

DESCRIPTION

Title of the Invention:

LIQUID DETERGENT COMPOSITION FOR HARD SURFACES

Field of the Invention

[0001]

The present invention relates to a liquid detergent composition for hard surfaces, and a method for preventing stains from adhering to hard surfaces.

Background of the Invention

[0002]

In living environment facilities surrounding people, there exist various hard surfaces made of materials such as tiles, plastics, and metals, and these hard surfaces are exposed to environments where various stains adhere to the hard surfaces in living scenes. Among others, hard surfaces used in toilets, bathrooms, kitchens and others are surfaces that come in daily contact with humans; and thus, many stains are likely to remain and accumulate, and further, they are difficult to be removed through washing.

[0003]

For example, JP-A 2010-100861 discloses a composition for cleaning or rinsing hard surfaces in an aqueous or aqueous alcoholic medium, which contains

at least one surfactant and at least one polybetaine (B), wherein the polybetaine (B) carries a permanent anionic overall charge and a permanent cationic overall charge within a pH range from 1 to 14 (each individual betaine unit carrying as many permanent anionic charges as permanent cationic charges), exhibits an absolute weight-average molecular weight (Mw) ranging from 5,000 to 3,000,000 g/mol.

In addition, US-A 2009/0197791 discloses a copolymer containing a unit A containing a betaine group and a cationic unit B.

Summary of the Invention

[0004]

JP-A 2010-100861 and US-A 2009/0197791 are not considered to be sufficient in terms of satisfying the foaming, the sterilization performance and the antifouling property. Especially, the present inventors have found that when a polymer having a betaine group and a cationic surfactant are used in combination as described in JP-A 2010-100861, further use of other surfactant such as a nonionic surfactant, an amphoteric surfactant or an anionic surfactant for improvement of foaming reduces the antifouling performance to hard surfaces.

[0005]

In addition, JP-A 2010-100861 and US-A 2009/0197791

are not considered to be sufficient in terms of satisfying the scale removal detergency (hereinafter, also referred to simply as detergency), the sterilization performance and the antifouling property. Especially, the present inventors have found that when a polymer having a betaine group and a cationic surfactant are used in combination as described in JP-A 2010-100861, further use of a chelating agent for improvement of the detergency reduces the antifouling performance to hard surfaces.

[0006]

The present invention relates to a liquid detergent composition for hard surfaces, which is excellent in the prevention of stain adhesion to a hard surface, that is, excellent in the antifouling performance, in addition to maintaining the sterilization performance and being excellent in the foaming.

[0007]

The present invention relates to a liquid detergent composition for hard surfaces, which is excellent in the prevention of stain adhesion to a hard surface, that is, excellent in the antifouling performance, in addition to maintaining the sterilization performance and being excellent in the detergency.

[0008]

The present inventors have found that use of: a polymer having a specific betaine group and a specific

cationic group; a cationic surfactant; and a nonionic surfactant, an amphoteric surfactant or an anionic surfactant can produce excellent effects all in the antifouling performance, the foaming (hereinafter, also referred to as foaming property), and the sterilization performance.

[0009]

The present invention provides a liquid detergent composition for hard surfaces, which contains:

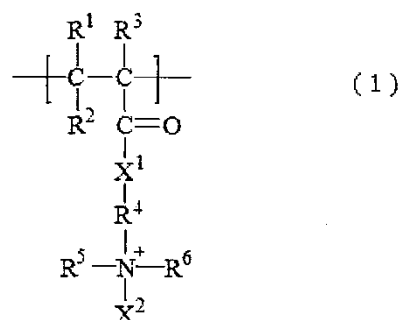
(a) a copolymer containing a constituent unit (a1) represented by the following formula (1) and a constituent unit (a2) represented by the following formula (2), wherein a molar ratio between the constituent unit (a1) and the constituent unit (a2), constituent unit (a1)/constituent unit (a2), is 30/70 or more and 99.9/0.1 or less;

(b) a cationic surfactant; and

(c) one or more surfactants [hereinafter, referred to as component (c)] selected from amphoteric surfactants, nonionic surfactants and anionic surfactants,

[0010]

[Chemical formula 1]



[0011]

wherein

R¹ to R³ are the same or different and represent a hydrogen atom or an alkyl group with 1 or 2 carbons; R⁴ represents an alkylene group with 1 or more and 4 or less carbons or -Y¹-OPO₃⁻-Y²-,

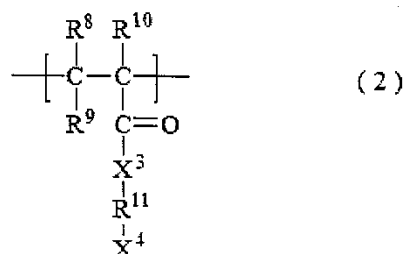
Y¹ and Y² are the same or different and represent an alkylene group with 1 or more and 4 or less carbons; R⁵ and R⁶ are the same or different and represent a hydrocarbon group with 1 or more and 4 or less carbons; X¹ is O or NR⁷, and R⁷ represents a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons; and

X² represents a hydrogen atom, a hydrocarbon group with 1 or more and 4 or less carbons, R¹⁷SO₃⁻ or R¹⁷COO⁻, with the proviso that: when R⁴ is an alkylene group with 1 or more and 4 or less carbons, X² is R¹⁷SO₃⁻ or R¹⁷COO⁻, wherein R¹⁷ is an alkylene group with 1 or more and 4 or less carbons; and when R⁴ is -Y¹-OPO₃⁻-Y²-, X² is a hydrogen atom or a hydrocarbon group with 1 or more and

4 or less carbons,

[0012]

[Chemical formula 2]



[0013]

wherein

R⁸ to R¹⁰ are the same or different and represent a hydrogen atom or an alkyl group with 1 or 2 carbons;

X³ represents O;

R¹¹ represents an alkylene group with 1 or more and 4 or less carbons; and

X⁴ is N⁺R¹²R¹³R¹⁴X⁵ or NR¹⁵R¹⁶, wherein R¹² to R¹⁶ are the same or different and represent a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons, and X⁵ represents an anion.

[0014]

In addition, the present inventors have found that use of: a polymer having a specific betaine group and a specific cationic group; a cationic surfactant; and a chelating agent can produce excellent effects all in the antifouling performance, the detergency and the sterilization performance.

[0015]

The present invention relates to a liquid detergent composition for hard surfaces, which contains:

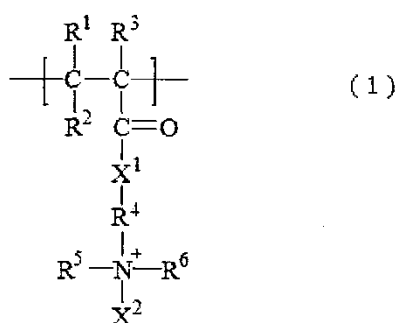
(a) a copolymer [hereinafter, referred to as component (a)] containing a constituent unit (a1) represented by the following formula (1) and a constituent unit (a2) represented by the following formula (2), wherein a molar ratio between the constituent unit (a1) and the constituent unit (a2), constituent unit (a1)/constituent unit (a2), is 30/70 or more and 99.9/0.1 or less;

(b) a cationic surfactant [hereinafter, referred to as component (b)]; and

(d) a chelating agent [hereinafter, referred to as component (d)],

[0016]

[Chemical formula 3]



[0017]

wherein

R¹ to R³ are the same or different and represent a

hydrogen atom or an alkyl group with 1 or 2 carbons;
 R^4 represents an alkylene group with 1 or more and 4 or less carbons or $-Y^1-OPO_3^--Y^2-$,

Y^1 and Y^2 are the same or different and represent an alkylene group with 1 or more and 4 or less carbons;

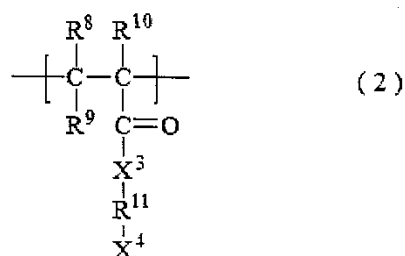
R^5 and R^6 are the same or different and represent a hydrocarbon group with 1 or more and 4 or less carbons;

X^1 is O or NR^7 , and R^7 represents a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons;
 and

X^2 represents a hydrogen atom, a hydrocarbon group with 1 or more and 4 or less carbons, $R^{17}SO_3^-$ or $R^{17}COO^-$, with the proviso that: when R^4 is an alkylene group with 1 or more and 4 or less carbons, X^2 is $R^{17}SO_3^-$ or $R^{17}COO^-$, wherein R^{17} is an alkylene group with 1 or more and 4 or less carbons; and when R^4 is $-Y^1-OPO_3^--Y^2-$, X^2 is a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons,

[0018]

[Chemical formula 4]



[0019]

wherein

R^8 to R^{10} are the same or different and represent a hydrogen atom or an alkyl group with 1 or 2 carbons;

X^3 represents O;

R^{11} represents an alkylene group with 1 or more and 4 or less carbons; and

X^4 is $N^+R^{12}R^{13}R^{14}X^5$ or $NR^{15}R^{16}$, wherein R^{12} to R^{16} are the same or different and represent a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons, and X^5 represents an anion.

[0020]

Hereafter, when the liquid detergent composition for hard surfaces of the present invention is referred to, it includes the above two liquid detergent compositions for hard surfaces.

[0021]

In addition, the present invention relates to a method for preventing a stain from adhering to a hard surface, which includes treating the hard surface with the liquid detergent composition for hard surfaces of the present invention.

[0022]

According to the present invention, there is provided a liquid detergent composition for hard surfaces, which is excellent in the prevention of stain adhesion to hard surfaces, that is, excellent in the antifouling performance, in addition to maintaining

the sterilization performance and being excellent in the foaming.

[0023]

In addition, according to the present invention, there is provided a liquid detergent composition for hard surfaces, which is excellent in the prevention of stain adhesion to hard surfaces, that is, excellent in the antifouling performance, in addition to maintaining the sterilization performance and being excellent in the detergency.

Description of Embodiments

[0024]

[Liquid detergent composition for hard surfaces]

According to one aspect, the liquid detergent composition for hard surfaces of the present invention is a liquid detergent composition for hard surfaces, which contains component (a), component (b) and component (c).

<Component (a)>

Component (a) is a copolymer containing a constituent unit (a1) represented by the above formula (1) and a constituent unit (a2) represented by the above formula (2).

Constituent unit (a1) represented by the above formula (1) may be a constituent unit derived from an unsaturated monomer having a betaine group. Also,

constituent unit (a2) represented by the above formula (2) may be a constituent unit derived from an unsaturated monomer having a cationic group.

[0025]

[Weight average molecular weight of component (a)]

The weight average molecular weight of component (a) is, from the viewpoint of enhancing the antifouling performance of component (a), preferably 500 or more, more preferably 5000 or more, further preferably 10000 or more, and further more preferably 30000 or more; and from the same viewpoint, preferably 200000 or less, more preferably 150000 or less, and further preferably 100000 or less. The weight average molecular weight can be measured by the method described in the examples.

[0026]

[Molar ratio between constituent units (a1) and (a2)]

The molar ratio between constituent units (a1) and (a2) of component (a) is, from the viewpoint of the antifouling performance, in terms of constituent unit (a1)/constituent unit (a2), 30/70 or more and 99.9/0.1 or less. The molar ratio of constituent unit (a1)/constituent unit (a2) is, from the same viewpoint, preferably 50/50 or more, more preferably 55/45 or more, further preferably 60/40 or more, further more preferably 75/25 or more, and further more preferably 90/10 or more; and from the viewpoint of enhancing the antifouling performance of component (a), preferably

98/2 or less, and more preferably 96/4 or less.

[0027]

[Constituent unit (a1)]

(Content of constituent unit (a1))

A content of constituent unit (a1) in component (a) is, from the viewpoint of enhancing the antifouling performance of component (a), preferably 30 mol% or more, more preferably 50 mol% or more, further preferably 70 mol% or more, further more preferably 80 mol% or more, and further more preferably 90 mol% or more; and from the same viewpoint, preferably 99 mol% or less, more preferably 98 mol% or less, and further preferably 95 mol% or less.

In addition, the content of constituent unit (a1) in the component (a) is, from the viewpoint of enhancing the antifouling performance of component (a), preferably 30 mass% or more, more preferably 50 mass% or more, further preferably 70 mass% or more, further more preferably 80 mass% or more, and further more preferably 90 mass% or more; and from the same viewpoint, preferably 99 mass% or less, more preferably 98 mass% or less, and further preferably 95 mass% or less.

[0028]

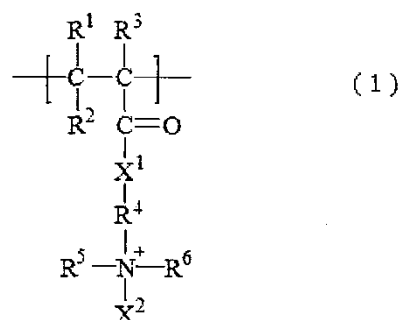
(Structure of constituent unit (a1))

Constituent unit (a1) of component (a) is a constituent unit represented by the following formula

(1):

[0029]

[Chemical formula 5]



[0030]

wherein

R¹ to R³ are the same or different and represent a hydrogen atom or an alkyl group with 1 or 2 carbons; R⁴ represents an alkylene group with 1 or more and 4 or less carbons or -Y¹-OPO₃⁻-Y²-,

Y¹ and Y² are the same or different and represent an alkylene group with 1 or more and 4 or less carbons; R⁵ and R⁶ are the same or different and represent a hydrocarbon group with 1 or more and 4 or less carbons; X¹ is O or NR⁷, and R⁷ represents a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons; and

X² represents a hydrogen atom, a hydrocarbon group with 1 or more and 4 or less carbons, R¹⁷SO₃⁻ or R¹⁷COO⁻, with the proviso that: when R⁴ is an alkylene group with 1 or more and 4 or less carbons, X² is R¹⁷SO₃⁻ or R¹⁷COO⁻,

wherein R^{17} is an alkylene group with 1 or more and 4 or less carbons; and when R^4 is $-Y^1-OPO_3^--Y^2-$, X^2 is a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons.

[0031]

In the formula (1), from the viewpoint of the availability of unsaturated monomers, the viewpoint of the polymerizability of monomers and the viewpoint of enhancing the antifouling performance of component (a), R^1 and R^2 are each preferably a hydrogen atom.

In the formula (1), from the viewpoint of the availability of unsaturated monomers, the viewpoint of the polymerizability of monomers and the viewpoint of enhancing the antifouling performance of component (a), R^3 is preferably a hydrogen atom or a methyl group, and more preferably a methyl group.

In the formula (1), from the viewpoint of the availability of unsaturated monomers, the viewpoint of the polymerizability of monomers and the viewpoint of enhancing the antifouling performance of component (a), X^1 is preferably O. The alkylene group with 1 or more and 4 or less carbons of R^4 is, from the same viewpoints, preferably an alkylene group with 2 or 3 carbons, and more preferably an alkylene group with 2 carbons.

In the formula (1), R^4 is, from the viewpoint of enhancing the antifouling performance, preferably an

alkylene group with 1 or more and 4 or less carbons, and more preferably an alkylene group with 2 or 3 carbons.

In the formula (1), Y^1 and Y^2 are each preferably an alkylene group with 2 or 3 carbons, and more preferably an alkylene group with 2 carbons.

In the formula (1), from the viewpoint of the availability of unsaturated monomers, the viewpoint of the polymerizability of monomers and the viewpoint of enhancing the antifouling performance of component (a), R^5 and R^6 are each preferably a methyl group or an ethyl group, and more preferably a methyl group.

In the formula (1), X^2 is a hydrogen atom, a hydrocarbon group with 1 or more and 4 or less carbons, $R^{17}SO_3^-$ or $R^{17}COO^-$. However, when R^4 is an alkylene group with 1 or more and 4 or less carbons, X^2 is $R^{17}SO_3^-$ or COO^- . When R^4 is $-Y^1-OPO_3--Y^2-$, X^2 is a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons. When R^4 is $-Y^1-OPO_3--Y^2-$, from the viewpoint of enhancing the antifouling performance, X^2 is preferably a hydrocarbon group with 1 or more and 4 or less carbons, and more preferably a methyl group. When R^4 is an alkylene group with 1 or more and 4 or less carbons, from the same viewpoint, X^2 is preferably $R^{17}SO_3^-$.

In addition, R^{17} is preferably an alkylene group with 1 or more and 3 or less carbons, and more preferably

an alkylene group with 2 or more and 3 or less carbons.

[0032]

[Constituent unit (a2)]

(Content of constituent unit (a2))

A content of constituent unit (a2) in component (a) is, from the viewpoint of enhancing the antifouling performance, preferably 1 mol% or more, more preferably 2 mol% or more, and further preferably 5 mol% or more; and from the same viewpoint, preferably 70 mol% or less, more preferably 50 mol% or less, further preferably 30 mol% or less, further preferably 20 mol% or less, and further preferably 10 mol% or less.

