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(54) **OIL-RESISTANT AGENT FOR PAPER**
ÖLBESTÄNDIGES MITTEL FÜR PAPIER
AGENT RÉSISTANT À L'HUILE POUR PAPIER

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Description

Technical Field

5 **[0001]** The present disclosure relates to an oil-resistant agent for paper, and paper treated therewith.

Background Art

[0002] Paper may be required to have oil resistance.

10 **[0003]** For example, food packaging and food containers which are made of paper are required to prevent water and oil contained in food from oozing out. Accordingly, an oil-resistant agent is internally or externally applied to the paper.

[0004] Several proposals have been made to impart oil resistance to paper.

[0005] JP-A-2015-129365 discloses a method of forming a cellulose article, comprising: attaching cellulose fibers to a compound comprising an aqueous dispersion comprising at least one polymer selected from the group consisting of an ethylene thermoplastic polymer, a propylene thermoplastic polymer, and a mixture thereof; at least one polymer stabilizer; and water.

[0006] WO 2015/008868 discloses a fine cellulose fiber sheet comprising fine cellulose fibers having an average fiber diameter of 2-1,000 nm, wherein a weight ratio of the fine cellulose fibers is 50-99 wt.%, and the block polyisocyanate aggregate is contained in a weight ratio of 1-100 wt.%, based on the fine cellulose fiber weight.

20 **[0007]** JP-A-2004-148307 discloses a method for producing a coated support comprising: a) forming a composite multilayer free-flowing curtain comprising at least two layers imparting barrier functionalities, and b) bringing the curtain into contact with a continuous web support to give a coated support.

Summary of Invention

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Technical Problem

[0008] An object of the present disclosure is to provide an oil-resistant agent capable of imparting excellent oil resistance to paper.

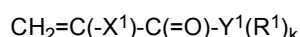
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Solution to Problem

[0009] The present disclosure provides an agent, which is a paper oil-resistant agent which is added to interior of paper, comprising:

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(1) a fluorine-free acrylic polymer having 30-95 wt.%, based on the fluorine-free polymer, of repeating units formed from a monomer (a) which has a long-chain hydrocarbon group and is a monomer of the formula:



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wherein

R¹ each independently is a C₇₋₄₀-hydrocarbon group,

X¹ is H, halogen other than F, or a monovalent organic group, and preferably is H or methyl,

45 Y¹ is a di- to tetravalent group composed of at least one of a hydrocarbon group having one carbon atom, -C₆H₄-, -O-, -C(=O)-, -S(=O)₂-, or -NH-, provided that a hydrocarbon group is excluded, and k is 1-3; and

(2) at least one type of particles selected from inorganic particles or organic particles,

50 wherein the amount of the particles (2) is 1-99.9 wt.%, based on the total weight of the polymer (1) and the particles (2).

[0010] Also, the present invention provides a paper, which is oil-resistant paper comprising the agent of the present invention in the interior of the paper.

[0011] Yet further, the present invention provides a method for producing oil-resistant paper, comprising preparing a formulated pulp slurry by adding the agent of the present invention to a slurry in which pulp is dispersed in an aqueous medium, making an oil-resistant paper intermediate, followed by dehydrating and then drying to obtain the oil-resistant paper.

[0012] Preferred embodiments of the invention are as defined in the appended dependent claims and/or in the following

detailed description.

Advantageous Effects of Invention

5 **[0013]** In the oil-resistant agent, the fluorine-free polymer is favorably dispersed in an aqueous medium, particularly water.

[0014] The oil-resistant agent imparts high oil resistance to paper. The oil-resistant agent can impart high water resistance and high gas barrier properties.

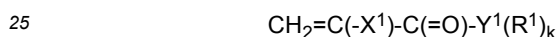
10 Description of Embodiment

[0015] The oil-resistant agent comprises (1) a fluorine-free polymer, and (2) particles. The oil-resistant agent may be a one-, two-, or three-part liquid. The one-part liquid is a liquid comprising the fluorine-free polymer (1) and the particles (2). The two-part liquid (two components) is a combination of a liquid comprising fluorine-free polymer (1) and a liquid comprising the particles (2) (or only particles (2)). In the three-part liquid (three components), a liquid comprising an additive for paper is added for use. The liquid comprising the particles (2) may be a solid (for example, particles only).

(1) Fluorine-free polymer

20 **[0016]** The fluorine-free polymer is an acrylic polymer. The acrylic polymer preferably has an ester bond and/or an amide bond.

[0017] The fluorine-free polymer has 30-95 wt.%, based on the fluorine-free polymer, of repeating units formed from a monomer (a) which has a long-chain hydrocarbon group and is a monomer of the formula:



wherein

R¹ each independently is a C₇₋₄₀-hydrocarbon group,

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X¹ is H, halogen other than F, or a monovalent organic group, and preferably is H or methyl,

Y¹ is a di- to tetravalent group composed of at least one of a hydrocarbon group having one carbon atom, -C₆H₄-, -O-, -C(=O)-, -S(=O)₂-, or

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-NH-, provided that a hydrocarbon group is excluded, and k is 1-3.

[0018] The fluorine-free polymer preferably has:

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(a) a repeating unit formed from the above monomer (a), and

(b) a repeating unit formed from an acrylic monomer having a hydrophilic group.

[0019] Moreover, the fluorine-free polymer preferably has a repeating unit formed of (c) a monomer having an ion donating group in addition to the monomers (a) and (b).

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[0020] The fluorine-free polymer may have a repeating unit formed from (d) another monomer, in addition to the monomers (a), (b), and (c).

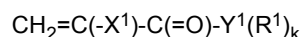
(a) Monomer (a)p

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[0021] The monomer (a) has a long-chain C₇₋₄₀-hydrocarbon group. The long-chain C₇₋₄₀-hydrocarbon group is preferably a linear or branched C₇₋₄₀-hydrocarbon group. The number of carbon atoms of the long-chain hydrocarbon group is preferably 10-40, such as 12-30, particularly 15-30. Alternatively, the number of carbon atoms of the long-chain hydrocarbon group may be 18-40 carbon atoms.

[0022] The acrylic monomer having a long-chain hydrocarbon group (a) is a monomer of the formula:

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wherein

R¹ each independently is a C₇₋₄₀-hydrocarbon group,

X¹ is H, halogen other than F, or a monovalent organic group, and preferably is H or methyl,

Y¹ is a di- to tetravalent group composed of at least one of a hydrocarbon group having one carbon atom, -C₆H₄-, -O-, -C(=O)-, -S(=O)₂-, or -NH-, provided that a hydrocarbon group is excluded, and

k is 1-3.

[0023] X¹ may be H, methyl, halogen other than F, optionally substituted benzyl, or optionally substituted phenyl. Examples of X¹ include H, methyl, Cl, Br, I, and cyano. X¹ is preferably H, methyl, or Cl. X¹ is particularly preferably H.

[0024] Y¹ is a di- to tetravalent group, preferably a divalent group, and is composed of at least one selected from a hydrocarbon group having one carbon atom, -C₆H₄-, -O-, -C(=O)-, -S(=O)₂-, or -NH-, provided that a hydrocarbon group is excluded. Examples of the hydrocarbon group having one carbon atom include -CH₂-, -CH= having a branched structure, and -C≡ having a branched structure.

[0025] Y¹ 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 a direct bond, -O-, -NH-, or -S(=O)₂-, and

R' is -(CH₂)_m- wherein m is an integer of 1-5, or -C₆H₄-(phenylene).

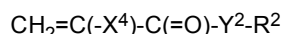
[0026] Specific examples of Y¹ include -O-, -NH-, -O-C(=O)-, -C(=O)-NH-, -NH-C(=O)-, -O-C(=O)-NH-, -NH-C(=O)-O-, -NH-C(=O)-NH-, -O-C₆H₄-, -O-(CH₂)_m-O-, -NH-(CH₂)_m-NH-, -O-(CH₂)_m-NH-, -NH-(CH₂)_m-O-, -O-(CH₂)_m-O-C(=O)-, -O-(CH₂)_m-C(=O)-O-, -NH-(CH₂)_m-O-C(=O)-, -NH-(CH₂)_m-C(=O)-O-, -O-(CH₂)_m-O-C(=O)-NH-, -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 1-5, particularly 2 or 4.

[0027] Y¹ 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 1-5, particularly 2 or 4. Y¹ is more preferably -O- or -O-(CH₂)_m-NH-C(=O)-, particularly -O-(CH₂)_m-NH-C(=O)-.

[0028] R¹ is preferably a linear or branched hydrocarbon group. The hydrocarbon group may be particularly a linear hydrocarbon group. The hydrocarbon group is preferably an aliphatic hydrocarbon group, particularly a saturated aliphatic hydrocarbon group, and especially an alkyl group. The number of carbon atoms of the hydrocarbon group is preferably 12-30, such as 16-26 or 15-26, particularly 18-22 or 17-22.

[0029] Examples of the monomer (a) include:

(a1) a monomer (a1) of the formula:

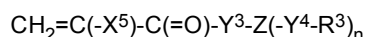


wherein

R² is a C₇₋₄₀-hydrocarbon group,
X⁴ is H, halogen or a monovalent organic group, and
Y² is -O- or -NH-;

and

(a2) a monomer of the formula:



wherein

R³ each independently is a C₇₋₄₀-hydrocarbon group,
X⁵ is H, halogen or a monovalent organic group,

- Y³ is -O- or -NH-,
 Y⁴ each independently is a group composed of at least one of a direct bond, -O-, -C(=O)-, -S(=O)₂-, or -NH-,
 Z is a direct bond or a di- or trivalent C₁₋₅-hydrocarbon group, and
 n is 1 or 2.

Acrylic monomer (a1)

[0030] The acrylic monomer (a1) is of the formula shown above and is a long-chain acrylate ester monomer wherein Y² is -O- or a long-chain acrylamide monomer wherein Y² is -NH-.

[0031] R² is preferably an aliphatic hydrocarbon group, particularly a saturated aliphatic hydrocarbon group, and especially an alkyl group. In R², the number of carbon atoms of the hydrocarbon group is preferably 12-30, such as 16-26, particularly 18-22.

[0032] X⁴ may be H, methyl, halogen other than F, optionally substituted benzyl, or optionally substituted phenyl, and is preferably H, methyl or Cl.

[0033] Preferable specific examples of the long-chain acrylate ester monomer include lauryl (meth)acrylate, stearyl (meth)acrylate, icosyl (meth)acrylate, behenyl (meth)acrylate, stearyl α -chloroacrylate, icosyl α -chloroacrylate, and behenyl α -chloroacrylate.

[0034] Preferable specific examples of the long-chain acrylamide monomer include stearyl (meth)acrylamide, icosyl (meth)acrylamide, and behenyl (meth)acrylamide.

Acrylic monomer(a2)

[0035] The monomer (a2) is of the formula shown above and is a monomer 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-, or -NH-.

[0036] R³ is preferably an aliphatic hydrocarbon group, particularly a saturated aliphatic hydrocarbon group, and especially an alkyl group. In R³, the number of carbon atoms of the hydrocarbon group is preferably 12-30, such as 16-26 or 15-26, particularly 18-22 or 17-22.

[0037] X⁵ may be H, methyl, halogen other than F, optionally substituted benzyl, or optionally substituted phenyl, and is preferably H, methyl, or Cl.

[0038] Y⁴ 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' each is independently a direct bond, -O-, -NH-, or -S(=O)₂-, and

R' is -(CH₂)_m- wherein m is an integer of 1-5, a linear C₁₋₅-hydrocarbon group having an unsaturated bond, a C₁₋₅-hydrocarbon group having a branched structure, or -(CH₂)_l-C₆H₄-(CH₂)_l- wherein l each is independently an integer of 0-5, and -C₆H₄- is phenylene.

