

DESCRIPTION

Title of Invention

LIQUID DETERGENT FOR CLOTHING

5 Technical Field

[0001]

The present invention relates to a liquid detergent for clothing.

Priority is claimed on Japanese Patent Application No. 2015-173800, filed on September 3, 2015, the content of which is incorporated herein by reference.

10 Background Art

[0002]

In recent years, environmental consciousness has been increasing, and detergents for clothing with less burden on the environment are desired. A

"concentrated type" liquid detergent for clothing which has higher concentration of washing components than detergents in the related art and requires less use of detergents has been studied as the liquid detergent for clothing with less burden on the environment.

[0003]

There is a problem with the concentrated type liquid detergent for clothing that increase in the concentration of a surfactant as a washing component easily causes deterioration of liquid stability such as remarkable increase in viscosity (gelation) and decrease in fluidity.

[0004]

Various liquid detergents for clothing have been proposed to improve the liquid stability of such a concentrated type liquid detergent for clothing. For example, a liquid detergent for clothing containing a specific nonionic surfactant and a specific anionic

surfactant at a specific ratio has been proposed in PTL 1. A liquid detergent for clothing containing a specific nonionic surfactant, a specific anionic surfactant, and an alkyl polysaccharide surfactant has been proposed in PTL 2. A liquid detergent for clothing containing a specific nonionic surfactant and a specific anionic surfactant at a specific ratio has been proposed in PTL 3. A liquid detergent for clothing containing a specific nonionic surfactant, at least one selected from an anionic surfactant and a cationic surfactant, and a specific compound has been proposed in PTL 4.

[0005]

In addition, a concentrated type liquid detergent for clothing blended with enzymes has been studied in order to improve the detergency with a small amount of detergent.

However, when enzymes are added to the concentrated type liquid detergent for clothing, there is a problem of deterioration of enzyme stability such as enzyme deactivation.

[0006]

While concentrated type liquid detergents for clothing are being developed, use of "water-saving type" washing machines which require less amount of water than washing machines in the related art as washing means with less environmental burden has also been studied.

However, in a case where a liquid detergent for clothing in the related art is used in a water-saving type washing machine, the concentration of stains in the washing liquid increases as the amount of water used decreases. Therefore, there is a problem in that re-contamination occurs since stains which have been removed once adhere to the clothes again.

Citation List

Patent Literature

[0007]

[PTL 1] Japanese Unexamined Patent Application, First Publication No.

2012-102285

5 [PTL 2] Japanese Unexamined Patent Application, First Publication No.

H06-299191

[PTL 3] Japanese Unexamined Patent Application, First Publication No.

2010-265333

[PTL 4] Japanese Unexamined Patent Application, First Publication No.

10 2011-201996

Summary of Invention

Technical Problem

[0008]

The present invention has been made from the viewpoint of the above-described
15 circumstances, and an object of the present invention is to provide a liquid detergent for
clothing which has liquid stability, an excellent effect of suppressing re-contamination,
and excellent enzyme stability.

Solution to Problem

[0009]

20 As a result of intensive studies, the inventors have found that it is effective to
increase the blending amount of an anionic surfactant in order to suppress the
re-contamination. On the basis of the obtained findings, the inventors have found that
the following liquid detergent for clothing can solve the above-described problem.

That is, the present invention has the following aspects.

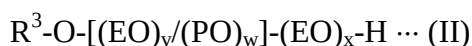
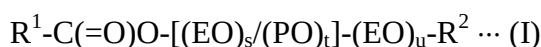
25 [1] A liquid detergent for clothing, including: a component (A); a component

(B); a component (C); a component (D); and a component (E),

in which the mass ratio represented by component (A) / [component (B) + component (C)] is 0.5 to 3.5,

5 in which the mass ratio represented by component (B) / component (C) is 90/10 to 10/90,

in which the component (A) is a nonionic surfactant represented by General Formula (I) or (II),



10 (in Formula (I), R^1 is a hydrocarbon group having 7 to 22 carbon atoms, R^2 is an alkyl group having 1 to 6 carbon atoms, s represents an average repeating number of EO which is 6 to 20, t represents an average repeating number of PO which is 0 to 6, u represents an average repeating number of EO which is 0 to 20, EO represents an oxyethylene group, and PO represents an oxypropylene group, and