In addition, the content of constituent unit (a2) in component (a) is, from the viewpoint of enhancing the antifouling performance, preferably 1 mass% or more, more preferably 2 mass% or more, and further preferably 5 mass% or more; and from the viewpoint of enhancing the antifouling performance of component (a), preferably 70 mass% or less, more preferably 50 mass% or less, further preferably 30 mass% or less, further preferably 20 mass% or less, and further preferably 10 mass% or less.

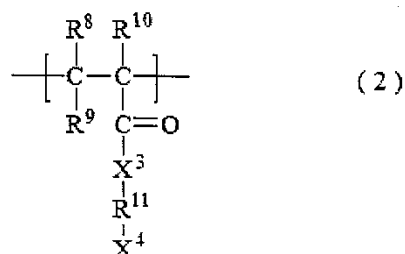
[0033]

(Structure of constituent unit (a2))

Constituent unit (a2) of component (a) is a constituent unit represented by the following formula (2):

[0034]

[Chemical formula 6]



[0035]

wherein

R⁸ to R¹⁰ are the same or different and represent a hydrogen atom or an alkyl group with 1 or 2 carbons;

X³ represents O or NH,

R¹¹ represents an alkylene group with 1 or more and 4 or less carbons; and

X⁴ is N⁺R¹²R¹³R¹⁴X⁵ or NR¹⁵R¹⁶, wherein R¹² to R¹⁶ are the same or different and represent a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons, and X⁵ represents an anion.

[0036]

In the formula (2), from the viewpoint of the availability of unsaturated monomers, the viewpoint of the polymerizability of monomers and the viewpoint of enhancing the antifouling performance of component (a), R⁸ and R⁹ are each preferably a hydrogen atom.

In the formula (2), from the viewpoint of the polymerizability of monomers and the viewpoint of

enhancing the antifouling performance of component (a), R^{10} is preferably a hydrogen atom or a methyl group, and more preferably a methyl group.

In the formula (2), from the viewpoint of the polymerizability of monomers and the viewpoint of enhancing the antifouling performance of component (a), X^3 is preferably O.

In the formula (2), from the viewpoint of the polymerizability of monomers and the viewpoint of enhancing the antifouling performance of component (a), R^{11} is preferably an alkylene group with 2 or 3 carbons, and more preferably an alkylene group with 2 carbons.

In the formula (2), from the viewpoint of enhancing the antifouling performance of component (a) and the viewpoint of the easiness of quaternarization reaction, X^4 is $N^+R^{12}R^{13}R^{14}X^5$ or $NR^{15}R^{16}$, preferably $N^+R^{12}R^{13}R^{14}X^5$, and R^{12} , R^{13} and R^{14} are each, from the same viewpoints, preferably a methyl group or an ethyl group.

In the formula (2), from the viewpoint of enhancing the antifouling performance of component (a) and the viewpoint of the easiness of quaternarization reaction, R^{15} and R^{16} are preferably a methyl group or an ethyl group, and more preferably a methyl group.

In the formula (2), X^5 is an anion, preferably a halogen ion or $C_2H_5SO_4^-$, and more preferably $C_2H_5SO_4^-$.

[0037]

[Constituent unit other than constituent units (a1) and (a2)]

Component (a) may contain a constituent unit other than constituent units (a1) and (a2) in such a range that effects of the present invention are not deteriorated. The constituent unit other than constituent units (a1) and (a2) is preferably a constituent unit derived from an unsaturated monomer other than an unsaturated monomer having a sulfobetaine group, and more preferably a constituent unit derived from a hydrophobic unsaturated monomer such as styrene.

[0038]

A content of the constituent unit other than constituent units (a1) and (a2) in component (a) is, from the viewpoint of the antifouling property, preferably 10 mol% or less, more preferably 5 mol% or less, more preferably 1 mol% or less, further preferably 0.5 mol% or less, and further more preferably 0.1 mol% or less. The content of the constituent unit other than constituent units (a1) and (a2) in component (a) may be 0 mol%.

[0039]

The content of the constituent unit other than constituent units (a1) and (a2) in component (a) is, from the viewpoint of the antifouling property, preferably 10 mass% or less, more preferably 5 mass%

or less, further preferably 1 mass% or less, further preferably 0.5 mass% or less, and further more preferably 0.1 mass% or less. The content of the constituent unit other than constituent units (a1) and (a2) in component (a) may be 0 mass%.

[0040]

The total content of constituent units (a1) and (a2) in component (a) is, from the viewpoint of the antifouling property, preferably 90 mol% or more, more preferably 95 mol% or more, further preferably 99 mol% or more, further more preferably 99.5 mol% or more, and further more preferably 99.9 mol% or more. The total content of constituent units (a1) and (a2) in component (a) may be 100 mol%.

The total content of constituent units (a1) and (a2) in component (a) is, from the viewpoint of the antifouling property, preferably 90 mass% or more, more preferably 95 mass% or more, further preferably 99 mass% or more, further more preferably 99.5 mass% or more, and further more preferably 99.9 mass% or more. The total content of constituent units (a1) and (a2) in component (a) may be 100 mass%.

[0041]

[Production method of component (a)]

As a method for producing component (a), any method may be employed, but specific examples thereof include the following methods (i) and (ii). From the viewpoint

of the availability of raw materials and the easiness of production, method (ii) is preferred.

(i) method for obtaining by copolymerizing unsaturated monomers having a betaine group and a cationic group; and

(ii) method for obtaining by copolymerizing unsaturated monomers having an amino group and a cationic group, and then quaternarizing with a betainizing agent.

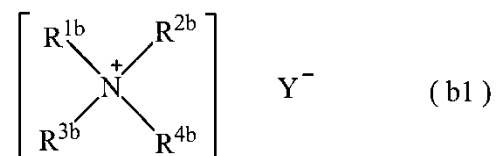
[0042]

<Component (b)>

Component (b) is a cationic surfactant. As the cationic surfactant, mono- or di- long-chain alkyl quaternary ammonium salt is preferred. As component (b), preferred is a cationic surfactant selected from compounds represented by the following general formula (b1) and compounds represented by the general formula (b2):

[0043]

[Chemical formula 7]



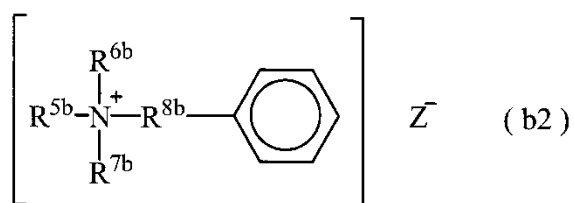
[0044]

wherein at least one selected from R^{1b} and R^{2b} represents

an alkyl group with 8 or more and 18 or less carbons, an alkenyl group with 8 or more and 18 or less carbons or a hydroxyalkyl group with 8 or more and 18 or less carbons, and the remainder represents an alkyl group with 1 or more and 3 or less carbons, a hydroxyalkyl group with 1 or more and 3 or less carbons or a polyoxyethylene group with an average number of added moles of 10 or less; R^{3b} and R^{4b} are the same or different and each represent an alkyl group with 1 or more and 3 or less carbons, a hydroxyalkyl group with 1 or more and 3 or less carbons or a polyoxyethylene group with an average number of added moles of 10 or less; and Y^- represents a halogen atom, or an anionic residue of a sulfonic ester or a sulfuric ester with 1 or more and 5 or less carbons,

[0045]

[Chemical formula 8]



[0046]

wherein R^{5b} represents an alkyl group with 8 or more and 18 or less carbons, an alkenyl group with 8 or more and 18 or less carbons or a hydroxyalkyl group with 8 or more and 18 or less carbons, R^{6b} and R^{7b} are the same

or different and each represent an alkyl group with 1 or more and 3 or less carbons, a hydroxyalkyl group with 1 or more and 3 or less carbons or a polyoxyethylene group with an average number of added moles of 10 or less, and R^{8b} represents an alkylene group with 1 or more and 3 or less carbons. Z- represents a halogen atom, or an anionic residue of a sulfonic ester or a sulfuric ester with 1 or more and 5 or less carbons. [0047]

When component (b) is a mono long-chain alkyl quaternary ammonium salt, it is preferred that in the general formula (b1), R^{1b} is an alkyl group, an alkenyl group or a hydroxyalkyl group with 8 or more and 16 or less carbons, R^{2b} , R^{3b} and R^{4b} are the same or different and are each an alkyl group or a hydroxyalkyl group with 1 or more and 3 or less carbons, or a polyoxyethylene group with an average number of added moles of 10 or less.

When component (b) is a di long-chain alkyl quaternary ammonium salt, it is preferred that in the general formula (b1), R^{1b} and R^{2b} are the same or different and are each an alkyl group, an alkenyl group or a hydroxyalkyl group with 8 or more and 16 or less carbons, and R^{3b} and R^{4b} are the same or different and are each an alkyl group or a hydroxyalkyl group with 1 or more and 3 or less carbons, or a polyoxyethylene group with an average number of added moles of 10 or

less.

[0048]

In the general formula (b2), R^{5b} is preferably a straight-chain alkyl group with 12 or more and 16 or less carbons, R^{6b} and R^{7b} are each preferably a methyl group, R^{8b} is preferably a methylene group, and Z^- is preferably a halogen ion, or further a chloride ion (Cl^-).

[0049]

Component (b) is preferably a cationic surfactant selected from compounds represented by the above general formula (b2).

[0050]

<Component (c)>

Component (c) is one or more surfactants selected from amphoteric surfactants, nonionic surfactants and anionic surfactants. From the viewpoint of the mixing stability, component (c) is preferably one or more surfactants selected from amphoteric surfactants and nonionic surfactants.

[0051]

[Amphoteric surfactant]

As the amphoteric surfactant, from the viewpoint of the mixing stability and the foaming property, it is preferable to contain one of more amphoteric surfactants selected from amine oxide, sulfobetaine and carbobetaine; it is more preferable to contain one

or more amphoteric surfactants selected from sulfobetaine and carbobetaine; and it is more preferable to contain carbobetaine. Two or more of these may also be used.

[0052]

Of the amphoteric surfactants, a content of one or more amphoteric surfactants selected from amine oxide, sulfobetaine and carbobetaine is, from the viewpoint of the mixing stability and the foaming property, preferably 50 mass% or more, more preferably 70 mass% or more, further preferably 80 mass% or more, further more preferably 90 mass% or more, further more preferably 95 mass% or more, and further more preferably 99 mass% or more; and preferably 100 mass% or less.

In addition, of the amphoteric surfactants, a content of one or more amphoteric surfactants selected from sulfobetaine and carbobetaine is, from the viewpoint of the mixing stability and the foaming property, preferably 50 mass% or more, more preferably 70 mass% or more, further preferably 80 mass% or more, further more preferably 90 mass% or more, further more preferably 95 mass% or more, and further more preferably 99 mass% or more; and preferably 100 mass% or less.

[0053]

As the sulfobetaine, exemplified are:

N-alkyl-N,N-dimethyl-N-sulfopropyl ammonium sulfobetaine wherein an alkyl group has, from the viewpoint of the mixing stability and the foaming property, preferably 10 or more carbons, and preferably 18 or less, and more preferably 14 or less carbons; N-alkyl-N,N-dimethyl-N-(2-hydroxysulfopropyl) ammonium sulfobetaine wherein an alkyl group has, from the viewpoint of the mixing stability and the foaming property, preferably 10 or more carbons, and preferably 18 or less and more preferably 14 or less carbons; N-alkanoyl aminopropyl-N,N-dimethyl-N-sulfopropyl ammonium sulfobetaine wherein an alkanoyl group has, from the viewpoint of the mixing stability and the foaming property, preferably 10 or more carbons, and preferably 18 or less, and more preferably 14 or less carbons; and N-alkanoyl aminopropyl-N,N-dimethyl-N-(2-hydroxysulfopropyl) ammonium sulfobetaine wherein an alkanoyl group has, from the viewpoint of the mixing stability and the foaming property, preferably 10 or more carbons, and preferably 18 or less and more preferably 14 or less carbons.

[0054]

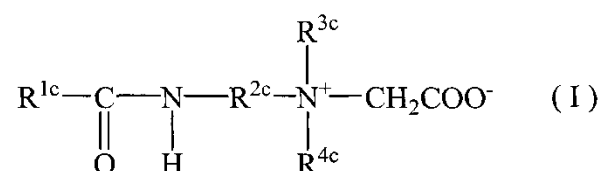
As the carbobetaine, exemplified are:

N-alkyl-N,N-dimethyl-N-carboxymethyl ammonium betaine wherein an alkyl group has, from the viewpoints of the mixing stability and the foaming property, preferably 10 or more carbons, and preferably 18 or

less, more preferably 14 or less carbons; and compounds represented by the following general formula (I). From the viewpoints of the mixing stability and the foaming property, compounds represented by the following general formula (I) are preferred:

[0055]

[Chemical formula 9]



[0056]

wherein R^{1c} represents an alkyl group or an alkenyl group with 7 or more and 21 or less carbons, R^{2c} represents a propylene group, and R^{3c} and R^{4c} each independently represent an alkyl group with 1 or more and 3 or less carbons.

[0057]

In the general formula (I), R^{1c} is, from the viewpoints of the mixing stability and the foaming property, an alkyl group or an alkenyl group with preferably 9 or more, and more preferably 11 or more carbons, and preferably 15 or less and more preferably 13 or less carbons; and it is preferably a nonyl group, a decyl group, an undecyl group, a dodecyl group and a tridecyl group.

In the general formula (I), R^{3c} and R^{4c} are, from the viewpoints of the mixing stability and the foaming property, preferably a methyl group.

Examples of the compound represented by the general formula (I) include almond amidopropyl betaine, apricot amidopropyl betaine, avocado amidopropyl betaine, babassu amidopropyl betaine, behenamidopropyl betaine, canola amidopropyl betaine, capryl/capramidopropyl betaine, cocamidopropyl betaine, coco/oleamidopropyl betaine, isostearamidopropyl betaine, lauramidopropyl carbobetaine, milk amidopropyl betaine, mink amidopropyl betaine, myristamidopropyl betaine, oleamidopropyl betaine, olive amidopropyl betaine, palmamidopropyl betaine, palmitamide propyl betaine, amidopropyl betaine ricinoleate, sesamidopropyl betaine, soy amidopropyl betaine, stearamidopropyl betaine, tallowamidopropyl betaine, undecylene amidopropyl betaine, and wheat germ amidopropyl betaine.

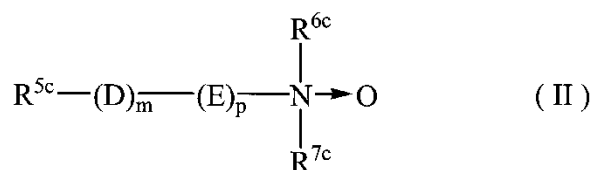
Among these, from the viewpoints of the mixing stability and the foaming property, one or more types selected from lauramidopropyl carbobetaine, myristamidopropyl betaine, oleamidopropyl betaine, and cocamidopropyl betaine are preferred. These are compounds wherein R^{3c} and R^{4c} in the general formula (I) are each a methyl group.

[0058]

As the amine oxide, compounds of the following general formula (II) are suitable:

[0059]

[Chemical formula 10]



[0060]

wherein R^{5c} represents a hydrocarbon group with 8 or more and 22 or less carbons, preferably an alkyl group or alkenyl group, more preferably an alkyl group, and R^{6c} and R^{7c} each independently represent an alkyl group with 1 or more and 3 or less carbons. D represents -NHC(=O)- group or -C(=O)NH- group, and E represents an alkylene group with 1 or more and 5 or less carbons. m and p represent that m=0 and p=0, or m=1 and p=1.

[0061]

In the above general formula (II), R^{5c} is, from the viewpoints of the mixing stability and the foaming property, preferably an alkyl group with 10 or more and 18 or less carbons, more preferably an alkyl group with 12 or more and 16 or less carbons, further preferably an alkyl group with 12 or more and 14 or less carbons, and further more preferably an alkyl group with 12

carbons. R^{6c} and R^{7c} are, from the viewpoint of the mixing stability, preferably a methyl group with 1 carbon.

[0062]

Preferable specific examples of the amine oxide include:

(1) alkyl (8 or more and 22 or less carbons) dialkyl (1 or more and 3 or less carbons) amine oxides such as capryl dimethyl amine oxide, caprin dimethyl amine oxide, lauryl dimethyl amine oxide, myristyl dimethyl amine oxide; and

(2) fatty acid (8 or more and 22 or less carbons) amidopropyl dialkyl (1 or more and 3 or less carbons) amine oxide such as amido propyl dimetnyl amine oxide laurate, amido propyl dimethyl amine oxide myristate, and amido propyl dimethyl amine oxide palmitate.