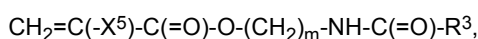
[0039] Specific examples of Y⁴ include a direct bond, -O-, -NH-, -O-C(=O)-, -C(=O)-O-, -C(=O)-NH-, -NH-C(=O)-, -NH-S(=O)₂-, -S(=O)₂-NH-, -O-C(=O)-NH-, -NH-C(=O)-O-, -NH-C(=O)-NH-, -O-C₆H₄-, -NH-C₆H₄-, -O-(CH₂)_m-O-, -NH-(CH₂)_m-NH-, -O-(CH₂)_m-NH-, -NH-(CH₂)_m-O-, -O-(CH₂)_m-O-C(=O)-, -O-(CH₂)_m-C(=O)-O-, -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-(CH₂)_m-NH-C(=O)-, -O-(CH₂)_m-NH-C(=O)-NH-, -O-(CH₂)_m-O-C₆H₄-, -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- wherein m is an integer of 1-5.

[0040] Y⁴ 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-C₆H₄-. Y⁴ is more preferably -NH-C(=O)-, -C(=O)-NH-, -O-C(=O)-NH-, -NH-C(=O)-O-, or -NH-C(=O)-NH-.

[0041] Z is a direct bond or a divalent or trivalent C₁₋₅-hydrocarbon group, and may have a linear structure or a branched structure. The number of carbon atoms of Z is preferably 2-4, particularly 2. Specific examples of Z include a direct bond, -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, -CH₂CH₂CH₂CH₂-, -CH₂CH₂CH₂CH₂CH₂-, -CH₂CH= having a branched structure, -CH₂(CH-)CH₂- having a branched structure, -CH₂CH₂CH= having a branched structure, -CH₂CH₂CH₂CH₂CH= having a branched structure, -CH₂CH₂(CH-)CH₂- having a branched structure, and -CH₂CH₂CH₂CH= having a branched structure.

[0042] Z is preferably not a direct bond, and Y⁴ and Z are simultaneously not direct bonds.

[0043] The monomer (a2) is preferably



$\text{CH}_2=\text{C}(-\text{X}^5)-\text{C}(=\text{O})-\text{O}-(\text{CH}_2)_m-\text{O}-\text{C}(=\text{O})-\text{NH}-\text{R}^3$,
 $\text{CH}_2=\text{C}(-\text{X}^5)-\text{C}(=\text{O})-\text{O}-(\text{CH}_2)_m-\text{NH}-\text{C}(=\text{O})-\text{O}-\text{R}^3$, or
 $\text{CH}_2=\text{C}(-\text{X}^5)-\text{C}(=\text{O})-\text{O}-(\text{CH}_2)_m-\text{NH}-\text{C}(=\text{O})-\text{NH}-\text{R}^3$, wherein R^3 and X^5 are as defined above.

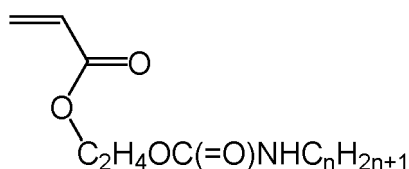
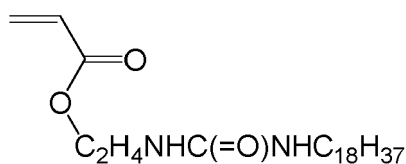
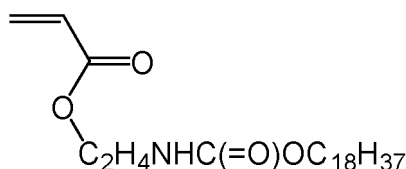
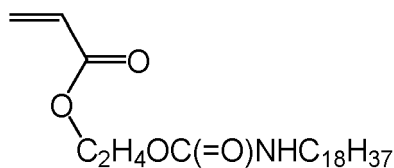
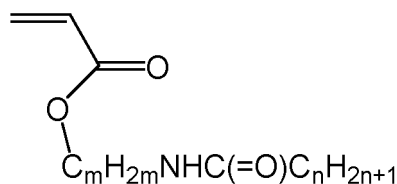
[0044] The monomer (a2) is particularly preferably $\text{CH}_2=\text{C}(-\text{X}^5)-\text{C}(=\text{O})-\text{O}-(\text{CH}_2)_m-\text{NH}-\text{C}(=\text{O})-\text{R}^3$.

[0045] The monomer (a2) can be produced by reacting hydroxyalkyl (meth)acrylate or hydroxyalkyl (meth)acrylamide with long-chain alkyl isocyanate. Examples of the long-chain alkyl isocyanate include lauryl isocyanate, myristyl isocyanate, cetyl isocyanate, stearyl isocyanate, oleyl isocyanate, and behenyl isocyanate.

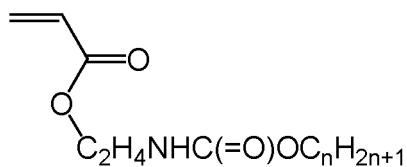
[0046] Alternatively, the monomer (a2) can also be produced by reacting (meth)acrylate having an isocyanate group in a side chain, such as 2-methacryloyloxyethyl methacrylate, with long-chain alkylamine or long-chain alkyl alcohol. Examples of the long-chain alkylamine include laurylamine, myristylamine, cetylamine, stearylamine, oleylamine, and behenylamine. Examples of the long-chain alkyl alcohol include lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, and behenyl alcohol.

[0047] Preferable examples of the long-chain hydrocarbon group-containing acrylic monomer are as follows:

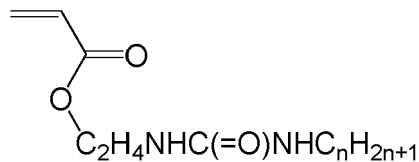
stearyl (meth)acrylate, behenyl (meth)acrylate, stearyl α -chloroacrylate, behenyl α -chloroacrylate;
 stearyl (meth)acrylamide, behenyl (meth)acrylamide;



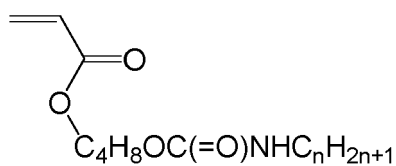
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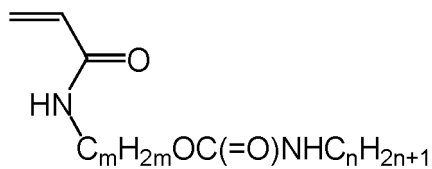
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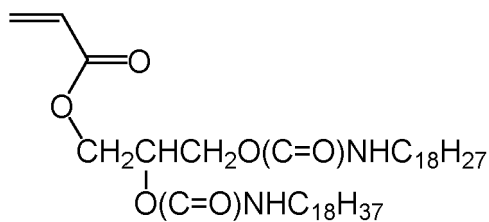
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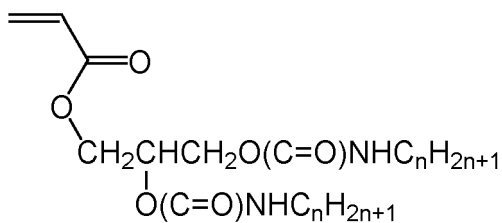


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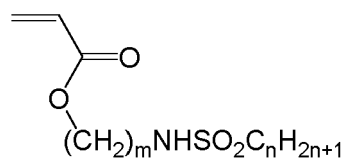
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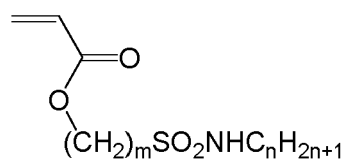


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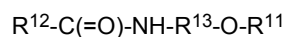
wherein n is a number of 7-40, and m is a number of 1-5.

[0048] The compounds of the above chemical formulae are acrylic compounds in which the α -position is H, and specific examples may be methacrylic compounds in which the α -position is methyl and α -chloroacrylic compounds in which the α -position is Cl.

[0049] The melting point of the acrylic monomer having a long-chain hydrocarbon group (a) is preferably $\geq 10^\circ\text{C}$, and more preferably $\geq 25^\circ\text{C}$.

[0050] The monomer group (a) is preferably an acrylate in which X^1 , X^4 , and X^5 are H.

[0051] The monomer (a2) is preferably an amide group-containing monomer or the formula:



wherein

R^{11} is an organic residue having an ethylenically unsaturated polymerizable group,

R^{12} is a C_{7-40} -hydrocarbon group, and

R^{13} is a C_{1-5} -hydrocarbon group.

[0052] R^{11} is an organic residue having an ethylenically unsaturated polymerizable group, and is not limited as long as there is a carbon-carbon double bond. Specific examples include organic residues having an ethylenically unsaturated polymerizable group such as $-C(=O)CR^{14}=CH_2$, $-CHR^{14}=CH_2$, and $-CH_2CHR^{14}=CH_2$, and R^{14} is H or C_{1-4} -alkyl. R^{11} may have various organic groups other than the ethylenically unsaturated polymerizable group, e.g., organic groups such as chain hydrocarbons, cyclic hydrocarbons, polyoxyalkylene groups, and polysiloxane groups, and these organic groups may be substituted with various substituents. R^{11} is preferably $-C(=O)CR^{14}=CH_2$.

[0053] R^{12} is a C_{7-40} -hydrocarbon group and preferably an alkyl group, such as a chain hydrocarbon group or a cyclic hydrocarbon group. Among them, a chain hydrocarbon group is preferable, and a linear saturated hydrocarbon group is particularly preferable. The number of carbon atoms of R^{12} is 7-40, preferably 11-27, and particularly preferably 15-23.

[0054] R^{13} is a C_{1-5} -hydrocarbon group, and preferably an alkyl group. The C_{1-5} -hydrocarbon group may be either linear or branched, may have an unsaturated bond, and is preferably linear. The number of carbon atoms of R^{13} is preferably 2-4, and particularly preferably 2. R^{13} is preferably an alkylene group.

[0055] The amide group-containing monomer may be a monomer having one type of R^{12} (for example, a compound in which R^{12} has 17 carbon atoms) or a monomer having a combination of multiple types of R^{12} (for example, a mixture of a compound in which R^{12} has 17 carbon atoms and a compound in which R^{12} has 15 carbon atoms).

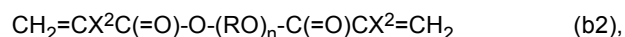
[0056] An example of the amide group-containing monomer is carboxylic acid amide alkyl (meth)acrylate.

[0057] Specific examples of the amide group-containing monomer 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 ethylamide (meth)acrylate, oleic acid ethylamide (meth)acrylate, tert-butylcyclohexylcaproic 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 mixtures thereof.

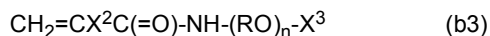
[0058] The amide group-containing monomer is preferably stearic acid amide ethyl (meth)acrylate. The amide group-containing monomer may be a mixture comprising stearic acid amide ethyl (meth)acrylate. In a mixture comprising stearic acid amide ethyl (meth)acrylate, the amount of stearic acid amide ethyl (meth)acrylate is, for example, 55-99 wt.%, preferably 60-85 wt.%, and more preferably 65-80 wt.%, based on the weight of the entirety of the amide group-containing monomer, and the remainder of the monomer may be, for example, palmitic acid amide ethyl (meth)acrylate.