15 in Formula (II), R^3 is a branched hydrocarbon having 7 to 22 carbon atoms, carbon atom bonded to oxygen atom is a secondary carbon atom, v represents an average repeating number of EO which is 3 to 20, w represents an average repeating number of PO which is 0 to 6, x represents an average repeating number of EO which is 0 to 20, EO represents an oxyethylene group, and PO represents an oxypropylene group)

20 in which the component (B) is polyoxyalkylene alkyl ether sulfuric acid or a salt thereof,

in which the component (C) is linear alkylbenzene sulfonic acid or a salt thereof,

in which the component (D) is an enzyme, and

in which the component (E) is water.

25 [2] The liquid detergent for clothing according to [1],

in which the content of the component (E) is 10 to 50 mass% with respect to the total mass of the liquid detergent for clothing.

[0010]

[3] The liquid detergent for clothing according to [1] or [2],

5 in which the total amount of the components (A) to (C) is 30 to 60 mass% with respect to the total mass of the liquid detergent for clothing.

[4] The liquid detergent for clothing according to any one of [1] to [3],

in which the component (A) is the nonionic surfactant represented by Formula (I).

10 [5] The liquid detergent for clothing according to [4],

in which in Formula (I), R^2 is a methyl group or an ethyl group.

[6] The liquid detergent for clothing according to any one of [1] to [5],

in which the component (B) is a compound represented by the General Formula (IV),

15 $R^4-O-[(EO)_m/(PO)_n]-SO_3^-M^+ \dots (IV)$

(in Formula (IV), R^4 is a linear or branched alkyl group having 8 to 20 carbon atoms, EO represents an oxyethylene group, PO represents an oxypropylene group, m represents an average repeating number of EO and is greater than or equal to 0, n represents an average repeating number of PO and is 0 to 6, and M^+ is a counter cation.)

20 [7] The liquid detergent for clothing according to [6], in which the component (B) contains 35 to 55 mass% of a component (b0), in which m is 0 and n is 0 in General Formula (IV), with respect to the total mass of the component (B).

[8] The liquid detergent for clothing according to any one of [1] to [7], in which the linear alkyl group of the component (C) has 8 to 16 carbon atoms.

25 [9] The liquid detergent for clothing according to any one of [1] to [8], in

which the component (D) is at least one enzyme selected from the group consisting of protease, amylase, lipase, cellulase, and mannanase.

[10] The liquid detergent for clothing according to any one of [1] to [9], in which the content of the component (A) is 5 to 80 mass% with respect to the total mass of the liquid detergent for clothing.

[11] The liquid detergent for clothing according to any one of [1] to [10], in which the content of the component (B) is 1 to 35 mass% with respect to the total mass of the liquid detergent for clothing.

[12] The liquid detergent for clothing according to any one of [1] to [11], in which the content of the component (C) is 1 to 30 mass% with respect to the total mass of the liquid detergent for clothing.

[13] The liquid detergent for clothing according to any one of [1] to [12], in which the content of the component (D) is 0.01 to 3.0 mass% with respect to the total mass of the liquid detergent for clothing.

[14] The liquid detergent for clothing according to any one of [1] to [13], in which the content of the surfactant is 30 to 60 mass% with respect to the total mass of the liquid detergent for clothing.

Advantageous Effects of Invention

[0011]

The liquid detergent for clothing of the present invention has liquid stability, an excellent effect of preventing re-contamination, and excellent enzyme stability.

Description of Embodiments

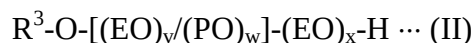
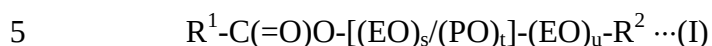
[0012]

The liquid detergent for clothing of the present invention is a composition containing Components (A) to (E).