From the viewpoint of the mixing stability, (1) alkyl (8 or more and 22 or less carbons) dialkyl (1 or more and 3 or less carbons) amine oxide is more preferred.

[0063]

[Nonionic surfactant]

As a nonionic surfactant, preferred is one or more types selected from the group consisting of (c1) monoalkyl glyceryl ether [hereinafter, referred to as component (c1)], (c2) polyoxyalkylene monoalkyl or alkenyl ether [hereinafter, referred to as component (c2)], (c3) alkyl polyglycoside (glycoside-type

nonionic surfactant) [hereinafter, referred to as component (c3)], (c4) a sorbitan-based nonionic surfactant [hereinafter, referred to as component (c4)], (c5) aliphatic alkanolamide [hereinafter, referred to as component (c5)], (c6) fatty acid monoglyceride [hereinafter, referred to as component (c6)], and (c7) sucrose fatty acid ester [hereinafter, referred to as component (c7)].

[0064]

From the viewpoints of the mixing stability and the foaming property, the nonionic surfactant preferably includes one or more types selected from component (c1), component (c2) and component (c3), and further preferably includes component (c3).

In the nonionic surfactant, a total content of components (c1), (c2) and (c3) is, from the viewpoints of the mixing stability and the foaming property, preferably 50 mass% or more, more preferably 70 mass% or more, further preferably 80 mass% or more, further more preferably 90 mass% or more, further more preferably 95 mass% or more, and further more preferably 99 mass% or more; and preferably 100 mass% or less.

In the nonionic surfactant, a content of component (c3) is, from the viewpoints of the mixing stability and the foaming property, preferably 50 mass% or more, more preferably 70 mass% or more, further preferably

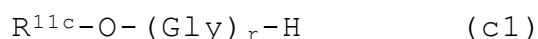
80 mass% or more, further more preferably 90 mass% or more, further more preferably 95 mass% or more, and further more preferably 99 mass% or more; and preferably 100 mass% or less.

[0065]

Component (c1)

Component (c1) is a monoalkyl glyceryl ether.

As component (c1), specifically, compounds represented by the following general formula (c1) are suitable:



wherein R^{11c} represents an alkyl group with 6 or more and 18 or less carbons, Gly represents a constituent unit derived from glycerin, preferably a residue in which one hydroxyl group and one hydrogen atom are removed from glycerin, and r represents a number of 1 or more and 4 or less.

[0066]

In the general formula (c1), R^{11c} is, from the viewpoints of the foaming property and the mixing stability, an alkyl group having preferably 6 or more carbons, more preferably 7 or more carbons, and further preferably 8 or more carbons; and preferably 18 or less carbons, more preferably 12 or less carbons, and further preferably 10 or less carbons, and a

straight-chain alkyl group such as a hexyl group, a heptyl group, an octyl group, a nonyl group and a decyl group may be used. In the present invention, from the viewpoint of the mixing stability, an alkyl group having a branched chain is suitable. As a specific alkyl group having a branched chain of R^{1c} , a group selected from 2-ethyl hexyl group, sec-octyl group, isononyl group and isodecyl group is preferred, 2-ethyl hexyl group or isodecyl group is further preferred, and 2-ethyl hexyl group is more preferred.

[0067]

In the general formula (c1), r is preferably 1 or more and preferably 2 or less. A compound wherein r is 1 is more preferred. A more preferred compound is a compound wherein R^{1c} is 2-ethyl hexyl group and r is 1.

The structure indicated by Gly is a structure represented by $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ wherein hydroxy groups at positions 1 and 3 of glycerin are bonded, or a structure represented by $-\text{CH}(\text{CH}_2\text{OH})\text{CH}_2-$ wherein hydroxy groups at positions 1 and 2 of glycerin are bonded; and it is varied depending on the catalyst or reaction condition.

[0068]

For obtaining a compound of the general formula (c1), usable is a production method wherein an alkyl alcohol indicated by $R^{1c}\text{-OH}$, for example, is used as an alcohol

with 6 to 10 carbons, and reacted with an epoxy compound such as epihalohydrin or glycidol by use of an acid catalyst such as BF_3 or an aluminum catalyst. When 2-ethylhexanol, for example, is used, obtained 2-ethyl hexyl monoglyceryl ether is a mixture that may contain a plurality of products as described in JP-A 2001-49291.

[0069]

Component (c2)

Component (c2) is polyoxyalkylene monoalkyl or alkenyl ether.

In the nonionic surfactant of component (c2), the carbon number of an alkyl group or alkenyl group is, from the viewpoints of the mixing stability and the foaming property, preferably 6 or more, more preferably 8 or more, further preferably 10 or more, and further more preferably 12 or more; and from the same viewpoints, preferably 22 or less, more preferably 18 or less, further preferably 16 or less, and further more preferably 14 or less.

[0070]

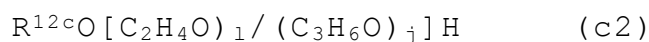
In the nonionic surfactant of component (c2), alkylene oxide has an average number of added moles of, from the viewpoints of the mixing stability and the foaming property, preferably over 0, more preferably 1 or more, and further preferably 3 or more; and from the same viewpoints, preferably 50 or less, more

preferably 30 or less, further preferably 20 or less, and further more preferably 10 or less.

The alkylene oxide is, from the viewpoints of the mixing stability and the foaming property, preferably one or more types selected from ethylene oxide, propylene oxide and butylene oxide, and more preferably one or more types selected from ethylene oxide and propylene oxide.

[0071]

Preferred examples of the nonionic surfactant as component (c2) include nonionic surfactants represented by the following general formula (c2):



wherein R^{12c} represents a hydrocarbon group with 6 or more and 22 or less carbons. l and j represent an average number of added moles; l represents a number of 0 or more and 30 or less; j represents a number of 0 or more and 30 or less; and l and j are not simultaneously zero. The sign "/" indicates that an oxyethylene group and an oxypropylene group may be added in either of random and block states regardless of the order thereof.

[0072]

The carbon number of R^{12c} in the above general formula (c2) is, from the viewpoints of the mixing stability

and the foaming property, preferably 8 or more, more preferably 10 or more, and further preferably 12 or more; and from the same viewpoints, preferably 18 or less, more preferably 16 or less, and further preferably 14 or less.

R^{12c} is, from the viewpoints of the mixing stability and the foaming property, preferably an alkyl group or an alkenyl group, more preferably an alkyl group, and from the viewpoints of the mixing stability and the foaming property, a secondary alkyl group. The secondary alkyl group used herein refers to an alkyl group wherein in $R^{12c}O$ of the general formula (c2), a carbon of R^{12c} to be bonded to O is a secondary carbon.

Specific examples of the alkyl group include various octyl groups (including 2-ethyl hexyl group), various nonyl groups, various decyl groups, various undecyl groups, various dodecyl groups (lauryl groups), various tridecyl groups, various tetradecyl groups, various pentadecyl groups, various hexadecyl groups, various heptadecyl groups, and various octadecyl groups.

Examples of the alkenyl group include various octanyl groups, various nonanyl groups, various decanyl groups, various undecanyl groups, various dodecanyl groups, various tridecanyl groups, various tetradecanyl groups, various pentadecanyl groups, various hexadecanyl groups, various heptadecanyl

groups, and various octadecanyle groups (for example, oleyl group, linoleic group). The term "various" used herein means various isomers including n-, sec-, tert-, and iso-isomers.

[0073]

Polyoxyalkylene mono-alkyl or alkenyl ether, further the nonionic surfactant represented by the general formula (c2) has an HLB value of, from the viewpoints of the mixing stability and the foaming property, preferably 5 or more, and more preferably 7 or more; and from the same viewpoints, preferably 19 or less, more preferably 15 or less, and further preferably 13 or less.

The HLB values used herein is defined by the Griffin's formula described below:

$$\text{HLB value} = 20 \times \text{Mw} / \text{M}$$

wherein M is a molecular weight of the nonionic surfactant, and Mw is a molecular weight of a hydrophilic portion of the nonionic surfactant. Note that in the general formula (c2), the hydrophilic portion is a total of portions of an oxyethylene group and an oxypropylene group.

[0074]

Component (c3)

Component (c3) is an alkyl polyglycoside

(glycoside-type nonionic surfactant).

The nonionic surfactant of component (c3) is preferably a nonionic surfactant represented by the following general formula (c3):



wherein R^{13c} represents a straight- or branched-chain alkyl group, alkenyl group or alkylphenyl group with 8 or more and 18 or less carbons, and preferably 12 or more and 14 or less carbons; preferably an alkyl group. R^{14c} represents an alkylene group with 2 or more and 4 or less carbons. G represents a residue derived from reducing sugar with 5 or 6 carbons. s represents an average number of added moles and is a number of 0 or more and 5 or less. t represents a number of 1 or more and 5 or less, which is an average value thereof.

[0075]

In the general formula (c3), R^{13c} is, from the viewpoints of the mixing stability and the foaming property, a straight- or branched-chain alkyl group with 8 or more, and preferably 10 or more carbons; and 18 or less, and preferably 14 or less carbons.

In the general formula (c3), s is, from the viewpoints of the mixing stability and the foaming property, 0 or more, and 2 or less, and more preferably 0. t is, from the viewpoints of the mixing stability

and the foaming property, preferably 1.1 or more; and preferably 1.5 or less, and more preferably 1.4 or less. Note that t is a value measured by proton NMR method.

In the general formula (c3), in terms of the availability and the cost, exemplified as G is a residue derived from one or more monosaccharides selected from glucose and fructose. In addition, exemplified as G is a residue derived from one or more polysaccharides selected from maltose and sucrose. G is preferably a residue derived from a monosaccharide of glucose.

[0076]

Components (c4) to (c7)

(c4) a sorbitan-based nonionic surfactant, (c5) aliphatic alkanolamide, (c6) fatty acid monoglyceride and (c7) sucrose fatty acid ester each have a straight- or branched-chain alkyl group with preferably 8 or more and 18 or less carbons, and more preferably 12 or more and 14 or less carbons.

[0077]

[Anionic surfactant]

The anionic surfactant is preferably an anionic surfactant having a sulfuric ester group, a phosphoric ester group, a phosphonic acid group, a sulfonic acid group or a carboxy group.

The anionic surfactant has a hydrocarbon group. From the viewpoints of the mixing stability and the foaming property, the hydrocarbon group possessed by

the anionic surfactant has a carbon number of preferably 5 or more, more preferably 6 or more, further preferably 7 or more, further more preferably 8 or more, further more preferably 10 or more, and further more preferably 12 or more; and preferably 21 or less, more preferably 18 or less, further preferably 16 or less, and further more preferably 14 or less. The hydrocarbon group is preferably a straight- or branched-chain alkyl group, alkylene group or aryl group.

[0078]

The anionic surfactant is preferably one or more anionic surfactants selected from the group consisting of: (c8) sulfosuccinate or salt thereof having a hydrocarbon group with 5 or more and 18 or less carbons [hereinafter, referred to as component (c8)]; (c9) an anionic surfactant having a hydrocarbon group with 8 or more and 21 or less carbons and having a sulfuric ester group or a sulfonic acid group [provided that component (c8) is excluded] [hereinafter, referred to as component (c9)]; (c10) an anionic surfactant having a hydrocarbon group with 7 or more and 21 or less carbons and having a carboxy group [hereinafter, referred to as component (c10)]; and (c11) an anionic surfactant having a hydrocarbon group with 8 or more and 21 or less carbons and having a phosphoric ester group [hereinafter, referred to as component (c11)]. These

may be used in combination of two or more thereof.

[0079]

From the viewpoints of the mixing stability and the foaming property, the anionic surfactant preferably includes one or more types selected from the group consisting of component (c8) and component (c9), and more preferably includes component (c9).

In addition, a content of component (c9) in the anionic surfactant is, from the viewpoints of the mixing stability and the foaming property, preferably 50 mass% or more, more preferably 70 mass% or more, further preferably 80 mass% or more, further more preferably 90 mass% or more, further more preferably 95 mass% or more, and further more preferably 99 mass% or more; and preferably 100 mass% or less.

Note that a content (mass%) of each component in the anionic surfactant is calculated based on the amount in terms of sodium salts.

[0080]

Component (c9) used in the present invention is an anionic surfactant [provided that component (c8) is excluded] having a hydrocarbon group with 8 or more and 21 or less carbons and having a sulfuric ester group or a sulfonic acid group.

[0081]

The hydrocarbon group of component (c9) has a carbon number of, from the viewpoints of the mixing stability

and the foaming property, preferably 8 or more, preferably 10 or more, and more preferably 12 or more; and 21 or less, preferably 18 or less, more preferably 14 or less, and further preferably 12 or less. The hydrocarbon group of component (c9) is preferably an alkyl group or aryl group.

[0082]

As the anionic surfactant of component (c9), preferred is one or more types selected from an alkyl sulfuric ester salt, a polyoxyalkylene alkyl ether sulfuric ester salt, and an alkane sulfonic acid salt.

[0083]

As the anionic surfactant having a sulfuric ester group, suitable is, from the viewpoints of the mixing stability and the foaming property, an alkyl sulfuric ester salt having a straight- or branched chain alkyl group with 8 or more, and preferably 10 or more carbons; and 21 or less, preferably 18 or less, more preferably 14 or less, and further preferably 12 or less carbons.

In addition, as the anionic surfactant having a sulfuric ester group and a polyoxyalkylene group, suitable is a polyoxyalkylene alkyl ether sulfuric ester salt having a straight- or branched-chain alkyl group with 8 or more, and preferably 10 or more; and 21 or less, preferably 18 or less, more preferably 14 or less, and further preferably 12 or less carbons; and having a polyoxyalkylene group wherein the average

number of added moles of the oxyalkylene group with 2 or more and 3 or less carbons is preferably 0.1 or more, more preferably 0.3 or more, and further preferably 0.4 or more; and preferably 6 or less, more preferably 5 or less, and further preferably 4 or less.

In addition, as the anionic surfactant having a sulfonic acid group, from the viewpoints of the mixing stability and the foaming property, suitable is one or more anionic surfactants selected from:

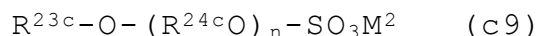
- (1) an alkylbenzene sulfonic acid salt having an alkyl group with 6 or more and 15 or less carbons; and
- (2) an alkane sulfonic acid salt with 8 or more, and preferably 10 or more; and 21 or less, preferably 18 or less, more preferably 14 or less, and further preferably 12 or less carbons.

[0084]

As a salt of the anionic surfactant of component (c9), suitable are an inorganic salt selected from a sodium salt, an ammonium salt, a potassium salt, and a magnesium salt, and an organic ammonium salt selected from a monoethanol ammonium salt, a diethanol ammonium salt, a triethanol ammonium salt, and a morpholinium salt.

[0085]

As component (c9), compounds of the following general formula (c9) are suitable from the viewpoints of the mixing stability and the foaming property:



wherein R^{23c} is a straight- or branched-chain alkyl group with 8 or more and 21 or less carbons, R^{24c} is an ethylene group and/or a propylene group, and n is an average number of added moles of 0 or more and 6 or less. M^2 is a hydrogen atom or a cation, and preferably an inorganic or organic cation.

[0086]

In the general formula (c9), R^{23c} is, from the viewpoint of the detergency, a straight- or branched-chain alkyl group, with 8 or more, and preferably 10 or more; and 21 or less, preferably 18 or less, more preferably 14 or less, and further preferably 12 or less carbons, and preferably a straight-chain alkyl group. Specifically, R^{23c} is preferably an alkyl group selected from an octyl group, a decyl group, a dodecyl group, a tridecyl group and a tetradecyl group, and more preferably a dodecyl group.

[0087]

In the general formula (c9), n is, from the viewpoint of the foaming property, preferably 0 or more; and preferably 6 or less, more preferably 4 or less, further preferably 3 or less, and further more preferably 1.5 or less. Also, n may be 0.

In the general formula (c9), when R^{24c} is an ethylene group, n is, from the viewpoint of the foaming property, a number of preferably 0.1 or more, and more preferably 0.5 or more; and preferably 6 or less, and more preferably 3 or less.

In addition, when R^{24c} in the general formula (c9) is a propylene group, n is, from the viewpoint of the foaming property, a number of preferably 0.1 or more, more preferably 0.2 or more, and further preferably 0.4 or more; and preferably 1.5 or less, more preferably 1.0 or less, and further preferably 0.8 or less.

In addition, when R^{24c} in the general formula (c9) is an ethylene group and a propylene group, n may be selected from the above-described scope for each of these groups.

