
Acid anhydride	$O(C(=O)-Z^O)_2$
Carboxylic acid	$HO(O)C-Z^O$
Isocyanate	$O=C=N-Z^O$
Thioisocyanate	$S=C=N-Z^O$
Epoxy	$(CH_2OCH)CH_2O-Z^O$
Halide	$G-Z^O$
Amine	H_2N-Z^O
Hydroxy	$HO-Z^O$

[In the formula, Z^O is as described above, and G is a halogen atom (e.g., F, Cl, Br or I)].

[0272] Z^O in the structure of the above modifying agent may be replaced with any group constituting the modifying group. For example, Z^O may be a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or a monovalent polysiloxane group, and Z^O may be $-Y^O-Z^O_n$.

[0273] The modified body of polyol may also be synthesized by reacting polyol and a modifying agent. For example, the modified body of polyol may be synthesized by forming an ester bond by reacting a modifying agent, which is an acid halide compound, acid anhydride or carboxylic acid, with the hydroxy group of polyol. Alternatively, the modified body of polyol may be produced by forming an ether bond by reacting a modifying agent, which is a halide compound or an epoxy compound, with the hydroxy group of polyol. Conditions of the reaction between polyol and the modifying agent may be suitably designed by a person skilled in the art, including use of a catalyst (e.g., acid catalyst and base catalyst) and use of a condensing agent depending on the intended product.

{Modified body of polycarboxylic acid}

[0274] The modified body of polycarboxylic acid will be described as an example of the liquid repellent compound. A modified body of polycarboxylic acid is a compound prepared by chemically modifying polycarboxylic acid so that polycarboxylic acid exhibits liquid repellency.

[Structure]

[0275] The modified body of polycarboxylic acid may be a low molecular weight compound (having a weight average molecular weight of, for example, less than 1,500, less than 1,000 or 500 or less) and/or a high molecular weight compound. The modified body of polycarboxylic acid may have a weight average molecular weight of 100 or more, 200 or more, 300 or more, 400 or more, 500 or more, 1,000 or more, 3,000 or more, 5,000 or more, 10,000 or more, 30,000 or more, 100,000 or more, 300,000 or more, or 500,000 or more, and may have a weight average molecular weight of 1,000,000 or less, 750,000 or less, 500,000 or less, 300,000 or less, 100,000 or less, 75,000 or less, 50,000 or less, 30,000 or less, 10,000 or less, 9,000 or less, 8,000 or less, 7,000 or less, 6,000 or less, 5,000 or less, 3,000 or less, 2,000 or less, 1,000 or less, or 500 or less.

[0276] The weight average molecular weight (Mw) and the number average molecular weight (Mn) of the modified body of polycarboxylic acid may be measured by GFC using polyethylene glycol/ polyethylene oxide as a standard sample by

the following apparatus under the following conditions.

Separation column: SB-806M (8 mm × 30 mm, Shodex)

Column temperature: 40°C

Solvent for mobile phase: ion-exchanged water

Flow rate of mobile phase: 1.0 mL/min

Sample concentration: 0.5 wt%

Injection amount: 50 µL

Detector: RI detector (Waters 2414 made by Waters)

[0277] The weight average molecular weight (Mw), the number average molecular weight (Mn) and polydispersity (Mw/Mn) of the modified body of polycarboxylic acid in terms polystyrene may be determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as an eluent and Shodex KF400RL and KF400RH columns (polystyrene gel) made by SHOWA DENKO K.K.

[0278] The hydroxy group substitution ratio of the modified body of polycarboxylic acid may be 1% or more, 3% or more, 5% or more, 10% or more, 20% or more, 30% or more, 40% or more, 50% or more, 60% or more, 70% or more, 80% or more, 90% or more, or 100%, and is preferably 10% or more, for example, 30% or more, 40% or more, 50% or more, 60% or more, 70% or more, particularly 80% or more, and 100% or less, 95% or less, 85% or less, 75% or less, 65% or less, 55% or less, 45% or less, 35% or less, 25% or less, 15% or less, and is for example, 95% or less. The "substitution ratio" means the proportion (mol%) of modified hydroxy groups out of the hydroxy groups derived from polycarboxylic acid, and may mean the proportion (mol%) of hydroxy groups modified by a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent, or by a monovalent polysiloxane group.

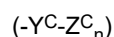
[0279] The residual ratio of hydroxyl groups in the modified body of carboxylic acid may be 1% or more, 3% or more, 5% or more, 10% or more, 20% or more, 30% or more, 40% or more, 50% or more, 60% or more, 70% or more, 80% or more, or 90% or more, and for example, is 5% or more, and may be 100% or less, 95% or less, 85% or less, 75% or less, 65% or less, 55% or less, 45% or less, 35% or less, 25% or less, 15% or less, or 5% or less, and for example, 50% or less, 30% or less, or 10% or less. In this regard, the "residual ratio" means the proportion (mol%) of hydroxyl groups without modification, out of the hydroxy groups derived from carboxylic acid.

[0280] The number of modifying groups that the modified body of polycarboxylic acid has may be 2 or more, 5 or more, 7 or more, 10 or more, 15 or more, 30 or more, or 50 or more, and 1,000 or less, 750 or less, 500 or less, 300 or less, 100 or less, 50 or less, 30 or less, or 20 or less. In this regard, the modifying group is preferably a monovalent hydrocarbon group optionally having a substituent, or a monovalent polysiloxane group.

[0281] The modifying group equivalent of the modified body of polycarboxylic acid may be 150 or more, 250 or more, 350 or more, 450 or more, 550 or more, 650 or more, 750 or more, or 1,000 or more, and 2,500 or less, 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, 500 or less, or 400 or less. The modifying group equivalent is obtained by dividing the weight average molecular weight of modified body of polyol by the number of modifying groups. In this regard, the modifying group is preferably a monovalent hydrocarbon group optionally having a substituent, or a monovalent polysiloxane group.

[0282] In the modified body of polycarboxylic acid, one or more of hydroxy groups in polycarboxylic acid are modified by a modifying group. The modifying group is preferably a monovalent hydrocarbon group optionally having a substituent, or a monovalent polysiloxane group. The modifying group is preferably a monovalent hydrocarbon group optionally having a substituent, or a monovalent polysiloxane group. In the modified body of polycarboxylic acid, polycarboxylic acid may have an alkyl group having 6 or more and 40 or less carbon atoms and optionally having a substituent from the viewpoint of the improvement in liquid repellency.

[0283] Details of the monovalent hydrocarbon group optionally having a substituent and the monovalent polysiloxane group are as described in the above (Monovalent hydrocarbon group optionally having a substituent) and (Monovalent polysiloxane group).



[0284] In the modified body of polycarboxylic acid in the present disclosure, one or more hydroxyl groups in the carboxyl group in polycarboxylic acid are substituted by a group represented by the following formula: $-Y^C-Z^{C_n}$ [wherein Y^C is a 1+n valent group composed of one or more selected from the group consisting of Y^{C1} and Y^{C2} ,

Y^{C1} is a group composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -C(=NR')-, -S-, -S(=O)₂-, -C(=S)-, -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 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms),

Y^{C2} is a group composed of one or more selected from the group consisting of a divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms and optionally having a substituent, a divalent to tetravalent

hydrocarbon aromatic ring optionally having a substituent, and a divalent to tetravalent heterocyclic ring optionally having a substituent,

Z^C is a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or a monovalent polysiloxane group, and

n is an integer of 1 or more and 3 or less].

(Y^C)

[0285]

Y^C is a 1+n valent group composed of one or more selected from the group consisting of Y^{C1} and Y^{C2},

Y^{C1} is a group composed of one or more selected from the group consisting of a direct bond, -O-, -C(=O)-, -C(=NR')-, -S-, -S(=O)₂-, -C(=S)-, -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 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms),

Y^{C2} is a group composed of one or more selected from the group consisting of a divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms and optionally having a substituent, a divalent to tetravalent hydrocarbon aromatic ring optionally having a substituent, and a divalent to tetravalent heterocyclic ring optionally having a substituent,

n is the number of Z^C bonded to Y^C, 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, and for example, 2 or less.

[0286] Y^C may have a molecular weight of 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, 500 or more, or 750 or more, and 3,000 or less, 2,500 or less, 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, 500 or less, 300 or less, 200 or less, 100 or less, or 50 or less.

[0287] Y^C may include at least an amide group, a urethane group, a urea group, an imide group, a thioamide group, a thiourethane group, a thiourea group, a thioimide group, a sulfone amide group, a sulfone urea group, a sulfone urethane group, or a sulfone imide group. For example, Y^C may be -C(=O)-NR'-, -O-C(=O)-NR'-, -NR'-C(=O)-, -NR'-C(=O)-NR'- or -SO₂NR'-. Inclusion of these groups in Y^C may improve liquid repellency.

◦ Y^{C1}

Y^{C1} is a non-hydrocarbon linker.

[0288] Y^{C1} is a direct bond or a divalent or higher valent group. Y^{C1} may have a valence of 2 to 4, 2 or 3, or 2. It is preferable that Y^{C1} is not limited to direct bond.

[0289] Y^{C1} may have a molecular weight of 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, or 500 or more, and 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, or 500 or less.

[0290] Y^{C1} may be 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 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms). Examples of Y^{C1} include: a direct bond,

-O-,

-O-C(=O)-,

-O-C(=O)-O-,

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

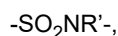
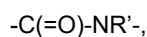
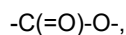
-NR'-,

-NR'-C(=O)-,

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

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

-C(=O)-,



wherein R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms.

[0291] Y^{C1} may include at least an amide group, a urethane group, a urea group, an imide group, a thioamide group, a thiourethane group, a thiourea group, a thioimide group, a sulfone amide group, a sulfone urea group, a sulfone urethane group, or a sulfone imide group. For example, Y^{C2} may include -C(=O)-NR'-, -O-C(=O)-NR'-, -NR'-C(=O)-, -NR'-C(=O)-NR'- or -SO₂NR'-. Inclusion of these groups in Y^{C1} may improve liquid repellency.

Y^{C2}

Y^{C2} is a hydrocarbon optionally having a substituent, a hydrocarbon aromatic ring optionally having a substituent or a heterocyclic linker optionally having a substituent.

[0292] Y^{C2} may be a hydrocarbon group or a non-hydrocarbon group (including a heteroatom). Y^{C2} may be aliphatic or aromatic. Y^{C2} may be linear, branched or cyclic.

[0293] Y^{C2} is a divalent or higher valent group. Y^{C2} may have a valence of, for example, 2 to 4, 2 or 3, or 2.

[0294] Y^{C2} may have 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 carbon atoms, and 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 carbon atoms.

[0295] Y^{C2} is composed of one or more selected from the group consisting of a divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms and optionally having a substituent, a divalent to tetravalent hydrocarbon aromatic ring optionally having a substituent, and a divalent to tetravalent heterocyclic ring optionally having a substituent.

[0296] The divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms may be a cyclic, branched or linear hydrocarbon group. The divalent to tetravalent aliphatic hydrocarbon group having 1 to 40 carbon atoms may be a saturated or unsaturated (e.g., saturated) aliphatic hydrocarbon group. The aliphatic hydrocarbon group having 1 to 40 carbon atoms may have 1 or more, 2 or more, 3 or more, 4 or more, 6 or more, 8 or more, or 10 or more carbon atoms, and 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, 10 or less, or 5 or less carbon atoms. The aliphatic hydrocarbon group may have a valence of 2 or more, 3 or more, or 4, and 4 or less, 3 or less, or 2.

[0297] The aliphatic hydrocarbon group may have a substituent. Examples of substituents include -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 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may or may not have active hydrogen. The number of substituents may be 6 or less, 5 or less, 4 or less, 3 or less, 2 or less, 1 or less, or 0. In the aliphatic hydrocarbon group having a substituent, the amount of carbon atom relative to the carbon atom and the heteroatom 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, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, or 80 mol% or less.

[0298] 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 atoms of the hydrocarbon aromatic ring is 3 to 20, 4 to 16, or 5 to 12 and preferably 5 to 12. The 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.

[0299] The hydrocarbon aromatic ring may have a substituent. Examples of substituents include -R', -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 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may have or be free of active hydrogen. The number of substituents 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 aromatic ring having a substituent, the amount of carbon atom relative to the amount of carbon atom and heteroatom may be 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and preferably 75 mol% or more, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, or 80 mol% or less.

[0300] 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 atoms 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 valence of 2 or more, 3 or more, or 4, and 4 or less, 3 or less, or 2. **[0301]** The heterocyclic ring may have a substituent. Examples of substituents include -R', -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 30, 1 to 20, 1 to 10, or 1 to 4 carbon atoms). The substituent may have or be free of active hydrogen. The number of substituents may be 6 or less, 5 or less, 4 or less, 3 or less, 2 or less, 1 or less, or 0. In the heterocyclic ring having a substituent, the amount of carbon atom relative to the amount of carbon atom and heteroatom may be 60 mol% or more, 70 mol% or more, 80 mol% or more, 90 mol% or more, 95 mol% or more, or 99 mol% or more, and for example 65 mol% or more, and may be 95 mol% or less, 90 mol% or less, 85 mol% or less, 80 mol% or less, or 70 mol% or less.

[0302] Examples of Y^{C2} include -Ali-

-Cy-

-Ali(-)₂

-Cy(-)₂

(-)₂Ali-

(-)₂Cy-

(-)₂Ali(-)₂

(-)₂Cy(-)₂

-Ali-Cy-

-Cy-Ali-

-Cy-Ali-Cy-

and

-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].

[0303] Specific examples of Y^{C2} include:

-(CH₂)_p- (p is 1 to 40, 1 to 20, or 1 to 10),

a linear hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms and having an unsaturated bond, a branched hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms, and

-(CH₂)_q-Cy-(CH₂)_r- (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 Y^C)

[0304] Examples of Y^C will be described. In the following, R' is independently at each occurrence a hydrogen atom or a hydrocarbon group having 1 to 30 (for example, 1 to 20, 1 to 10, or 1 to 4) carbon atoms.

[0305] When Y^C is divalent, examples of Y^C include -YC1-, -YC1-YC2-, -YC1-YC2-YC1-, -YC1-YC2-YC1-YC2-, -YC2-, -YC2-YC1-, -YC2-YC1-YC2-, and -YC2-YC1-YC2-YC1-.