(b) Acrylic monomer having hydrophilic group

[0059] The acrylic monomer having a hydrophilic group (b) is a monomer different from the monomer (a), and is a hydrophilic monomer. The hydrophilic group is preferably an oxyalkylene group (the number of carbon atoms of the alkylene group is 2-6). Particularly, the monomer (b) is preferably polyalkylene glycol mono(meth)acrylate, polyalkylene glycol di(meth)acrylate, and/or polyalkylene glycol mono(meth)acrylamide. Polyalkylene glycol mono(meth)acrylate, polyalkylene glycol di(meth)acrylate, and polyalkylene glycol mono(meth)acrylamide are preferably those of the formulae:



or



wherein,

X^2 each is independently H or methyl,

X^3 each independently is H or an unsaturated or saturated C_{1-22} -hydrocarbon group,

R each is independently C_{2-6} -alkylene, and

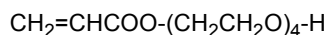
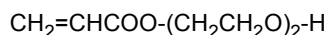
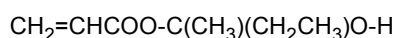
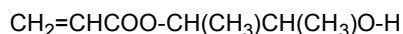
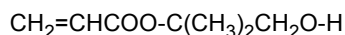
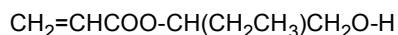
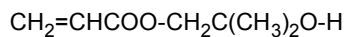
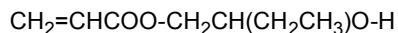
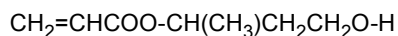
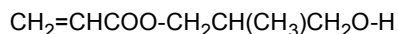
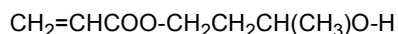
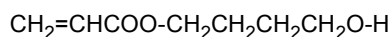
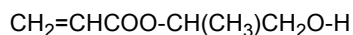
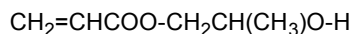
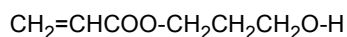
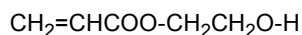
n is an integer of 1-90. n may be, for example, 1-50, particularly 1-30, and especially 1-15 or 2-15. Alternatively, n may be, for example, 1.

[0060] R may be linear or branched alkylene such as a group of the formula $-(\text{CH}_2)_x-$ or $-(\text{CH}_2)_{x1}-(\text{CH}(\text{CH}_3))_{x2}-$ wherein $x1$ and $x2$ are 0-6 such as 2-5, and the sum of $x1$ and $x2$ is 1-6; and the order of $-(\text{CH}_2)_{x1}-$ and $-(\text{CH}(\text{CH}_3))_{x2}-$ is not limited to the formula shown, and may be random.

[0061] In $-(\text{RO})_n-$, there may be two or more types (such as 2-4 types, particularly 2 types) of R, and thus $-(\text{RO})_n-$ may be a combination of, for example, $-(\text{R}^1\text{O})_{n1}-$ and $-(\text{R}^2\text{O})_{n2}-$ wherein R^1 and R^2 are mutually different and a C_{2-6} -alkylene group, $n1$ and $n2$ are a number of ≥ 1 , and the sum of $n1$ and $n2$ is 2-90.

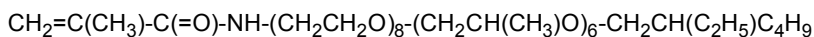
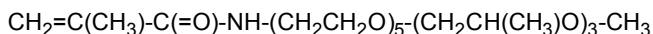
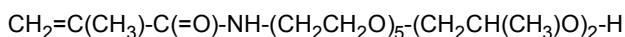
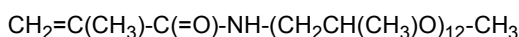
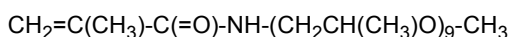
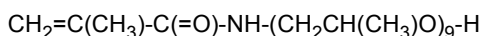
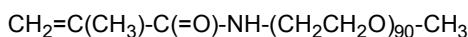
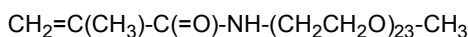
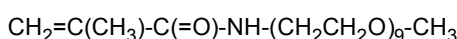
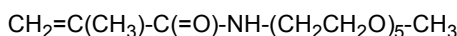
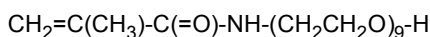
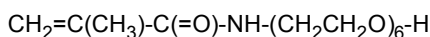
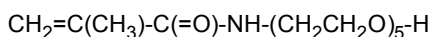
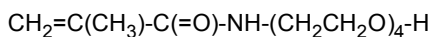
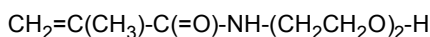
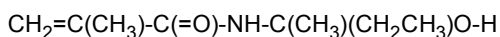
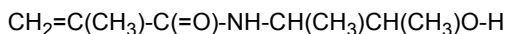
[0062] R in general formulae (b1), (b2), and (b3) is particularly preferably ethylene, propylene, or butylene. R in general formulae (b1), (b2), and (b3) may be a combination of two or more types of alkylene groups. In this case, at least one R is preferably ethylene, propylene, or butylene. Examples of the combination of R include a combination of ethylene / propylene, a combination of ethylene / butylene, and a combination of propylene / butylene. The monomer (b) may be a mixture of two or more types. In this case, in at least one monomer (b), R in general formula (b1), (b2), or (b3) is preferably ethylene, propylene, or butylene. Polyalkylene glycol di(meth)acrylate of formula (b2) is not preferably used solely as the monomer (b), and is preferably used in combination with the monomer (b1). In this case as well, the compound of formula (b2) is preferably < 30 wt.% in the monomer (b) used.

[0063] Specific examples of the acrylic monomer having a hydrophilic group (b) include the following.



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

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



[0064] The monomer (b) is preferably acrylate or acrylamide in which X^2 is H. Particularly, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, or hydroxyethyl acrylamide is preferable.

(c) Monomer having ion donating group

[0065] The monomer having an ion donating group (c) is a monomer different from the monomer (a) and the monomer (b). The monomer (c) is preferably a monomer having an olefinic carbon-carbon double bond and an ion donating group. The ion donating group is an anion donating group and/or a cation donating group.

[0066] Examples of the monomer having an anion donating group include monomers having a carboxyl group, a sulfonic acid group, or a phosphoric acid group. Specific examples of the monomer having an anion donating group include (meth)acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, vinyl sulfonic acid, (meth)allylsulfonic acid, styrenesulfonic acid, phosphoric acid (meth)acrylate, vinylbenzenesulfonic acid, acrylamide tert-butyl sulfonic acid, and salts thereof.

[0067] Examples of salts of the anion donating group include alkali metal salts, alkaline earth metal salts, and ammonium salts, such as a methyl ammonium salt, an ethanol ammonium salt, and a triethanol ammonium salt.

[0068] In the monomer having a cation donating group, examples of the cation donating group include an amino group and preferably a tertiary amino group and a quaternary amino group. In the tertiary amino group, two groups bonded to the nitrogen atom are the same or different and are preferably a C_{1-5} -aliphatic group (particularly alkyl), a C_{6-20} -aromatic group (aryl), or a C_{7-25} -araliphatic group (particularly aralkyl such as benzyl ($\text{C}_6\text{H}_5-\text{CH}_2-$)). In the quaternary amino group, three groups bonded to the nitrogen atom are the same or different and are preferably a C_{1-5} -aliphatic group (particularly alkyl), a C_{6-20} -aromatic group (aryl), or a C_{7-25} -araliphatic group (particularly aralkyl such as benzyl ($\text{C}_6\text{H}_5-\text{CH}_2-$)). In the tertiary and quaternary amino groups, the remaining one group bonded to the nitrogen atom may have a carbon-carbon double bond. The cation donating group may be in the form of a salt.

[0069] A cation donating group which is a salt is a salt formed with an acid (an organic acid or an inorganic acid). Organic acids such as C₁₋₂₀-carboxylic acids (particularly, monocarboxylic acids such as acetic acid, propionic acid, butyric acid, and stearic acid) are preferable. Dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, and salts thereof are preferable.

[0070] Specific examples of the monomer having a cation donating group are as follows.

CH₂=CHCOO-CH₂CH₂-N(CH₃)₂ and salts thereof (such as acetate)
 CH₂=CHCOO-CH₂CH₂-N(CH₂CH₃)₂ and salts thereof (such as acetate)
 CH₂=C(CH₃)COO-CH₂CH₂-N(CH₃)₂ and salts thereof (such as acetate)
 CH₂=C(CH₃)COO-CH₂CH₂-N(CH₂CH₃)₂ and salts thereof (such as acetate)
 CH₂=CHC(O)N(H)-CH₂CH₂CH₂-N(CH₃)₂ and salts thereof (such as acetate)
 CH₂=CHCOO-CH₂CH₂-N(-CH₃)(-CH₂-C₆H₅) and salts thereof (such as acetate)
 CH₂=C(CH₃)COO-CH₂CH₂-N(-CH₂CH₃)(-CH₂-C₆H₅) and salts thereof (such as acetate)
 CH₂=CHCOO-CH₂CH₂-N⁺(CH₃)₃Cl⁻
 CH₂=CHCOO-CH₂CH₂-N⁺(-CH₃)₂(-CH₂-C₆H₅)Cl⁻
 CH₂=C(CH₃)COO-CH₂CH₂-N⁺(CH₃)₃Cl⁻
 CH₂=CHCOO-CH₂CH(OH)CH₂-N⁺(CH₃)₃Cl⁻
 CH₂=C(CH₃)COO-CH₂CH(OH)CH₂-N⁺(CH₃)₃Cl⁻
 CH₂=C(CH₃)COO-CH₂CH(OH)CH₂-N⁺(-CH₂CH₃)₂(-CH₂-C₆H₅)Cl⁻
 CH₂=C(CH₃)COO-CH₂CH₂-N⁺(CH₃)₃Br⁻
 CH₂=C(CH₃)COO-CH₂CH₂-N⁺(CH₃)₃I⁻
 CH₂=C(CH₃)COO-CH₂CH₂-N⁺(CH₃)₃O-SO₃CH₃
 CH₂=C(CH₃)COO-CH₂CH₂-N⁺(CH₃)(-CH₂-C₆H₅)₂Br⁻

[0071] The monomer (c) is preferably methacrylic acid, acrylic acid, and dimethylaminoethyl methacrylate, and more preferably methacrylic acid and dimethylaminoethyl methacrylate.

(d) Another monomer

[0072] Another monomer (d) is a monomer different from the monomers (a), (b), and (c). Examples of the other monomer include ethylene, vinyl acetate, vinyl chloride, vinyl fluoride, halogenated vinyl styrene, α-methylstyrene, p-methylstyrene, polyoxyalkylene mono(meth)acrylate, (meth)acrylamide, diacetone (meth)acrylamide, methylolated (meth)acrylamide, N-methylol (meth)acrylamide, alkyl vinyl ether, halogenated alkyl vinyl ether, alkyl vinyl ketone, butadiene, isoprene, chloroprene, glycidyl (meth)acrylate, aziridinyl (meth)acrylate, benzyl (meth)acrylate, isocyanate ethyl (meth)acrylate, cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, short-chain alkyl (meth)acrylate, maleic anhydride, (meth)acrylate having a polydimethylsiloxane group, and N-vinylcarbazole.

[0073] The amount of the repeating unit formed from the monomer (a) may be 30-95 wt.%, preferably 40-88 wt.%, and more preferably 50-85 wt.%, based on the fluorine-free polymer (particularly, an acrylic polymer).

[0074] The amount of the repeating unit formed from the monomer (b) may be 5-70 wt.%, preferably 8-50 wt.%, and more preferably 10-40 wt.%, based on the fluorine-free polymer.

[0075] The amount of the repeating unit formed from the monomer (c) may be 0.1-30 wt.%, preferably 0.5-20 wt.%, and more preferably 1-15 wt.%, based on the fluorine-free polymer.

[0076] The amount of the repeating unit formed from the monomer (d) may be 0-20 wt.%, such as 1-15 wt.%, particularly 2-10 wt.%, based on the fluorine-free copolymer.

[0077] The weight-average molecular weight of the fluorine-free polymer may be 1,000-10,000,000, preferably 5,000-8,000,000, and more preferably 10,000-4,000,000. The weight-average molecular weight is a value obtained in terms of polystyrene by gel permeation chromatography.

[0078] Herein, "(meth)acryl" means acryl or methacryl. For example, "(meth)acrylate" means acrylate or methacrylate.

[0079] From the viewpoint of oil resistance, the fluorine-free polymer (particularly, an acrylic polymer) is preferably a random copolymer rather than a block copolymer.