[0088]

In the general formula (c9), M^2 is: a hydrogen atom; an inorganic cation such as sodium ion, ammonium ion, potassium ion, and magnesium ion; and an organic cation such as monoethanol ammonium ion, diethanol ammonium ion, triethanol ammonium ion and morpholinium ion, and M^2 is preferably an inorganic cation selected from sodium ion, potassium ion, ammonium ion and magnesium ion.

[0089]

When obtaining a compound in which R^{23c} is a branched-chain alkyl group in the general formula (c9),

exemplified as an alcohol represented by R^{23c} -OH being a raw material are: an alcohol obtained by hydroformylating 1-alkene with 8 or more and 14 or less carbons (containing 15 mol% or more and 70 mol% or less of alkyl group wherein a methyl group is branched at position β relative to an OH group); a Guerbet-type alcohol obtained by condensing and reducing aldehyde with 4 or more and 8 or less carbons (containing 100 mol% of alcohol having a structure where an alkyl group with 3 or more and 6 or less carbons is branched at β position relative to an OH group); 3,5,5-trimethyl hexanol obtained by hydroformylating a dimer of isobutene; a multiple-branched tridecanol obtained by hydroformylating a trimer of isobutene (branching fraction of 100 mol%); and a synthesized alcohol obtained by using petroleum or coal (an alkyl group wherein the branching fraction is approximately 20 mol% or more and 100 mol% or less).

[0090]

Component (c10) used in the present invention is an anionic surfactant having a hydrocarbon group with 7 or more and 21 or less carbons and having a carboxy group.

Specifically, exemplified are a higher fatty acid or salt thereof, a polyoxyethylene alkyl ether carboxylic acid or salt thereof, and N-acyl amino acid or salt thereof.

[0091]

As the higher fatty acid or salt thereof, those represented by the following general formula (c10-1) are preferred:



wherein R^{25c} represents an alkyl group or alkenyl group with 7 or more and 21 or less carbons, and X^{1c} represents a hydrogen atom, an alkaline metal, an alkaline-earth metal, ammonium, alkanol ammonium or a basic amino acid.

More specifically, exemplified as the higher fatty acid or salt thereof are lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, oleic acid, arachidic acid, behenic acid, and salts thereof. Among these, lauric acid, myristic acid, palmitic acid, and salts thereof are preferred.

[0092]

The polyoxyethylene alkyl ether carboxylic acid or salt thereof is preferably one represented by the following general formula (c10-2):



wherein R^{26c} represents an alkyl group or alkenyl group with 7 or more, preferably 8 or more and 21 or less

carbons, g is an average number of added moles of ethylene oxide and represents a number of 0.5 or more and 10 or less, and X^{2c} represents a hydrogen atom, an alkali metal, an alkaline-earth metal, ammonium, alkanol ammonium or a basic amino acid.

[0093]

In another aspect, the liquid detergent composition for hard surfaces of the present invention is a liquid detergent composition for hard surfaces containing component (a), component (b) and component (d). For the liquid detergent composition for hard surfaces, specific examples and preferred embodiments of components (a) and (b) are as described above.

[0094]

<Component (d)>

Component (d) is a chelating agent. The chelating agent is preferably one or more compounds selected from aminocarboxylic acid, hydroxycarboxylic acid, hydroxyphosphonic acid, and salts thereof.

As the aminocarboxylic acid and salts thereof, exemplified are one or two or more types selected from ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), iminodiacetic acid, diethylene triamine penta-acetic acid (DTPA), N-hydroxyethyl-ethylene diamine triacetic acid (HEDTA), methylglycinediacetic acid (MGDA), asparaginediacetic acid (ASDA), glutaminediacetic

acid (GLDA), and salts thereof. The aminocarboxylic acid and salts thereof are preferably one or two or more types selected from ethylenediaminetetraacetic acid and salt thereof, methylglycinediacetic acid and salt thereof, and L-glutaminediacetic acid and salt thereof.

As the hydroxycarboxylic acid and salts thereof, preferred is a compound selected from aliphatic hydroxycarboxylic acids and salts thereof. As the hydroxycarboxylic acid and salts thereof, exemplified is a compound selected from malic acid, citric acid and salts thereof.

As the hydroxyphosphonic acid and salts thereof, exemplified is a compound selected from 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) and salts thereof.

Examples of salts of the chelating agent include alkaline metal salts, ammonium salts, amine salts and others. They are preferably alkaline metal salts, more preferably sodium salts or potassium salts.

The chelating agent is preferably one or more compounds selected from aminocarboxylic acid, hydroxycarboxylic acid, and salts thereof, more preferably aminocarboxylic acid or salt thereof, and further preferably ethylenediaminetetraacetic acid or salt thereof.

[0095]

<Composition, optional component, etc.>

In the liquid detergent composition for hard surfaces of the present invention, a content of component (a) is, from the viewpoints of hydrophilizing a hard surface and imparting a stain prevention effect, preferably 0.01 mass% or more, more preferably 0.05 mass% or more, and further preferably 0.1 mass% or more; and from the viewpoint of the mixing stability, preferably 3 mass% or less, more preferably 2 mass% or less, further preferably 1 mass% or less, further more preferably 0.8 mass% or less, further more preferably 0.5 mass% or less, and further more preferably 0.4 mass% or less.

[0096]

In addition, in the liquid detergent composition for hard surfaces, a content of component (b) is, from the viewpoint of the sterilization capability, preferably 0.01 mass% or more, more preferably 0.05 mass% or more, further preferably 0.1 mass% or more, and further more preferably 0.2 mass% or more; and from the viewpoint of the mixing stability, preferably 5 mass% or less, more preferably 4 mass% or less, further preferably 3 mass% or less, further more preferably 2 mass% or less, and further more preferably 1.5 mass% or less.

[0097]

In the liquid detergent composition for hard surfaces of the present invention, a mass ratio of

(a)/(b) is, from the viewpoint of the stain adhesion prevention, preferably 0.01 or more, more preferably 0.05 or more, further preferably 0.1 or more, and further more preferably 0.15 or more; and from the viewpoint of the mixing stability, preferably 5 or less, more preferably 4 or less, further preferably 3 or less, further more preferably 2 or less, and further more preferably 1 or less. When the liquid detergent composition for hard surfaces of the present invention contains component (d), the above upper limits are preferred from the viewpoint of the sterilization performance.

[0098]

In addition, in the liquid detergent composition for hard surfaces of the present invention containing component (c), a content of component (c) is, from the viewpoint of the foaming property, preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further preferably 0.15 mass% or more; and from the viewpoint of the economic efficiency (low cost), preferably 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, and further more preferably 3 mass% or less.

[0099]

In addition, when component (c) includes an amphoteric surfactant, a content of the amphoteric surfactant in the liquid detergent composition for hard

surfaces of the present invention containing component (c) is, from the viewpoint of the foaming property, preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further preferably 0.15 mass% or more; and from the viewpoint of the economic efficiency (low cost), preferably 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, and further more preferably 3 mass% or less.

In addition, when component (c) includes a nonionic surfactant, a content of the nonionic surfactant in the liquid detergent composition for hard surfaces of the present invention containing component (c) is, from the viewpoint of the foaming property, preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further preferably 0.15 mass% or more; and from the viewpoint of the economic efficiency (low cost), preferably 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, and further more preferably 3 mass% or less.

In addition, when component (c) includes an anionic surfactant, a content of the anionic surfactant in the liquid detergent composition for hard surfaces of the present invention containing component (c) is, from the viewpoint of the foaming property, preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further preferably 0.15 mass% or more; and from the viewpoints of the economic efficiency (low cost) and

the mixing stability, preferably 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, further more preferably 3 mass% or less, and further more preferably 1 mass% or less.

[0100]

In addition, in the liquid detergent composition for hard surfaces of the present invention containing component (c), a mass ratio of (b)/(c) is, from the viewpoint of the sterilization performance, preferably 0.05 or more, more preferably 0.1 or more, and further preferably 0.15 or more; and from the viewpoint of the foaming, preferably 30 or less, more preferably 25 or less, further preferably 20 or less, and further more preferably 10 or less.

[0101]

In addition, in the liquid detergent composition for hard surfaces of the present invention containing component (d), a content of component (d) is, from the viewpoint of the detergency, preferably 0.01 mass% or more, more preferably 0.05 mass% or more, further preferably 0.1 mass% or more, further more preferably 0.2 mass% or more, and further more preferably 0.5 mass% or more; and from the viewpoints of the economic efficiency and the mixing stability, preferably 10 mass% or less, more preferably 9 mass% or less, further preferably 8 mass% or less, further more preferably 6 mass% or less, further more preferably 5 mass% or less,

and further more preferably 4 mass% or less. Note that the mass of component (d) is an acid conversion value (the same is applied to other quantity ratios related to the mass of component (d)).

[0102]

In addition, in the liquid detergent composition for hard surfaces of the present invention containing component (d), a mass ratio of (b)/(d) is, from the viewpoint of the sterilization performance, preferably 0.01 or more, more preferably 0.03 or more, further preferably 0.05 or more, further preferably 0.1 or more, and further more preferably 0.15 or more; and from the viewpoints of the mixing stability and the detergency, preferably 10 or less, more preferably 5 or less, further preferably 3 or less, further more preferably 1 or less, and further more preferably 0.8 or less.

[0103]

The liquid detergent composition for hard surfaces of the present invention containing component (d) may contain a surfactant other than component (d). Exemplified as such a surfactant is component (c), that is, one or more surfactants selected from amphoteric surfactants, nonionic surfactants and anionic surfactants. From the viewpoint of the mixing stability, component (c) is preferably one or more surfactants selected from amphoteric surfactants and

nonionic surfactants. In this case, specific examples and preferred embodiments of component (c) are as described above. In addition, for the liquid detergent composition for hard surfaces of the present invention containing component (d), the viewpoint of the detergency may be added to the viewpoints as the reasons that component (c) is preferred,.

[0104]

When the liquid detergent composition for hard surfaces of the present invention containing component (d) contains component (c), a content of component (c) in the composition is, from the viewpoint of the foaming, preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further more preferably 0.15 mass% or more; and from the viewpoint of the low cost, preferably 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, and further more preferably 3 mass% or less.

[0105]

In addition, when the liquid detergent composition for hard surfaces of the present invention containing component (d) contains an amphoteric surfactant, a content of the amphoteric surfactant in the composition is, from the viewpoint of the foaming property, preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further preferably 0.15 mass% or more; and from the viewpoint of the economic efficiency

(low cost), preferably 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, and further more preferably 3 mass% or less.

In addition, when the liquid detergent composition for hard surfaces of the present invention containing component (d) contains a nonionic surfactant, a content of the nonionic surfactant in the composition is, from the viewpoint of the foaming property, preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further preferably 0.15 mass% or more; and from the viewpoint of the economic efficiency (low cost), preferably 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, and further more preferably 3 mass% or less.

In addition, when the liquid detergent composition for hard surfaces of the present invention containing component (d) contains an anionic surfactant, a content of the anionic surfactant in the composition is, from the viewpoint of the foaming property, preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further preferably 0.15 mass% or more; and from the viewpoints of the economic efficiency (low cost) and the mixing stability, preferably 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, further preferably 3 mass% or less, and further more preferably 1 mass% or less.

[0106]

The liquid detergent composition for hard surfaces of the present invention contains water. That is, the remainder other than component (a), component (b), component (c) and/or component (d), and an optional component is water.

In the liquid detergent composition for hard surfaces of the present invention, a content of water is preferably 30 mass% or more, more preferably 50 mass% or more, and further preferably 60 mass% or more; and preferably 95 mass% or less, and more preferably 93 mass% or less.

The water to be used is preferably ion-exchanged water, sterilized ion-exchanged water, etc.

[0107]

The liquid detergent composition for hard surfaces of the present invention has a pH at 20°C of preferably 4 or more, more preferably 5 or more, and further preferably 6 or more; and preferably 10 or less, more preferably 9 or less, and further preferably 8 or less.

[0108]

The liquid detergent composition for hard surfaces of the present invention may additionally contain, in such a range that objects of the present invention are not deteriorated, a polyvalent carboxylic acid such as polyacrylic acid, polymethacrylic acid, polymaleic acid, poly 2-acrylamide-2-methylpropane sulfonic acid and poly p-styrene sulfonic acid; a lower alcohol such

as ethyl alcohol and isopropyl alcohol;
a solvent such as diethylene glycol monobutyl ether;
a solubilizing agent such as toluenesulfonate,
xylenesulfonate and urea; a viscosity modifier such as
clay mineral and a water-soluble polymer compound
(provided that component (a) is excluded); a
water-insoluble abrasive such as calcite, silica
stone, calcium phosphate, zeolite, calcium carbonate,
polyethylene, nylon and polystyrene; a humectant such
as glycerin and sorbitol; a touch improver such as
cationized cellulose (provided that component (a) is
excluded); an alkali builder such as sodium carbonate
and sodium silicate; enzyme; coloring matter; perfume;
and antiseptic·antifungal agent.

[0109]

[Method for preventing stain adhesion on hard surfaces]

The present invention relates to a method for
preventing a stain from adhering to a hard surface,
which includes treating the hard surface with the
liquid detergent composition for hard surfaces of the
present invention.

[0110]

The hard surface is not particularly limited, and
examples thereof include solid hard surfaces of: glass,
earthenware, porcelain, porcelain enamel, tile,
ceramics; metals such as aluminum, stainless and brass;
synthetic resins such as polyethylene, polypropylene,

a melamine resin, a polyamide resin, an ABS resin, and FRP; natural fibers such as cotton, silk and wool; and synthetic fibers such as polyester, nylon and rayon. Fiber is suitably in the form of fiber products having a shape or strength suitable for treatment with the liquid detergent composition for hard surfaces of the present invention.

As the surface to which the composition and the treatment method of the present invention are applicable, hydrophilic hard surfaces are preferred. The term "hydrophilic" used herein for a hard surface means that a stationary contact angle relative to water is less than 70° . Note that such a stationary contact angle can be measured by the method described in the examples.

As the hard surface suitable for the present invention, exemplified are one or two or more hard surfaces selected from glass, earthenware, porcelain, plastics, stainless and silicon wafer.

[0111]

Targets of the present invention are hard surfaces, specifically, articles having a hard surface. Examples of articles having a hard surface include a toilet bowl, a bathtub, a kitchen sink, window glass, a mirror and a faucet.

[0112]

In the method for preventing stain adhesion of the

prevent invention, it is preferred to use the liquid detergent composition for hard surfaces of the present invention containing component (a), component (b), component (c) and/or component (d) in the above amounts.

[0113]

Treatment of a hard surface with the liquid detergent composition for hard surfaces of the present invention can be carried out by bringing the hard surface into contact with the liquid detergent composition for hard surfaces of the present invention. A method for providing contact between the liquid detergent composition for hard surfaces of the present invention and the hard surface is not particularly limited. Examples thereof include the following methods (i) and (ii).

(i) a method for soaking an article having a hard surface in a liquid detergent composition for hard surfaces of the present invention

(ii) a method for spraying or applying the liquid detergent composition for hard surfaces of the present invention onto a hard surface

[0114]

In the above method (i), a period for soaking is, from the viewpoints of enhancing the antifouling property and the economic efficiency, preferably 0.5 minutes or longer, and more preferably 1 minute or

longer; and preferably 60 minutes or shorter, and more preferably 50 minutes or shorter.

In the above method (ii), a method for spraying or applying the liquid detergent component for hard surfaces of the present invention onto a hard surface can be appropriately selected depending on the size (area) of a hard surface. A method including spraying the liquid detergent composition for hard surfaces of the present invention onto a hard surface by a spray, etc. and drying it is preferred. In accordance with the necessity, rinsing with water may be carried out after spraying. In addition, the composition may be thinly spread by use of a sponge after being sprayed. Alternatively, the liquid detergent composition for hard surfaces of the present invention may be discharged from a discharging container such as a squeeze bottle and directly applied to a hard surface.

The amount of the liquid detergent composition for hard surfaces of the present invention to be sprayed or applied to a hard surface is preferably 0.01 mL or and 1 mL or less, more preferably 0.01 mL or more and 0.1 mL or less, for example, per 10 cm².

[0115]

The temperature of the liquid detergent composition for hard surfaces of the present invention for treating a hard surface is, from the viewpoint of enhancing the antifouling performance and the viewpoint of the

easiness of treatment method, preferably 5°C or higher, more preferably 10°C or higher, and further preferably 15°C or higher; and preferably 50°C or lower, more preferably 40°C or lower, and further preferably 30°C or lower.

[0116]

In addition, from the viewpoints of imparting the hydrophilicity to a hard surface and enhancing the antifouling performance, a stationary contact angle relative to water of a hard surface, preferably a hydrophilic hard surface, and more preferably a glass surface, which are treated with the liquid detergent composition for hard surfaces of the present invention, is preferably 20° or less, more preferably 15° or less, further preferably 10° or less, and further more preferably 8° or less; and preferably 1° or more. Imparting the hydrophilicity to a hard surface in this way can enhance the antifouling performance onto a hard surface relative to a hydrophobic substance. The stationary contact angle of a glass surface relative to water can be obtained by the method described in the examples.