[0013]

<Component (A)>

The component (A) is a nonionic surfactant represented by General Formula (I) or (II),



(in Formula (I), R^1 is a hydrocarbon group having 7 to 22 carbon atoms, R^2 is an alkyl group having 1 to 6 carbon atoms, s represents an average repeating number of EO which is 6 to 20, t represents an average repeating number of PO which is 0 to 6, u represents an average repeating number of EO which is 0 to 20, EO represents an oxyethylene group, and PO represents an oxypropylene group, and

in Formula (II), R^3 is a branched hydrocarbon having 7 to 22 carbon atoms, carbon atom bonded to oxygen atom is a secondary carbon atom, v represents an average repeating number of EO which is 3 to 20, w represents an average repeating number of PO which is 0 to 6, x represents an average repeating number of EO which is 0 to 20, EO represents an oxyethylene group, and PO represents an oxypropylene group)

[0014]

In Formula (I), R^1 is a hydrocarbon group having 7 to 22 carbon atoms. The number of carbon atoms of R^1 is preferably 9 to 21 and more preferably 11 to 21.

20 R^1 is preferably an alkyl group or an alkenyl group.

R^1 may be either linear or branched.

From the viewpoint of further improving the detergency, R^1 is preferably a linear or branched alkyl group having 7 to 22 carbon atoms or a linear or branched alkenyl group having 7 to 22 carbon atoms.

25 R^2 is an alkyl group having 1 to 6 carbon atoms and may be either linear or

branched.

Among them, a methyl group and an ethyl group are preferable.

In Formula (I), s and u each independently represent an average repeating number of EO.

5 s + u is preferably 6 to 20, more preferably 6 to 18, and still more preferably 11 to 18. In a case where s + u is greater than or equal to the above-described lower limit value, the stability of the component (D) is more easily improved. In a case where s + u is lower than or equal to the above-described upper limit value, the detergency is more easily improved.

10 In Formula (I), t is a number representing an average repeating number of PO. t is 0 to 6, preferably 0 to 3, and more preferably 0. In a case where the average repeating number of t is lower than or equal to the above-described upper limit value, the liquid stability is more easily improved.

15 In a case where t is greater than or equal to 1, the oxyethylene group and the oxypropylene group in [(EO)_s / (PO)_t] may be random polymerization or block polymerization.

In the present specification, the average repeating number can be measured through gas chromatography or the like.

20 The distribution of EO or PO in Formula (I) varies depending on the reaction method during production. For example, in a case where ethylene oxide or propylene oxide is added to raw materials using sodium hydroxide, potassium hydroxide, or the like which is a general alkaline catalyst, the distribution of s or t becomes relatively wide. In a case where ethylene oxide or propylene oxide is added to raw materials using a specific alkoxylation catalyst such as magnesium oxide to which metal ions such as Al³⁺, Ga³⁺, In³⁺, Tl³⁺, Co³⁺, Sc³⁺, La³⁺, and Mn²⁺ described in Japanese Examined Patent

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Application, Second Publication No. H06-15038 are added, the distribution of s or t becomes relatively narrow.

[0015]

In Formula (II), R^3 is a branched hydrocarbon group having 7 to 22 carbon atoms, and carbon atoms bonded to oxygen atoms (-O-) are secondary carbon atoms.

In Formula (II), the number of carbon atoms of R^3 is preferably 10 to 22, more preferably 10 to 20, still more preferably 10 to 18 from the viewpoint of further improving the detergency.

Preferred examples of R^3 -O- include groups represented by General Formula (III).



(in Formula (III), R^{101} and R^{102} each independently represent a chain-like hydrocarbon group, the total number carbon atoms of R^{101} and R^{102} is 6 to 21, and the total number of carbon atoms of R^{101} and R^{102} is preferably 9 to 21, more preferably 9 to 19, and still more preferably 9 to 17)

R^{101} and R^{102} are preferably linear or branched alkyl groups.

In Formula (II), v and x each independently represent an average repeating number of EO.

v + x is preferably 3 to 20, more preferably 5 to 18, still more preferably 6 to 18, and particularly preferably 11 to 18. In a case where v + x is greater than or equal to the above-described lower limit value, the stability of the component (D) is more easily improved. In a case where v + x is lower than or equal to the above-described upper limit value, the detergency is more easily improved.