[0080] Polymerization for the fluorine-free polymer is not limited, and various polymerization methods can be selected, such as bulk polymerization, solution polymerization, emulsion polymerization, and radiation polymerization. For example, in general, solution polymerization involving an organic solvent, and emulsion polymerization involving water or involving an organic solvent and water in combination, are selected. The fluorine-free copolymer after polymerization is diluted with water to be emulsified in water and thus formed into a treatment liquid.

[0081] Herein, it is preferable that after polymerization (for example, solution polymerization or emulsion polymerization, preferably solution polymerization), water is added, and then the solvent is removed to disperse the polymer in water. An emulsifier does not need to be added, and a self-dispersive product can be produced.

[0082] Examples of organic solvents include ketones such as acetone and methyl ethyl ketone, esters such as ethyl acetate and methyl acetate, glycols such as propylene glycol, dipropylene glycol monomethyl ether, N-methyl-2-pyrrolidone (NMP), dipropylene glycol, tripropylene glycol, and low molecular weight polyethylene glycol, and alcohols such as ethyl alcohol and isopropanol.

[0083] For example, peroxide, an azo compound, or a persulfate compound can be used as a polymerization initiator. The polymerization initiator is, in general, water-soluble and/or oil-soluble.

[0084] Specific examples of the oil-soluble polymerization initiator preferably include 2,2'-azobis(2-methylpropionitrile), 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile), 1,1'-azobis(cyclohexan-1-carbonitrile), dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis(2-isobutyronitrile), benzoyl peroxide, di-tert-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxyphthalate, diisopropyl peroxydicarbonate, and t-butyl perphthalate.

[0085] Specific examples of the water-soluble polymerization initiator preferably include 2,2'-azobisisobutylamidine dihydrochloride, 2,2'-azobis(2-methylpropionamidine) hydrochloride, 2,2'-azobis[2-(2-imidazolin-2-yl)propane] hydrochloride, 2,2'-azobis[2-(2-imidazolin-2-yl)propane] sulfate hydrate, 2,2'-azobis[2-(5-methyl-2-imidazolin-2-yl)propane] hydrochloride, potassium persulfate, barium persulfate, ammonium persulfate, and hydrogen peroxide.

[0086] The polymerization initiator is used in the range of 0.01-5 parts by weight (pbw), based on 100 pbw of the monomers.

[0087] In order to regulate the molecular weight, a chain transfer agent such as a mercapto group-containing compound may be used, and specific examples thereof include 2-mercaptoethanol, thiopropionic acid, and alkyl mercaptan. The mercapto group-containing compound is used in the range of ≤ 10 pbw, or 0.01-5 pbw, based on 100 pbw of the monomers.

[0088] Specifically, the fluorine-free polymer can be produced as follows.

[0089] In solution polymerization, a method is employed that involves dissolving the monomers in an organic solvent, performing nitrogen purge, then adding a polymerization initiator, and heating and stirring the mixture, for example, in the range of 40-120°C for 1-10 hours. The polymerization initiator may be, in general, an oil-soluble polymerization initiator.

[0090] The organic solvent is inert to and dissolves the monomers, and examples include ketones such as acetone and methyl ethyl ketone, esters such as ethyl acetate and methyl acetate, glycols such as propylene glycol, dipropylene glycol monomethyl ether, N-methyl-2-pyrrolidone (NMP), dipropylene glycol, tripropylene glycol, and low molecular weight polyethylene glycol, alcohols such as ethyl alcohol and isopropanol, and hydrocarbon solvents such as n-heptane, n-hexane, n-octane, cyclohexane, methylcyclohexane, cyclopentane, methylcyclopentane, methylpentane, 2-ethylpentane, isoparaffin hydrocarbon, liquid paraffin, decane, undecane, dodecane, mineral spirit, mineral turpen, and naphtha. Preferable examples of the solvent include acetone, chloroform, HCHC 225, isopropyl alcohol, pentane, hexane, heptane, octane, cyclohexane, benzene, toluene, xylene, petroleum ether, tetrahydrofuran, 1,4-dioxane, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, tetrachlorodifluoroethane, trichlorotrifluoroethane, N-methyl-2-pyrrolidone (NMP), and dipropylene glycol monomethyl ether (DPM). The organic solvent is used in the range of 50-2,000 pbw, such as 50-1,000 pbw, based on total 100 pbw of the monomers.

[0091] In emulsion polymerization, a method is employed that involves emulsifying the monomers in water in the presence of an emulsifier, performing nitrogen purge, then adding a polymerization initiator, and stirring the mixture in the range of 40-80°C for 1-10 hours for polymerization. As the polymerization initiator, a water-soluble polymerization initiator such as 2,2'-azobisisobutylamidine dihydrochloride, 2,2'-azobis(2-methylpropionamidine) hydrochloride, 2,2'-azobis[2-(2-imidazolin-2-yl)propane] hydrochloride, 2,2'-azobis[2-(2-imidazolin-2-yl)propane] sulfate hydrate, 2,2'-azobis[2-(5-methyl-2-imidazolin-2-yl)propane] hydrochloride, potassium persulfate, barium persulfate, ammonium persulfate, or hydrogen peroxide; or an oil-soluble polymerization initiator such as 2,2'-azobis(2-methylpropionitrile), 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile), 1,1'-azobis(cyclohexan-1-carbonitrile), dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis(2-isobutyronitrile), benzoyl peroxide, di-tert-butyl peroxide, lauryl peroxide, cumene hydroperoxide, t-butyl peroxyphthalate, diisopropyl peroxydicarbonate, or t-butyl perphthalate is used. The polymerization initiator is used in the range of 0.01-10 pbw, based on 100 pbw of the monomers.

[0092] In order to obtain a water dispersion of the polymer, that has excellent stability when being left to stand, it is desirable that the monomers are formed into particles in water by using an emulsifying apparatus capable of applying strong crushing energy such as a high-pressure homogenizer or an ultrasonic homogenizer, and polymerized by using an oil-soluble polymerization initiator. Various anionic, cationic, or nonionic emulsifiers can be used as emulsifiers, and are used in the range of 0.5-20 pbw, based on 100 pbw of the monomers. An anionic and/or nonionic and/or cationic emulsifier is preferably used. When the monomers are not completely compatible, a compatibilizer such as a water-soluble organic solvent or a low molecular weight monomer that causes the monomers to be sufficiently compatible is preferably added. By adding a compatibilizer, emulsifiability and copolymerizability can be increased.

[0093] Examples of the water-soluble organic solvent include acetone, propylene glycol, dipropylene glycol monomethyl ether (DPM), dipropylene glycol, tripropylene glycol, ethanol, N-methyl-2-pyrrolidone (NMP), 3-methoxy-3-methyl-

1-butanol, or isoprene glycol, and the water-soluble organic solvent may be used in the range of 1-50 pbw, such as 10-40 pbw, based on 100 pbw of water. By adding NMP or DPM or 3-methoxy-3-methyl-1-butanol or isoprene glycol (a preferable amount is, for example, 1-20 wt.%, and particularly 3-10 wt.%, based on the composition), the stability of the composition (particularly, the emulsion) is increased. Examples of the low molecular weight monomer include methyl methacrylate, glycidyl methacrylate, and 2,2,2-trifluoroethyl methacrylate, and the low molecular weight monomer may be used in the range of 1-50 pbw, such as 10-40 pbw, based on total 100 pbw of the monomers.

[0094] The amount of the fluorine-free polymer (1) is 0.1-99 wt.%, based on the total weight of the fluorine-free polymer (1) and the particles (2). The lower limit of the amount of the fluorine-free polymer (1) may be 1 wt.%, such as 5 wt.%, particularly 10 wt.%, and especially 20 wt.% or 30 wt.%. The upper limit of the amount of the fluorine-free polymer (1) may be 90 wt.%, such as 70 wt.%, particularly 60 wt.%, and especially 50 wt.% or 40 wt.%.

(2) Particle

[0095] The particles (2) comprise at least one type of inorganic particles or organic particles. The particles (2) preferably comprise organic particles. The particles (2) more preferably comprise both inorganic particles and organic particles.

[0096] The inorganic particles are particles made of inorganic materials. Examples of the inorganic materials constituting the inorganic particles include calcium carbonate, talc, kaolin (and calcined kaolin), clay (and calcined clay), mica, aluminum hydroxide, barium sulfate, calcium silicate, calcium sulfate, silica, zinc carbonate, zinc oxide, titanium oxide, bentonite, and white carbon. Calcium carbonate, silica, and calcined clay are preferable. Calcium carbonate is particularly preferable.

[0097] The organic particles are particles made of organic materials. Examples of the organic materials constituting the organic particles include polysaccharides and thermoplastic resins (such as polyvinyl alcohol, polyolefin, polystyrene). The organic particles (such as particles of polysaccharides and particles of thermoplastic resins) may be modified (for example, cation-modified or anion-modified). Polysaccharides are preferable.

[0098] The polysaccharides are biopolymers synthesized in biological systems by the condensation and polymerization of various monosaccharides, including those that have been chemically modified (denatured). Examples of polysaccharides include starch, cellulose, modified cellulose, amylose, amylopectin, pullulan, curdlan, xanthan, chitin, and chitosan. Examples of modified cellulose include hydroxymethyl cellulose, hydroxyethyl cellulose, and carboxymethyl cellulose.

[0099] The polysaccharides are preferably starch. Starch particles have excellent dispersibility in the pulp slurry. The starch may be an undenatured starch. Examples of the starches include rice flour starch, wheat starch, corn starch, potato starch, tapioca starch, sweet potato starch, adzuki bean starch, mung bean starch, kudzu starch, and dogtooth violet starch. The starch may be those that have been denatured, such as enzymatic denaturation, thermochemical denaturation, acetate esterification, phosphate esterification, carboxy etherification, hydroxy etherification, and cationic denaturation. Since it gives high air permeability and high oil resistance, the starch is preferably amphoterized starch (starch having a cation group and an anion group) or cationized starch (starch having a cation group). A combination of amphoterized starch and cationized starch (at a preferred weight ratio of (0.1:9.9)-(4:6) or (0.5:9.5)-(2:8)) is preferable since it also increases water resistance.

[0100] In the particles (2), the cation group (particularly, the cation group in the amphoterized starch or the cationized starch) may be a cation group similar to the cation group in the monomer having the ion donating group (c), such as an amino group, and the anion group (particularly, the anion group in the amphoterized starch) may be an anion group similar to the anion group in the monomer having the ion donating group (c), such as a carboxyl group, a sulfonic acid group, and a phosphoric acid group.

[0101] The particles (2) may e.g. have a powdery, granular, fibrous or flaky form.

[0102] The particles (inorganic particles and organic particles) are preferably insoluble in water at 40°C. Insoluble in water means that the solubility in 100 g of water at 40°C is ≤ 1 g, such as ≤ 0.5 g.

[0103] The average particle size of the particles may be 0.01-100 μm , such as 0.1-50 μm , particularly 1.0-20 μm .

[0104] The average particle size can be measured by a laser diffraction particle size distribution measurement apparatus (applying light scattering theory) using a water dispersion of the particles.

[0105] The dissolution temperature of organic particles in water is preferably $\geq 55^\circ\text{C}$ (for example, 60-100°C). The "dissolution temperature" means the highest temperature at which the appearance of the liquid changes from cloudy to transparent after adding 5 pbw of organic particles based on 100 pbw of water maintained at the target temperature with stirring by visual observation under atmospheric pressure (the liquid might be cloudy at the time of addition), and maintaining the liquid at the temperature for 30 minutes with continuous stirring.

[0106] Examples of such organic particles that can be dissolved in water are undenatured starch, denatured starch (such as cationized starch), locust bean gum, carboxymethyl cellulose, and polyvinyl alcohol.