[0306] When Y^C is trivalent, examples of Y^C include -YC1(-)₂, -YC1-YC2(-)₂, -YC1-(YC2-)₂, -YC1-YC2-YC1(-)₂, -YC1-YC2(-YC1-)₂, -YC1-(YC2-YC1-)₂, -YC1-YC2-YC1-YC2(-)₂, -YC1-YC2-YC1-(YC2-)₂, -YC1-YC2-(YC1-YC2-)₂, -YC1-(YC2-YC1-YC2-)₂, -YC2(-)₂, -YC2-YC1(-)₂, -YC2-(YC1-)₂, -YC2-YC1-YC2(-)₂, -YC2-YC1-(YC2-)₂, -YC2-(YC1-YC2-)₂, -YC2-YC1-YC2-YC1(-)₂,

$-\text{YC}_2-\text{YC}_1-\text{YC}_2-(\text{YC}_1)_2$, $-\text{YC}_2-\text{YC}_1-(\text{YC}_2-\text{YC}_1)_2$, and $-\text{YC}_2-(\text{YC}_1-\text{YC}_2-\text{YC}_1)_2$.

[0307] When Y^{C} is tetravalent, examples of Y^{C} include $-\text{YC}_1(-)_3$, $-\text{YC}_1-\text{YC}_2(-)_3$, $-\text{YC}_1-(\text{YC}_2)_3$, $-\text{YC}_1-\text{YC}_2-\text{YC}_1(-)_3$, $-\text{YC}_1-\text{YC}_2(-\text{YC}_1)_3$, $-\text{YC}_1-(\text{YC}_2-\text{YC}_1)_3$, $-\text{YC}_1-\text{YC}_2-\text{YC}_1-\text{YC}_2(-)_3$, $-\text{YC}_1-\text{YC}_2-\text{YC}_1-(\text{YC}_2)_3$, $-\text{YC}_1-\text{YC}_2-(\text{YC}_1-\text{YC}_2)_3$, $-\text{YC}_1-(\text{YC}_2-\text{YC}_1-\text{YC}_2)_3$, $-\text{YC}_2(-)_3$, $-\text{YC}_2-\text{YC}_1(-)_3$, $-\text{YC}_2-(\text{YC}_1)_3$, $-\text{YC}_2-\text{YC}_1-\text{YC}_2(-)_3$, $-\text{YC}_2-\text{YC}_1-(\text{YC}_2)_3$, $-\text{YC}_2-(\text{YC}_1-\text{YC}_2)_3$, $-\text{YC}_2-\text{YC}_1-\text{YC}_2-\text{YC}_1(-)_3$, $-\text{YC}_2-\text{YC}_1-\text{YC}_2-(\text{YC}_1)_3$, $-\text{YC}_2-\text{YC}_1-(\text{YC}_2-\text{YC}_1)_3$, $-\text{YC}_2-(\text{YC}_1-\text{YC}_2-\text{YC}_1)_3$.

[0308] Preferred examples of Y^{C} include $-\text{YC}_1-$, $-\text{YC}_1-\text{YC}_2-$, $-\text{YC}_1-\text{YC}_2-\text{YC}_1-$, $-\text{YC}_1-\text{YC}_2(-)_2$, $-\text{YC}_2-$, $-\text{YC}_2-\text{YC}_1-$, $-\text{YC}_2-\text{YC}_1-\text{YC}_2-$, $-\text{YC}_2-\text{YC}_1(-)_2$.

(Preferred Example of Y^{C})

[0309] Preferably Y^{C} may be

$-\text{YC}_{11}-$

or

$-\text{YC}_{11}-\text{YC}_{21}-\text{YC}_{12}-$

wherein, independently at each occurrence,

YC_{11} is $-\text{O}-$ or $-\text{NR}'-$,

YC_{21} is a hydrocarbon group having 1 to 40 carbon atoms and

YC_{12} is $-\text{O}-$, $-\text{O}-\text{C}(=\text{O})-$, $-\text{O}-\text{C}(=\text{O})-\text{O}-$, $-\text{C}(=\text{O})-\text{NR}'-$, $-\text{O}-\text{C}(=\text{O})-\text{NR}'-$, $-\text{NR}'-$, $-\text{NR}'-\text{C}(=\text{O})-$, $-\text{NR}'-\text{C}(=\text{O})-\text{O}-$, $-\text{NR}'-\text{C}(=\text{O})-\text{NR}'-$, $-\text{C}(=\text{O})-$, $-\text{C}(=\text{O})-\text{O}-$, $-\text{C}(=\text{O})-\text{NR}'-$, $-\text{SO}_2-$, $-\text{SO}_2\text{NR}'-$, $-\text{C}(\text{OR}')\text{R}'-$, or $-\text{C}(\text{OR}')(-)_2$.

[0310] YC_{11} is a non-hydrocarbon linker, and is a direct bond or divalent or higher valent group.

[0311] YC_{11} may have a molecular weight of 2,000 or less, 1,500 or less, 1,000 or less, 750 or less, or 500 or less, and 10 or more, 50 or more, 100 or more, 200 or more, 300 or more, or 500 or more.

[0312] YC_{11} may be a direct bond, $-\text{C}(=\text{O})-$, $-\text{C}(=\text{O})-\text{NR}'-$ or $-\text{C}(=\text{S})-\text{NR}'-$.

[0313] YC_{21} is a divalent hydrocarbon linker, and may be a hydrocarbon group having 1 to 40 carbon atoms.

[0314] YC_{21} may have 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, and 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 carbon atoms.

[0315] The hydrocarbon group having 1 to 40 carbon atoms may be cyclic, branched or linear, and may be a saturated or unsaturated (e.g., saturated) aliphatic hydrocarbon group.

[0316] Specific examples YC_{21} include:

$-(\text{CH}_2)_p-$ (p is 1 to 40, 1 to 20, or 1 to 10),

a linear hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms and having an unsaturated bond,

a branched hydrocarbon group having 1 to 40, 1 to 20, or 1 to 10 carbon atoms, and

$-(\text{CH}_2)_q-\text{Cy}-(\text{CH}_2)_r-$ (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).

[0317] YC_{12} may be $-\text{O}-$, $-\text{O}-\text{C}(=\text{O})-$, $-\text{O}-\text{C}(=\text{O})-\text{O}-$, $-\text{O}-\text{C}(=\text{O})-\text{NR}'-$, $-\text{NR}'-$, $-\text{NR}'-\text{C}(=\text{O})-$, $-\text{NR}'-\text{C}(=\text{O})-\text{O}-$, $-\text{NR}'-\text{C}(=\text{O})-\text{NR}'-$, $-\text{C}(=\text{O})-$, $-\text{C}(=\text{O})-\text{O}-$, $-\text{C}(=\text{O})-\text{NR}'-$, $-\text{SO}_2-$, $-\text{SO}_2\text{NR}'-$, $-\text{C}(\text{OR}')\text{R}'-$, or $-\text{C}(\text{OR}')(-)_2$.

[0318] YC_{12} may include at least an amide group, a urethane group, a urea group, an imide group, a thioamide group, a thiourethane group, a thiourea group, a thioimide group, a sulfone amide group, a sulfone urea group, a sulfone urethane group, or a sulfone imide group. For example, YC_{12} may include $-\text{C}(=\text{O})-\text{NR}'-$, $-\text{O}-\text{C}(=\text{O})-\text{NR}'-$, $-\text{NR}'-\text{C}(=\text{O})-$, $-\text{NR}'-\text{C}(=\text{O})-\text{NR}'-$ or $-\text{SO}_2\text{NR}'-$. Inclusion of these groups in YC_{12} may improve liquid repellency.

(Z^{C})

[0319] Z^{C} is a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or a monovalent polysiloxane group. The same explanation in the above (Monovalent hydrocarbon group optionally having a substituent) and (Monovalent polysiloxane group) applies.

[Other modifying groups]

[0320] The hydroxy group of polycarboxylic acid may be substituted by a modifying group other than $-\text{Y}^{\text{C}}-\text{Z}^{\text{C}}_n$. Examples

of modifying groups include an anionic group and/or a cationic group. The anionic group and/or cationic group are as described in [Other modifying groups] in the polyol described above.

[Production Method]

[0321] The modified body of polycarboxylic acid may be produced by reacting a modifying agent including a modifying group (or a precursor structure of the modifying group) with the hydroxy group of polycarboxylic acid.

(Polycarboxylic acid)

[0322] Polycarboxylic acid has two or more carboxyl groups and is a raw material of the modified body of polycarboxylic acid. Polycarboxylic acid has two or more carboxyl groups in the molecule. Polycarboxylic acid may be aliphatic or aromatic, and is preferably aliphatic.

[0323] Polycarboxylic acid may be a low molecular weight compound (having a weight average molecular weight of, for example, less than 1,000 or 500 or less) and/or a high molecular weight compound. Polycarboxylic acid may have a weight average molecular weight of 100 or more, 300 or more, 500 or more, 1,000 or more, 3,000 or more, 5,000 or more, 10,000 or more, 30,000 or more, 100,000 or more, 300,000 or more, or 500,000 or more, and 1,000,000 or less, 7,500,000 or less, 500,000 or less, 3,000,000 or less, 100,000 or less, 75,000 or less, 50,000 or less, 30,000 or less, 10,000 or less, 5,000 or less, 3,000 or less, 2,000 or less, 1,000 or less, or 500 or less.

[0324] Polycarboxylic acid may have 2 or more, 5 or more, 7 or more, 10 or more, 15 or more, 30 or more, 50 or more, or 100 or more carboxyl groups, and 3,000 or less, 1,000 or less, 750 or less, 500 or less, 300 or less, 100 or less, 50 or less, 30 or less, or 20 or less carboxyl groups.

[0325] The carboxyl group equivalent of polycarboxylic acid may be 20 or more, 40 or more, 60 or more, 80 or more, 100 or more, 120 or more, 150 or more, and 1,000 or less, 800 or less, 600 or less, 400 or less, 200 or less, 100 or less, or 75 or less. The carboxyl group equivalent is obtained by dividing the weight average molecular weight of polycarboxylic acid by the number of carboxyl groups.

[0326] Polycarboxylic acid may be a natural product. The natural product may be a high molecular weight natural product, a low molecular weight natural product, or a derivative thereof. The above natural product also includes a compound converted from microorganisms.

[0327] Polycarboxylic acid may be at least one selected from the group consisting of a dicarboxylic acid, a tricarboxylic acid, a tetracarboxylic acid, a polymer of a carboxyl group-containing compound.

[0328] Dicarboxylic acid has two carboxyl groups, and examples thereof include oxalic acid, malonic acid, succinic acid, maleic acid, fumaric acid, adipic acid, phthalic acid, terephthalic acid, malic acid, tartaric acid, aldarc acid and a salt thereof.

[0329] Tricarboxylic acid has three carboxyl groups, and examples thereof include citric acid, tricarballic acid, t-aconitic acid, trimellitic acid and a salt thereof.

[0330] Tetracarboxylic acid has four carboxyl groups, and examples thereof include pyromellitic acid and a salt thereof.

[0331] The polymer of a carboxyl group-containing compound has five or more carboxyl groups, and examples thereof include alginic acid, gum tragacanth, gum arabic, polyacrylic acid, polymethacrylic acid, polymaleic acid, polyaspartic acid, polyglutamic acid, hyaluronic acid, heparin, xanthan gum, gellan gum, carboxymethyl cellulose alginate, galacturonic acid, mannuronic acid and a salt thereof.

(Modifying agent)

[0332] The modifying agent is preferably a compound which is reactive to polycarboxylic acid and comprises the above monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent or monovalent polysiloxane group.

[0333] Examples of modifying agents are as follows:

Epoxy	$(\text{CH}_2\text{OCH})\text{CH}_2\text{O}-\text{Z}^{\text{C}}$
Amine	$\text{H}_2\text{N}-\text{Z}^{\text{C}}$
Hydroxy	$\text{HO}-\text{Z}^{\text{C}}$

[In the formula, Z^{C} is as described above].

[0334] Z^{C} in the structure of the above modifying agent may be replaced with any group constituting the modifying group. For example, Z^{C} may be a monovalent hydrocarbon group having 1 or more and 40 or less carbon atoms and optionally having a substituent, and for example, Z^{C} may be $-\text{Y}^{\text{C}}-\text{Z}^{\text{C}}_{\text{n}}$.

[0335] The modified body of polycarboxylic acid may also be synthesized by reacting polycarboxylic acid and a modifying agent. For example, modified body of polycarboxylic acid may be synthesized by forming an ester bond by reacting a modifying agent, which is an epoxy compound, with the carboxy group of polycarboxylic acid. Conditions of the reaction between polycarboxylic acid and the modifying agent may be suitably designed by a person skilled in the art, including use of a catalyst (e.g., acid catalyst and base catalyst) and use of a condensing agent depending on the intended product.

{Vinyl polymer}

[0336] The vinyl polymer will be described as an example of the liquid repellent compound. The vinyl polymer is prepared by polymerizing a vinyl monomer, and exhibits liquid repellency. In this regard, the vinyl monomer may be a compound having a polymerizable carbon-carbon double bond ($>C=C<$), and may be a monomer having a vinyl group, a vinylene group, a vinylidene group, an acryloyl group, a methacryloyl group, or a monomer having a derivative group thereof. In particular, the vinyl polymer may be a (meth)acrylic polymer.

[Characteristics]

[0337] The vinyl polymer is preferably a compound with carbon of biobased origin. The biobased content is measured in accordance with ASTM D6866. The vinyl polymer may have a biobased content of 20% or more, and is preferably 30% or more, more preferably 50% or more, even more preferably 60% or more, still more preferably 70% or more, and most preferably 80% or more or 90% or more, and for example, 100%. A high biobased content means that the amount of use of fossil resource materials, which are typically petroleum, is small, and a higher biobased content of the vinyl monomer is preferred from that point of view.

[0338] The vinyl polymer may have a melting point of 30°C or more, 40°C or more, 60°C or more, 80°C or more, 100°C or more, or 120°C or more, and is preferably 40°C or more, and may have a melting point of 250°C or less, 225°C or less, 200°C or less, 150°C or less, 130°C or less, 120°C or less, 110°C or less, 100°C or less, 80°C or less, or 50°C or less.

[Structure]

[0339] The vinyl polymer may have a weight average molecular weight of 3,000 or more, 5,000 or more, 10,000 or more, 30,000 or more, 100,000 or more, 300,000 or more, or 500,000 or more, and 5,000,000 or less, 3,000,000 or less, 1,000,000 or less, 750,000 or less, 500,000 or less, 300,000 or less, 100,000 or less, 75,000 or less, 50,000 or less, 30,000 or less, 10,000 or less, or 5,000 or less. The weight average molecular weight may be measured by GPC in terms of polystyrene.

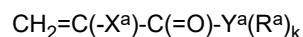
(a) Hydrocarbon group-containing monomer

[0340] The vinyl polymer may have a repeating unit derived from a monomer (a) having a hydrocarbon group having 6 or more and 40 or less carbon atoms.