In Formula (II), w is a number representing an average repeating number of PO.

w is 0 to 6, preferably 0 to 3, and more preferably 0. In a case where the

average repeating number of w is lower than or equal to the above-described upper limit value, the liquid stability is more easily improved.

In a case where w is greater than 0, the oxyethylene group and the oxypropylene group in $[(EO)_v / (PO)_w]$ may be random polymerization or block polymerization.

5 The distribution of EO or PO in Formula (II) varies depending on the reaction method during production. For example, in a case where ethylene oxide or propylene oxide is added to raw materials using sodium hydroxide, potassium hydroxide, or the like which is a general alkaline catalyst, the distribution of v or w becomes relatively wide. In a case where ethylene oxide or propylene oxide is added to raw materials using a
10 specific alkoxylation catalyst such as magnesium oxide to which metal ions such as Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Co^{3+} , Sc^{3+} , La^{3+} , and Mn^{2+} described in Japanese Examined Patent Application, Second Publication No. H06-15038 are added, the distribution of v or w becomes relatively narrow.

[0016]

15 As the component (A), a compound represented by Formula (I) is more preferable, a compound (that is, polyoxyethylene fatty acid alkyl ester) in which t in Formula (I) is 0 is still more preferable, and polyoxyethylene fatty acid methyl ester (hereinafter referred to as "MEE") in which R^2 in Formula (I) is a methyl group is particularly preferable from the viewpoint of improving detergency or solubility of a
20 liquid detergent for clothing.

 The liquid detergent for clothing of the present invention containing the polyoxyethylene fatty acid alkyl ester has excellent solubility in water, and high detergency is more easily obtained therewith. In addition, it is possible to make a concentrated type liquid detergent for clothing which is not liable to cause a remarkable
25 increase in viscosity (gelation) even if it contains a surfactant at high concentration and

which has superior liquid stability having favorable fluidity.

The polyoxyethylene fatty acid alkyl ester (in particular, MEE) is a nonionic surfactant in which orientation of molecules in an aqueous solution system is weak and micelles are unstable. Therefore, gelation or the like does not occur in the high

5 concentration region, and a large amount of single type of polyoxyethylene fatty acid alkyl ester can be blended with the liquid detergent for clothing. In addition, the solubility in water is favorable. Furthermore, it has favorable fluidity even at high concentration. Accordingly, polyoxyethylene fatty acid alkyl ester rapidly becomes uniform in a washing liquid after being put into water in a washing machine drum.

10 Accordingly, in a case where the polyoxyethylene fatty acid alkyl ester is used, the washing liquid can come into contact with the washing objects at a predetermined concentration from the beginning of cleaning. Therefore, high detergency can be obtained.

In addition, polyoxyethylene fatty acid alkyl ester in which the content ratio of
15 an ethylene oxide adduct, in which the addition molar number of EO is less than or equal to 2, is less than or equal to 0.5 mass% with respect to the entirety of the polyoxyethylene fatty acid alkyl ester is preferable as the polyoxyethylene fatty acid alkyl ester, and polyoxyethylene fatty acid alkyl ester in which the content ratio thereof is less than or equal to 0.2 mass% is more preferable as the polyoxyethylene fatty acid alkyl
20 ester. In a case where the total content ratio is less than or equal to 0.5 mass%, a liquid detergent for clothing having a lower raw material odor derived from polyoxyethylene fatty acid alkyl ester is easily obtained.

[0017]

The nonionic surfactant represented by Formula (I) and the nonionic surfactant
25 represented by Formula (II) preferably have a narrow ratio greater than or equal to 20

mass% and more preferably have a narrow ratio greater than or equal to 25 mass%.

More favorable detergency is obtained as the narrow ratio is higher. In addition, in a case where the narrow ratio is greater than or equal to 20 mass%, in particular, greater than or equal to 25 mass%, a liquid detergent for clothing with less raw material odor of
5 a surfactant is easily obtained.

In a case where the nonionic surfactant represented by Formula (I) is produced through a usual method, a component not contributing to detergency, for example, fatty acid ester which is a raw material of the nonionic surfactant represented by Formula (I) or an ethylene oxide adduct in which s of the nonionic surfactant represented by Formula
10 (I) is 1 or 2 coexists in a product in addition to the nonionic surfactant represented by Formula (I). Thus, the narrow ratio decreases. For this reason, in a case where the narrow ratio is high, the amount of coexisting components becomes sufficiently small. Therefore, deterioration of detergency and problems such as raw material odor are less likely to occur. The same applies to the case of the nonionic surfactant represented by
15 Formula (II).