In addition, the hard surface treated with the liquid detergent composition for hard surfaces of the present invention is preferably treated uniformly from the viewpoint of enhancing the antifouling performance. The uniformity of surface treatment can be determined

by visual observation of a treated hard surface.

Further, when the hard surface is a toilet bowl, the liquid detergent composition for hard surfaces of the present invention can be used in a method including dissolving the composition in washing water in a tank and continuously washing the toilet bowl. In this case, a predetermined amount of the composition may be dropped automatically or manually into a toilet tank.
[0117]

<Embodiments of the present invention>

Hereafter, embodiments of the present invention are exemplified. The matters mentioned for a liquid detergent composition for hard surfaces and a method for stain adhesion prevention of the present invention are appropriately applicable to these embodiments.
[0118]

<1a>

A liquid detergent composition for hard surfaces containing:

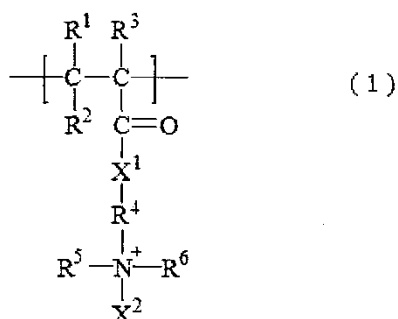
(a) a copolymer [hereinafter, referred to as component (a)] containing a constituent unit (a1) represented by the following formula (1) and a constituent unit (a2) represented by the following formula (2), wherein a molar ratio between the constituent unit (a1) and the constituent unit (a2), constituent unit (a1)/constituent unit (a2), is 30/70 or more and 99.9/0.1 or less;

(b) a cationic surfactant [hereinafter, referred to as component (b)]; and

(c) one or more surfactants [hereinafter, referred to as component (c)] selected from amphoteric surfactants, nonionic surfactants and anionic surfactants,

[0119]

[Chemical formula 11]



[0120]

wherein

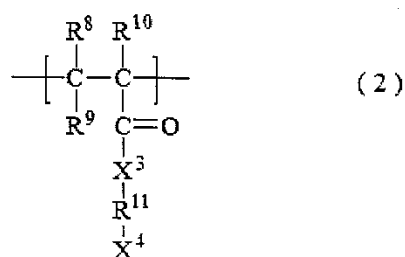
R¹ to R³ are the same or different and represent a hydrogen atom or an alkyl group with 1 to 2 carbons; R⁴ represents an alkylene group with 1 or more and 4 or less carbons or -Y¹-OPO₃⁻-Y²-,

Y¹ and Y² are the same or different and represent an alkylene group with 1 or more and 4 or less carbons; R⁵ and R⁶ are the same or different and represent a hydrocarbon group with 1 or more and 4 or less carbons; X¹ is O or NR⁷, and R⁷ represents a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons; and

X² represents a hydrogen atom, a hydrocarbon group with 1 or more and 4 or less carbons, R¹⁷SO₃⁻ or R¹⁷COO⁻, with the proviso that: when R⁴ is an alkylene group with 1 or more and 4 or less carbons, X² is R¹⁷SO₃⁻ or R¹⁷COO⁻, wherein R¹⁷ is an alkylene group with 1 or more and 4 or less carbons; and when R⁴ is -Y¹-OPO₃⁻-Y²-, X² is a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons,

[0121]

[Chemical formula 12]



[0122]

wherein

R⁸ to R¹⁰ are the same or different and represent a hydrogen atom or an alkyl group with 1 or 2 carbons; X³ represents O;

R¹¹ represents an alkylene group with 1 or more and 4 or less carbons; and

X⁴ is N⁺R¹²R¹³R¹⁴X⁵ or NR¹⁵R¹⁶, wherein R¹² to R¹⁶ are the same or different and represent a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons, and X⁵ represents an anion.

[0123]

<2a>

The liquid detergent composition for hard surfaces described in <1a>, wherein component (a) has a weight average molecular weight of preferably 500 or more, more preferably 5000 or more, further preferably 10000 or more, and further more preferably 30000 or more; and preferably 200000 or less, more preferably 150000 or less, and further preferably 100000 or less.

[0124]

<3a>

The liquid detergent composition for hard surfaces described in <1a> or <2a>, wherein a molar ratio of constituent units (a1) and (a2) of component (a), constituent unit (a1)/constituent unit (a2), is 30/70 or more, preferably 50/50 or more, more preferably 55/45 or more, further preferably 60/40 or more, further more preferably 75/25 or more, and further more preferably 90/10 or more; and 99.9/0.1 or less, preferably 98/2 or less, and more preferably 96/4 or less.

[0125]

<4a>

The liquid detergent composition for hard surfaces described in any of <1a> to <3a>, wherein a content of constituent unit (a1) in component (a) is preferably 30 mol% or more, more preferably 50 mol% or more, further preferably 70 mol% or more, further more preferably 80

mol%, and further more preferably 90 mol% or more; and preferably 99 mol% or less, more preferably 98 mol% or less, and further preferably 95 mol% or less.

[0126]

<5a>

The liquid detergent composition for hard surfaces described in any of <1a> to <4a>, wherein a content of constituent unit (a2) in component (a) is preferably 1 mol% or more, more preferably 2 mol% or more, and further preferably 5 mol% or more; and preferably 70 mol% or less, more preferably 50 mol% or less, further preferably 30 mol% or less, further preferably 20 mol% or less, and further preferably 10 mol% or less.

[0127]

<6a>

The liquid detergent composition for hard surfaces described in any of <1a> to <5a>, wherein a content of constituent units other than constituent units (a1) and (a2) in component (a) is preferably 10 mol% or less, more preferably 5 mol% or less, more preferably 1 mol% or less, further preferably 0.5 mol% or less, and further more preferably 0.1 mol% or less, or 0 mol%.

[0128]

<7a>

The liquid detergent composition for hard surfaces described in any of <1a> to <6a>, wherein a total content of constituent units (a1) and (a2) in component (a) is

preferably 90 mol% or more, more preferably 95 mol% or more, further preferably 99 mol% or more, further more preferably 99.5 mol% or more, and further more preferably 99.9 mol% or more, or 100 mol%.

[0129]

<8a>

The liquid detergent composition for hard surfaces described in any of <1a> to <7a>, wherein component (b) is a cationic surfactant selected from mono- or di-long-chain alkyl quaternary ammonium salts.

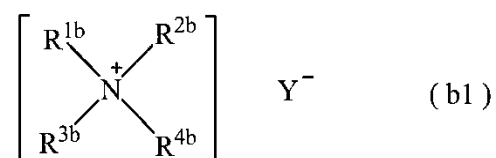
[0130]

<9a>

The liquid detergent composition for hard surfaces described in any of <1a> to <8a>, wherein component (b) is a cationic surfactant selected from compounds represented by the following general formula (b1) and compounds represented by the following formula (b2):

[0131]

[Chemical formula 13]



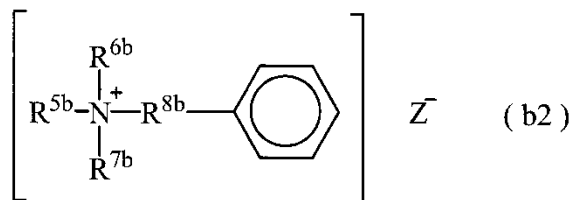
[0132]

wherein at least one selected from R^{1b} and R^{2b} represents an alkyl group with 8 or more and 18 or less carbons, an alkenyl group with 8 or more and 18 or less carbons

or a hydroxyalkyl group with 8 or more and 18 or less carbons, and the remainder represents an alkyl group with 1 or more and 3 or less carbons, a hydroxyalkyl group with 1 or more and 3 or less carbons or a polyoxyethylene group with an average number of added moles of 10 or less; R^{3b} and R^{4b} are the same or different and each represent an alkyl group with 1 or more and 3 or less carbons, a hydroxyalkyl group with 1 or more and 3 or less carbons or a polyoxyethylene group with an average number of added moles of 10 or less; and Y^- represents a halogen atom, or an anionic residue of a sulfonic acid ester or a sulfuric ester with 1 or more and 5 or less carbons,

[0133]

[Chemical formula 14]



[0134]

wherein R^{5b} represents an alkyl group with 8 or more and 18 or less carbons, an alkenyl group with 8 or more and 18 or less carbons or a hydroxyalkyl group with 8 or more and 18 or less carbons, R^{6b} and R^{7b} are the same or different and each represent an alkyl group with 1 or more and 3 or less carbons, a hydroxyalkyl group with 1 or more and 3 or less carbons or a polyoxyethylene

group with an average number of added moles of 10 or less, and R^{8b} represents an alkylene group with 1 or more and 3 or less carbons. Z- represents a halogen atom, or an anionic residue of a sulfonic acid ester or a sulfuric ester with 1 or more and 5 or less carbons.

[0135]

<10a>

The liquid detergent composition for hard surfaces described in any of <1a> to <9a>, wherein component (c) is one or more surfactants selected from amphoteric surfactants and nonionic surfactants.

[0136]

<11a>

The liquid detergent composition for hard surfaces described in any of <1a> to <10a>, wherein the amphoteric surfactant is one or more amphoteric surfactants selected from amine oxide, sulfobetaine and carboxobetaine, preferably one or more amphoteric surfactants selected from sulfobetaine and carboxobetaine, and more preferably carboxobetaine.

[0137]

<12a>

The liquid detergent composition for hard surfaces described in any of <1a> to <11a>, wherein a content of one or more amphoteric surfactants selected from amine oxide, sulfobetaine and carboxobetaine in the amphoteric surfactant is preferably 50 mass% or more,

more preferably 70 mass% or more, further preferably 80 mass% or more, further more preferably 90 mass% or more, further more preferably 95 mass% or more, and further more preferably 99 mass% or more; and preferably 100 mass% or less.

[0138]

<13a>

The liquid detergent composition for hard surfaces described in any of <1a> to <12a>, wherein a content of one or more amphoteric surfactants selected from sulfobetaine and carbobetaine in the amphoteric surfactant is preferably 50 mass% or more, more preferably 70 mass% or more, further preferably 80 mass% or more, further more preferably 90 mass% or more, further more preferably 95 mass% or more, and further more preferably 99 mass% or more; and preferably 100 mass% or less.

[0139]

<14a>

The liquid detergent composition for hard surfaces described in any of <1a> to <13a>, wherein the nonionic surfactant is one or more nonionic surfactants selected from the group consisting of (c1) monoalkyl glyceryl ether [hereinafter, referred to as component (c1)], (c2) polyoxyalkylene monoalkyl or alkenyl ether [hereinafter, referred to as component (c2)], (c3) alkyl polyglycoside (glycoside-type nonionic

surfactant) [hereinafter, referred to as component (c3)], (c4) a sorbitan-based nonionic surfactant [hereinafter, referred to as component (c4)], (c5) aliphatic alkanolamide [hereinafter, referred to as component (c5)], (c6) fatty acid monoglyceride [hereinafter, referred to as component (c6)], and (c7) sucrose fatty acid ester [hereinafter, referred to as component (c7)].

[0140]

<15a>

The liquid detergent composition for hard surfaces described in <14a>, wherein the nonionic surfactant is one or more nonionic surfactants selected from component (c1), component (c2) and component (c3), and preferably (c3).

[0141]

<16a>

The liquid detergent composition for hard surfaces described in <14a> or <15a>, wherein a content of component (c3) in the nonionic surfactant is preferably 50 mass% or more, more preferably 70 mass% or more, further preferably 80 mass% or more, further more preferably 90 mass% or more, further more preferably 95 mass% or more, and further more preferably 99 mass% or more; and preferably 100 mass% or less.

[0142]

<17a>

The liquid detergent composition for hard surfaces described in <1a> to <16a>, wherein the anionic surfactant is an anionic surfactant having a sulfuric ester group, a phosphoric ester group, a phosphonic acid group, sulfonic acid group or a carboxy group.

[0143]

<18a>

The liquid detergent composition for hard surfaces described in <1a> to <17a>, wherein the anionic surfactant has a hydrocarbon group, the hydrocarbon group has preferably 5 or more, more preferably 6 or more, further preferably 7 or more, further more preferably 8 or more, further more preferably 10 or more, and further more preferably 12 or more carbons; and preferably 21 or less, more preferably 18 or less, further preferably 16 or less, and further more preferably 14 or less carbons, and the hydrocarbon group is a straight- or branched-chain alkyl group, alkylene group or aryl group.

[0144]

<19a>

The liquid detergent composition for hard surfaces described in any <1a> to <18a>, wherein the anionic surfactant is one or more anionic surfactants selected from the group consisting of (c8) sulfosuccinate or salt thereof having a hydrocarbon group with 5 or more and 18 or less carbons [hereinafter, referred to as

component (c8)], (c9) an anionic surfactant having a hydrocarbon group with 8 or more and 21 or less carbons and having a sulfuric ester group or a sulfonic acid group [provided that component (c8) is excluded] [hereinafter, referred to as component (c9)], (c10) an anionic surfactant having a hydrocarbon group with 7 or more and 21 or less carbons and having a carboxy group [hereinafter, referred to as component (c10)], and (c11) an anionic surfactant having a hydrocarbon group with 8 or more and 21 or less carbons and having a phosphoric ester group [hereinafter, referred to as component (c11)].

[0145]

<20a>

The liquid detergent composition for hard surfaces described in <19a>, wherein the anionic surfactant is one or more anionic surfactants selected from the group consisting of component (c8) and component (c9), preferably one or more anionic surfactants selected from component (c9).

[0146]

<21a>

The liquid detergent composition for hard surfaces described in any of <19a> or <20a>, wherein a content of component (c9) in the anionic surfactant is preferably 50 mass% or more, preferably 70 mass% or more, further preferably 80 mass% or more, further more

preferably 90 mass% or more, further more preferably 95 mass% or more, an further more preferably 99 mass% or more; and preferably 100 mass% or less.

[0147]

<22a>

The liquid detergent composition for hard surfaces described in any of <1a> to <21a>, wherein a content of component (a) is preferably 0.01 mass% or more, more preferably 0.05 mass% or more, and further preferably 0.1 mass% or more; and preferably 3 mass% or less, more preferably 2 mass% or less, further preferably 1 mass% or less, further more preferably 0.8 mass% or less, further more preferably 0.5 mass% or less, and further more preferably 0.4 mass% or less.

[0148]

<23a>

The liquid detergent composition for hard surfaces described in any <1a> to <22a>, wherein a content of component (b) is preferably 0.01 mass% or more, more preferably 0.05 mass% or more, further preferably 0.1 mass% or more, and further more preferably 0.2 mass% or more; and preferably 5 mass% or less, more preferably 4 mass% or less, further preferably 3 mass% or less, further more preferably 2 mass% or less, and further more preferably 1.5 mass% or less.

[0149]

<24a>

The liquid detergent composition for hard surfaces described in any of <1a> to <23a>, wherein a content of component (c) is preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further preferably 0.15 mass% or more; and 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, and further more preferably 3 mass% or less.

[0150]

<25a>

The liquid detergent composition for hard surfaces described in any of <1a> to <24a>, wherein a mass ratio of (a)/(b) is preferably 0.01 or more, more preferably 0.05 or more, further preferably 0.1 or more, and further more preferably 0.15 or more; and preferably 5 or less, more preferably 4 or less, further preferably 3 or less, furthermore preferably 2 or less, and further more preferably 1 or less.

[0151]

<26a>

The liquid detergent composition for hard surfaces described in any of <1a> to <25a>, wherein a mass ratio of (b)/(c) is preferably 0.05 or more, more preferably 0.1 or more, and further preferably 0.15 or more; and preferably 30 or less, more preferably 25 or less, further preferably 20 or less, and further more preferably 10 or less.

[0152]

<27a>

The liquid detergent composition for hard surfaces described in any of <1a> to <26a>, wherein a content of water is preferably 30 mass% or more, more preferably 50 mass% or more, and further preferably 60 mass% or more; and preferably 95 mass% or less, and more preferably 93 mass% or less.

[0153]

<28a>

The liquid detergent composition for hard surfaces described in any of <1a> to <27a>, wherein the hard surface is a hydrophilic hard surface.

[0154]

<29a>

The liquid detergent composition for hard surfaces described in any of <1a> to <28a>, wherein a hard surface, preferably a hydrophilic hard surface, and more preferably a glass surface, which are treated with the liquid detergent composition for hard surfaces, have a stationary contact angle relative to water of preferably 20° or less, more preferably 15° or less, further preferably 10° or less, and further more preferably 8° or less.

[0155]

<30a>

A method for preventing a stain from adhering to a hard surface including treating the hard surface with

the liquid detergent composition for hard surfaces described in any of <1a> to <29a>.