[0341] The hydrocarbon group which the monomer (a) has may be an aromatic hydrocarbon group or an aliphatic hydrocarbon group, and is preferably an aliphatic hydrocarbon group, and in particular a saturated aliphatic hydrocarbon group (an alkyl group). The hydrocarbon group is branched or linear, and preferably linear. The hydrocarbon group may be saturated or unsaturated. The hydrocarbon group is preferably a saturated aliphatic hydrocarbon group (alkyl group). The hydrocarbon group may have 6 or more, 8 or more, 10 or more, 12 or more, 14 or more, 16 or more, 18 or more, 20 or more, or 22 or more carbon atoms, and is preferably 10 or more, 12 or more, 14 or more, or 16 or more carbon atoms, and may have 40 or less, 35 or less, 30 or less, 25 or less, 20 or less, 15 or less, or 10 or less carbon atoms, and is preferably 30 or less, 25 or less, or 20 or less carbon atoms.

[0342] The monomer (a) may have an amide group, a urea group or a urethane group. The hydrocarbon monomer may be a combination of a hydrocarbon monomer having an amide group, a urea group or a urethane group and a hydrocarbon monomer which does not have an amide group, a urea group or an urethane group. Inclusion of these groups in the monomer (a) allows the effect of the present disclosure to be achieved well.

[0343] The monomer (a) having a hydrocarbon group having 6 or more and 40 or less carbon atoms is preferably a group represented by the formula:



[wherein R^a is each independently a hydrocarbon group having 6 or more and 40 or less carbon atoms,

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

Y^a is a group composed of at least one selected from a divalent to tetravalent hydrocarbon group having 1 carbon atom (in particular, -CH₂-, -CH(-)₂-, -C₆H₄-, -O-, -C(=O)-, -S(=O)₂- and -NH-, and k is 1 to 3].

[0344] X^a may be a hydrogen atom, a methyl group, a halogen excluding a fluorine atom, a substituted or non-substituted benzyl group, or a substituted or non-substituted phenyl group. Examples of X^a include a hydrogen atom, a methyl group, a chlorine atom, a bromine atom, an iodine atom and a cyano group. X^a is preferably a hydrogen atom, a methyl group or a chlorine atom. X^a is particularly preferably a hydrogen atom.

[0345] Y^a is a divalent to tetravalent group. Y^a is preferably a divalent group

[0346] Y^a is a group composed of at least one selected from a hydrocarbon group having 1 carbon atom, -C₆H₄-, -O-, -C(=O)-, -S(=O)₂- and -NH-. It is preferable that Y^a is not a hydrocarbon group. Examples of hydrocarbon groups having 1 carbon atom include -CH₂-, -CH(-)₂ or -C(-)₃. A hydrocarbon group having 1 carbon atom may be repeatedly linked to form a hydrocarbon group having 2 or more carbon atoms, such as -(CH₂)_m- (m is an integer from 1 to 5). Y^a may have an NH group.

[0347] Y^a may be -Y'-, -Y'-Y'-, -Y'-C(=O)-, -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'-,

[wherein Y' is a direct bond, -O-, -NH- or -S(=O)₂-,

and R' is -(CH₂)_m- in which m is an integer of 1 to 5, or -C₆H₄- (a phenylene group)].

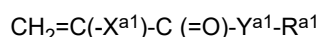
[0348] Specific examples of Y^a include -O-, -NH-, -O-C(=O)-, -C(=O)-NH-, -NH-C(=O)-, -O-C(=O)-NH-, -NH-C(=O)-O-, -NH-C(=O)-NH-, -O-C₆H₄-, -O-(CH₂)_m-O-, -NH-(CH₂)_m-NH-, -O-(CH₂)_m-NH-, -NH-(CH₂)_m-O-, -O-(CH₂)_m-O-C(=O)-, -O-(CH₂)_m-C(=O)-O-, -NH-(CH₂)_m-O-C(=O)-, -NH-(CH₂)_m-C(=O)-O-, -O-(CH₂)_m-O-C(=O)-NH-, -O-(CH₂)_m-NH-C(=O)-O-, -O-(CH₂)_m-C(=O)-NH-, -O-(CH₂)_m-NH-C(=O)-, -O-(CH₂)_m-NH-C(=O)-NH-, -O-(CH₂)_m-O-C₆H₄-, -O-(CH₂)_m-NH-S(=O)₂-, -O-(CH₂)_m-S(=O)₂-NH-, -NH-(CH₂)_m-O-C(=O)-NH-, -NH-(CH₂)_m-NH-C(=O)-O-, -NH-(CH₂)_m-C(=O)-NH-, -NH-(CH₂)_m-NH-C(=O)-, -NH-(CH₂)_m-NH-C(=O)-NH-, -NH-(CH₂)_m-O-C₆H₄-, -NH-(CH₂)_m-NH-C₆H₄-, -NH-(CH₂)_m-NH-S(=O)₂-, or -NH-(CH₂)_m-S(=O)₂-NH- wherein m is 1 to 5, in particular 2 or 4.

[0349] Y^a is preferably -O-, -NH-, -O-(CH₂)_m-O-C(=O)-, -O-(CH₂)_m-NH-C(=O)-, -O-(CH₂)_m-O-C(=O)-NH-, -O-(CH₂)_m-NH-C(=O)-O-, -O-(CH₂)_m-NH-C(=O)-NH-, -O-(CH₂)_m-NH-S(=O)₂-, -O-(CH₂)_m-S(=O)₂-NH-, -NH-(CH₂)_m-NH-S(=O)₂-, or -NH-(CH₂)_m-S(=O)₂-NH- wherein m is an integer of 1 to 5, in particular 2 or 4. Y^a is more preferably -O- or -O-(CH₂)_m-NH-C(=O)-, in particular -O-(CH₂)_m-NH-C(=O)-.

[0350] R^a is preferably a linear or branched hydrocarbon group. The hydrocarbon group may be a linear hydrocarbon group. The hydrocarbon group is preferably an aliphatic hydrocarbon group, particularly preferably a saturated aliphatic hydrocarbon group and especially preferably an alkyl group. The hydrocarbon group has preferably 12 to 30, for example, 16 to 26 or 15 to 26, in particular 18 to 22 or 17 to 22 carbon atoms.

[0351] Examples of monomers (a) include:

(a1) a monomer represented by the formula:

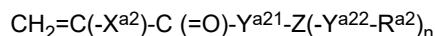


wherein R^{a1} is a hydrocarbon group having 6 to 40 carbon atoms,

X^{a1} is a hydrogen atom, a monovalent organic group or a halogen atom, and

Y^{a1} is -O- or -NH-; and

(a2) a monomer represented by the formula:



wherein R^{a2} is each independently a hydrocarbon group having 6 to 40 carbon atoms,

X^{a2} is a hydrogen atom, a monovalent organic group or a halogen atom,

Y^{a2} is -O- or -NH-

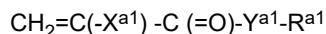
Y^{a22} is each independently a direct bond or a group composed of at least one selected from -O-, -C(=O)-, -S(=O)₂-, -NH- and -CH₂-

Z is a direct bond or a divalent or trivalent hydrocarbon group having 1 to 5 carbon atoms, and

n is 1 or 2.

(a1) Monomer

[0352] The monomer (a1) is a compound represented by the formula:



wherein R^{a1} is a hydrocarbon group having 6 to 40 carbon atoms,
 X^{a1} is a hydrogen atom, a monovalent organic group or a halogen atom, and
 Y^{a1} is -O- or -NH-.

[0353] The monomer (a1) is a long chain acrylate ester monomer in which Y^{a1} is -O-, or a long chain acrylamide monomer in which Y^{a1} is -NH-.

[0354] R^{a1} is preferably an aliphatic hydrocarbon group, particularly preferably a saturated aliphatic hydrocarbon group and especially preferably an alkyl group. In R^{a1} , the hydrocarbon group has preferably 12 to 30, for example, 16 to 26, in particular 18 to 22 carbon atoms.

[0355] X^{a1} may be a hydrogen atom, a methyl group, a halogen excluding a fluorine atom, a substituted or non-substituted benzyl group, or a substituted or non-substituted phenyl group. X^{a1} is preferably a hydrogen atom, a methyl group or a chlorine atom.

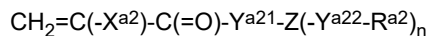
[0356] Preferred examples of long chain acrylate ester monomers include lauryl (meth)acrylate, stearyl (meth)acrylate, icosyl (meth)acrylate, behenyl (meth)acrylate, stearyl α -chloroacrylate, icosyl α -chloroacrylate and behenyl α -chloroacrylate.

[0357] Examples of long chain acrylamide monomers include stearyl (meth)acrylamide, icosyl (meth)acrylamide and behenyl (meth)acrylamide.

(a2) Monomer

[0358] The monomer (a2) is different from the monomer (a1). The monomer (a2) is (meth)acrylate or (meth)acrylamide having a group composed of at least one selected from -O-, -C(=O)-, -S(=O)₂-, -NH- and -CH₂-.

[0359] The monomer (a2) may be a compound represented by the formula:



wherein R^{a2} is each independently a hydrocarbon group having 6 to 40 carbon atoms,
 X^{a2} is a hydrogen atom, a monovalent organic group or a halogen atom,
 Y^{a21} is -O- or -NH-
 Y^{a22} is each independently a direct bond or a group composed of at least one selected from -O-, -C(=O)-, -S(=O)₂-, -NH- and -CH₂-
 Z is a direct bond or a divalent or trivalent hydrocarbon group having 1 to 5 carbon atoms, and
 n is 1 or 2. Y^{a22} and/or Z may not be a direct bond. Y^{a22} and Z may not be simultaneously a direct bond.

[0360] R^{a2} is preferably an aliphatic hydrocarbon group, particularly preferably a saturated aliphatic hydrocarbon group and especially preferably an alkyl group. In R^{a2} , the hydrocarbon group has preferably 12 to 30, for example, 16 to 26 or 15 to 26, in particular 18 to 22 or 17 to 22 carbon atoms.

[0361] X^{a2} may be a hydrogen atom, a methyl group, a halogen excluding a fluorine atom, a substituted or non-substituted benzyl group, or a substituted or non-substituted phenyl group. X^{a2} is preferably a hydrogen atom, a methyl group or a chlorine atom.

[0362] Y^{a22} may be -Y'-, -Y'-Y'-, -Y'-C(=O)-, -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 each independently a direct bond, -O-, -NH- or -S(=O)₂-,
 R' is -(CH₂)_m- in which m is an integer of 1 to 5, a linear hydrocarbon group having 1 to 5 carbon atoms and having an unsaturated bond, a hydrocarbon group having 1 to 5 carbon atoms and having a branched structure or -
 (CH₂)_l-C₆H₄-(CH₂)_l- in which l is each independently an integer of 0 to 5 and -C₆H₄- is a phenylene group.

[0363] Specific examples of Y^{a22} 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-C₆H₄-, -NH-C₆H₄-, -O-(CH₂)_m-O-, -NH-(CH₂)_m-NH-, -O-(CH₂)_m-NH-, -NH-(CH₂)_m-O-, -O-(CH₂)_m-O-C(=O)-, -O-(CH₂)_m-C(=O)-O-, -NH-(CH₂)_m-O-C(=O)-, -NH-(CH₂)_m-C(=O)-O-, -O-(CH₂)_m-O-C(=O)-NH-, -O-(CH₂)_m-NH-C(=O)-O-, -O-(CH₂)_m-C(=O)-NH-,

$-O-(CH_2)_m-NH-C(=O)-$, $-O-(CH_2)_m-NH-C(=O)-NH-$, $-O-(CH_2)_m-O-C_6H_4-$, $-NH-(CH_2)_m-O-C(=O)-NH-$, $-NH-(CH_2)_m-NH-C(=O)-O-$, $-NH-(CH_2)_m-C(=O)-NH-$, $-NH-(CH_2)_m-NH-C(=O)-$, $-NH-(CH_2)_m-NH-C(=O)-NH-$, $-NH-(CH_2)_m-O-C_6H_4-$, $-NH-(CH_2)_m-NH-C_6H_4-$, wherein m is an integer of 1 to 5.

[0364] Y^{a22} is preferably $-O-$, $-NH-$, $-O-C(=O)-$, $-C(=O)-O-$, $-C(=O)-NH-$, $-NH-C(=O)-$, $-NH-S(=O)_2-$, $-S(=O)_2-NH-$, $-O-C(=O)-NH-$, $-NH-C(=O)-O-$, $-NH-C(=O)-NH-$, or $-O-C_6H_4-$. Y^{a22} is more preferably $-NH-C(=O)-$, $-C(=O)-NH-$, $-O-C(=O)-NH-$, $-NH-C(=O)-O-$ or $-NH-C(=O)-NH-$. Y^{a22} is more preferably $-NH-C(=O)-$, $-C(=O)-NH-$, $-O-C(=O)-NH-$, $-NH-C(=O)-O-$ or $-NH-C(=O)-NH-$. Y^{a22} may not be a direct bond. Y^{a22} may have an NH group.

[0365] Z is a direct bond or a divalent or trivalent hydrocarbon group having 1 to 5 carbon atoms, and may have a linear structure or a branched structure. Z has preferably 2 to 4, particularly preferably 2 carbon atoms. Specific examples of Z include a direct bond, $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2CH_2-$, $-CH_2CH(-)_2$, $-CH_2(CH-)CH_2-$, $-CH_2CH_2CH(-)_2$, $-CH_2CH_2CH_2CH_2CH(-)_2$, $-CH_2CH_2(CH-)CH_2-$, and $-CH_2CH_2CH_2CH(-)_2$. Z may not be a direct bond.

[0366] The monomer (a2) is preferably $CH_2=C(X^{a2})-C(=O)-O-(CH_2)_m-NH-C(=O)-R^{a2}$, $CH_2=C(X^{a2})-C(=O)-O-(CH_2)_m-O-C(=O)-NH-R^{a2}$, $CH_2=C(X^{a2})-C(=O)-O-(CH_2)^m-NH-C(=O)-O-R^{a2}$, $CH_2=C(X^{a2})-C(=O)-O-(CH_2)_m-NH-C(=O)-NH-R^{a2}$ wherein R^{a2} and X^{a2} are as described above.

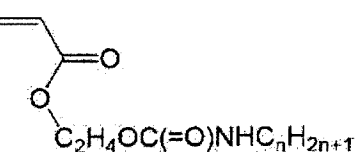
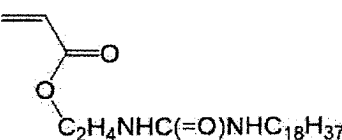
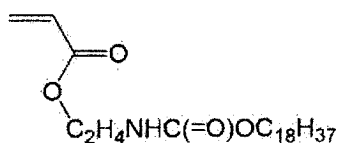
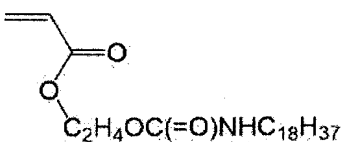
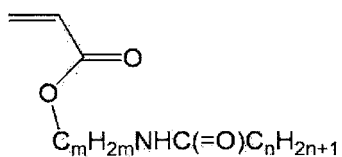
[0367] The monomer (a2) is particularly preferably $CH_2=C(X_{a2})-C(=O)-O-(CH_2)_m-NH-C(=O)-R_{a2}$.