The upper limit value of the narrow ratio is not particularly limited. However, it is preferable that the upper limit value thereof is substantially less than or equal to 80 mass%.

The narrow ratio is more preferably 20 to 50 mass% and still more preferably 25
20 to 45 mass% due to improvement of liquid stability and solubility.

Here, the "narrow ratio" indicates the ratio of distribution of ethylene oxide adducts having different addition molar numbers of EO, and is represented by Equation (S).

[0018]

$$\text{Narrow ratio} = \sum_{i=n_{\max}-2}^{i=n_{\max}+2} Y_i \quad \cdot \cdot \cdot \quad (S)$$

[0019]

[in the equation, $n_{\max}$ indicates an addition molar number of EO of an ethylene oxide adduct which is present in the largest amount in the entire ethylene oxide adducts, i

5 indicates an addition molar number of EO, and Y_i represents the proportion (mass%) of an ethylene oxide adduct in which the addition molar number of EO is i and which is present in the entire ethylene oxide adducts]

[0020]

The narrow ratio can be controlled through, for example, a method for

10 producing a nonionic surfactant represented by Formula (I) or (II). The method for producing a nonionic surfactant represented by Formula (I) is not particularly limited. However, the nonionic surfactant represented by Formula (I) can be easily produced through, for example, a method for subjecting ethylene oxide to addition polymerization to fatty acid alkyl ester using a surface-modified composite metal oxide catalyst (refer to

15 Japanese Unexamined Patent Application, First Publication No. 2000-144179). The method for producing a nonionic surfactant represented by Formula (II) is not particularly limited. However, the nonionic surfactant represented by Formula (II) can be produced through, for example, a method for subjecting ethylene oxide to addition polymerization to a secondary alcohol having 7 to 22 carbon atoms using a

20 surface-modified composite metal oxide catalyst.

Specific examples of the surface-modified composite metal oxide catalyst used in such a method include a composite metal oxide catalyst such as magnesium oxide to which metal ions (such as Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Co^{3+} , Sc^{3+} , La^{3+} , and Mn^{2+})

surface-modified with metal hydroxide or the like are added; or a calcined substance catalyst of hydrotalcite surface-modified with metal hydroxide and/or metal alkoxide.

In the surface modification using the composite metal oxide catalyst, it is preferable to use a composite metal oxide in combination with metal hydroxide and/or metal alkoxide. In this case, the ratio of metal hydroxide and/or metal alkoxide with respect to 100 parts by mass of the composite metal oxide is preferably 0.5 to 10 parts by mass and more preferably 1 to 5 parts by mass.

[0021]

As the component (A), a commercially available product may be used or a component produced through a well-known synthesis method may be used. It is possible to produce the nonionic surfactant represented by Formula (I), for example, through a method for subjecting ethylene oxide and/or propylene oxide to addition polymerization to fatty acid alkyl ester as the well-known production method. It is possible to produce the nonionic surfactant represented by Formula (II), for example, through a method for subjecting ethylene oxide and/or propylene oxide to addition polymerization to a secondary alcohol having 7 to 22 carbon atoms.

[0022]

The component (A) may be one type or may be two or more types.

The content of the component (A) in the liquid detergent for clothing with respect to the total mass of the liquid detergent for clothing is preferably 5 to 80 mass%, more preferably 10 to 70 mass%, still more preferably 15 to 60 mass%, still more preferably 20 to 50 mass%, and most preferably 25 to 35 mass%.

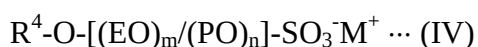
In a case where the content of the component (A) is greater than or equal to the above-described lower limit value, detergency of the liquid detergent for clothing is more easily improved. In a case where the content of the component (A) is lower than or

equal to the above-described upper limit value, liquid stability of the liquid detergent for clothing is more easily improved.