[0107] The organic particles may be ionic or nonionic. If the pulp is ionic, the organic particles are preferably ionic, more specifically anionic, cationic, or amphoteric organic particles, so that they can be easily anchored to the pulp in the pulp slurry and the product. Particularly, if the pulp is ionic, it is preferable to use organic particles having the opposite

ionic part to the pulp, so that the organic particles can be effectively anchored to the pulp (preferably together with an oil-resistant agent) and the gas barrier properties of the finally obtained molded pulp container can be enhanced. Pulp are usually anionic, and for such pulps, it is preferable that the organic particles have a cationic moiety, or more particularly are cationized or amphotericized.

[0108] Organic particles having cation moieties include cationized starch, amphoteric starch, and cation-modified polyvinyl alcohol.

[0109] The amount of the particles (2) is 1-99.9 wt.%, based on the total weight of the fluorine-free polymer (1) and the particles (2). The lower limit of the amount of the particles (2) may be 10 wt.%, such as 30 wt.% or 40 wt.%, particularly 50 wt.% or 60 wt.%, and especially 65 wt.% or 70 wt.%. The upper limit of the amount of the particles (2) may be 99 wt.% or 98 wt.%, such as 97 wt.% or 95 wt.%, particularly 90 wt.%, and especially 80 wt.% or 70 wt.%. Alternatively, the amount of the particles (2) may be 60-99 wt.%, such as 65-98 wt.%, particularly 70-97 wt.%, based on the total weight of the fluorine-free polymer (1) and the particles (2).

(3) Another component

[0110] The oil-resistant agent may comprise another component (3) other than the fluorine-free polymer (1) and the particles (2). Examples of the other component (3) include an aqueous medium and an emulsifier.

[0111] The aqueous medium is water or a mixture of water and an organic solvent (an organic solvent miscible with water). The amount of the aqueous medium may be 50-99.99 wt.%, based on the total amount of the fluorine-free polymer (1) (and the particles (2), if necessary) and the aqueous medium.

[0112] The amount of the emulsifier may be 0-30 pbw, such as 0.1-10 pbw, based on 100 pbw of the fluorine-free polymer (1).

[Oil-resistant agent]

[0113] The oil-resistant agent may be in the form of a solution, an emulsion, or an aerosol. The oil-resistant agent may comprise the fluorine-free polymer (1) and a liquid medium. The liquid medium is, for example, an organic solvent and/or water, and preferably an aqueous medium. The aqueous medium is water or a mixture of water and an organic solvent (such as polypropylene glycol and/or a derivative thereof).

[0114] In the case of a dispersion (emulsion) form, the fluorine-free polymer is a water dispersion type which is dispersed in an aqueous medium, and the fluorine-free polymer(1) may be self-emulsified, dispersed in the aqueous medium in the form of a neutralized salt, or emulsified using an emulsifier.

[0115] The particles (2) may be used in the form of solid or dispersed in a liquid medium. The fluorine-free polymer(1) and the particles (2) may be dispersed in the same liquid medium or may be dispersed in different liquid media. In the oil-resistant agent, the concentration of the fluorine-free polymer may be, for example, 0.01-50 wt.%. The oil-resistant agent may either comprise or not comprise an emulsifier, but it is preferable not to comprise an emulsifier.

[0116] The oil-resistant agent can be used to treat a paper substrate. The "treatment" means that the oil-resistant agent is applied to interior and/or exterior of paper.

[0117] The oil-resistant agent can be applied to the substrate by a conventionally known method. The oil-resistant agent is mainly present inside the paper through internal treatment.

[0118] Examples of the paper substrate to be treated include paper, a container made of paper, and a molded article made of paper (for example, molded pulp).

[0119] The fluorine-free polymer favorably adheres to the paper substrate.

[0120] The oil-resistant agent should be used such that the amount of fluorine-free polymer (1) and the particles (2) is 0.01-75 pbw, such as 0.1-60 pbw, based on 100 pbw of pulp solids.

[Papermaking]

[0121] Paper can be produced by a conventionally known papermaking method. An internal treatment method in which the oil-resistant agent is added to a pulp slurry before papermaking, or an external treatment method in which the oil-resistant agent is applied to paper after papermaking, can be used. The method of treatment with the oil-resistant agent in the present disclosure is preferably an internal treatment method. Even if the oil-resistant agent of the present disclosure is used in the internal treatment, no new equipment is required.

[0122] In the internal treatment method, paper treated by the oil-resistant agent may be produced by mixing the oil-resistant agent with pulp slurry and paper making. The paper treated by the oil-resistant agent is oil-resistant paper having oil resistance. The oil-resistant paper can be thin or thick, or molded pulp.

[0123] Paper thus treated, after rough drying at room temperature or high temperature, is optionally subjected to a heat treatment that can have a temperature range of up to 300°C, such as up to 200°C, particularly 80-180°C, depending

on the properties of the paper, and thus shows excellent oil resistance and water resistance.

[0124] The present disclosure can be used in, for example, gypsum board base paper, coated base paper, wood containing paper, commonly used liner and corrugating medium, neutral machine glazed paper, neutral liner, rustproof liner and metal laminated paper, and kraft paper. The present disclosure can also be used in neutral printing writing paper, neutral coated base paper, neutral PPC paper, neutral heat sensitive paper, neutral pressure sensitive base paper, neutral inkjet paper, and neutral communication paper.

[0125] A pulp (pulp raw material) may be any of bleached or unbleached chemical pulp such as kraft pulp or sulfite pulp, bleached or unbleached high yield pulp such as ground pulp, mechanical pulp, or thermomechanical pulp, waste paper pulp such as waste newspaper, waste magazine, waste corrugated cardboard, or waste deinked paper, and non-wood pulp such as bagasse pulp, kenaf pulp, or bamboo pulp. The pulp raw material may be a combination of one or more of these. A mixture of the above pulp raw material and one or more of e.g. synthetic fiber of asbestos, polyamide, polyimide, polyester, or polyolefin can be used as well.

[0126] In the internal treatment, a pulp slurry having a pulp concentration of 0.5-5.0 wt.% (such as 2.5-4.0 wt.%) is preferably formed into paper. An additive (such as a sizing agent, a paper strengthening agent, a flocculant, a retention aid, or a coagulant) and the fluorine-free polymer can be added to the pulp slurry. Since the pulp is generally anionic, at least one of the additive and the fluorine-free polymer is preferably cationic or amphoteric such that the additive and the fluorine-free polymer are favorably anchored to paper. A combination of a cationic or amphoteric additive and an anionic fluorine-free polymer, a combination of an anionic additive and a cationic or amphoteric fluorine-free polymer, and a combination of a cationic or amphoteric additive and fluorine-free polymer are preferably used.

[0127] Other components (additives) may be used in addition to the oil-resistant agent. Examples of the other components are cationic coagulants, water-resistant agents, paper strength additives, flocculants, fixing agents, and yield improvers.

[0128] Cationic coagulants, paper strength additives, flocculants, fixing agents, and yield improvers can be polymers or inorganic materials which are cationic or amphoteric. The cationic coagulants, paper strength additives, flocculants, fixing agents, and yield improvers can effectively anchor the oil-resistant agent consisting of the fluorine-free polymer (1) and the particles (2) to the pulp, which is generally anionic, and the gas barrier properties and/or water resistance and oil resistance of the finally obtained molded pulp container can be enhanced.

[0129] Examples of cationic coagulants, paper strength additives, flocculants, fixing agents, and yield improvers include a polyamine epichlorohydrin resin, a polyamide epichlorohydrin resin, cationic polyacrylamide (e.g. an acrylamide-allylamine copolymer, an acrylamide-dimethylaminoethyl (meth)acrylate copolymer, an acrylamide-diethylaminoethyl (meth)acrylate copolymer, an acrylamide-quaternized dimethylaminoethyl (meth)acrylate copolymer, or an acrylamide-quaternized diethylaminoethyl (meth)acrylate copolymer., polydiallyldimethylammonium chloride, polyallylamine, polyvinylamine, polyethyleneimine, an N-vinylformamide-vinylamine copolymer, a melamine resin, a polyamide epoxy resin, sulfate band, PAC (polyaluminum chloride), aluminum chloride, and ferric chloride. Particularly, polyamidopolyamine-epichlorohydrin (PAE), polydiallyldimethylammonium chloride (poly-DADMAC), and polyacrylamide (PAM) can be used.

[0130] A water-resistant agent may be used in addition to the oil-resistant agent. In the present disclosure, the "water-resistant agent" refers to a component that, when added to the pulp slurry, is capable of increasing the water resistance of a molded pulp product as compared to the case where it is not added (provided that the above-described oil-resistant agent is excluded). Due to the water-resistant agent, the water resistance of the finally obtained molded pulp container can be increased. The above-described cationic coagulant is generally incapable of increasing water resistance by itself and can be understood as being different from the water-resistant agent.

[0131] A sizing agent used in ordinary papermaking is usable as a water-resistant agent. Examples of the water-resistant agent include cationic sizing agents, anionic sizing agents, and rosin-based sizing agents (such as acidic rosin-based sizing agents or neutral rosin-based sizing agents), and cationic sizing agents are preferable. Particularly, a styrene-containing polymer such as a styrene-(meth)acrylate copolymer, an alkenyl succinic anhydride, and an alkyl ketene dimer are preferable.

[0132] If necessary, a dye, a fluorescent dye, a slime control agent, an antislip agent, an antifoaming agent, and a pitch control agent which are usually used as paper making chemicals in paper treatment agents may also be used.

[0133] Paper is preferably a molded pulp product. The molded pulp product can be produced by a producing method comprising: preparing a formulated pulp slurry by adding an oil-resistant agent to a slurry in which pulp is dispersed in an aqueous medium, making a molded pulp intermediate, followed by dehydrating and then at least drying to obtain a molded pulp product.

[0134] The preparation of the formulated pulp slurry is preferably performed such that the organic particles remain in a solid state. For example, the formulated pulp slurry is prepared at a temperature lower than, for example, a temperature at least 5°C lower than the dissolution temperature of the organic particles. In the formulated pulp slurry prepared, the organic particles remain in a solid state (e.g. powdery, granular, fibrous, or flaky, depending on the organic particles used as a raw material), and for example, when starch powder is used as a raw material, the starch powder may remain dispersed in an aqueous medium.

[0135] The oil-resistant agent and the organic particles, and optionally the cationic coagulant and/or the water-resistant agent may be added to the pulp slurry in any order as long as the organic particles remain in a solid state.

[0136] The content of each component in the formulated pulp slurry (based on all components) can be suitably selected so as to attain a high freeness suitable for papermaking and dehydrating and the physical properties desired of a molded pulp product, and, for example, can be as follows.

Aqueous medium: 89.5-99.89 wt.%, particularly 94.5-99.69 wt.%

Pulp: 0.1-5 wt.%, particularly 0.3-2.5 wt.%

Oil-resistant agent (solids): 0.00001-1 wt.%, particularly 0.0001-0.5 wt.%

Cationic coagulant (solids): 0-1 wt.%, particularly 0-0.5 wt.% (when added, for example, ≥ 0.00005 wt.%)

Water-resistant agent (solids): 0-1 wt.%, particularly 0-0.5 wt.% (when added, for example, ≥ 0.00005 wt.%)

[0137] When each component is in the form of, for example, a dispersion, the above content indicates the solid content (based on all components) of each component in the formulated pulp slurry.

[0138] From another viewpoint, the content of each of the pulp and the oil-resistant agent based on the aqueous medium in the formulated pulp slurry can be suitably selected so as to attain a high freeness suitable for papermaking and dehydrating, and for example, can be as follows.

Pulp: 0.1-5.58 wt.%, particularly 0.3-2.64 wt.%

Oil-resistant agent (solids): 0.001-2.79 wt.%, particularly 0.005-1.05 wt.%

[0139] When the organic particles are dissolved in the aqueous medium (or when an aqueous solution in which the organic particles such as starch are dissolved in advance in the aqueous medium is added to a pulp slurry), the resulting aqueous composition has a reduced freeness. On the other hand, in the formulated pulp slurry, the organic particles remain in a solid state without being dissolved in the aqueous medium, and therefore, as compared to the case where the organic particles are dissolved in the aqueous medium, a larger amount of the organic particles can be added while maintaining the high freeness of the formulated pulp slurry.