[0368] The monomer (a2) may be produced by reacting hydroxyalkyl (meth)acrylate or hydroxyalkyl (meth)acrylamide with long chain alkyl isocyanate. Examples of long chain alkyl isocyanate include lauryl isocyanate, myristyl isocyanate, cetyl isocyanate, stearyl isocyanate, oleyl isocyanate and behenyl isocyanate.

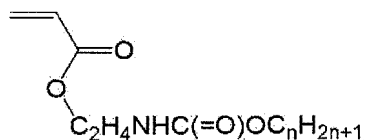
[0369] The monomer (a2) may also be produced by reacting (meth) acrylate having an isocyanate group in the side chain, such as 2-methacryloyloxyethyl methacrylate, with long chain alkylamine or long chain alkyl alcohol. Examples of long chain alkylamine include laurylamine, myristylamine, cetylamine, stearylamine, oleylamine and behenylamine. Examples of long chain alkyl alcohol include lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol and behenyl alcohol.

[0370] Preferred examples of monomers (a) are as follows:

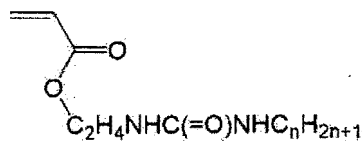
Stearyl (meth)acrylate, behenyl (meth)acrylate, stearyl α -chloroacrylate, behenyl α -chloroacrylate
Stearyl (meth)acrylamide, behenyl (meth)acrylamide;



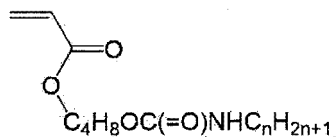
5



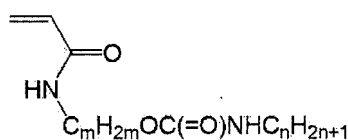
10



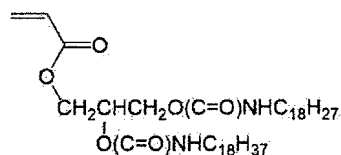
15



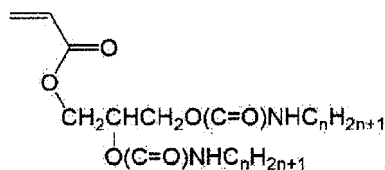
20



25

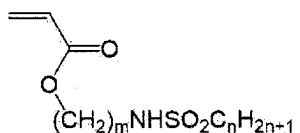


30

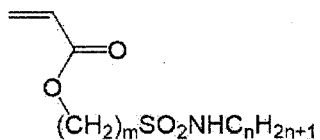


35

40



45



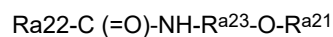
wherein n is a number of 6 to 40 and m is a number of 1 to 5.

50

[0371] The compounds of the above formula are an acrylic compound having a hydrogen atom at the α position, and specific examples thereof may also include a methacrylic compound having a methyl group at the α position and an α -chloroacrylic compound having a chlorine atom at the α position.

[0372] The monomer (a2) is preferably an amide-group containing monomer represented by the formula:

55



wherein Ra^{21} is an organic residue having an ethylenically unsaturated polymerizable group,

R^{a22} is a hydrocarbon group having 6 to 40 carbon atoms, and

R^{a23} is a hydrocarbon group having 1 to 5 carbon atoms.

[0373] R^{a21} is an organic residue having an ethylenically unsaturated polymerizable group, and is not limited as long as it has a carbon - carbon double bond. Specific examples thereof include an organic residue having an ethylenically unsaturated polymerizable group, such as -C(=O)CR^{a211}=CH₂, -CHR^{a211}=CH₂ and -CH₂CHR^{a211}=CH₂, in which R^{a211} is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms. R^{a21} may have various organic groups other than the ethylenically unsaturated polymerizable group, including, for example, an organic group such as chain hydrocarbon, cyclic hydrocarbon, a polyoxyalkylene group and a polysiloxane group. These organic groups may be substituted by a substituent. R^{a21} is preferably -C(=O)CR^{a211}=CH₂.

[0374] R^{a22} is a hydrocarbon group having 6 or more and 40 or less carbon atoms, and preferably an alkyl group, a chain hydrocarbon group, and a cyclic hydrocarbon group. Of them, a chain hydrocarbon group is preferred, and a linear saturated hydrocarbon group is particularly preferred. R^{a22} has 6 or more and 40 or less, preferably 11 to 27, and particularly preferably 15 to 23 carbon atoms.

[0375] R^{a23} is a hydrocarbon group having 1 to 5 carbon atoms, preferably an alkyl group. The hydrocarbon group having 1 to 5 carbon atoms may be linear or branched, and may have an unsaturated bond, and is preferably linear. R^{a23} has preferably 2 to 4, and particularly preferably 2 carbon atoms. R^{a23} is preferably an alkylene group.

[0376] The amide group-containing monomer may be a monomer with only one type of R^{a22} (e.g., a compound with only R^{a22} having 17 carbon atoms), or a monomer in which more than one R^{a22}'s are combined (e.g., a mixture of a compound with R^{a22} having 17 carbon atoms and a compound with R^{a22} having 15 carbon atoms).

[0377] Examples of amide group-containing monomers include carboxylic acid amide alkyl (meth)acrylate.

[0378] Specific examples of amide group-containing monomers include palmitic acid amide ethyl (meth)acrylate, stearic acid amide ethyl (meth)acrylate, behenic acid amide ethyl (meth)acrylate, myristic acid amide ethyl (meth)acrylate, lauric acid amide ethyl (meth)acrylate, isostearic acid ethyl amide (meth)acrylate, oleic acid ethylamide (meth)acrylate, t-butyl cyclohexylcaproic acid amide ethyl (meth)acrylate, adamantanecarboxylic acid ethylamide (meth)acrylate, naphthalenecarboxylic acid amide ethyl (meth)acrylate, anthracenecarboxylic acid amide ethyl (meth)acrylate, palmitic acid amide propyl (meth)acrylate, stearic acid amide propyl (meth)acrylate, palmitic acid amide ethyl vinyl ether, stearic acid amide ethyl vinyl ether, palmitic acid amide ethyl allyl ether, stearic acid amide ethyl allyl ether and a mixture thereof.

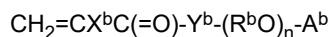
[0379] It is preferable that the amide group-containing monomer is stearic acid amide ethyl (meth)acrylate. The amide group-containing monomer may be a mixture containing stearic acid amide ethyl (meth)acrylate. The amount of stearic acid amide ethyl (meth)acrylate in the mixture containing stearic acid amide ethyl (meth)acrylate may be, for example, 40% by weight or more, 50% by weight or more, 60% by weight or more, or 70% by weight or more, and 90% by weight or less, 80% by weight or less, or 70% by weight or less based on the total weight of the amide group-containing monomers. The rest of the monomers may be, for example, palmitic acid amide ethyl (meth)acrylate.

[0380] The amount of the monomer (a2) out of the monomers (a) may be 10% by weight or more, 20% by weight or more, 30% by weight or more, 40% by weight or more, 50% by weight or more, 60% by weight or more, 70% by weight or more, or 80% by weight or more, and is preferably 30% by weight or more.

(b) Hydrophilic group-containing monomer

[0381] The vinyl polymer may comprise a hydrophilic group-containing monomer (b). The monomer (b) is different from the monomer (a), and has a hydrophilic group. The hydrophilic group is preferably an oxyalkylene group (in which the alkylene group has 2 to 6 carbon atoms), and particularly preferably an oxyethylene group. The monomer (b) is preferably oxyalkylene (meth)acrylate, for example, polyalkylene (or monoalkylene) glycol mono(meth)acrylate and/or polyalkylene (or monoalkylene) glycol di (meth)acrylate, polyalkylene (or monoalkylene) glycol mono(meth)acrylamide.

[0382] The monomer (b) is preferably oxyalkylene (meth)acrylate represented by the formula:



wherein X^b is a hydrogen atom or a methyl group,

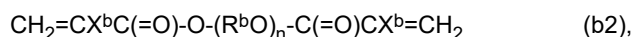
Y^b is -O- or -NH-,

R^b is each independently an alkylene group having 2 to 6 carbon atoms,

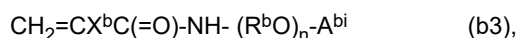
A^b is a hydrogen atom, an unsaturated or saturated hydrocarbon group having 1 to 22 carbon atoms or CH₂=CX^bC(=O)-, and

n is an integer of 1 to 90.

[0383] Examples of monomer (b) are preferably those represented by the formula:



5 or



wherein

10

X^b is each independently a hydrogen atom or a methyl group,

A^{bi} is each independently a hydrogen atom or an unsaturated or saturated hydrocarbon group having 1 to 22 carbon atoms,

R^b is each independently an alkylene group having 2 to 6 carbon atoms, and

15

n is an integer of 1 to 90.

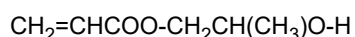
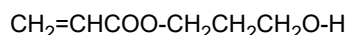
[0384] n is, for example, 1 to 50, in particular 1 to 30, especially 1 to 15 or 2 to 15. Or, n may be, for example, 1.

[0385] R^b may be a linear or branched alkylene group, and may be, for example, a group represented by the formula - (CH₂)_x- or - (CH₂)_{x1}-(CH(CH₃))_{x2}- wherein x₁ and x₂ are 0 to 6, for example, 2 to 5, and the sum of x₁ and x₂ is 1 to 6, and the order of - (CH₂)_{x1}- and - (CH(CH₃))_{x2}- is not limited to the order in the formula described, and may be random.

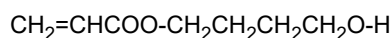
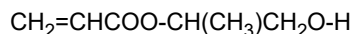
[0386] In -(R^bO)_n-, there may be 2 or more types of Rs (e.g., 2 to 4 types, in particular, 2 types). -(R^bO)_n- may be, for example, a combination of -(R¹O)_{n1}- and -(R²O)_{n2}- wherein R¹ and R² are different from each other and are an alkylene group having 2 to 6 carbon atoms, n₁ and n₂ are a number of 1 or more, and the sum of n₁ and n₂ is 2 to 90.

[0387] In the formula (b1), (b2) and (b3), R^b is preferably an ethylene group, a propylene group or a butylene group, and particularly preferably a butylene group. In the formula (b1), (b2) and (b3), R^b may be a combination of two or more alkylene groups. In that case, at least one R is preferably an ethylene group, propylene group or a butylene group. Examples of combinations of R^b include a combination of an ethylene group/ a propylene group, a combination of an ethylene group/ a butylene group and a combination of a propylene group/ a butylene group. The monomer (b) may be a mixture of two or more. In that case, at least one of the monomer (b) is preferably a monomer in which R^b in the formula (b1), (b2) and (b3) is an ethylene group, a propylene group or a butylene group. When polyalkylene glycol di(meth)acrylate represented by the formula (b2) is used, using only polyalkylene glycol di(meth)acrylate as the monomer (b) is not preferred, and using it together with the monomer (b1) is preferred. Even in that case, it is preferable to keep the proportion of the compound represented by the formula (b2) at less than 30% by weight in the monomers (b) used.

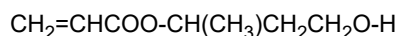
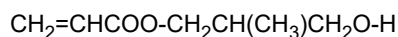
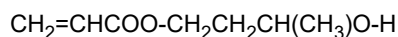
[0388] Specific examples of monomers (b) include, but are not limited to, the following monomers: CH₂=CHCOO-CH₂CH₂O-H



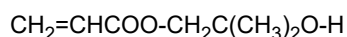
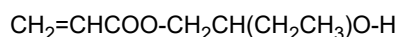
40



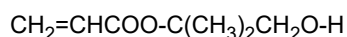
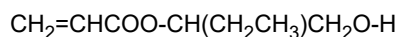
45



50



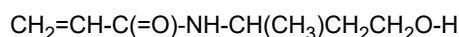
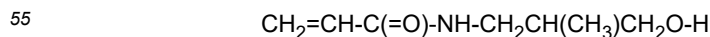
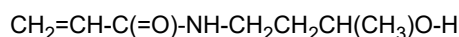
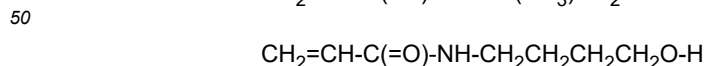
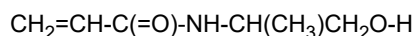
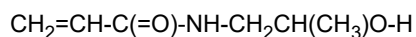
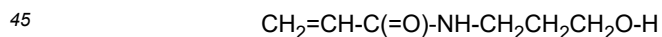
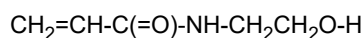
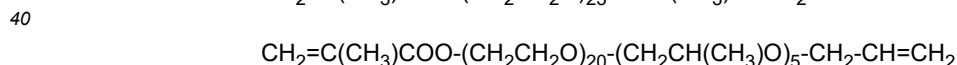
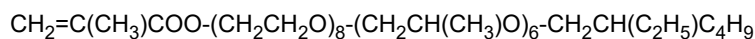
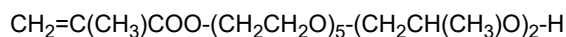
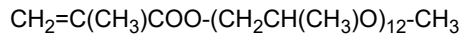
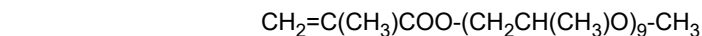
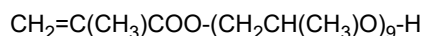
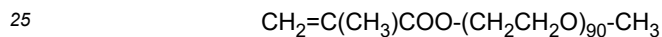
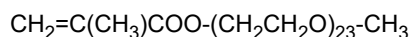
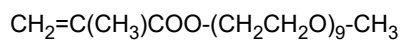
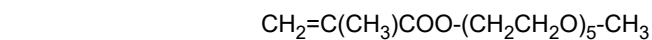
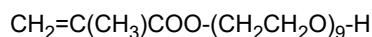
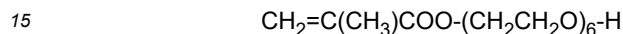
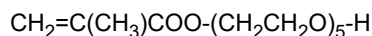
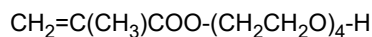
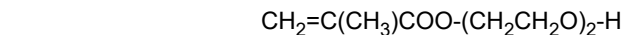
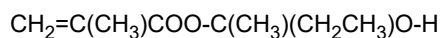
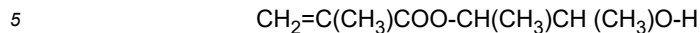
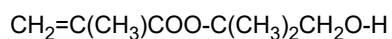
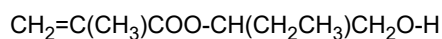
55