[0156]

<31a>

The method for preventing a stain from adhering to a hard surface described in <30a>, wherein the hard surface is a hydrophilic hard surface.

[0157]

<32a>

The method for preventing a stain from adhering to a hard surface described in <30a> or <31a>, wherein the hard surface is a solid hard surface of: glass, earthenware, porcelain, porcelain enamel, tile, ceramics; metals such as aluminum, stainless and brass; synthetic resins such as polyethylene, polypropylene, a melamine resin, a polyamide resin, an ABS resin, and FRP; natural fibers such as cotton, silk and wool; and synthetic fibers such as polyester, nylon and rayon.

[0158]

<33a>

The method for preventing a stain from adhering to a hard surface described in any of <30a> to <32a>, wherein the hard surface is one or two or more hard surfaces selected glass, earthenware, porcelain, plastics, stainless and silicon wafer.

[0159]

<34a>

The method for preventing a stain from adhering to a hard surface described in any of <30a> to <33a>, including treating an article having a hard surface, further an article having a hard surface selected from a toilet bowl, a bathtub, a kitchen sink, window glass, a mirror and a faucet.

[0160]

<35a>

The method for preventing a stain from adhering to a hard surface described in any of <30a> to <34a>, wherein a hard surface, preferably a hydrophilic hard surface, and more preferably a glass surface, which are treated with the liquid detergent composition for hard surfaces, have a stationary contact angle relative to water of preferably 20° or less, more preferably 15° or less, further preferably 10° or less, and further more preferably 8° or less.

[0161]

<36a>

Use of the composition described in any of <1a> to <29a> as a liquid detergent composition for hard surfaces.

[0162]

<1b>

A liquid detergent composition for hard surfaces containing:

(a) a copolymer [hereinafter, referred to as

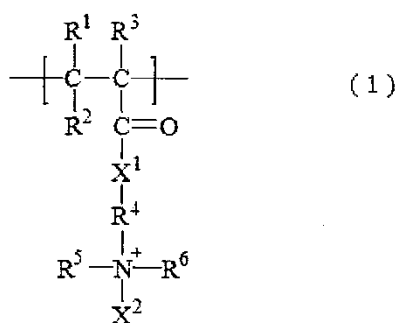
component (a)] containing a constituent unit (a1) represented by the following formula (1) and a constituent unit (a2) represented by the following formula (2), wherein a molar ratio between the constituent unit (a1) and the constituent unit (a2), constituent unit (a1)/constituent unit (a2), is 30/70 or more and 99.9/0.1 or less;

(b) a cationic surfactant [hereinafter, referred to as component (b)]; and

(d) a chelating agent [hereinafter, referred to as component (d)],

[0163]

[Chemical formula 15]



[0164]

wherein

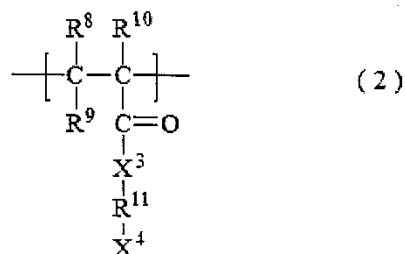
R¹ to R³ are the same or different and represent a hydrogen atom or an alkyl group with 1 to 2 carbons; R⁴ represents an alkylene group with 1 or more and 4 or less carbons or -Y¹-OPO₃⁻-Y²-, Y¹ and Y² are the same or different and represent an alkylene group with 1 or more and 4 or less carbons;

R⁵ and R⁶ are the same or different and represent a hydrocarbon group with 1 or more and 4 or less carbons; X¹ is O or NR⁷, and R⁷ represents a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons; and

X² represents a hydrogen atom, a hydrocarbon group with 1 or more and 4 or less carbons, R¹⁷SO₃⁻ or R¹⁷COO⁻, with the proviso that: when R⁴ is an alkylene group with 1 or more and 4 or less carbons, X² is R¹⁷SO₃⁻ or R¹⁷COO⁻, wherein R¹⁷ is an alkylene group with 1 or more and 4 or less carbons; and when R⁴ is -Y¹-OPO₃⁻-Y²-, X² is a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons,

[0165]

[Chemical formula 16]



[0166]

wherein

R⁸ to R¹⁰ are the same or different and represent a hydrogen atom or an alkyl group with 1 or 2 carbons; X³ represents O;

R¹¹ represents an alkylene group with 1 or more and 4 or less carbons; and

X^4 is $N^+R^{12}R^{13}R^{14}X^5$ or $NR^{15}R^{16}$, wherein R^{12} to R^{16} are the same or different and represent a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons, and X^5 represents an anion.

[0167]

<2b>

The liquid detergent composition for hard surfaces described in <1b>, wherein component (a) has a weight average molecular weight of preferably 500 or more, more preferably 5000 or more, further preferably 10000 or more, and further more preferably 30000 or more; and preferably 200000 or less, more preferably 150000 or less, and further preferably 100000 or less.

[0168]

<3b>

The liquid detergent composition for hard surfaces described in <1b> or <2b>, wherein a molar ratio of constituent units (a1) and (a2) of component (a), constituent unit (a1)/constituent unit (a2), is 30/70 or more, preferably 50/50 or more, more preferably 55/45 or more, further preferably 60/40 or more, further more preferably 75/25 or more, and further more preferably 90/10 or more; and 99.9/0.1 or less, preferably 98/2 or less, and more preferably 96/4 or less.

[0169]

<4b>

The liquid detergent composition for hard surfaces described in any of <1b> to <3b>, wherein a content of constituent unit (a1) in component (a) is preferably 30 mol% or more, more preferably 50 mol% or more, further preferably 70 mol% or more, further more preferably 80 mol%, and further more preferably 90 mol% or more; and preferably 99 mol% or less, more preferably 98 mol% or less, and further preferably 95 mol% or less.

[0170]

<5b>

The liquid detergent composition for hard surfaces described in any of <1b> to <4b>, wherein a content of constituent unit (a2) in component (a) is preferably 1 mol% or more, more preferably 2 mol% or more, an further preferably 5 mol% or more; and preferably 70 mol% or less, more preferably 50 mol% or less, further preferably 30 mol% or less, further preferably 20 mol% or less, and further preferably 10 mol% or less.

[0171]

<6b>

The liquid detergent composition for hard surfaces described in any of <1b> to <5b>, wherein a content of constituent units other than constituent units (a1) and (a2) in component (a) is preferably 10 mol% or less, more preferably 5 mol% or less, more preferably 1 mol% or less, further preferably 0.5 mol% or less, and further more preferably 0.1 mol% or less, or 0 mol%.

[0172]

<7b>

The liquid detergent composition for hard surfaces described in any of <1b> to <6b>, wherein a total content of constituent units (a1) and (a2) in component (a) is preferably 90 mol% or more, more preferably 95 mol% or more, further preferably 99 mol% or more, further more preferably 99.5 mol% or more, and further more preferably 99.9 mol% or more, or 100 mol%.

[0173]

<8b>

The liquid detergent composition for hard surfaces described in any of <1b> to <7b>, wherein component (b) is a mono- or di- long-chain alkyl quaternary ammonium salt.

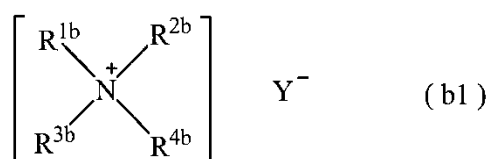
[0174]

<9b>

The liquid detergent composition for hard surfaces described in any of <1b> to <8b>, wherein component (b) is a cationic surfactant selected from compounds represented by the following general formula (b1) and compounds represented by the following formula (b2):

[0175]

[Chemical formula 17]

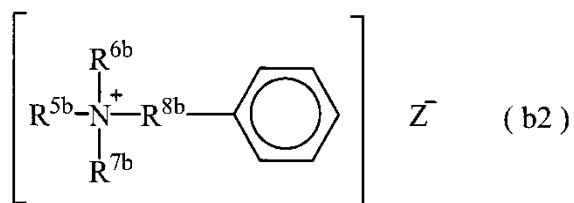


[0176]

wherein at least one selected from R^{1b} and R^{2b} represents an alkyl group with 8 or more and 18 or less carbons, an alkenyl group with 8 or more and 18 or less carbons or a hydroxyalkyl group with 8 or more and 18 or less carbons, and the remainder represents an alkyl group with 1 or more and 3 or less carbons, a hydroxyalkyl group with 1 or more and 3 or less carbons or a polyoxyethylene group with an average number of added moles of 10 or less; R^{3b} and R^{4b} are the same or different and each represent an alkyl group with 1 or more and 3 or less carbons, a hydroxyalkyl group with 1 or more and 3 or less carbons or a polyoxyethylene group with an average number of added moles of 10 or less; and Y^- represents a halogen atom, or an anionic residue of a sulfonic acid ester or a sulfuric ester with 1 or more and 5 or less carbons,

[0177]

[Chemical formula 18]



[0178]

wherein R^{5b} represents an alkyl group with 8 or more and 18 or less carbons, an alkenyl group with 8 or more and 18 or less carbons or a hydroxyalkyl group with 8

or more and 18 or less carbons, R^{6b} and R^{7b} are the same or different and each represent an alkyl group with 1 or more and 3 or less carbons, a hydroxyalkyl group with 1 or more and 3 or less carbons or a polyoxyethylene group with an average number of added moles of 10 or less, and R^{8b} represents an alkylene group with 1 or more and 3 or less carbons. Z- represents a halogen atom, or an anionic residue of a sulfonic acid ester or a sulfuric ester with 1 or more and 5 or less carbons.

[0179]

<10b>

The liquid detergent composition for hard surfaces described in any of <1b> to <9b>, wherein component (d) is one or more components selected from aminocarboxylic acid, hydroxycarboxylic acid, hydroxyphosphonic acid, and salts thereof.

[0180]

<11b>

The liquid detergent composition for hard surfaces described in any of <1b> to <10b>, wherein component (d) is one or more compounds selected from aminocarboxylic acids, hydroxycarboxylic acids and salts thereof, preferably aminocarboxylic acid or salt thereof, and more preferably ethylenediaminetetraacetic acid or salt thereof.

[0181]

<12b>

The liquid detergent composition for hard surfaces described in any of <1b> to <11b>, wherein a content of component (a) is preferably 0.01 mass% or more, more preferably 0.05 mass% or more, and further preferably 0.1 mass% or more; and preferably 3 mass% or less, more preferably 2 mass% or less, further preferably 1 mass% or less, further more preferably 0.8 mass% or less, further more preferably 0.5 mass% or less, and further more preferably 0.4 mass% or less.

[0182]

<13b>

The liquid detergent composition for hard surfaces described in any of <1b> to <12b>, wherein a content of component (b) is preferably 0.01 mass% or more, more preferably 0.05 mass% or more, further preferably 0.1 mass% or more, and further more preferably 0.2 mass% or more; and preferably 5 mass% or less, more preferably 4 mass% or less, further preferably 3 mass% or less, further more preferably 2 mass% or less, and further more preferably 1.5 mass% or less.

[0183]

<14b>

The liquid detergent composition for hard surfaces described in any of <1b> to <13b>, wherein a content of component (d) is preferably 0.01 mass% or more, more preferably 0.05 mass% or more, further preferably 0.1 mass% or more, further more preferably 0.2 mass% or

more, and further more preferably 0.5 mass% or more; and preferably 10 mass% or less, more preferably 9 mass% or less, further preferably 8 mass% or less, further more preferably 6 mass% or less, further more preferably 5 mass% or less, and further more preferably 4 mass% or less.

[0184]

<15b>

The liquid detergent composition for hard surfaces described in any of <1b> to <14b>, wherein a mass ratio of (a)/(b) is preferably 0.01 or more, more preferably 0.05 or more, further preferably 0.1 or more, and further more preferably 0.15 or more; and preferably 5 or less, more preferably 4 or less, further preferably 3 or less, further more preferably 2 or less, and further more preferably 1 or less.

[0185]

<16b>

The liquid detergent composition for hard surfaces described in any of <1b> to <15b>, wherein a mass ratio of (b)/(d) is 0.01 or more, more preferably 0.03 or more, further preferably 0.05 or more, further preferably 0.1 or more, and further more preferably 0.15 or more; and preferably 10 or less, more preferably 5 or less, further preferably 3 or less, further more preferably 1 or less, and further more preferably 0.8 or less.

[0186]

<17b>

The liquid detergent composition for hard surfaces described in any of <1b> to <16b>, containing a surfactant other than component (b) [hereinafter, referred to as component (c)].

[0187]

<18b>

The liquid detergent composition for hard surfaces described in <17b>, wherein component (c) is one or more surfactants selected from amphoteric surfactants, nonionic surfactants and anionic surfactants, and preferably one or more surfactants selected from amphoteric surfactants and nonionic surfactants.

[0188]

<19b>

The liquid detergent composition for hard surfaces described in <18b>, wherein the amphoteric surfactant is one or more amphoteric surfactants selected from amine oxide, sulfobetaine and carbobetaine, and preferably one or more amphoteric surfactants selected from sulfobetaine and carbobetaine.

[0189]

<20b>

The liquid detergent composition for hard surfaces described in <18b> or <19b>, wherein the nonionic surfactant is one or more nonionic surfactants selected from the group consisting of (c1) monoalkyl glyceryl

ether, (c2) polyoxyalkylene monoalkyl or alkenyl ether, (c3) alkyl polyglycoside (glycoside-type nonionic surfactant), (c4) a sorbitan-based nonionic surfactant, (c5) aliphatic alkanolamide, (c6) fatty acid monoglyceride, and (c7) sucrose fatty acid ester.

[0190]

<21b>

The liquid detergent composition for hard surfaces described in any <18b> to <20b>, wherein the anionic surfactant is one or more anionic surfactants selected from the group consisting of (c8) sulfosuccinate or salt thereof having a hydrocarbon group with 5 or more and 18 or less carbons, (c9) an anionic surfactant having a hydrocarbon group with 8 or more and 21 or less carbons and having a sulfuric ester group or a sulfonic acid group [provided that component (c8) is excluded], (c10) an anionic surfactant having a hydrocarbon group with 7 or more and 21 or less carbons and having a carboxy group, and (c11) an anionic surfactant having a hydrocarbon group with 8 or more and 21 or less carbons and having a phosphoric ester group.

[0191]

<22b>

The liquid detergent composition for hard surfaces described in any of <17b> to <21b>, wherein a content of component (c) is preferably 0.05 mass% or more, more preferably 0.1 mass% or more, and further preferably

0.15 mass% or more; and 10 mass% or less, more preferably 8 mass% or less, further preferably 5 mass% or less, and further more preferably 3 mass% or less.

[0192]

<23b>

The liquid detergent composition for hard surfaces described in any of <1b> to <22b>, wherein a content of water is preferably 30 mass% or more, more preferably 50 mass% or more, and further preferably 60 mass% or more; and preferably 95 mass% or less, and more preferably 93 mass% or less.

[0193]

<24b>

The liquid detergent composition for hard surfaces described in any of <1b> to <23b>, wherein the hard surface is a hydrophilic hard surface.

[0194]

<25b>

A method for preventing a stain from adhering to a hard surface including treating the hard surface with the liquid detergent composition for hard surfaces described in any of <1b> to <24b>.

[0195]

<26b>

The method for preventing a stain from adhering to a hard surface described in <25b>, wherein the hard surface is a hydrophilic hard surface.

[0196]

<27b>

The method for preventing a stain from adhering to a hard surface described in <25b> or <26b>, wherein the hard surface is a solid hard surface of: glass, earthenware, porcelain, porcelain enamel, tile, ceramics; metals such as aluminum, stainless and brass; synthetic resins such as polyethylene, polypropylene, a melamine resin, a polyamide resin, an ABS resin, and FRP; natural fibers such as cotton, silk and wool; and synthetic fibers such as polyester, nylon and rayon.

[0197]

<28b>

The method for preventing a stain from adhering to a hard surface described in any of <25b> to <27b>, wherein the hard surface is one or two or more hard surfaces selected glass, earthenware, porcelain, plastics, stainless and silicon wafer.

[0198]

<29b>

The method for preventing a stain from adhering to a hard surface described in any of <25b> to <28b>, including treating an article having a hard surface, further an article having a hard surface selected from a toilet bowl, a bathtub, a kitchen sink, window glass, a mirror and a faucet.

[0199]

<30b>

The liquid detergent composition for hard surfaces described in any of <25b> to <29b>, wherein a hard surface, preferably a hydrophilic hard surface, and more preferably a glass surface, which are treated with the liquid detergent composition for hard surfaces, have a stationary contact angle relative to water of preferably 20° or less, more preferably 15° or less, further preferably 10° or less, and further more preferably 8° or less; and preferably 1° or more.

[0200]

<31b>

Use of the composition described in any of <1b> to <24b> as a liquid detergent composition for hard surfaces.