[0140] Next, the formulated pulp slurry prepared above is made to form a molded pulp intermediate, the molded pulp intermediate is dehydrated and then at least dried to obtain a molded pulp product.

[0141] Papermaking, dehydrating, and drying can be performed according to conventionally known methods concerning molded pulp.

[0142] For example, by straining the formulated pulp slurry to dehydrate it (for example, by suction and/or pressure reduction) using a mold which has a desired shape and which is provided with numerous holes (and that may be equipped with a filter as necessary), the aqueous medium can be at least partially removed from the formulated pulp slurry, and a molded pulp intermediate having a shape that corresponds to the mold can be obtained.

[0143] The process from the preparation to the dehydration of the formulated pulp slurry is performed, with the organic particles remaining in a solid state. For example, after preparation, dehydrating is performed at a temperature lower than, such as a temperature at least 5°C lower than the dissolution temperature of the organic particles. As for papermaking and dehydrating, the aqueous medium is removed from the formulated pulp slurry through a mold (and optionally a filter), and therefore, an excessively lowered freeness of the formulated pulp slurry due to dissolution of the organic particles makes it substantially impossible to perform papermaking and dehydrating and is thus not preferable. On the other hand, with the organic particles remaining in a solid state, the freeness of the formulated pulp slurry is not lowered, and papermaking and dehydrating can be appropriately performed.

[0144] After dehydrating, in the resulting molded pulp intermediate, the organic particles remain in a solid state (e.g. powdery, granular, fibrous or flaky, depending on the organic particles used as raw materials) and, for example, when starch powder is used as a raw material, the starch powder may be dispersed in the pulp.

[0145] Drying does not need to be performed such that the organic particles remain in a solid state, and can be performed at a temperature at which the remaining aqueous medium can be effectively removed (if applicable, it can be a temperature equal to or higher than the dissolution temperature of the organic particles), for example, 90-250°C, particularly 100-200°C. The drying time is not limited, and can be selected such that the aqueous medium remaining in the molded pulp intermediate is substantially removed. The drying atmosphere is not limited, and may be conveniently an ambient atmosphere (air under normal pressure).

[0146] During and/or after drying, other steps which are conventionally known concerning molded pulp, for example, press molding (including heat pressing), may be performed if necessary.

[0147] During drying and/or press molding, causing the organic particles to at least partially dissolve makes it possible to obtain even higher gas barrier properties. The organic particles do not need to dissolve entirely, and the organic particles may partially remain in a solid state.

[0148] Thus, a molded pulp product can be produced. This molded pulp product comprises a pulp, an oil-resistant

agent, and can achieve high gas barrier properties and excellent water resistance and oil resistance.

[0149] In the molded pulp product of the present disclosure, the content of the organic particles based on the pulp is 0.0001-75 wt.%, such as 0.1-60 wt.%, particularly 2-50 wt.%.

[0150] When a molded pulp product is obtained by adding an aqueous solution in which organic particles such as starch are dissolved in advance in an aqueous medium to a pulp slurry to increase strength, a sufficient strength improving effect can be obtained even when the content of organic particles based on the pulp is low, and it was thus not required to increase the content of the organic particles based on the pulp.

[0151] In the present disclosure, the content of the organic particles based on the pulp is preferably high, and the lower limit of the content of the organic particles based on the pulp may be 3 wt.% or 5 wt.%, such as 8 wt.% or 10 wt.%, particularly 15 wt.%. The upper limit of the content of the organic particles based on the pulp may be 60 wt.%, such as 50 wt.% or 40 wt.%, particularly 30 wt.% or 20 wt.%. The content of the organic particles based on the pulp may be 3-70 wt.% or 5-60 wt.%, such as 8-50 wt.% or 8-40 wt.%. In other words, the content of the organic particles may be 3-70 pbw or 5-60 pbw, such as 8-50 pbw or 8-40 pbw, based on the 100 pbw of the pulp. With such a high content of the organic particles, it is possible to not only obtain high gas barrier properties but also further increase water resistance and oil resistance.

[0152] In the molded pulp product, the organic particles may be derived from starch powder dispersed in the aqueous medium (in the formulated pulp slurry).

[0153] The proportions of the pulp, the organic particles, the oil-resistant agent, and optionally the cationic coagulant and/or the water-resistant agent contained in the molded pulp product can be considered substantially the same as the solid contents of these components used as raw materials (usually, the aqueous medium and, if present, other liquid media can be removed by drying and press molding, but the solids can remain without being removed or decomposed).

[0154] In the molded pulp product, the content of each component (a component that can remain in the molded pulp product) based on the pulp (solids) can be suitably selected according to the physical properties desired of the molded pulp product, and, for example, can be as follows.

Oil-resistant agent (solids): 0.01-50 wt.% or 0.01-20 wt.%, particularly 0.05-10 wt.%

Cationic coagulant (solids): 0-20 wt.%, particularly 0-10 wt.% (if present, such as ≥ 0.001 wt.%)

water-resistant agent (solids): 0-20 wt.%, particularly 0-10 wt.% (if present, such as ≥ 0.001 wt.%)

[0155] The oil-resistant agent are internally added to the molded pulp product (they are added to a pulp slurry, and the molded pulp product is produced by a pulp molding method). Accordingly, after the molded pulp product is used, the entirety of the product can be crushed to bring it back to the original raw materials, and is thus suitable for recycle use. Furthermore, it is possible to utilize the intrinsic biodegradability of the pulp, the molded pulp product can extremely reduce and preferably can substantially eliminate the environmental burden. Also, with the molded pulp product, the texture of the pulp can be maintained on the front side of the product, and the appearance is not impaired unlike when the front side is laminated with a plastic film and becomes glossy.

[0156] The molded pulp product can be suitably used as food containers (including e.g. trays), for example, storage containers for frozen food and chilled food.

[0157] Since the present molded pulp product has excellent water resistance and oil resistance, moisture and oil derived from food do not impregnate the molded pulp product (a container), and it is thus possible to prevent deterioration of container strength resulting from impregnation with water and oil and prevent staining of e.g. the table surface facing the bottom surface of the container with moisture and oil permeated through the container. Also, the present molded pulp product has high gas barrier properties and unlikely allows gas and water vapor to permeate, and thus, when accommodating hot and wet food or when heated in a microwave with food being accommodated therein, it is possible to prevent the problem that gas and water vapor derived from food permeate through the container and leak to the outside and, particularly, condense on e.g. the table surface facing the bottom surface of the container. Further, the present molded pulp product has high gas barrier properties and unlikely allow gas and water vapor (or moisture) to permeate, and thus, when refrigerating accommodated food, evaporation of water from food and exposure of food to oxygen can be effectively reduced, freezer burn resulting therefrom can be effectively prevented, and the flavor of food can be maintained for a long period of time.

Examples

[0158] Next, the present disclosure will now be described in detail by way of Examples, Comparative Examples, and Test Examples.

[0159] Below, a part, %, and a ratio indicate a part by weight, wt.%, and a weight ratio, respectively, unless otherwise specified.

[0160] The test methods used below are as follows.

[High-temperature oil resistance]

[0161] First, 100 ml of an evaluation liquid (corn oil) at 90°C was poured into a molded pulp product molded into a container shape, the molded pulp product was left to stand still for 30 minutes, then the evaluation liquid was discarded, and the extent of impregnation of the molded pulp product (the container) with the evaluation liquid was visually evaluated according to the following criteria.

- 4: Almost no oil stains observed in the interior of the bottom of the molded pulp container
- 3: No oil stains observed on the exterior of the bottom of the molded pulp container
- 2: Oil stains observed on < 5% of the exterior area of the bottom of the molded pulp container
- 1: Oil stains observed on 5 to < 50% of the exterior area of the bottom of the molded pulp container
- 0: Oil stains observed on ≥ 50% of the exterior area of the bottom of the molded pulp container

[High-temperature water resistance]

[0162] First, 100 ml of an evaluation liquid (tap water) at 90°C was poured into a molded pulp product molded into a container shape, the molded pulp product was left to stand still for 30 minutes, then the evaluation liquid was discarded, and the extent of impregnation of the molded pulp product (the container) with the evaluation liquid was visually evaluated according to the following criteria.

- 4: Almost no water stains observed in the interior of the bottom of the molded pulp container
- 3: No water stains observed on the exterior of the bottom of the molded pulp container
- 2: Water stains observed on < 5% of the exterior area of the bottom of the molded pulp container
- 1: Water stains observed on 5% to < 50 % of the exterior area of the bottom of the molded pulp container
- 0: Water stains observed on ≥ 50% of the exterior area of the bottom of the molded pulp container

[Air permeance]

[0163] The air permeance (air resistance) at the bottom part of a molded pulp product molded into a container shape was measured in accordance with JIS P 8117 (2009) using an automatic Gurley densometer manufactured by YASUDA SEIKI SEISAKUSHO, LTD. (Product No. 323-AUTO, vent hole diameter 28.6 ± 0.1 mm). The measured value of air permeance was evaluated according to the following criteria.

Evaluation Criteria

[0164]

- Excellent: ≥ 500 seconds
- Good: ≥ 300 seconds
- Fair: ≥ 100 seconds
- Poor: < 100 seconds

Synthesis Example 1

[0165] A reactor having a volume of 500 ml and equipped with a stirrer, a thermometer, a reflux condenser, a dropping funnel, a nitrogen inlet, and a heater was provided, and 100 parts of a methyl ethyl ketone (MEK) solvent was added. Subsequently, while the solvent is stirred, a monomer composed of 78 parts of stearyl acrylate (StA, melting point: 30°C), 16 parts of hydroxyethyl acrylate (HEA), and 6 parts of methacrylic acid (MAA) (the monomer being 100 parts in total) as well as 1.2 parts of a perbutyl PV (PV) initiator were added in this order, and the mixture was mixed by being stirred for 12 hours in a nitrogen atmosphere at 65-75°C to carry out copolymerization. The solid content concentration of the resulting copolymer-containing solution was 50 wt.%. When the molecular weight of the resulting copolymer was analyzed by gel permeation chromatography, the weight-average molecular weight in terms of polystyrene was 230,000.

[0166] As a post-treatment, 142 g of a 0.3% aqueous NaOH solution was added to 50 g of the resulting copolymer solution and dispersed, then MEK was distilled off under reduced pressure while heating the mixture by using an evaporator, and thus a milky white water dispersion of a copolymer was obtained (the content of the volatile organic solvent was ≤ 1 wt.%). Moreover, ion-exchanged water was added to the water dispersion, and thus a water dispersion having a solid content concentration of 15 wt.% was obtained.

[0167] The melting point of the copolymer was 48°C.

Synthesis Example 2

[0168] A reactor having a volume of 500 ml and equipped with a stirrer, a thermometer, a reflux condenser, a dropping funnel, a nitrogen inlet, and a heater was provided, and 100 parts of a methyl ethyl ketone (MEK) solvent was added. Subsequently, while the solvent is stirred, a monomer composed of 78 parts of stearic acid amide ethyl acrylate (C18AmEA, melting point: 70°C), 16 parts of hydroxybutyl acrylate (HBA, Tg: -40°C), and 6 parts of dimethylaminoethyl methacrylate (DM) (the monomer being 100 parts in total) as well as 1.2 parts of a perbutyl PV (PV) initiator were added in this order, and mixed by being stirred for 12 hours in a nitrogen atmosphere at 65-75°C to carry out copolymerization. The solid content concentration of the resulting copolymer-containing solution was 50 wt. %.

[0169] As a post-treatment, 142 g of a 0.4% aqueous acetic acid solution was added to 50 g of the resulting copolymer solution and dispersed, then the mixture was heated by using an evaporator to distill off MEK under reduced pressure, and thus a light brown copolymer-water dispersion liquid (the content of the volatile organic solvent was ≤ 1 wt. %) was obtained. Moreover, ion-exchanged water was added to the water dispersion, and thus a water dispersion having a solid content concentration of 15 wt. % was obtained.