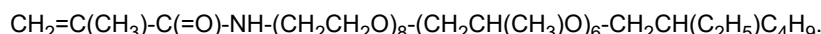
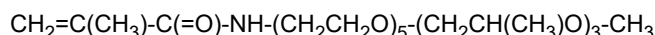
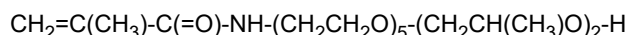
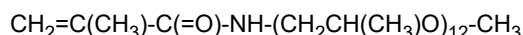
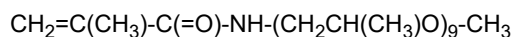
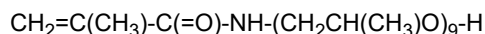
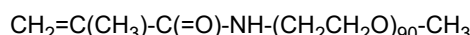
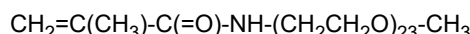
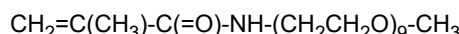
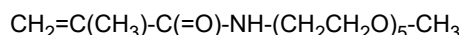
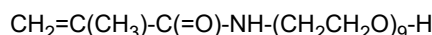
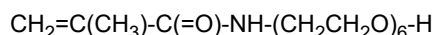
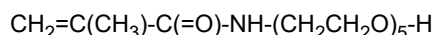
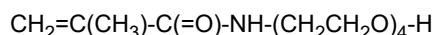
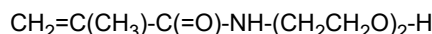
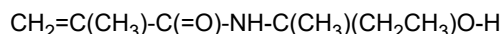
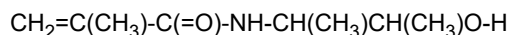
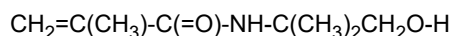
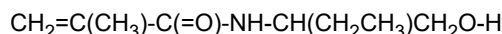
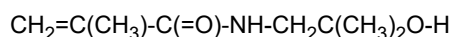
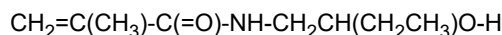


EP 4 575 089 A1

	$\text{CH}_2=\text{CHCOO}-\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{O}-\text{H}$
	$\text{CH}_2=\text{CHCOO}-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)\text{O}-\text{H}$
5	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_2-\text{H}$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_4-\text{H}$
10	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_5-\text{H}$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_6-\text{H}$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_5-\text{CH}_3$
15	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_9-\text{CH}_3$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_{23}-\text{CH}_3$
20	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_{90}-\text{CH}_3$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_9-\text{H}$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_9-\text{CH}_3$
25	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{12}-\text{CH}_3$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_5-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_2-\text{H}$
30	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_5-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_3-\text{CH}_3$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_8-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_6-\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_{23}-\text{OOC}(\text{CH}_3)\text{C}=\text{CH}_2$
35	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_{20}-(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_5-\text{CH}_2-\text{CH}=\text{CH}_2$
	$\text{CH}_2=\text{CHCOO}-(\text{CH}_2\text{CH}_2\text{O})_9-\text{H}$
40	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}_2\text{CH}_2\text{O}-\text{H}$
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{H}$
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-\text{H}$
45	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-\text{H}$
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{H}$
50	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-\text{H}$
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-\text{H}$
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{O}-\text{H}$
55	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{O}-\text{H}$
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{CH}_2\text{C}(\text{CH}_3)_2\text{O}-\text{H}$

EP 4 575 089 A1





[0389] Acrylate and acrylamide in which X^2 is a hydrogen atom are preferred as the monomer (b). The monomer (b) is particularly preferably hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate or hydroxyethyl acrylamide.

(c) Ionic group-containing monomer

[0390] The vinyl polymer may comprise an ionic group-containing monomer (c). The monomer (c) is preferably a monomer having an olefinic carbon - carbon double bond and an ionic group (in particular, an acrylic monomer). The ionic group is an anionic group and/ or a cationic group.

[0391] Examples of monomers having an anionic group include a monomer having a carboxyl group, a sulfonic acid group or a phosphate group. Specific examples of monomers having an anionic group include (meth)acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, vinylsulfonic acid, (meth)allylsulfonic acid, styrene sulfonic acid, phosphoric acid (meth)acrylate, vinylbenzene sulfonic acid, acrylamide t-butylsulfonic acid and a salt thereof.

[0392] Examples of salts of the anionic group include alkaline metal salt, alkaline earth metal salt, and an ammonium salt such as methyl ammonium salt, ethanol ammonium salt and triethanol ammonium salt.

[0393] In the monomer having a cationic group, examples of cationic groups include an amino group, which is preferably a tertiary amino group and a quaternary amino group. It is preferable that in the tertiary amino group, two groups bonded to

a nitrogen atom, which are the same or different, are an aliphatic group having 1 to 5 carbon atoms (in particular alkyl group), an aromatic group having 6 to 20 carbon atoms (an aryl group), or an aromatic aliphatic group having 7 to 25 carbon atoms (in particular an aralkyl group, e.g., a benzyl group ($C_6H_5-CH_2-$)). It is preferable that in the quaternary amino group, three groups bonded to a nitrogen atom, which are the same or different, are an aliphatic group having 1 to 5 carbon atoms (in particular alkyl group), an aromatic group having 6 to 20 carbon atoms (an aryl group), or an aromatic aliphatic group having 7 to 25 carbon atoms (in particular an aralkyl group, e.g., benzyl group ($C_6H_5-CH_2-$)). In the tertiary amino group and the quaternary amino group, the last group bonded to the nitrogen atom may have a carbon-carbon double bond. The cationic group may be in the form of salt.

[0394] The cationic group in the form of salt is a salt with an acid (an organic acid or an inorganic acid). An organic acid such as a carboxylic acid having 1 to 20 carbon atoms (in particular, a monocarboxylic acid such as acetic acid, propionic acid, butyric acid and stearic acid) are preferred. Dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate and a salt thereof are preferred.

[0395] Specific examples of monomers having a cationic group are as follows:

$CH_2=CHCOO-CH_2CH_2-N(CH_3)_2$ and a salt thereof (e.g., acetate)
 $CH_2=CHCOO-CH_2CH_2-N(CH_2CH_3)_2$ and a salt thereof (e.g., acetate)
 $CH_2=C(CH_3)COO-CH_2CH_2-N(CH_3)_2$ and a salt thereof (e.g., acetate)
 $CH_2=C(CH_3)COO-CH_2CH_2-N(CH_2CH_3)_2$ and a salt thereof (e.g., acetate)
 $CH_2=CHC(O)N(H)-CH_2CH_2CH_2-N(CH_3)_2$ and a salt thereof (e.g., acetate)
 $CH_2=CHCOO-CH_2CH_2-N(CH_3)(-CH_2-C_6H_5)$ and a salt thereof (e.g., acetate)
 $CH_2=C(CH_3)COO-CH_2CH_2-N(-CH_2CH_3)(-CH_2-C_6H_5)$ and a salt thereof (e.g., acetate)

$CH_2=CHCOO-CH_2CH_2-N^+(CH_3)_3Cl^-$

$CH_2=CHCOO-CH_2CH_2-N^+(-CH_3)_2(-CH_2-C_6H_5)Cl^-$

$CH_2=C(CH_3)COO-CH_2CH_2-N^+(CH_3)_3Cl^-$

$CH_2=CHCOO-CH_2CH(OH)CH_2-N^+(CH_3)_3Cl^-$

$CH_2=C(CH_3)COO-CH_2CH(OH)CH_2-N^+(CH_3)_3Cl^-$

$CH_2=C(CH_3)COO-CH_2CH(OH)CH_2-N^+(-CH_2CH_3)_2(-CH_2-C_6H_5)Cl^-$

$CH_2=C(CH_3)COO-CH_2CH_2-N^+(CH_3)_3Br^-$

$CH_2=C(CH_3)COO-CH_2CH_2-N^+(CH_3)_3I^-$

$CH_2=C(CH_3)COO-CH_2CH_2-N^+(CH_3)_3O^-SO_3CH_3$

$CH_2=C(CH_3)COO-CH_2CH_2-N^+(CH_3)(-CH_2-C_6H_5)_2Br^-$

[0396] Methacrylic acid, acrylic acid and dimethylaminoethyl methacrylate are preferred, and methacrylic acid and dimethylaminoethyl methacrylate are more preferred as the ionic group-containing monomer (c).

(d) Halogenated olefin monomer (d)

[0397] The vinyl polymer may comprise a repeating unit derived from a halogenated olefin monomer (d). The halogenated olefin monomer (d) may not have a fluorine atom. The halogenated olefin monomer (d) is preferably an olefin having 2 to 20 carbon atoms and substituted by 1 to 10 chlorine atoms, bromine atoms or iodine atoms. The halogenated olefin monomer (d) is preferably chlorinated olefin having 2 to 20 carbon atoms, and particularly preferably an olefin having 2 to 5 carbon atoms and 1 to 5 chlorine atoms. Preferred examples of halogenated olefin monomers (d) include halogenated vinyl such as vinyl chloride, vinyl bromide and vinyl iodide, and halogenated vinylidene such as vinylidene chloride, vinylidene bromide and vinylidene iodide. Vinyl chloride and vinylidene chloride are preferred because they increase water-repellency, in particular, durability of water-repellency. The presence of the repeating unit derived from a halogenated olefin monomer (d) improves wash durability provided by the vinyl polymer.

(e) Cross-linkable monomer

[0398] The vinyl monomer may comprise a cross-linkable monomer having at least two reactive groups and/or an ethylenically unsaturated double bond (preferably a (meth)acrylate group). The cross-linkable monomer (e) may be a monomer which does not include a fluorine atom. The cross-linkable monomer (e) may be a compound which does not include a fluorine atom. The cross-linkable monomer (e) may be a compound having at least two ethylenically unsaturated double bonds (preferably a (meth)acrylate group), or a compound having at least one ethylenically unsaturated double bond and at least one reactive group. Examples of reactive groups include a hydroxyl group, an epoxy group, chloromethyl group, a blocked isocyanate group, an amino group and a carboxyl group.

[0399] The crosslinkable monomer may be mono(meth)acrylate, di(meth)acrylate or di(meth)acrylamide having a reactive group.

[0400] An example of the crosslinkable monomer is a vinyl monomer having a reactive group.

[0401] Examples of crosslinkable monomers include, but are not limited to, diacetone (meth)acrylamide, 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 neopentylglycol di(meth)acrylate.

(f) Cyclic hydrocarbon group-containing monomer

[0402] The vinyl polymer may comprise a repeating unit derived from a cyclic hydrocarbon group-containing monomer (f). The cyclic hydrocarbon group-containing monomer (f) has a cyclic hydrocarbon group, and may have an ethylenically unsaturated double bond and a cyclic hydrocarbon group.

[0403] The cyclic hydrocarbon group-containing monomer (f) preferably has a (meth)acrylic group as the ethylenically unsaturated double bond, and for example, may have a (meth)acrylate group or a (meth)acrylamide group as the ethylenically unsaturated double bond.

[0404] 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, a polycyclic group, or a bridged-ring group, and is preferably a bridged-ring group. The cyclic hydrocarbon group may have a chain group (e.g., a linear or branched hydrocarbon group).

[0405] The cyclic hydrocarbon group may have 4 or more, 6 or more, or 8 or more, and 30 or less, 26 or less, 22 or less, 18 or less, or 14 or less carbon atoms.

[0406] Specific examples of cyclic hydrocarbon groups include a cyclohexyl group, a t-butylcyclohexyl group, an adamantyl group, a 2-methyl-2-adamantyl group, a 2-ethyl-2-adamantyl group, a bornyl group, an isobornyl group, a norbornyl group, a dicyclopentanyl group, a dicyclopentenyl group, a benzyl group, a phenyl group, a naphthyl group, a 2-t-butylphenyl group, a residue formed by eliminating one or more hydrogen atoms from those groups (e.g., a cyclohexylene group, an adamantylene group, a phenylene group and a naphthylene group), and a substituted group thereof.

[0407] Specific examples of cyclic hydrocarbon group-containing monomers 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 and a compound in which such acrylate is substituted with acrylamide. These may be used alone, or two or more of them may be used in combination.

(g) Other monomers

[0408] Other monomers are not limited to those examples, and include acrylonitrile, organosiloxane-containing (meth)acrylate, short-chain alkyl (meth)acrylate, vinyl acetate, styrene, α -methylstyrene, p-methylstyrene and vinyl alkyl ether. Other monomers (d) may be used alone, or two or more of them may be used in combination.

[Composition of polymer]

[0409] The combination of the monomers (a) to (g) constituting the repeating unit of the vinyl polymer is not limited, and is for example, as follows (parentheses omitted).

a

a+b

a+b+c

$a+c$ $a+d$

5 $a+b+c+d$

$$a+b+c+d+e$$
$$10 \quad a+b+c+d+e+f$$

[0410] Other monomers (g) may also be used together with the above combinations. When the vinyl polymer is used for a pulp product, preferably the monomer (a), the monomer (b) and the monomer (c) are used together.

15 **[0411]** The amount of the repeating unit derived from the monomer (a) may be 1% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 40% by weight or more, 50% by weight or more, 60% by weight or more, 70% by weight or more, 80% by weight or more, or 90% by weight or more, and 95% by weight or less, 85% by weight or less, 75% by weight or less, 65% by weight or less, 55% by weight or less, 45% by weight or less, 35% by weight or less, 25% by weight or less, 15% by weight or less, or 5% by weight or less based on the vinyl polymer.

20 **[0412]** The amount of the repeating unit derived from the monomer (b) may be 1% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 40% by weight or more, 50% by weight or more, 60% by weight or more, 70% by weight or more, 80% by weight or more, or 90% by weight or more, and 95% by weight or less, 85% by weight or less, 75% by weight or less, 65% by weight or less, 55% by weight or less, 45% by weight or less, 35% by weight or less, 25% by weight or less, 15% by weight or less, or 5% by weight or less based on the vinyl polymer

25 **[0413]** The amount of the repeating unit derived from the monomer (b) 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, 75 parts by weight or more, 100 parts by
weight or more, 300 parts by weight or more, 500 parts by weight or more, and 1,000 parts by weight or more, and 3,000
parts by weight or less, 2,000 parts by weight or less, 1,000 parts by weight or less, 750 parts by weight or less, 500 parts by
30 weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 50 parts by weight or
less, 30 parts by weight or less, 10 parts by weight or less, or 1 part by weight or less based on 100 parts by mass of the
repeating unit derived from the monomer (a).

[0414] The amount of the repeating unit derived from the monomer (c) may be 1% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 40% by weight or more, 50% by weight or more, 60% by weight or more, 70% by weight or more, 80% by weight or more, or 90% by weight or more, and 95% by weight or less, 85% by weight or less, 75% by weight or less, 65% by weight or less, 55% by weight or less, 45% by weight or less, 35% by weight or less, 25% by weight or less, 15% by weight or less, or 5% by weight or less based on the vinyl polymer.