Examples

[0201]

Production Example 1 [Production of copolymer A1]
(Process 1)

126.30 g of ethanol (manufactured by Wako Pure Chemical Industries, Ltd.) was charged into a 1000-mL four-necked flask, heated to 78°C and refluxed. To the resultant product, each of: a solution prepared by mixing 181.12 g of 2-(dimethylamino)ethyl methacrylate (manufactured by Wako Pure Chemical Industries, Ltd.), 23.60 g of 2-(dimethylamino)ethyl methacrylate diethyl

sulfate (manufactured by Kao Corporation/90% aqueous solution), and 53.20 g of ethanol with one another; and a solution prepared by mixing 5.83 g of 2,2'-azobis(2-methylbutyronitrile) (manufactured by Wako Pure Chemical Industries, Ltd.) and 10.00 g of ethanol with each other was dropped for 2 hours. After 4-hour aging, the resultant product was cooled, so that a polymer solution was obtained.

[0202]

(Process 2)

94.70 g of the obtained polymer solution, 3.15 g of sodium hydrogencarbonate (manufactured by Wako Pure Chemical Industries, Ltd.), and 150.00 g of water was charged into a 1000-mL four-necked flask, and heated to 50°C. To the resultant product, 38.70 g of 1,3-propanesultone (manufactured by Tokyo Chemical Industry Co., Ltd.) was dropped for 1 hour to cause a reaction. After 3-hour aging, ethanol was distilled off by heating under reduced pressure for 2 hours at 90°C and 20 kPa, so that an aqueous solution containing copolymer A1 was obtained.

[0203]

Copolymer A1 had constituent unit (a1) having the following structure in the formula (1) and constituent unit (a2) having the following structure in the formula (2), wherein a molar ratio of constituent unit (a1)/constituent unit (a2) was 95/5.

Constituent unit (a1): $R^1=R^2=H$, $R^3=CH_3$, $R^4=C_2H_4$,
 $R^5=R^6=CH_3$, $X^1=O$, $X^2=R^{17}SO_3^-$, $R^{17}=C_3H_6$
Constituent unit (a2): $R^8=R^9=H$, $R^{10}=CH_3$, $X^3=O$, $R^{11}=C_2H_4$,
 $X^4=N^+R^{12}R^{13}R^{14}X^5$, $R^{12}=R^{13}=CH_3$, $R^{14}=C_2H_5$, $X^5=C_2H_5CO_4^-$

In addition, copolymer A1 had a weight average molecular weight of 63000.

[0204]

Production Example 2 [Production of copolymer A2]
(Process 1)

37.95 g of ethanol was charged into a 1000-mL four-necked flask, heated to 78°C and refluxed. To the resultant product, a solution prepared by mixing 122.94 g of 2-(dimethylamino)ethyl methacrylate, 30.06 g of 2-(dimethylamino)ethyl methacrylate diethyl sulfate, and 28.88 g of ethanol with one another; and a solution prepared by mixing 1.67 g of 2,2'-azobis(2-methylbutyronitrile) and 3.90 g of ethanol with each other were separately dropped for 2 hours to cause polymerization. After 4-hour aging, the resultant product was cooled, so that a polymer solution was obtained.

(Process 2)

230.77 g of the obtained polymer solution, 6.56 g of sodium hydrogencarbonate, and 308.91 g of water were charged into a 1000-mL four-necked flask, and heated

to 50°C. To the resultant product, 102.21 g of 1,3-propanesultone was dropped for 1 hour to cause a reaction. After 3-hour aging, ethanol was distilled off by heating under reduced pressure for 2 hours at 90°C and 20 kPa, so that an aqueous polymer solution containing copolymer A2 was obtained.

[0205]

Copolymer A2 had the same constituent units (a1) and (a2) as copolymer A1 and a molar ratio of constituent unit (a1)/constituent unit (a2) of 90/10.

In addition, copolymer A2 had a weight average molecular weight of 69000.

[0206]

Production Example 3 (Production of copolymer A3)
(Process 1)

94.46 g of ethanol was charged into a 1000-mL four-necked flask, heated to 78°C and refluxed. To the resultant product, a solution prepared by mixing 267.52 g of 2-(dimethylamino)ethyl methacrylate, 147.20 g of 2-(dimethylamino)ethyl methacrylate diethyl sulfate, and 78.29 g of ethanol with one another; and a solution prepared by mixing 4.09 g of 2,2'-azobis(2-methylbutyronitrile) and 9.54 g of ethanol with each other were separately dropped for 2 hours to cause polymerization. After 4-hour aging, the resultant product was cooled, so that a polymer solution was obtained.

(Process 2)

307.82 g of the obtained polymer solution, 7.15 g of sodium hydrogencarbonate, and 394.56 g of water were charged into a 1000-mL four-necked flask, and heated to 50°C. To the resultant product, 111.20 g of 1,3-propanesultone was dropped for 1 hour to cause a reaction. After 3-hour aging, ethanol was distilled off by heating under reduced pressure for 2 hours at 90°C and 20 kPa, so that an aqueous polymer solution containing copolymer A3 was obtained.

[0207]

Copolymer A3 had the same constituent units (a1) and (a2) as copolymer A1 and a molar ratio of constituent unit (a1)/constituent unit (a2) of 80/20.

In addition, copolymer A3 had a weight average molecular weight of 78000.

[0208]

Production Example 4 (Production of copolymer A4)

(Process 1)

33.27 g of ethanol was charged into a 1000-mL four-necked flask, heated to 78°C and refluxed. To the resultant product, a solution prepared by mixing 81.13 g of 2-(dimethylamino)ethyl methacrylate, 76.52 g of 2-(dimethylamino)ethyl methacrylate diethyl sulfate, and 29.76 g of ethanol with one another; and a solution prepared by mixing 1.42 g of 2,2'-azobis(2-methylbutyronitrile) and 3.31 g of

ethanol with each other were separately dropped for 2 hours to cause polymerization. After 4-hour aging, the resultant product was cooled, so that a polymer solution was obtained.

(Process 2)

230.77 g of the obtained polymer solution, 4.34 g of sodium hydrogencarbonate, and 285.67 g of water were charged into a 1000-mL four-necked flask, and heated to 50°C. To the resultant product, 67.45 g of 1,3-propanesultone was dropped for 1 hour to cause a reaction. After 3-hour aging, ethanol was distilled off by heating under reduced pressure for 2 hours at 90°C and 20 kPa, so that an aqueous polymer solution containing copolymer was obtained.

[0209]

Copolymer A4 had the same constituent units (a1) and (a2) as copolymer A1 and a molar ratio of constituent unit (a1)/constituent unit (a2) of 70/30.

In addition, copolymer A4 had a weight average molecular weight of 81000.

[0210]

Production Example 5 [Production of polymer A'1]

(Process 1)

53.23 g of ethanol was charged into a 500-mL four-necked flask, heated to 78°C and refluxed. To the resultant product, a solution prepared by mixing 150.00 g of 2-(dimethylamino)ethyl methacrylate, and 16.60 g

of ethanol with each other; and a solution prepared by mixing 0.92 g of 2,2'-azobis(2-methylbutyronitrile) and 10.00 g of ethanol with each other were separately dropped for 2 hours to cause polymerization. After 4-hour aging, the resultant product was cooled, so that a polymer solution was obtained.

(Process 2)

75.76 g of the obtained polymer solution, 3.47 g of sodium hydrogencarbonate, and 150.00 g of water were charged into a 1000-mL four-necked flask, and heated to 50°C. To the resultant product, 42.73 g of 1,3-propanesultone was dropped for 1 hour to cause a reaction. After 3-hour aging, ethanol was distilled off by heating under reduced pressure for 2 hours at 90°C and 20 kPa, so that an aqueous polymer solution containing polymer A'1 was obtained.

[0211]

Polymer A'1 was a polymer containing, as a constituent unit, only constituent unit (a1) which is the same as that of copolymer A1 (100 mol% of constituent unit (a1)).

In addition, polymer A'1 had a weight average molecular weight of 40000.

[0212]

Note that the weight average molecular weights of copolymers A1 to A4 were measured by gel permeation chromatography (pullulan) under the following

conditions.

Column: two columns of TSKgel α -M (manufactured by Tosoh Corporation) were used and connected in series.

Column temperature: 40°C

Eluent: 0.15 mol Na₂SO₄/1%CH₃COOH/water

Flow rate: 1.0 ml/min.

Detector: a differential refractometer

[0213]

In addition, the weight average molecular weight of polymer A'1 was measured by SLS (static light scattering method). That is, the weight average molecular weight was calculated by using a light scattering photometer "DLS-7000" (manufactured by Otsuka Electronics Co., Ltd.) to measure static light scattering under the conditions described below, and producing a Zimm-plot. In addition, a refractive index increment required for calculation of the molecular weight was measured by use of a differential refractometer "DRM3000" (manufactured by Otsuka Electronics Co., Ltd.)

Wavelength: 632.8 nm (helium-neon laser)

Scattering angle: measured for each 10° from 30° to 150°

Temperature: 25°C

Solvent: trifluoroethanol

[0214]

Examples 1a to 17a and Comparative Examples 1a to 8a

Formulation components described below were used to

prepare liquid detergent compositions for hard surfaces shown in Tables 1 and 2, and evaluation was made on the following items. Results are shown in Tables 1 and 2. Note that in the tables, component (a') is regarded as component (a) for convenience to indicate (a)/(b) mass ratio.

Note that all of the numeral values expressed by "mass%" for formulation components in Tables 1 and 2 are values based on the effective amount. In addition, component (c) or an anionic surfactant is indicated with mass% based on the amount of sodium salt.

pH was adjusted by a very small amount of sodium hydroxide and hydrochloric acid.

[0215]

<Formulation component>

Component (a)

· Copolymers A1 to A4 were used.

Component (a') (comparative component of component (a))

· Polymer A'1 was used.

Component (b)

· Cationic surfactant: alkyl dimethyl benzyl ammonium chloride: alkyl group with 8 carbons (product name "SANISOL 08", manufactured by Kao Corporation)

Component (c)

· Nonionic surfactant: alkyl polyglycoside: alkyl (12 to 16 carbons) polyglucose (average sugar condensation

degree of 1 to 2) (product name "AG124" manufactured by Kao Corporation)

· Amphoteric surfactant: lauramidopropyl betaine (product name "Amphitol 20AB" manufactured Kao Corporation)

· Anionic surfactant: polyoxyethylene alkyl ether sodium sulfate, alkyl group with 12 to 16 carbons, an average number of added moles of ethylene oxide of 4.0 (product name "ES-4K" manufactured by Kao Corporation)
[0216]

<Contact angle>

A glass plate (manufacture by Matsunami Glass Ind., Ltd., with a size of 76 mm × 26 mm × 1 mm) was coated with 1 mL of a liquid detergent composition for hard surfaces and allowed to stand for 5 minutes, and thereafter, was rinsed with tap water at 25°C (flow rate: 50 mL/sec.) for 20 seconds. In a temperature and humidity controlled test chamber at 25°C and 40%RH, a stationary contact angle of the above treated glass plate relative to ion exchanged water was measured. For measurement, a fully automatic contact angle meter DM-500 manufactured by Kyowa Interface Science Co., Ltd. was used, water droplets of 20 µl of ion exchanged water were applied onto the treated surface, a contact angle was measured 10 times at intervals of 1 second from 3 seconds after droplet application, and average values thereof were described as data. Note that a

pre-treated glass plate had a stationary contact angle of 25°. A smaller contact angle, in other words, smaller than the stationary contact angle of the pre-treated glass plate, indicates hydrophilization. [0217]

<Antifouling property (stain adhesion prevention property)>

The entire surface of one side of a glass plate (manufacture by Matsunami Glass Ind., Ltd., with a size of 76 mm × 26 mm × 1 mm) was coated with 1 mL of a liquid detergent composition for hard surfaces and allowed to stand for 5 minutes; thereafter, was rinsed with tap water at 25°C (flow rate: 50 mL/sec) for 20 seconds; and was used for the following evaluation.

450 ml of water and 50 ml of a model oil solution (model oil: oleic acid, coloring matter: Sudan III (0.1 parts by mass relative to 100 parts by mass of oleic acid)) were mixed in a 500 ml beaker with a diameter of 10 cm, and a solution having two separated layers of water as a lower layer and oil as an upper layer was prepared.

The entire of the glass plate was soaked so that it was soaked in the lower layer for 10 seconds after it was passed through the upper layer, and it was then pulled out.

Thereafter, the soaked glass plate was dried, a photograph of the glass plate was taken, image

processing (by use of ImageJ) was carried out on the photograph to measure an oil remaining area in the glass plate, an oil residual factor was calculated (first try) based on the treated area of a glass plate.

Thereafter, that glass plate was used as-is, and an operation of soaking for 10 second and pulling out the plate was again carried out, and a residual factor was calculated by the same method (second try). When the treated area of glass was taken as 100, a residual factor (%) was calculated based on how much oil coated the surface (the degree of coating).

[0218]

<Foaming>

A liquid detergent composition for hard surfaces was charged in a trigger-type spray container (Toilet Magiclean Deodorant and Detergent Sprayer manufactured by Kao Corporation), and sprayed 10 times into a 200-mL graduated cylinder (with an inner diameter of 40 mm) in a wide foaming mode of the container. After spraying, a mass of the 200-mL graduated cylinder was measured by use of a 4-digit balance, and a difference from a mass of the graduated cylinder before spraying was regarded as an amount of foam coating (g) (a). In addition, the volume of foam (mL) in the graduated cylinder after spraying was visually read (b). A foam specific volume was calculated by the following formula. Results are shown in Tables 1 and 2.

Foam specific volume (mL/g) = (b)/(a)

A larger foam specific volume indicates excellence in the foaming.

[0219]

<Sterilization capability>

Staphylococcus aureus (NBRC12732 strain) was cultured twice on a nutrient agar medium (Nutrient Agar reagent available from Difco was prepared by following its description) at 37°C for 24 hours and scratched off; it was suspended and dispersed in a 1/2 nutrient liquid medium (Nutrient Agar reagent available from Difco was prepared at a half concentration of the description), so that a bacterial concentration was adjusted to 2.5 to 13×10^8 cfu/mL by use of the 1/2 nutrient liquid medium; and it was mixed with 3 mass% bovine serum albumin aqueous solution at an equivalent volume, thereby providing a test bacterial suspension. A stainless steel disk plate of a surface grade 2B with a diameter of 20 mm and a thickness of 1 mm was placed in a laboratory dish with an inner diameter of 75 mm, and 10 μ l of the test bacterial suspension was inoculated by a micropipette (Gilson, product name PIPETMAN) and spread on a disk surface. The laboratory dish was allowed to stand with no lid under the condition of $25 \pm 1^\circ\text{C}$. After it was confirmed that the bacterial

suspension was dried, a liquid prepared by diluting a liquid detergent composition for hard surfaces by 100 times with water having an adjusted hardness of 4°dH was promptly adhered. Adhesion of the liquid prepared by diluting the liquid detergent composition for hard surfaces by 100 times with water having an adjusted hardness of 4°dH was carried out by applying and spreading, by a micropipette (Gilson, product name PIPETMAN), 10 μ L of the liquid prepared by diluting the liquid detergent composition for hard surfaces by 100 times with water having an adjusted hardness of 4°dH onto 3.14 cm² of surface area of the stainless steel disk plate with a diameter of 20 mm (equivalent to 0.32 g/100 cm²). After 5 minutes of the adhesion, the disk was put into a predetermined amount of LP water diluted solution (one manufactured by Nissui Pharmaceutical Co., Ltd. was prepared by following the description) carefully so that the adhered composition was not flown down to inactivate the sterilization performance of the composition, and a bacterial concentration in the LP water diluted solution was counted by a pour culture method. The same operation (inoculating and spreading 10 μ l by the micropipette onto a disk surface, and after 5 minutes of inoculation, putting the disk into an LP diluted solution) was carried out as a control operation by using physiological saline solution instead of the composition; and a logarithm difference

in the bacterial count from the control operation in the LP water diluted solution was calculated and used as an index for sterilization performance in accordance with the following criteria.

* Criteria for evaluating the sterilization capability

A: logarithm difference in the bacterial count of 2 or more

B: logarithm difference in the bacterial count of less than 2

[0220]

<Mixing stability>

An appearance immediately after the preparation of a liquid detergent composition for hard surfaces was visually observed at a liquid temperature of 20°C, and evaluated in accordance with the following criteria.