Example 1

[0170] 2,400 g of a 0.5 wt. % of the water dispersion of a mixture of 70 parts of leaf bleached kraft pulp and 30 parts of needle bleached kraft pulp beaten to a freeness (Canadian Freeness) of 550 cc, was added with contiguous stirring. Next, 1.2 g of calcium carbonate was added and kept stirring for 1 minute, and 2.4 g of a 5% solid aqueous solution of amphoterized starch was added and kept stirring for 1 minute. Then, 0.72 g of a 5% solid aqueous solution of alkyl ketene dimer (AKD) was added and kept stirring for 1 minute, and subsequently 3.6 g of the water dispersion of the fluorine-free copolymer of Synthesis Example 2 diluted with water to a solid content of 10% was added and kept stirring for 1 minute.

[0171] The above pulp slurry was placed in a metal tank. In the lower part of the tank, a metal pulp mold with many suction holes was present with a reticular body placed on top of the mold. From the side opposite to the side where the reticular body of the pulp mold was placed, the pulp-containing aqueous composition was suctioned and dehydrated through the pulp mold and the reticular body using a vacuum pump, and the solids (such as a pulp) contained in the pulp-containing aqueous composition were deposited on the reticular body to obtain a molded pulp intermediate. Next, the resulting molded pulp intermediate was dried by applying pressure from top and bottom with metal male and female molds heated to 60-200°C. As a result, a molded pulp product molded into a container shape was produced. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Example 2

[0172] 2,400 g of a 0.5 wt. % of the water dispersion of a mixture of 70 parts of leaf bleached kraft pulp and 30 parts of needle bleached kraft pulp beaten to a freeness (Canadian Freeness) of 550 cc, was added with contiguous stirring. Next, 0.6 g of calcium carbonate was added and kept stirring for 1 minute, and 1.2 g of cationized starch powder was added and kept stirring for 1 minute. Then, 2.4 g of a 5% solid aqueous solution of amphoterized starch was added and kept stirring for 1 minute, and 0.72 g of a 5% solid aqueous solution of alkyl ketene dimer (AKD) was added and kept stirring for 1 minute. Subsequently, 3.6 g of the water dispersion of the fluorine-free copolymer of Synthesis Example 2 diluted with water to a solid content of 10% was added and kept stirring for 1 minute.

[0173] Thereafter, molded pulp products were produced in the same manner as in Example 1, except that the above pulp slurry was used. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Example 3

[0174] The experiment was performed in the same manner as in Example 1, except that 1.2 g of calcium carbonate in Example 2 was added, and 2.4 g of cationized starch powder was added. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Example 4

[0175] The experiment was performed in the same manner as in Example 1, except that 2.4 g of the water dispersion of the fluorine-free copolymer of Synthesis Example 2 in Example 3 diluted with water to a solid content of 10% was added. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Example 5

[0176] The experiment was performed in the same manner as in Example 1, except that 4.8 g of cationized starch powder in Example 4 was added. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Example 6

[0177] The experiment was performed in the same manner as in Example 1, except that calcium carbonate in Example 5 was not added, and 3.6 g of the water dispersion of the fluorine-free copolymer of Synthesis Example 2 diluted with water to a solid content of 10% was added. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Example 7

[0178] The experiment was performed in the same manner as in Example 1, except that a 5% solid aqueous solution of amphoterized starch in Example 5 was not added, and a 5% solid aqueous solution of alkyl ketene dimer (AKD) was not added. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Example 8

[0179] The experiment was performed in the same manner as in Example 1, except that 0.6 g of calcium carbonate in Example 1 was added. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Example 9

[0180] The experiment was performed in the same manner as in Example 1, except that 3.6 g of the water dispersion of the fluorine-free copolymer of Synthesis Example 2 in Example 8 diluted with water to a solid content of 10% was added and kept stirring for 1 minute, and then 6.0 g of the water dispersion of the fluorine-free copolymer of Synthesis Example 1 diluted with water to a solid content of 10% was added and kept stirring for 1 minute. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Example 10

[0181] The experiment was performed in the same manner as in Example 1, except that a 5% solid aqueous solution of the alkyl ketene dimer (AKD) in Example 3 was not added. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Comparative Example 1

[0182] The experiment was performed in the same manner as in Example 1, except that calcium carbonate in Example 1 was not added, and 3.6 g of styrene-butadiene latex diluted with water to a solid content of 10% was added in place

of the water dispersion of the fluorine-free copolymer of Synthesis Example 2 diluted with water to a solid content of 10%. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

Comparative Example 2

[0183] The experiment was performed in the same manner as in Example 1 except that 3.6 g of styrene-butadiene latex diluted with water to a solid content of 10% was added in place of the water dispersion of the fluorine-free copolymer of Synthesis Example 2 in Example 2 diluted with water to a solid content of 10%. Table 1 shows the results of evaluating the content of each component based on the pulp in the resulting molded pulp product, as well as high-temperature oil-resistant characteristics, high-temperature water-resistant characteristics, and air permeance.

[Table 1]

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Com. Ex. 1	Com. Ex. 2
Particles	Inorganic Particles	Calcium carbonate	solid%/ pulp	10%	10%	10%	10%	5%	5%	10%		5%
	Organic Particles	Cationized starch	solid%/ pulp	20%	40%	40%	40%			20%		10%
Aqueous starch solution		Amphoterized starch	solid%/ pulp	1%	1%	1%		1%	1%	1%	1%	1%
Water- resistant agent		Alkyl ketene dimer (AKD)	solid%/ pulp	0.3%	0.3%	0.3%		0.3%	0.3%		0.3%	0.3%
Treatment agent	Acrylic polymer	Syn. Ex. 1	solid%/ pulp						5%			
		Syn. Ex. 2	solid%/ pulp	3%	3%	2%	2%	3%	3%	3%		
	Styrene-butadiene latex		solid%/ pulp								3%	3%
High-temp. oil- resistance		Corn oil 90°C × 30 min.	3	3	4	3	4	2	3	4	0	0
High-temp. water- resistance		Tap water 90°C × 30 min.	3	3	3	3	1	3	3	1	4	4
Air permeance	Evaluation	Evaluation	Poor	Fair	Excell ent	Excell ent	Excell ent	Poor	Poor	Excell ent	Poor	Fair
		Measured value (sec.)	37	161	701	718	783	30	33	687	42	177

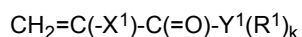
Industrial Applicability

[0184] The oil-resistant agent of the present disclosure is applicable to a variety of paper, particularly paper for use in a food container and a food packaging material. The oil-resistant agent is externally or internally, particularly internally incorporated into the paper.

Claims

1. An agent, which is a paper oil-resistant agent which is added to interior of paper, comprising:

(1) a fluorine-free acrylic polymer having 30-95 wt.%, based on the fluorine-free polymer, of repeating units formed from a monomer (a) which has a long-chain hydrocarbon group and is a monomer of the formula:



wherein

R¹ each independently is a C₇₋₄₀-hydrocarbon group,

X¹ is H, halogen other than F, or a monovalent organic group, and preferably is H or methyl,

Y¹ is a di- to tetravalent group composed of at least one of a hydrocarbon group having one carbon atom, -C₆H₄-, -O-, -C(=O)-, -S(=O)₂-, or -NH-, provided that a hydrocarbon group is excluded, and k is 1-3; and

(2) at least one type of particles selected from inorganic particles or organic particles,

wherein the amount of the particles (2) is 1-99.9 wt.%, based on the total weight of the polymer (1) and the particles (2).

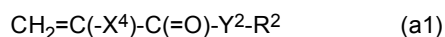
2. The agent of claim 1, wherein X¹ is H or methyl.

3. The agent of claim 1 or 2, wherein the at least one type of particles is selected from organic particles.

4. The agent of any of claims 1-3, wherein the amount of the particles (2) is 50-99.9 wt.%, based on the total weight of the polymer (1) and the particles (2).

5. The agent of any of claims 1-4, wherein the long-chain hydrocarbon group in the monomer (a) has ≥ 18 carbon atoms.

6. The agent of any of claims 1-5, wherein the monomer (a) is a monomer of the formula (a1) and/or (a2):

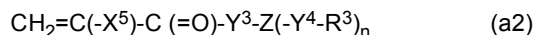


wherein

R² is a C₇₋₄₀-hydrocarbon group,

X⁴ is H, halogen or a monovalent organic group, and

Y² is -O- or -NH-;



wherein

R³ each independently is a C₇₋₄₀-hydrocarbon group,

X⁵ is H, halogen or a monovalent organic group,

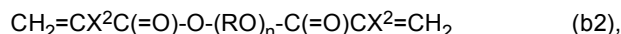
Y³ is -O- or -NH-,

Y⁴ each independently is a group composed of at least one of a direct bond, -O-, -C(=O)-, -S(=O)₂-, or -NH-,

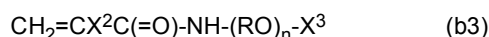
Z is a direct bond or a di- or trivalent C₁₋₅-hydrocarbon group, and

n is 1 or 2.

7. The agent of any of claims 1-6, wherein the fluorine-free polymer further has a repeating unit formed from a monomer (b) which is at least one oxyalkylene (meth)acrylate of the formula:



or



wherein

X² is H or methyl,

X³ is H or an unsaturated or saturated C₁₋₂₂-hydrocarbon group,

R each independently is C₂₋₆-alkylene, and

n is an integer of 1-90.

8. The agent of any of claims 1-7, wherein the fluorine-free polymer further comprises a repeating unit formed from a monomer (c) which is other than the monomers (a) and (b) and has an olefinic carbon-carbon double bond and has an anion donating group, preferably a carboxyl group, or a cation donating group, preferably an amino group.

9. The agent of any of claims 1-8, wherein, based on the copolymer, the amount of repeating units formed from monomer (a) is 30-90 wt.%, and the amount of repeating units formed from monomer (b) is 5-70 wt.%.

10. The agent of any of claims 1-9, wherein

the inorganic particles are made of at least one of calcium carbonate, talc, kaolin, clay, mica, aluminum hydroxide, barium sulfate, calcium silicate, calcium sulfate, silica, zinc carbonate, zinc oxide, titanium oxide, bentonite, and white carbon, and

the organic particles are made of at least one of polysaccharides and thermoplastic resins;

and preferably the inorganic particles are calcium carbonate, and the organic particles are starch.

11. The agent of any of claims 1-10, wherein the organic particles are insoluble in water at 40°C.

12. The agent of any of claims 1-11, further comprising a liquid medium which is water or a mixture of water and an organic solvent.

13. Paper, which is oil-resistant paper comprising the agent of any of claims 1-12 in the interior of the paper, and preferably is a molded pulp product.

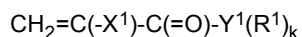
14. The paper of claim 13, which is a food packaging material or a food container.

15. A method for producing oil-resistant paper, comprising preparing a formulated pulp slurry by adding the agent of any of claims 1-12 to a slurry in which pulp is dispersed in an aqueous medium, making an oil-resistant paper intermediate, followed by dehydrating and then drying to obtain the oil-resistant paper.