[0415] The amount of the repeating unit derived from the monomer (c) 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, 75 parts by weight or more, 100 parts by weight or more, 300 parts by weight or more, 500 parts by weight or more, 1,000 parts by weight or more, and 3,000 parts by weight or less, 2,000 parts by weight or less, 1,000 parts by weight or less, 750 parts by weight or less, 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 50 parts by weight or less, 30 parts by weight or less, 10 parts by weight or less, or 1 part by weight or less based on 100 parts by mass of the repeating unit derived from the monomer (a).

[0416] The amount of the repeating unit derived from the monomer (d) may be 1% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 40% by weight or more, 50% by weight or more, 60% by weight or more, 70% by weight or more, 80% by weight or more, or 90% by weight or more, and 95% by weight or less, 85% by weight or less, 75% by weight or less, 65% by weight or less, 55% by weight or less, 45% by weight or less, 35% by weight or less, 25% by weight or less, 15% by weight or less, or 5% by weight or less based on the vinyl polymer.

[0417] The amount of the repeating unit derived from the monomer (d) 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, 75 parts by weight or more, 100 parts by weight or more, 300 parts by weight or more, 500 parts by weight or more, 1,000 parts by weight or more, and 3,000 parts by weight or less, 2,000 parts by weight or less, 1,000 parts by weight or less, 750 parts by weight or less, 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 50 parts by weight or less, 30

parts by weight or less, 10 parts by weight or less, or 1 part by weight or less based on 100 parts by mass of the repeating unit derived from the monomer (a).

[0418] The amount of the repeating unit derived from the monomer (e) may be 1% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 40% by weight or more, 50% by weight or more, 60% by weight or more, 70% by weight or more, 80% by weight or more, or 90% by weight or more, and 95% by weight or less, 85% by weight or less, 75% by weight or less, 65% by weight or less, 55% by weight or less, 45% by weight or less, 35% by weight or less, 25% by weight or less, 15% by weight or less, or 5% by weight or less based on the vinyl polymer.

[0419] The amount of the repeating unit derived from the monomer (e) 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, 75 parts by weight or more, 100 parts by weight or more, 300 parts by weight or more, 500 parts by weight or more, 1,000 parts by weight or more, and 3,000 parts by weight or less, 2,000 parts by weight or less, 1,000 parts by weight or less, 750 parts by weight or less, 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 50 parts by weight or less, 30 parts by weight or less, 10 parts by weight or less, or 1 part by weight or less based on 100 parts by mass of the repeating unit derived from the monomer (a).

[0420] The amount of the repeating unit derived from the monomer (f) may be 1% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 40% by weight or more, 50% by weight or more, 60% by weight or more, 70% by weight or more, 80% by weight or more, or 90% by weight or more, and 95% by weight or less, 85% by weight or less, 75% by weight or less, 65% by weight or less, 55% by weight or less, 45% by weight or less, 35% by weight or less, 25% by weight or less, 15% by weight or less, or 5% by weight or less based on the vinyl polymer.

[0421] The amount of the repeating unit derived from the monomer (f) 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, 75 parts by weight or more, 100 parts by weight or more, 300 parts by weight or more, 500 parts by weight or more, 1,000 parts by weight or more, and 3,000 parts by weight or less, 2,000 parts by weight or less, 1,000 parts by weight or less, 750 parts by weight or less, 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 50 parts by weight or less, 30 parts by weight or less, 10 parts by weight or less, or 1 part by weight or less based on 100 parts by mass of the repeating unit derived from the monomer (a).

[0422] The amount of the repeating unit derived from the monomer (g) may be 1% by weight or more, 5% by weight or more, 10% by weight or more, 20% by weight or more, 30% by weight or more, 40% by weight or more, 50% by weight or more, 60% by weight or more, 70% by weight or more, 80% by weight or more, or 90% by weight or more, and 95% by weight or less, 85% by weight or less, 75% by weight or less, 65% by weight or less, 55% by weight or less, 45% by weight or less, 35% by weight or less, 25% by weight or less, 15% by weight or less, or 5% by weight or less based on the vinyl polymer.

[0423] The amount of the repeating unit derived from the monomer (g) 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, 75 parts by weight or more, 100 parts by weight or more, 300 parts by weight or more, 500 parts by weight or more, 1000 parts by weight or more, and 3,000 parts by weight or less, 2,000 parts by weight or less, 1,000 parts by weight or less, 750 parts by weight or less, 500 parts by weight or less, 300 parts by weight or less, 200 parts by weight or less, 100 parts by weight or less, 50 parts by weight or less, 30 parts by weight or less, 10 parts by weight or less, or 1 part by weight or less based on 100 parts by mass of the repeating unit derived from the monomer (a).

[Polymerization method]

[0424] The vinyl polymer may be polymerized by a known polymerization method, and conditions of polymerization reaction may be optionally selected. Examples of polymerization methods include solution polymerization, suspension polymerization, emulsion polymerization, and condensation polymerization.

[0425] Solution polymerization uses a method in which monomer is dissolved in an organic solvent in the presence of a polymerization initiator, and after nitrogen replacement, the mixture is heated and stirred at 30 to 120°C for 1 to 10 hours. Examples of polymerization initiators include azobisisobutyronitrile, benzoyl peroxide, di-t-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxyvalate and diisopropyl peroxydicarbonate. 0.01 to 20 parts by weight, for example, 0.01 to 10 parts by weight of polymerization initiator is used based on 100 parts by weight of the monomer.

[0426] Organic solvents are inert to monomers and dissolves them. Examples thereof include ester (e.g., ester having 2 to 40 carbon atoms such as ethyl acetate and butyl acetate), ketone (e.g., ketone having 2 to 40 carbon atoms such as methyl ethyl ketone, diisobutyl ketone and methyl isobutyl ketone), alcohol (e.g., alcohol having 1 to 40 carbon atoms such

as ethanol, butanol and isopropyl alcohol). Specific examples of solvents include 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. 10 to 3,000 parts by weight, for example, 50 to 2,000 parts by weight of organic solvent is used based on 100 parts by weight of the total amount of the monomers.

[0427] Emulsion polymerization uses a method in which monomer is emulsified in water in the presence of a polymerization initiator and an emulsifier, and after nitrogen replacement, the monomer is polymerized by stirring at 50 to 80°C for 1 to 20 hours. As the polymerization initiator, a water-soluble initiator such as benzoyl peroxide, lauroyl peroxide, t-butyl perbenzoate, 1-hydroxycyclohexyl hydroperoxide, 3-carboxypropionyl peroxide, acetyl peroxide, azobisisobutylamidinium-dihydrochloride, sodium peroxide, potassium persulfate and ammonium persulfate, and an oil-soluble initiator such as azobisisobutyronitrile, benzoyl peroxide, di-t-butylperoxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxyphthalate and diisopropyl peroxydicarbonate are used. 0.01 to 10 parts by weight of polymerization initiator is used based on 100 parts by weight of the monomer.

[0428] To obtain an aqueous polymer dispersion having excellent standing stability, it is desirable to perform polymerization by forming fine particles of monomers in water by using an emulsification device which can offer high crush energy, such as a high pressure homogenizer and an ultrasonic homogenizer. The emulsifier may be anionic, cationic or nonionic, and 0.5 to 20 parts by weight of the emulsifier may be used based on 100 parts by weight of the monomer. It is preferable to use an anionic and/or nonionic and/or cationic emulsifier. If monomers are not completely dissolved, it is preferable to add a compatibilizer which dissolves the monomers completely, such as a water-soluble organic solvent or a low molecular weight monomer. Addition of the compatibilizer improves emulsifiability and copolymerizability.

[0429] The above organic solvent may be used as the aqueous organic solvent. Examples thereof include acetone, methyl ethyl ketone, ethyl acetate, propylene glycol, dipropylene glycol monomethyl ether, dipropylene glycol, tripropylene glycol and ethanol. 1 to 50 parts by weight, for example, 10 to 40 parts by weight of the organic solvent may be used based on 100 parts by weight of water. Examples of low molecular weight monomers include methyl methacrylate, glycidyl methacrylate and 2,2,2-trifluoroethyl methacrylate. 1 to 50 parts by weight, for example, 10 to 40 parts by weight of the low molecular weight monomer may be used based on 100 parts by weight of the total amount of the monomers.

[0430] A chain transfer agent may also be used in polymerization. The molecular weight of the polymer can be changed depending on the amount of use of the chain transfer agent. Examples of chain transfer agents include a mercaptan group-containing compound, in particular, alkyl mercaptan having 1 to 40 carbon atoms, such as lauryl mercaptan, thioglycol and thioglycerol, and an inorganic salt such as sodium hypophosphite and sodium hydrogen sulfide. 0.01 to 10 parts by weight, for example, 0.1 to 5 parts by weight of the chain transfer agent may be used based on 100 parts by weight of the total amount of the monomers.

{Dispersant}

[0431] The repellent of the present disclosure may comprise a dispersant. The dispersant may be at least one selected from an organic dispersant and an inorganic dispersant. The dispersant may be at least one selected from an anionic dispersant, a nonionic dispersant, a cationic dispersant, an amphoteric dispersant and an inorganic dispersant.

[0432] An organic dispersant and an inorganic dispersant may be used as the dispersant, respectively, or an organic dispersant and an inorganic dispersant may be used in combination.

[0433] An organic dispersant may be used as the dispersant. The organic dispersant may be classified into a nonionic dispersant, an anionic dispersant, a cationic dispersant and an amphoteric dispersant. The organic dispersant may mean a surfactant.

[0434] The dispersant may have no fluorine.

[Nonionic dispersant]

[0435] The dispersant may comprise a nonionic dispersant. The nonionic dispersant may be a nonionic surfactant.

[0436] The nonionic dispersant may be of low molecular weight or high molecular weight. The nonionic dispersant may have a molecular weight of 100 or more, 500 or more, 1,000 or more, 2,000 or more, 4,000 or more, or 6,000 or more, and 100,000 or less, 10,000 or less, 7,500 or less, 5,000 or less, 25,000 or less, 750 or less, or 250 or less.

[0437] Examples of nonionic dispersant include ether, ester, ester ether, alkanolamide, polyol and amine oxide.

[0438] The ether is, for example, a compound having an oxyalkylene group (preferably a polyoxyethylene group).

[0439] The ester is, for example, an ester of an alcohol and a fatty acid. The alcohol is, for example, an alcohol which is 1 to 30 hydric (particularly dihydric to decahydric) 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.

[0440] 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 1 to 30 hydric (particularly dihydric to decahydric) 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.

[0441] 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.

[0442] The polyol may be, for example, a dihydric to pentahydric alcohol having 10 to 30 carbon atoms.

[0443] The amine oxide may be an oxide (for example, having 5 to 50 carbon atoms) of an amine (secondary amine or preferably tertiary amine).

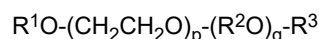
[0444] The nonionic dispersant is preferably a nonionic dispersant having an oxyalkylene group (preferably a polyoxyethylene group). The alkylene group in the oxyalkylene group preferably has 2 to 10 carbon atoms. The number of oxyalkylene groups in the molecule of the nonionic dispersant is generally preferably 2 to 100.

[0445] The nonionic dispersant is selected from the group consisting of an ether, an ester, an ester ether, an alkanolamide, a polyol, or an amine oxide, and is preferably a nonionic dispersant having an oxyalkylene group.

[0446] The nonionic dispersant 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 sorbitan ester of a linear and/or branched fatty acid (saturated and/or unsaturated), a glycerin ester of a linear and/or branched fatty acid (saturated and/or unsaturated), a polyglycerol ester of a linear and/or branched fatty acid (saturated and/or unsaturated), a sucrose ester of a linear and/or branched fatty acid (saturated and/or unsaturated), a polyoxyethylene (POE)/polyoxypropylene (POP) copolymer (random copolymer or block copolymer), and an alkylene oxide adduct of acetylene glycol. Among them, the nonionic dispersant is preferably a dispersant 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 or block copolymer, for example.).

[0447] Furthermore, the nonionic dispersant may not include an aromatic group.

[0448] The nonionic dispersant may be the compound represented by the formula:



[wherein R¹ is an alkyl group having 1 to 22 carbon atoms, an alkenyl group or an acyl group, having 2 to 22 carbon atoms,

R² is each independently the same or different and is an alkylene group having 3 or more carbon atoms (for example, 3 to 10),

R³ 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.].

[0449] R¹ preferably has 8 to 20 carbon atoms, particularly 10 to 18 carbon atoms. Preferred examples of R¹ include an octyl group, a nonyl group, a trimethylnonyl group, a lauryl group, a tridecyl group, an oleyl group and a stearyl group.

[0450] R² is, for example, a propylene group and a butylene group.

[0451] In the nonionic dispersant, 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, -(R²O)_q- may form, for example, a polyoxyalkylene chain.

[0452] The nonionic dispersant 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.

[0453] Specific examples of the nonionic dispersants include a condensation product of ethylene oxide with hexylphenol, isooctatylphenol, hexadecanol, oleic acid, an alkane(C₁₂-C₁₆) thiol, a sorbitan monofatty acid (C₇-C₁₉), an alkyl (C₁₂-C₁₈) amine, or the like, and a sorbitan fatty acid ester, a glycerin fatty acid ester, a polyglycerin fatty acid ester, a sucrose fatty acid ester, a propylene glycol fatty acid ester, a polyoxyethylene alkyl ether, a polyoxyethylene polyoxypropylene alkyl ether, a polyoxyethylene glycerin fatty acid ester, a polyoxyethylene sorbitan fatty acid ester, and a lecithin derivative. Examples of nonionic dispersants include polyoxyethylene alkyl ether, polyoxyethylene polyoxypropylene alkyl ether, polyoxyethylene polyoxybutylene alkyl ether, polyoxyethylene polyoxypropylene glycol and polyethyleneimine ethoxylate.

[0454] 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 dispersant (copolymer).

[0455] The average molecular weight of the nonionic dispersant is generally 300 to 5,000, for example, 500 to 3,000.

[0456] For example, the nonionic dispersant may be used singly or in admixture of two or more. The nonionic dispersant 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. More specifically, it is preferable to select the nonionic dispersant from polyoxyethylene alkyl ether, polyoxyethylene polyoxypropylene alkyl ether, polyoxyethylene and polyoxypropylene having an HLB of 1 to 18, sorbitan fatty acid ester, glycerol fatty acid ester, polyglycerol fatty acid ester, sucrose fatty acid ester, propylene glycol fatty acid ester, polyoxyethylene glycerol fatty acid ester and polyoxyethylene sorbitan fatty acid ester having an HLB of less than 7.