* Criteria for evaluating the mixing stability

A: uniformly dissolved

B: slight turbidity was observed

C: obviously turbid

[0221]

[Table 1]

Example														Comparative Example							
														1a	2a	3a	4a	5a	6a	7a	8a
Liquid detergent composition for hard surfaces	Formulation component (mass%)	(a)	Copolymer A1		1a	2a	3a	4a	5a	6a	7a	8a	9a	10a	11a						
		(a')	Polymer A'1																		
		(b)	Cationic surfactant		1.00	1.00	1.00	1.00	1.00	1.00	0.30	0.50	1.00	1.00	1.00	0.50	1.00	1.00	1.00	1.00	1.00
	(c)	Nonionic surfactant								0.5	2.0	2.0	2.0						0.5	2.0	
		Amphoteric surfactant		0.10	0.20	0.50	1.00	1.00	2.00								0.50	1.00			
		Anionic surfactant												0.30	1.00						1.00
		Ion exchanged water		Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
		Total		100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
		pH (20°C)		7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
		(a)/(b) (mass ratio)		0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.67	0.4	0.2	0.2	0.2	0.4	0.2	0.2	0.2	0.2	0.2
		(b)/(C) (mass ratio)		10	5	2	1	0.5	2	0.15	0.25	0.5	3.3	1	-	-	2	1	2	0.5	1
		Contact angle (°)		5	4	4	4	5	4	5	4	4	4	6	6	4	5	13	14	21	20
Antifouling property (residual factor [%])	1st try			5	5	6	6	6	5	4	4	6	4	5	5	8	7	11	14	15	19
		2nd try		7	7	9	9	9	8	8	7	9	7	7	7	10	9	23	24	26	35
	Foaming (foam specific volume [mL/g])		13.6	14.3	14.9	15.0	15.2	13.9	12.6	13.9	14.5	15.5	15.5	2.3	2.9	1.9	13.9	14.3	13.7	14.0	15.3
	Sterilization capability		A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
	Mixing stability (20°C)		A	A	A	A	A	A	A	A	A	A	A	C	C	C	A	A	A	A	C

[Table 2]

				Example							
				12a	4a	13a	14a	15a	16a	17a	
Liquid detergent composition for hard surfaces	Formulation component (mass%)	(a)	Copolymer A1	0.10	0.20	0.50	2.00				
			Copolymer A2					0.20			
			Copolymer A3						0.20		
			Copolymer A4							0.20	
		(b)	Cationic surfactant	1.00	1.00	1.00	1.00	1.00	1.00	1.00	
		(c)	Amphoteric surfactant	1.00	1.00	1.00	1.00	1.00	1.00	1.00	
		Ion exchanged water		Balance	Balance	Balance	Balance	Balance	Balance	Balance	
		Total		100	100	100	100	100	100	100	
		pH (20°C)			7.0	7.0	7.0	7.0	7.0	7.0	7.0
		(a)/(b) (mass ratio)			0.1	0.2	0.5	2	0.2	0.2	0.2
	(b)/(C) (mass ratio)			1	1	1	1	1	1	1	
	Contact angle (°)			5	4	3	3	3	4	7	
	Antifouling property (residual factor [%])			1st try	8	6	4	4	5	8	7
2nd try				9	9	7	5	8	7	10	
Foaming (foam specific volume [mL/g])				15.0	15.0	15.7	16.0	15.7	15.1	14.9	
Sterilization capability				A	A	A	A	A	A	A	
Mixing stability (20°C)				A	A	B	B	A	A	A	

[0223]

Examples 1b to 9b and Comparative Examples 1b to 4b

Formulation components described below were used to prepare liquid detergent compositions for hard surfaces shown in Table 3, and evaluation was made on the following items. Results are shown in Table 3. Note that all of the numeral values expressed by "mass%"

for formulation components in Table 3 are values based on the effective amount. Further, in the table, component (a') is regarded as component (a) for convenience to indicate (a)/(b) mass ratio. In addition, as the mass ratio of (b)/(d), a value calculated based on the acid-converted mass% of component (d) is shown.

In addition, pH was adjusted by a very small amount of sodium hydroxide and hydrochloric acid.

[0224]

<Formulation component>

Component (a)

· Copolymer A1 of Production Example 1 and copolymer A4 of Production Example 4 were used.

Component (a') (comparative component of component (a))

· Polymer A'1 of Production Example 5 was used.

Component (b)

· Cationic surfactant: alkyl dimethyl benzyl ammonium chloride: alkyl group with 8 carbons (product name "SANISOL 08", manufactured by Kao Corporation)

Component (d)

· EDTA: tetrasodium ethylenediaminetetraacetic acid, (figures in the table show mass% as sodium salt, and figures in parentheses show acid-converted mass%.)

Other components

· Nonionic surfactant: alkyl polyglycoside: alkyl (12

to 16 carbons) polyglucose (average sugar condensation degree of 1 to 2) (product name "AG124" manufactured by Kao Corporation)

· Amphoteric surfactant: lauramidopropyl betaine (product name "Amphitol 20AB" manufactured Kao Corporation)

[0225]

<Contact angle>

A stationary contact angle was measured by the same method as for Example 1a and others.

[0226]

<Antifouling property (stain adhesion prevention property)>

The entire surface of one side of a glass plate (manufacture by Matsunami Glass Ind., Ltd., with a size of 76 mm × 26 mm × 1 mm) was coated with 1 mL of a liquid detergent composition for hard surfaces and allowed to stand for 5 minutes; thereafter, was rinsed with tap water at 25°C (flow rate: 50 mL/sec) for 20 seconds; and was used for the following evaluation.

450 ml of water and 50 ml of a model oil solution (model oil: oleic acid, coloring matter: Sudan III (0.1 parts by mass relative to 100 parts by mass of oleic acid)) were mixed in a 500 ml beaker with a diameter of 10 cm, and a solution having two separated layers of water as a lower layer and oil as an upper layer was prepared.

The entire of the glass plate was soaked so that it was soaked in the lower layer for 10 seconds after it was passed through the upper layer, and it was then pulled out.

Thereafter, the soaked glass plate was dried, a photograph of the glass plate was taken, image processing (by use of ImageJ) was carried out on the photograph to measure an oil remaining area in the glass plate, and an oil residual factor was calculated based on the treated area of the glass plate. When the treated area of glass was taken as 100, a residual factor (%) was calculated based on how much oil coated the surface (the degree of coating). The residual factor was used to evaluate the antifouling property in accordance with the following criteria.

* Criteria for evaluating the antifouling property

A: residual factor of less than 10%

B: residual factor of 10% or more

[0227]

<Detergency (scale removal)>

For preparing a stain model, 2 ml of 0.5% calcium dihydrogen phosphate aqueous solution was uniformly applied onto a black earthenware plate (a 10 cm × 10 cm tile), and dried at 120°C for 30 minutes. This process was repeated 10 times to prepare a model stain plate, and this was used to conduct detergent test.

A composition (0.3 ml) was dropped onto the model

stain plate horizontally fixed and allowed to stand for 1 minute, and then, the plate was washed by rubbing it 10 times with a cotton swab. Images of the earthenware plate before stain application, the earthenware plate (model stain plate) after stain application and before washing, and the earthenware plate after washing were taken in a state where picture-taking conditions such as brightness were the same, and a gray scale for each earthenware plate was measured from the obtained images. While taking washing ratios of earthenware plate before stain washing and before stain application as 0% and 100%, respectively, a comparison was made on the state of the earthenware plate after washing to calculate a washing ratio of the earthenware plate. Note that image processing software ImageJ 1.47v was used for measurement of a gray scale.

[0228]

<Sterilization capability>

The sterilization capability was evaluated by the same method as for Example 1a and others.

[0229]

<Mixing stability>

The mixing stability was evaluated by the same method as for Example 1a and others.

[0230]

<Foaming>

A liquid detergent composition for hard surfaces was

charged in a trigger-type spray container (Toilet Magiclean Deodorant and Detergent Sprayer manufactured by Kao Corporation), and sprayed 10 times into a 200-mL graduated cylinder (with an inner diameter of 40 mm) in a wide foaming mode of the container. After spraying, a mass of the 200-mL graduated cylinder was measured by use of a 4-digit balance, and a difference from a mass of the graduated cylinder before spraying was regarded as an amount of foam coating (g) (a). In addition, the volume of foam (mL) in the graduated cylinder after spraying was visually read (b). A foam specific volume was calculated by the following formula. Results are shown in Table 3.

$$\text{Foam specific volume (mL/g)} = (b)/(a)$$

A larger foam specific volume indicates excellence in the foaming. From the foam specific value, the foaming performance was evaluated in accordance with the following criteria.

* Criteria for evaluating the foaming performance

A: foam specific volume of 10 mL/g or more

B: foam specific volume of 5 mL/g or more and less than 10 mL/g

C: foam specific volume of less than 5 mL/g

[0231]

Example										Comparative Example																			
										9b	8b	7b	6b	5b	4b	3b	2b	1b	3b	4b									
Liquid detergent composition for hard surfaces										0.20	0.20	0.20	0.50	0.20	0.20	0.20	0.20			0.20									
										(a)	Copolymer A1	0.20	0.20	0.20	0.50	0.20	0.20	0.20											0.20
										Copolymer A4																			
										(a')	Polymer A'1																		
										(b)	Cationic surfactant	0.20	0.30	0.50	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.50
										(d)	EDTA (acid conversion value in parentheses)	3.0 (2.1)	3.0 (2.1)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)	2.5 (1.75)
(c)																													
										Nonionic surfactant																			
Amphoteric surfactant																													
																													1.50
Ion exchanged water										Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance								
Total										100	100	100	100	100	100	100	100	100	100	100	100	100							
(a)/(b) (mass ratio)										1	0.67	0.4	0.2	0.5	0.2	0.2	0.2	0.2	0.2	-	-	-	-	0.4					
										(b)/(d) (mass ratio)	0.1	0.14	0.29	1.43	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57	-
pH (20°C)										7	7	7	7	7	7	7	7	7	7	7	7								
Contact angle (°)										7	6	6	5	6	5	4	8	5	25	31	4								
Antifouling property										A	A	A	A	A	A	A	A	A	A	B	A								
Stergency (scale removal) (washing ratio: ^a)										87	92	82	74	90	87	85	93	53	87	82	50								
Sterilization capability										A	A	A	A	A	A	A	A	A	A	A	A								
Mixing stability (20°C)										A	A	A	B	A	A	A	A	C	A	A	C								
Foaming										C	C	C	C	C	C	A	C	C	C	A	C								

CLAIMS

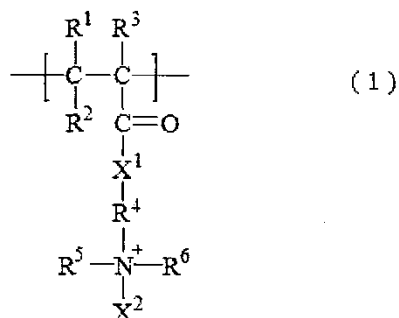
1. A liquid detergent composition for hard surfaces comprising:

(a) a copolymer [hereinafter, referred to as a component (a)] comprising a constituent unit (a1) represented by the following formula (1) and a constituent unit (a2) represented by the following formula (2), wherein a molar ratio between the constituent unit (a1) and the constituent unit (a2), is 30/70 or more and 99.9/0.1 or less;

(b) a cationic surfactant [hereinafter, referred to as a component (b)]; and

(c) one or more surfactants [hereinafter, referred to as a component (c)] selected from amphoteric surfactants, nonionic surfactants and anionic surfactants,

[Chemical formula 1]



wherein

R¹ to R³ are the same or different and represent a hydrogen atom or an alkyl group with 1 to 2 carbons; R⁴ represents an alkylene group with 1 or more and 4 or less carbons or -Y¹-OPO₃⁻-Y²-,

Y¹ and Y² are the same or different and represent an alkylene group with 1 or more and 4 or less carbons;

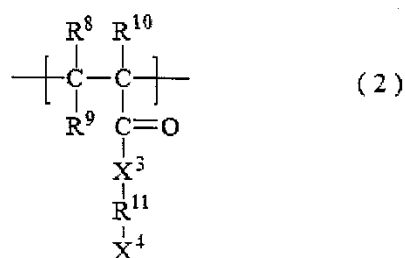
R⁵ and R⁶ are the same or different and represent a hydrocarbon group with 1 or more and 4 or less carbons;

X¹ is O or NR⁷, and R⁷ represents a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons;

and

X² represents a hydrogen atom, a hydrocarbon group with 1 or more and 4 or less carbons, R¹⁷SO₃⁻ or R¹⁷COO⁻, with the proviso that: when R⁴ is an alkylene group with 1 or more and 4 or less carbons, X² is R¹⁷SO₃⁻ or R¹⁷COO⁻, wherein R¹⁷ is an alkylene group with 1 or more and 4 or less carbons; and when R⁴ is -Y¹-OPO₃⁻-Y²-, X² is a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons,

[Chemical formula 2]



wherein

R^8 to R^{10} are the same or different and represent a hydrogen atom or an alkyl group with 1 or 2 carbons;

X^3 represents O;

R^{11} represents an alkylene group with 1 or more and 4 or less carbons; and

X^4 is $N^+R^{12}R^{13}R^{14}X^5$ or $NR^{15}R^{16}$, wherein R^{12} to R^{16} are the same or different and represent a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons, and X^5 represents an anion.

2. The liquid detergent composition for hard surfaces according to Claim 1, wherein a mass ratio of (b)/(c) is 0.05 or more and 30 or less.

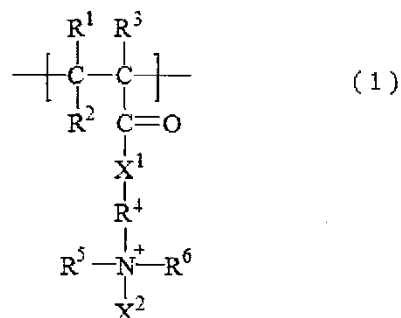
3. A liquid detergent composition for hard surfaces comprising:

(a) a copolymer [hereinafter, referred to as a component (a)] comprising a constituent unit (a1) represented by the following formula (1) and a constituent unit (a2) represented by the following formula (2), wherein a molar ratio between the constituent unit (a1) and the constituent unit (a2), constituent unit (a1)/constituent unit (a2), is 30/70 or more and 99.9/0.1 or less;

(b) a cationic surfactant [hereinafter, referred to as a component (b)]; and

(d) a chelating agent [hereinafter, referred to as a component (d)],

[Chemical formula 3]



wherein

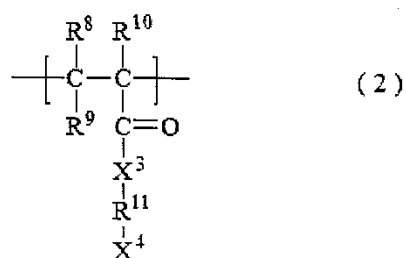
R¹ to R³ are the same or different and represent a hydrogen atom or an alkyl group with 1 to 2 carbons; R⁴ represents an alkylene group with 1 or more and 4 or less carbons or -Y¹-OPO₃⁻-Y²-,

Y¹ and Y² are the same or different and represent an alkylene group with 1 or more and 4 or less carbons; R⁵ and R⁶ are the same or different and represent a hydrocarbon group with 1 or more and 4 or less carbons; X¹ is O or NR⁷, and R⁷ represents a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons; and

X² represents a hydrogen atom, a hydrocarbon group with 1 or more and 4 or less carbons, R¹⁷SO₃⁻ or R¹⁷COO⁻, with the proviso that: when R⁴ is an alkylene group with 1 or more and 4 or less carbons, X² is R¹⁷SO₃⁻ or R¹⁷COO⁻,

wherein R¹⁷ is an alkylene group with 1 or more and 4 or less carbons; and when R⁴ is -Y¹-OPO₃⁻-Y²-, X² is a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons,

[Chemical formula 4]



wherein

R⁸ to R¹⁰ are the same or different and represent a hydrogen atom or an alkyl group with 1 or 2 carbons; X³ represents O;

R¹¹ represents an alkylene group with 1 or more and 4 or less carbons; and

X⁴ is N⁺R¹²R¹³R¹⁴X⁵ or NR¹⁵R¹⁶, wherein R¹² to R¹⁶ are the same or different and represent a hydrogen atom or a hydrocarbon group with 1 or more and 4 or less carbons, and X⁵ represents an anion.

4. The liquid detergent composition for hard surfaces according to Claim 3, wherein a mass ratio of (b)/(d) is 0.01 or more and 10 or less.

5. The liquid detergent composition for hard surfaces according to any one of Claims 1 to 4, wherein the content of the component (a) is 0.01 mass% or more and 3 mass% or less.

6. The liquid detergent composition for hard surfaces according to any one of Claims 1 to 5, wherein a mass ratio of (a)/(b) is 0.01 or more and 5 or less.

7. The liquid detergent composition for hard surfaces according to any one of Claims 1 to 6, wherein the hard surfaces are a hydrophilic hard surface.

8. A method for preventing a stain from adhering to a hard surface, comprising treating the hard surface with a liquid detergent composition for hard surfaces according to any one of Claims 1 to 7.