Patentansprüche

1. Mittel, das ein ölbeständiges Mittel für Papier ist, das dem Inneren von Papier zugesetzt wird, umfassend:

(1) ein fluorfreies Acrylpolymer, das, basierend auf dem fluorfreien Polymer, 30-95 Gew.-% Wiederholungseinheiten aufweist, die aus einem Monomer (a) gebildet sind, das eine langkettige Kohlenwasserstoffgruppe aufweist und ein Monomer der folgenden Formel ist:



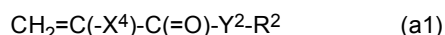
worin

- 5 R¹ jeweils unabhängig eine C₇₋₄₀-Kohlenwasserstoffgruppe ist,
X¹ H, Halogen außer F oder eine einwertige organische Gruppe ist und vorzugsweise H oder Methyl ist,
Y¹ eine zwei- bis vierwertige Gruppe ist, die aus mindestens einem von einer Kohlenwasserstoffgruppe
mit einem Kohlenstoffatom, -C₆H₄-, -O-, -C(=O)-, -S(=O)₂- oder -NH- besteht, mit der Maßgabe, dass eine
Kohlenwasserstoffgruppe ausgeschlossen ist, und
10 k 1-3 ist; und

(2) mindestens eine Art an Teilchen, ausgewählt aus anorganischen Teilchen oder organischen Teilchen,

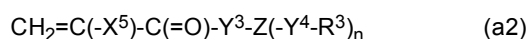
15 worin die Menge der Teilchen (2), basierend auf dem Gesamtgewicht des Polymers (1) und der Teilchen (2), 1-99,9 Gew.-% beträgt.

2. Mittel gemäß Anspruch 1, worin X¹ H oder Methyl ist.
3. Mittel gemäß Anspruch 1 oder 2, worin die mindestens eine Art an Teilchen aus organischen Teilchen ausgewählt ist.
4. Mittel gemäß einem der Ansprüche 1-3, worin die Menge der Teilchen (2), basierend auf dem Gesamtgewicht des Polymers (1) und der Teilchen (2), 50-99,9 Gew.-% beträgt.
5. Mittel gemäß einem der Ansprüche 1-4, worin die langkettige Kohlenwasserstoffgruppe im Monomer (a) ≥ 18 Kohlenstoffatome aufweist.
6. Mittel gemäß einem der Ansprüche 1-5, worin das Monomer (a) ein Monomer der Formel (a1) und/oder (a2) ist:



worin

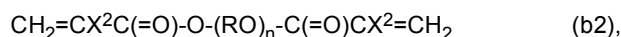
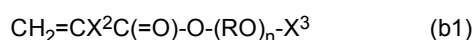
R² eine C₇₋₄₀-Kohlenwasserstoffgruppe ist,
X⁴ H, Halogen oder eine einwertige organische Gruppe ist, und
Y² -O- oder -NH- ist;



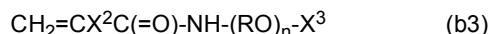
worin

R³ jeweils unabhängig eine C₇₋₄₀-Kohlenwasserstoffgruppe ist,
X⁵ H, Halogen oder eine einwertige organische Gruppe ist,
Y³ -O- oder -NH- ist,
Y⁴ jeweils unabhängig eine Gruppe ist, die aus mindestens einem aus einer direkten Bindung, -O-, -C(=O)-, -S(=O)₂- oder -NH- besteht,
Z eine direkte Bindung oder eine zwei- oder dreiwertige C₁₋₅-Kohlenwasserstoffgruppe ist, und
n 1 oder 2 ist.

7. Mittel gemäß einem der Ansprüche 1-6, worin das fluorfreie Polymer ferner eine Wiederholungseinheit aufweist, die aus einem Monomer (b) gebildet ist, das mindestens ein Oxyalkylen(meth) acrylat der folgenden Formel ist:



oder



worin

X² H oder Methyl ist,
 X³ H oder eine ungesättigte oder gesättigte C₁₋₂₂-Kohlenwasserstoffgruppe ist,
 R jeweils unabhängig C₂₋₆-Alkylen ist, und
 n eine ganze Zahl von 1-90 ist.

8. Mittel gemäß einem der Ansprüche 1-7, worin das fluorfreie Polymer ferner eine Wiederholungseinheit umfasst, die aus einem Monomer (c) gebildet ist, das anders als die Monomere (a) und (b) ist und eine olefinische Kohlenstoff-Kohlenstoff-Doppelbindung aufweist und einen Anionen-gebende Gruppe, vorzugsweise eine Carboxylgruppe, oder eine Kationen-gebende Gruppe, vorzugsweise eine Aminogruppe, aufweist.

9. Mittel gemäß einem der Ansprüche 1-8, worin, basierend auf dem Copolymer, die Menge der aus Monomer (a) gebildeten Wiederholungseinheiten 30-90 Gew.-% beträgt und die Menge der aus Monomer (b) gebildeten Wiederholungseinheiten 5-70 Gew.-% beträgt.

10. Mittel gemäß einem der Ansprüche 1-9, worin

die anorganischen Teilchen aus mindestens einem von Calciumcarbonat, Talk, Kaolin, Ton, Glimmer, Aluminiumhydroxid, Bariumsulfat, Calciumsilikat, Calciumsulfat, Kieselsäure, Zinkcarbonat, Zinkoxid, Titanoxid, Bentonit und Weißkohle sind, und
 die organischen Teilchen aus mindestens einem von Polysacchariden und thermoplastischen Harzen sind;
 und vorzugsweise die anorganischen Teilchen Calciumcarbonat sind und die organischen Teilchen Stärke sind.

11. Mittel gemäß einem der Ansprüche 1-10, worin die organischen Teilchen bei 40°C in Wasser unlöslich sind.

12. Mittel gemäß einem der Ansprüche 1-11, ferner umfassend ein flüssiges Medium, das Wasser oder ein Gemisch aus Wasser und einem organischen Lösungsmittel ist.

13. Papier, das ein ölbeständiges Papier ist, umfassend das Mittel gemäß einem der Ansprüche 1-12 im Inneren des Papiers, und vorzugsweise ein geformtes Zellstoffprodukt ist.

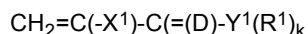
14. Papier gemäß Anspruch 13, das ein Lebensmittelverpackungsmaterial oder ein Lebensmittelbehälter ist.

15. Verfahren zur Herstellung von ölbeständigem Papier, umfassend das Bereiten einer formulierten Zellstoffaufschlämmung durch Zugabe des Mittels gemäß einem der Ansprüche 1-12 zu einer Aufschlämmung, in der Zellstoff in einem wässrigen Medium dispergiert ist, wodurch ein ölbeständiges Papierzwischenprodukt entsteht, gefolgt von Dehydratisierung und dann Trocknung, um das ölbeständige Papier zu erhalten.

Revendications

1. Agent, qui est un agent résistant à l'huile pour papier qui est ajouté à l'intérieur d'un papier, comprenant :

(1) un polymère acrylique sans fluor présentant de 30 à 95 % en poids, sur la base du polymère sans fluor, de motifs de répétition formés à partir d'un monomère (a) qui présente un groupe hydrocarbure à chaîne longue et est un monomère de la formule :



dans lequel

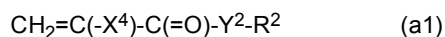
R¹ est chacun indépendamment un groupe hydrocarbure en C₇₋₄₀,
 X¹ est H, un halogène autre que F ou un groupe organique monovalent, et est préférablement H ou du méthyle,

Y¹ est un groupe divalent à tétravalent composé d'au moins un parmi un groupe hydrocarbure présentant un atome de carbone, -C₆H₄-, -O-, -C(=O)-, -S(=O)₂-, ou -NH-, à condition qu'un groupe hydrocarbure soit exclu, et
k vaut 1 à 3 ; et

(2) au moins un type de particules sélectionné parmi des particules inorganiques ou des particules organiques,

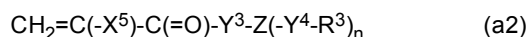
dans lequel la quantité des particules (2) va de 1 à 99,9 % en poids, par rapport au poids total du polymère (1) et des particules (2).

2. Agent selon la revendication 1, dans lequel X¹ est H ou du méthyle.
3. Agent selon la revendication 1 ou la revendication 2, dans lequel le au moins un type de particules est sélectionné parmi des particules organiques.
4. Agent selon l'une quelconque des revendications 1 à 3, dans lequel la quantité des particules (2) va de 50 à 99,9 % en poids, sur la base du poids total du polymère (1) et des particules (2).
5. Agent selon l'une quelconque des revendications 1 à 4, dans lequel le groupe hydrocarbure à longue chaîne dans le monomère (a) présente ≥ 18 atomes de carbone.
6. Agent selon l'une quelconque des revendications 1 à 5, dans lequel le monomère (a) est un monomère de la formule (a1) et/ou (a2) :



dans lequel

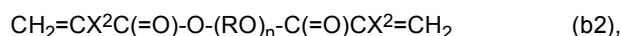
R² est un groupe hydrocarbure en C₇₋₄₀,
X⁴ est H, un halogène ou un groupe organique monovalent, et
Y² est -O- ou -NH- ;



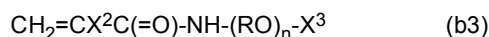
dans lequel

R³ est chacun indépendamment un groupe hydrocarbure en C₇₋₄₀,
X⁵ est H, un halogène ou un groupe organique monovalent,
Y³ est -O- ou -NH-,
Y⁴ est chacun indépendamment un groupe composé d'au moins un d'une liaison directe, -O-, -C(=O)-, -S(=O)₂- ou -NH-,
Z est une liaison directe ou un groupe hydrocarbure di- ou trivalent en C₁₋₅, et
n vaut 1 ou 2.

7. Agent selon l'une quelconque des revendications 1 à 6, dans lequel le polymère sans fluor présente en outre un motif de répétition formé à partir d'un monomère (b) qui est au moins un (méth)acrylate d'oxyalkylène de la formule :



ou



dans lequel

X² est H ou du méthyle,
 X³ est H ou un groupe hydrocarbure insaturé ou saturé en C₁₋₂₂,
 R est chacun indépendamment de l'alkylène en C₂₋₆, et
 n est un nombre entier de 1 à 90.

- 5
8. Agent selon l'une quelconque des revendications 1 à 7, dans lequel le polymère sans fluor comprend en outre un motif de répétition formé à partir d'un monomère (c) qui est autre que les monomères (a) et (b) et présente une double liaison carbone-carbone oléfinique et présente un groupe donneur d'anions, préférablement un groupe carboxyle ou groupe donneur de cations, préférablement un groupe aminé.
- 10
9. Agent selon l'une quelconque des revendications 1 à 8, dans lequel, sur la base du copolymère, la quantité de motifs de répétition formés à partir du monomère (a) est de 30 à 90 % en poids, et la quantité de motifs de répétition formés à partir du monomère (b) est de 5 à 70 % en poids.
- 15
10. Agent selon l'une quelconque des revendications 1 à 9, dans lequel
 les particules inorganiques sont composées d'au moins un parmi carbonate de calcium, talc, kaolin, argile, mica, hydroxyde d'aluminium, sulfate de baryum, silicate de calcium, sulfate de calcium, silice, carbonate de zinc, oxyde de zinc, oxyde de titane, bentonite et carbone blanc, et
 les particules organiques sont composées d'au moins un parmi polysaccharides et des résines thermoplastiques ;
 et préférablement les particules inorganiques sont du carbonate de calcium, et les particules organiques sont de l'amidon.
- 20
11. Agent selon l'une quelconque des revendications 1 à 10, dans lequel les particules organiques sont insolubles dans l'eau à 40 °C.
- 25
12. Agent selon l'une quelconque des revendications 1 à 11, comprenant en outre un milieu liquide qui est de l'eau ou un mélange d'eau et d'un solvant organique.
- 30
13. Papier, qui est un papier résistant à l'huile comprenant l'agent selon l'une quelconque des revendications 1 à 12 à l'intérieur du papier, et préférablement est un produit de pâte moulé.
- 35
14. Papier selon la revendication 13, qui est un matériau d'emballage alimentaire ou un récipient alimentaire.
- 40
15. Procédé de production de papier résistant à l'huile, comprenant le fait de préparer une suspension de pâte formulée en ajoutant l'agent selon l'une quelconque des revendications 1 à 12 à une suspension dans laquelle la pâte est dispersée dans un milieu aqueux, le fait de fabriquer un intermédiaire de papier résistant à l'huile, suivi du fait de déshydrater puis de sécher afin d'obtenir le papier résistant à l'huile.

REFERENCES CITED IN THE DESCRIPTION

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