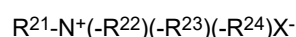
[Cationic dispersant]

[0457] The dispersant may comprise a cationic dispersant. The cationic dispersant may be a cationic surfactant. The cationic dispersant may be a compound not having an amide group.

[0458] The cationic dispersant may be of low molecular weight (with a molecular weight of 2,000 or less, in particular, 10,000 or less) or of high molecular weight (with a molecular weight of, for example, 2,000 or more). The cationic dispersant may not have an amide group. The cationic dispersant may have a molecular weight of 100 or more, 500 or more, 1,000 or more, 2,000 or more, 4,000 or more, or 6,000 or more, and 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, 10,000 or less, 7,500 or less, 5,000 or less, 25,000 or less, 750 or less, or 250 or less.

[0459] The cationic dispersant may be aliphatic or aromatic, and examples thereof include an ammonium salt (e.g., quaternary ammonium salt). The cationic dispersant may be oxyethylene-added ammonium salt. Specific examples thereof include an amine salt dispersant such as alkylamine salt, an amino alcohol fatty acid derivative, a polyamine fatty acid derivative and imidazoline; a quaternary ammonium salt dispersant such as alkyl trimethyl ammonium salt, dialkyl dimethyl ammonium salt, alkyl dimethyl benzyl ammonium salt, pyridinium salt, alkyl isoquinolinium salt, benzalkonium chloride and benzethonium chloride; and a polymer cationic dispersant such as polyquaternium-1 to 47. Examples of cationic dispersants include alkyl amine salt and quaternary ammonium salt.

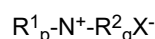
[0460] The low molecular weight cationic dispersant may be a compound represented by the formula:



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

[0461] Specific examples of R^{21} , R^{22} , R^{23} and $-R^{24}$ include an alkyl group (e.g., a methyl group, a butyl group, a stearyl group, a palmityl group). Specific examples of X include a halogen (e.g., chlorine) and an acid (e.g., hydrochloric acid and acetic acid). The cationic dispersant may be monoalkyltrimethylammonium salt (in which alkyl has 4 to 40 carbon atoms).

[0462] More specifically, the low molecular weight cationic dispersant may be an ammonium salt represented by the formula:



[wherein R^1 is a C_{12} or higher (e.g., C_{12} to C_{50}) linear and/or branched aliphatic (saturated and/or unsaturated) group,

R^2 is H or a C_1 to 4 alkyl group, a benzyl group, a polyoxyethylene group (in which the number of oxyethylene groups is for example, 1 (in particular 2, and especially 3) to 50) (particularly preferably CH_3 , C_2H_5),

X is a halogen atom (e.g., chlorine) or a C_1 to C_4 fatty acid salt or a C_1 to C_4 sulfonate,

p is 1 or 2, q is 2 or 3 and $p + q = 4$.]

R^1 may have 12 to 50, and for example 12 to 30 carbon atoms.

[0463] Examples of the low molecular weight cationic dispersants may include dodecyltrimethylammonium acetate, trimethyltetradecylammonium chloride, hexadecyltrimethylammonium bromide, trimethyloctadecylammonium chloride, (dodecylmethylbenzyl)trimethylammonium chloride, benzyl dodecyl dimethylammonium chloride, methyl dodecyl di(hydroxyethylene) ammonium chloride, benzyl dodecyl di(hydroxyethylene) ammonium chloride, and N-[2-(diethylamino)ethyl]oleamide hydrochloride.

[0464] The high molecular weight cationic dispersant may be a polymer having a cationic group (for example, an ammonium group, a quaternary ammonium group) (for example, polypolyquaternium-1 to 47). Examples of high molecular weight cationic dispersants include a cationic natural product (in particular, cationic sugar) such as cationic starch, cationic cellulose (e.g., O-(2-hydroxy-3-(trimethylammonio)propylhydroxyethyl cellulose chloride), cationic guar gum, cationic xanthan gum and chitosan; a polymer of a cationic group-containing monomer such as aziridine, vinyl imidazole, aminoalkyl methacrylate, N,N,N',N'-tetramethyl-2-butene-1,4-diamine, quaternary dimethyl ammonium ethyl

methacrylic acid, diallyldimethylammonium chloride, dimethylaminopropylamine and quaternary vinyl imidazole.

[Anionic dispersant]

5 **[0465]** The dispersant may comprise an anionic dispersant. The anionic dispersant may be an anionic surfactant. The dispersant may not include an anionic dispersant.

[0466] The anionic dispersant may be of low molecular weight or high molecular weight. The anionic dispersant may have a molecular weight of 100 or more, 500 or more, 1,000 or more, 2,000 or more, 4,000 or more, or 6,000 or more, and 100,000 or less, 10,000 or less, 7,500 or less, 5,000 or less, 25,000 or less, 750 or less, or 250 or less.

10 **[0467]** Examples of the anionic dispersant 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 dispersant, a phosphate mono- or diester dispersant, and a sulfosuccinic acid ester. Examples of anionic dispersants include a carboxylic acid salt (e.g., fatty acid salt).

15 [Amphoteric dispersant]

[0468] The dispersant may comprise an amphoteric dispersant. The amphoteric dispersant may be an amphoteric surfactant.

20 **[0469]** The amphoteric dispersant may be of low molecular weight or high molecular weight. The amphoteric dispersant may have a molecular weight of 100 or more, 500 or more, 1,000 or more, 2,000 or more, 4,000 or more, or 6,000 or more, and 100,000 or less, 10,000 or less, 7,500 or less, 5,000 or less, 25,000 or less, 750 or less, or 250 or less.

[0470] Examples of the amphoteric dispersants include, for example, alanines, imidazolinium betaines, amidobetaines, and acetic acid betaine, and specific examples of the amphoteric dispersants include, for example, lauryl betaine, stearyl betaine, lauryl carboxymethyl hydroxyethyl imidazolinium betaine, lauryl dimethylamino acetic acid betaine, and fatty acid
25 amidopropyl dimethylaminoacetic acid betaine.

[Inorganic dispersant]

[0471] The dispersant may comprise an inorganic dispersant.

30 **[0472]** The inorganic dispersant has an average primary particle size of 5 nm or larger, 30 nm or larger, 100 nm or larger, 1 μ m or larger, 10 μ m or larger, or 25 μ m or larger, and 100 μ m or smaller, 50 μ m or smaller, 10 μ m or smaller, 1 μ m or smaller, 500 nm or smaller, or 300 nm or smaller. The average primary particle size may be measured by a microscope, for example, a scanning electron microscope or a transmission electron microscope. The inorganic dispersant may be hydrophilic particles.

35 **[0473]** Examples of inorganic dispersants include polyvalent metal phosphate such as tricalcium phosphate, magnesium phosphate, aluminum phosphate, zinc phosphate and hydroxyapatite; carbonate such as calcium carbonate and magnesium carbonate; silicate such as calcium metasilicate; sulfate such as calcium sulfate and barium sulfate; and hydroxide such as calcium hydroxide, magnesium hydroxide and aluminum hydroxide.

40 [Amount of Dispersant]

[0474] The amount of dispersant 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, 15 parts by weight or more, 20 parts by weight or more, 50 parts by weight or more, 75 parts by weight or more, or 100 parts by weight or more, relative to 100 parts
45 by weight of the liquid-repellent compound, and 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 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, or 1 part by weight or less.

{Liquid medium}

50 **[0475]** The repellent in the present disclosure may comprise a liquid medium. The liquid medium may be water, an organic solvent, or a mixture of water and an organic solvent. The repellent may be a dispersion or a solution. The repellent in the present disclosure may include at least water.

[0476] 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
55

water-soluble organic solvent may include a compound having at least one hydroxy group (for example, polyol such as alcohol and glycol solvent, and an ether form of polyol (for example, a monoether form)). These may be used alone, or two or more of them may be used in combination.

5 [Amount of liquid medium]

[0477] The amount of liquid medium 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, 100 parts by weight or more, 200 parts by weight or more, 300 parts by weight or more, 500 parts by weight or more, or 1,000 parts by weight or more, and 3,000 parts by weight or less, 2,000 parts by weight or less, 1,000 parts by weight or less, 500 parts by weight or less, 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, or 10 parts by weight or less relative to 1 part by weight of the liquid-repellent compound.

[0478] The amount of water 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, 50 parts by weight or more, 100 parts by weight or more, 200 parts by weight or more, 300 parts by weight or more, 500 parts by weight or more, or 1,000 parts by weight or more, and 3,000 parts by weight or less, 2,000 parts by weight or less, 1,000 parts by weight or less, 500 parts by weight or less, 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, or 10 parts by weight or less based on 1 part by weight of the liquid-repellent compound.

[0479] The amount of the 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, 50 parts by weight or more, 100 parts by weight or more, 200 parts by weight or more, 300 parts by weight or more, 500 parts by weight or more, or 1,000 parts by weight or more, and 3,000 parts by weight or less, 2,000 parts by weight or less, 1,000 parts by weight or less, 500 parts by weight or less, 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, or 10 parts by weight or less relative to 1 part by weight of the liquid-repellent compound.

{Silicone}

[0480] 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.

[0481] 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.

[0482] A weight average molecular weight of the silicone may be 1,000 or more, 10,000 or more, or 50,000 or more, and may be 500,000 or less, 2,500,000 or less, 100,000 or less, or 50,000 or less.

[Amount of Silicone]

[0483] The amount of silicone is 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, 75 parts by weight or more, or 100 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound, and 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, 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.

{Wax}

[0484] The repellent in the present disclosure may include wax. Containing the wax can impart favorable liquid-repellency to a substrate.

[0485] Examples of 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. A hydrocarbon wax, in particular, paraffin wax is preferred. Specific examples of compounds constituting wax include

n-alkane (such as tricosan, tetracosane, pentacosane, hexacosane, heptacosan, octacosan, nonacosane, triacontane, hentriacontane, dotriacontane, tritriacontane, tetratriacontane, pentatriacontane, hexatriacontane), n-alkene (such as 1-icosene, 1-docosene, 1-tricosene, 1-tetracosene, 1-pentacosene, 1-hexacosene, 1-heptacosene, 1-octacosene, 1-nonacosene, 1-triacontene, 1-hentriacontene, 1-dotriacontene, 1-tritriacontene, 1-tetratriacontene, 1-pentatriacontene, 1-hexatriacontene). 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.

[0486] The wax may have a melting point of 50°C or higher, 55°C or higher, 60°C or higher, 65°C or higher, or 70°C or higher, preferably 55°C or higher, more preferably 60°C or higher. The melting point of wax is measured according to JIS K 2235-1991.

[Amount of Wax]

[0487] 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, 75 parts by weight or more, or 100 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound, and 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, 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.

{Organic Acid}

[0488] The repellent of the present disclosure 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]

[0489] 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, 75 parts by weight or more, or 100 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound, and 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, 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. 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}

[0490] The repellent of the present disclosure may contain a curing agent (active hydrogen-reactive compound or active hydrogen-containing compound).

[0491] 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 that the liquid-repellent compound has. 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.

[0492] 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.

[0493] 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.

[0494] 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-isocyanatomethyl-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.

[0495] Examples of the aromatic-aliphatic polyisocyanate include an aromatic-aliphatic diisocyanate and aromatic-aliphatic triisocyanate. Specific examples of the aromatic-aliphatic 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.

[0496] 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.

[0497] 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.

[0498] These polyisocyanates can be used singly or in combination of two or more thereof.

[0499] 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.

[0500] 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.

[0501] 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.

[0502] 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.

[0503] 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.

[0504] Specific examples of the ketone group-containing compound include, for example, a (poly)diacetone acrylamide, and diacetone alcohol.

[0505] Specific examples of the hydrazide compound include, for example, hydrazine, a carbohydrazide, and adipic acid hydrazide.

[0506] Specific examples of the melamine compound include, for example, a melamine resin and a methyl etherified melamine resin.

[Amount of Curing Agent]

[0507] The amount of the 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, 75 parts by weight or more, or 100 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound, and 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, 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, and 5 parts by weight or less.

{Other Component}

[0508] The repellent may contain a component other than the aforementioned components. Examples of the other components include, for example, polysaccharides, a paper strengthening agent, an agglomerating agent, a yield improver, a coagulant, a binder resin, an anti-slip agent, a sizing agent, a paper strengthening agent, a filler, 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.

[0509] In addition to the above components, as other components, for example, other water-repellent and/or oil-repellent agents, a dispersant, a texture modifier, a softening 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 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 a polyvinylpyrrolidone, a polymer dispersant, a soil release agent, a scum dispersant, a fluorescent brightening agent such as 4,4-bis(2-sulfostyryl)biphenyldisodium (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 agent, enzymes such as cellulase, amylase, protease, lipase, and keratinase as fiber surface modifiers, a foam inhibitor, and silk protein powder that can impart texture and functions of silk such as moisture absorption and release properties, and surface modified products or emulsified dispersions thereof (for example, 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 an alkylene terephthalate and/or an alkylene isophthalate units and a polyoxyalkylene unit (for example, FR627 manufactured by GOO CHEMICAL CO., LTD.), SRC-1 manufactured by Clariant (Japan), K. K.), can be compounded. These may be used singly or in combination of two or more thereof.

[Polysaccharide]

[0510] Examples of polysaccharides include starch, xanthan gum, karaya gum, welan gum, guar gum, pectin, tamarind gum, carrageenan, chitosan, gum arabic, locust bean gum, cellulose, alginic acid, agar, dextran, cellulose, carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, chitin nanofiber, cellulose nanofiber and pullulan. Polysaccharide may be a substituted modified polysaccharide (excluding the liquid-repellent compound described above), and in particular, may be a modified polysaccharide into which a hydroxyl group or a cationic group is introduced.

[Paper Strengthening Improver, Agglomerating agent, Yield Improver or Coagulant]

[0511] Examples of the paper strengthening improver, agglomerating agent, yield improver or coagulant include, for example, a styrenic polymer (styrene/maleic acid polymer, styrene/acrylic acid polymer), a ureaformaldehyde polymer, a polyethyleneimine, a melamineformaldehyde polymer, a polyamidoamine-epichlorohydrin polymer, a polyacrylamide-based polymer, a polyamine-based polymer, a polydiallyldimethylammonium chloride, an alkylamine-epichlorohydrin condensate, a condensate of alkylene dichloride and polyalkylenepolyamine, a dicyandiamide formalin condensate, a dimethyldiallylammonium chloride polymer, and an olefin/maleic anhydride polymer.

[Sizing Agent]

[0512] Examples of the sizing agent include a cellulose-reactive sizing agent, for example, a rosin-based sizing agent such as rosin-based soap, rosin-based emulsion/a dispersion, a cellulose-reactive sizing agent, for example, emulsion/-dispersions of acid anhydrides such as alkyl and alkenyl succinic anhydrides (ASA), an alkenyl and alkyl ketene dimers (AKD) and multimers thereof, and anionic, cationic and amphoteric polymers of ethylenically unsaturated monomers, for example, a styrene and acrylate copolymer.

[Antistatic Agent]

[0513] 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 as 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.

5 [Antiseptic Agent]

[0514] The antiseptic agent may be used mainly to enhance antiseptis 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.

10 [Ultraviolet Absorber]

[0515] 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, azolebased compounds, and 4-t-butyl-4'-methoxybenzoylmethane.

[Antibacterial Agent]

[0516] 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.

25 [Deodorant]

[0517] 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]

[0518] Each amount or the total amount of 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, 75 parts by weight or more, or 100 parts by weight or more, relative to 100 parts by weight of the liquid-repellent compound, and 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, 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.

[0519] 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

[0520] Hereinafter, the present disclosure will be described in detail with reference to Examples, but the present disclosure is not limited to these Examples.

<Test Method>

[0521] The test procedures are as follows.

[Practical water resistance test]

[0522] Mold was pre-treated by storing under conditions of 23°C and a humidity of 50% for 12 hours. After pouring 100 ml of corn oil at 65°C into the mold and allowing it to stand at room temperature for 45 minutes, the corn oil was removed from the mold, and the degree of oil staining in the mold was evaluated. The evaluation scores were set as follows according to the degree of staining.

- 5: No stains inside the pulp mold.
 4: Stains inside the pulp mold. No stains on the backside.
 3: Stains the inside the pulp mold. Slight stain bleed out on the backside.
 2: Stains inside the pulp mold. The area of stain bleed out to the backside is less than 50% of the total area.
 1: Stains inside the pulp mold. The area of stain bleed out to the backside is 50% or more and less than 100% of the total area.
 0: Stains over the backside.

[Practical water resistance test]

[0523] Mold was pre-treated by storing under conditions of 23°C and a humidity of 50% for 12 hours. After pouring 100 ml of water at 100°C into the mold and allowing it to stand at room temperature for 30 minutes, the water was removed from the mold, and the degree of staining in the mold was evaluated. Evaluation scores were set as follows depending on the degree of penetration.

- 5: No stains inside the mold.
 4: Stains inside the mold. No stains on the backside.
 3: Stains inside the mold. Slight stain bleed out on the backside.
 2: Stains inside the mold. The area of stain bleed out to the backside is less than 50% of the total area.
 1: Stains inside the mold. The area of stain bleed out to the backside is 50% or more and less than 100% of the total area.
 0: Stains over the backside.

Evaluation of amount of adhesion

[0524] The amount of adhesion of the liquid repellent compound to the pulp mold is less than the amount of the liquid repellent compound added. The amount of adhesion may be calculated by the following process.

[0525] In the first step, a paper plate of the pulp mold is weighed. In the second step, a solvent for evaluation is prepared by adding an internal standard (e.g., toluene, DMF) to a solvent in which the liquid repellent compound is dissolved (e.g., chloroform). In the third step, the solvent for evaluation is weighed, and the paper plate weighed is dipped in the solvent and heated if necessary to extract the liquid repellent compound. In the fourth step, a portion of the solution into which the liquid repellent compound is extracted is discharged and diluted with a heavy solvent and subjected to 1H-NMR measurement. When a heavy solvent is used as the solvent for evaluation, the solution into which the liquid repellent compound is extracted is not diluted and directly subjected to the measurement. The amount of the liquid repellent compound adhering to the mold is calculated based on the results of the 1H-NMR measurement.

<Examples 1-1 to 1-5, Comparative Examples 1-1>

[Preparation of repellent]

[0526] 2 g of decaglycerol dodecabenyl ester (degree of polymerization: 10, hydroxy group substitution ratio: 12/12*100 [100%], biobased ratio: 100%, melting point: 69°C), which was a liquid-repellent compound, 0.2 g of polyethylene oxide alkyl ether (in which alkyl has 6 to 16 carbon atoms, HLB: 7) and 17.8 g of water were mixed to give a precursor of water-dispersible repellent A. The precursor of water-dispersible repellent A was heated to 80°C and then allowed to cool with stirring by a magnetic stirrer to give a precursor of water-dispersible repellent B. The precursor of water-dispersible repellent B was treated twice in a high pressure wet pulverizer under a condition of 80 MPa to give a water-dispersible repellent. The resulting water-dispersible repellent had a volume abundance ratio of particles with a particle size of 100 μm or larger of 2% and a median diameter D50 of 16.2 μm.

[Preparation of pulp composition (pulp slurry)]

[0527] 1,300 ml of water was added to 700 g of a 1.4% by weight aqueous dispersion of a mixture of 70 parts of broad leaf tree bleached kraft pulp and 30 parts of needle bleached kraft pulp, which were beaten to a freeness (Canadian Standard Freeness) of 500 cc. The pulp composition was prepared by adding the water-dispersible repellent obtained above at a solid concentration of the liquid repellent compound of 3 parts by weight per weight of pulp while stirring.

[Preparation of pulp mold]

[0528] Pulp mold was formed using an automatic mold molding machine. In the lower part thereof, a reticular body was arranged on a pulp mold molding mold made of metal with many suction holes, a metal tank was arranged in the upper part, and the pulp composition was charged in the upper metal tank. From the opposite side of the pulp mold molding mold to the side where the reticular body was

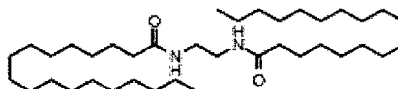
	Temperature (°C)	Time (s)	Temperature (°C)	Time (min)	Bottom	Side
Com. Ex. 1-1	180	60	-	-	1	1~2.5
Ex. 1-1			65	10	3.5~4	2~4
Ex. 1-2			65	30	4	2.5~3.5
Ex. 1-3			65	60	4	4
Ex. 1-4			80	10	4	3.5
Ex. 1-5			80	30	3~4	2~3.5

[0529] The amount of adhesion of the liquid repellent compositions of Examples 1 to 3 was 1.9% by weight based on the weight of the pulp.

<Examples 2-1 to 2-3, Comparative Examples 2-1 and 2-2>

[Preparation of repellent]

[0530] 2 g of a dry-ground powder of ethylene bis(stearic acid amide) represented by the following formula:



(biobased content: 97%, melting point: 143°C), which was the liquid repellent compound, 0.2 g of polyethylene glycol trimethylnonyl ether (HLB13) and 17.8 g of water were mixed to give a water-dispersible repellent (volume abundance ratio of particles with a particle size of 100 μm or more: 4.5%, volume median diameter: 19.2 μm).

arranged, the pulp composition was suctioned and dehydrated through the pulp mold molding mold and the reticular body by a vacuum pump, and solids (pulp, etc.) contained in the pulp composition were allowed to deposit on the reticular body to obtain a pulp mold intermediate.

[0531] Next, the resulting pulp mold intermediate was heated (preheated) from the tops and bottoms of heated male and female molding molds made of metal for 10 seconds at 80°C under a pressure of 0.3 MPa. Subsequently the first heating was performed at the temperature for the time shown in the following table to heat and dry the pulp mold intermediate so that the amount of the liquid medium was 10% by weight to give a pulp mold (a paper bowl).

[0532] Then the pulp mold was left at room temperature until the temperature of the pulp mold reached room temperature (15 to 40°C) (first cooling).

[0533] Subsequently the pulp mold after the first cooling was subjected to the second heating under the conditions shown in the following table.

[0534] The resulting pulp mold after the second heating was returned to room temperature (after the second cooling), and then subjected to the above tests. The results are shown in the following table.

	First heating condition	Second heating condition	Practical oil resistance (point (s))
--	-------------------------	--------------------------	--------------------------------------

[Preparation of pulp composition (pulp slurry)]

[0535] 1,300 ml of water was added to 700 g of a 1.4% by weight aqueous dispersion of a mixture of 70 parts of broad leaf tree bleached kraft pulp and 30 parts of needle bleached kraft pulp, which were beaten to a freeness (Canadian Standard Freeness) of 550 cc. The pulp composition was prepared by adding the water-dispersible repellent obtained above at a solid concentration of the liquid repellent compound of 1 part by weight per weight of pulp while stirring.

[Preparation of pulp mold]

[0536] Pulp mold was prepared and tested in the same manner as in Example 1-1 except for heating and cooling using the above pulp composition under conditions shown in the following table. The results are shown in the following table.

	First heating condition		First cooling condition	Second heating condition		Practical oil resistance (point(s))		Practical water resistance (point(s))	
	Temperature (°C)	Time (s)	Temperature (°C)	Temperature (°C)	Time (min)	Bottom	Side	Bottom	Side
Com. Ex. 2-1	180	60	25	-	-	1	1	0	0
Com. Ex. 2-2		180	25	-	-	0	0	0	0
Ex. 2-1		60	25	180	3	2.5	3	-	-
Ex. 2-2			25	180	5	3	4	-	-
Ex. 2-3			25	180	10	4	3.5	4	4

Claims

1. A method for producing a pulp product, comprising:

a first heating of heating a pulp composition comprising pulp and a liquid repellent compound to a first heating temperature, thereby preparing a precursor product in which the liquid repellent compound is adhered to the pulp;
a first cooling of cooling the precursor product to a first cooling temperature, thereby preparing a cooled precursor product; and
a second heating of heating the cooled precursor product to a second heating temperature, thereby preparing a pulp product.

2. The method for producing a pulp product according to claim 1, wherein

the first heating temperature is 40°C or higher,
the first cooling temperature is lower than 40°C, and
the second heating temperature is 40°C or higher.

3. The method for producing a pulp product according to claim 1 or 2, wherein

the first heating temperature is equal to or higher than the melting point of the liquid repellent compound, and
the first cooling temperature is lower than the melting point of the liquid repellent compound.

4. The method for producing a pulp product according to claim 3, wherein the second heating temperature is at least 0.7 times the melting point of the liquid repellent compound.

5. The method for producing a pulp product according to claim 3, wherein the second heating temperature is equal to or higher than the first cooling temperature +30°C, and equal to or higher than the melting point of the liquid repellent compound -50°C.

6. The method for producing a pulp product according to any one of claims 1 to 5, wherein

the first heating temperature is equal to or higher than the melting point of the liquid repellent compound,
the first cooling temperature is lower than 40°C, and
the second heating temperature is equal to or higher than the melting point of the liquid repellent compound -50°C, and equal to or lower than the melting point of the liquid repellent compound +100°C.

7. The method for producing a pulp product according to any one of claims 1 to 6, wherein

the pulp composition comprises a liquid medium, and
in the first heating step, the liquid medium is removed to an amount of 10% by weight or less in the pulp composition.

8. The method for producing a pulp product according to any one of claims 1 to 7, wherein

the pulp composition is formed in the first heating step and
the precursor product is a pulp mold.

9. The method for producing a pulp product according to any one of claims 1 to 8, wherein the liquid repellent compound has a biobased content of 30% or more.

10. The method for producing a pulp product according to any one of claims 1 to 9, wherein the liquid repellent compound has a hydrocarbon group having 6 or more and 40 or less carbon atoms.

11. The method for producing a pulp product according to any one of claims 1 to 10, wherein the liquid repellent compound is at least one selected from the group consisting of a fatty acid ester, a fatty acid amide, a linear hydrocarbon and a vinyl polymer.

12. The method for producing a pulp product according to any one of claims 1 to 11, wherein

the pulp composition comprises at least one repellent selected from the group consisting of a water-resistant agent, an oil-resistant agent, a water-repellent agent, an oil-repellent agent and an antifouling agent, and the repellent comprises the liquid repellent compound.

13. The method for producing a pulp product according to claim 12, wherein the repellent is at least one selected from the group consisting of a water-resistant agent and an oil-resistant agent.

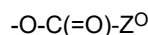
14. The method for producing a pulp product according to claim 12 or 13, wherein the repellent comprises a dispersant and water.

15. The method for producing a pulp product according to any one of claims 1 to 14, wherein the pulp product is prepared by internally adding the liquid repellent compound.

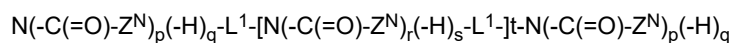
16. The method for producing a pulp product according to any one of claims 1 to 15, wherein the amount of the liquid repellent compound adhering to the pulp product is 3.0% by weight or less.

17. The method for producing a pulp product according to any one of claims 1 to 16, wherein

the liquid repellent compound is a modified body of polyol or a modified body of amine,
the modified body of polyol is a compound formed by replacing a hydroxy group of polyglycerol having a degree of polymerization of 1 or more and 15 or less with a group represented by the following formula:



wherein Z^O is an alkyl group having 14 or more and 24 or less carbon atoms,
the modified body of polyol has a hydroxy group substitution ratio of 50% or more, and
the modified body of amine is a compound represented by the following formula:



wherein Z^N is independently at each occurrence an alkyl group having 14 or more and 24 or less carbon atoms,

L^1 is independently at each occurrence a divalent aliphatic hydrocarbon group having 2 to 20 carbon

atoms or an aromatic hydrocarbon group,
 p is independently at each occurrence an integer of 1 or more and 2 or less,
 q is independently at each occurrence 0 or 1,
 p + q is 2 in each $N(-C(=O)-Z^N)_p(-H)_q$,
 r is independently at each occurrence 0 or 1,
 s is independently at each occurrence 0 or 1,
 r + s is 1 in each $N(-C(=O)-Z^N)_r(-H)_s$, and
 t is an integer of 0 or more and 3 or less.

5

10

15

20

25

30

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/027030

A. CLASSIFICATION OF SUBJECT MATTER

D21J 5/00(2006.01)i; **D21J 7/00**(2006.01)i
FI: D21J5/00; D21J7/00

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)
D21J5/00; D21J7/00

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2024
Registered utility model specifications of Japan 1996-2024
Published registered utility model applications of Japan 1994-2024

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 2002-88677 A (ROU, Kuwoku) 27 March 2002 (2002-03-27) paragraphs [0010]-[0021], fig. 1-2	1-2, 7-9, 12-16
Y		10-16
A		3-6, 17
Y	WO 2021/235452 A1 (AGC INC.) 25 November 2021 (2021-11-25) paragraphs [0013], [0038], [0085]-[0088]	10-16

☐ 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

“D” document cited by the applicant in the international application

“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

04 September 2024

Date of mailing of the international search report

17 September 2024

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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2024/027030

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP	2002-88677	A	27 March 2002	(Family: none)	
WO	2021/235452	A1	25 November 2021	US	2023/0062674 A1
				paragraphs [0042]-[0047], [0093], [0191]-[0197]	
				EP	4155329 A1
				CN	115667454 A

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 2002129499 A [0003]
- FR 627 [0509]
- WO 2012090580 A [0517]

Non-patent literature cited in the description

- JIS K 6953-1 [0097]
- ASTM D6400 [0097]
- The JOCS Standard Methods for the Analysis of Fats, Oils and Related Materials (I). 2003 [0195]
- JIS K 2235-1991 [0486]