[0023]

<Component (B)>

5 The component (B) is polyoxyalkylene alkyl ether sulfuric acid or a salt thereof. Specifically, the component (B) is preferably a compound represented by General Formula (IV).



(in Formula (IV), R^4 is a linear or branched alkyl group having 8 to 20 carbon
10 atoms, EO represents an oxyethylene group and PO represents an oxypropylene group, m represents an average repeating number of EO and is greater than or equal to 0, n represents an average repeating number of PO and is 0 to 6, and M^+ is a counter cation)

Polyoxyalkylene alkyl ether sulfate having a linear or branched alkyl group having 10 to 20 carbon atoms and having an average of 1 to 5 mol of alkylene oxide
15 added thereto is preferable as polyoxyalkylene alkyl ether sulfate.

The number of carbon atoms of the alkyl group is preferably 10 to 20 and more preferably 12 to 14. Specific examples thereof include a dodecyl group, a tridecyl group, and a tetradecyl group. Among them, a dodecyl group is preferable.

The average repeating number of EO is preferably 0 to 5, more preferably 0.5 to
20 3, particularly preferably 0.5 to 2.5, and most preferably 0.5 to 1.5.

The average repeating number of PO is preferably 0 to 3 and more preferably 0.

Examples of salts include alkali metal salts of sodium, potassium and the like, alkaline earth metal salts of magnesium and the like, and alkanolamine salts of monoethanolamine, diethanolamine, and the like.

25 Denaturation of the component (D) due to an anionic surfactant in a liquid

detergent for clothing can be suppressed using polyoxyalkylene alkyl ether sulfuric acid or a salt thereof as the component (B).

As the component (B), a commercially available product may be used or a component produced through well-known synthesis method may be used. The component can be produced through a method for reacting sulfuric anhydride with polyoxyalkylene alkyl ether or reacting chlorosulfonic acid with polyoxyalkylene alkyl ether as the well-known production method.

[0024]

The component (B) may be one type or may be two or more types. 35 to 55 mass% of a component (b0) in which m is 0 and n is 0 in General Formula (IV) is preferably contained with respect to the entirety of the component (B).

The content of the component (B) in the liquid detergent for clothing with respect to the total mass of the liquid detergent for clothing is preferably 1 to 35 mass%, more preferably 2 to 30 mass%, still more preferably 5 to 25 mass%, and particularly preferably 5 to 15 mass%.

In a case where the content of the component (B) is within the above-described range, the effect of preventing re-contamination and the enzyme stability are more easily improved. In addition, in a case where the content of the component (B) is greater than or equal to the above-described lower limit value, the effect of preventing re-contamination is more easily improved. In a case where the content of the component (B) is lower than or equal to the above-described upper limit value, the stability of the component (D) is more easily improved.

[0025]

<Component (C)>

The component (C) is linear alkylbenzene sulfonic acid or a salt thereof.

Linear alkylbenzene sulfonic acid or a salt thereof in which the number of carbon atoms of a linear alkyl group is 8 to 16 is preferable, and linear alkylbenzene sulfonic acid or a salt thereof in which the number of carbon atoms if a linear alkyl group is 10 to 14 is more preferable, as the linear alkylbenzene sulfonic acid or a salt thereof.

- 5 In a case where the number of carbon atoms of a linear alkyl group is within the above-described range, it is possible to improve the effect of preventing re-contamination. Specific examples thereof include a decyl group, an undecyl group, a dodecyl group, a tridecyl group, and a tetradecyl group.

- Examples of salts include alkali metal salts of sodium, potassium and the like,
10 alkaline earth metal salts of magnesium and the like, and alkanolamine salts of monoethanolamine, diethanolamine, and the like.

- As the component (C), a commercially available product may be used or a component produced through well-known synthesis method may be used. It is possible to produce the component through a method for sulfonating alkylbenzene with sulfuric
15 anhydride as the well-known production method.

The component (C) may be one type or may be two or more types.

The content of the component (C) in the liquid detergent for clothing with respect to the total mass of the liquid detergent for clothing is preferably 1 to 30 mass%, more preferably 2 to 15 mass%, and particularly preferably 5 to 12 mass%.

- 20 In a case where the content of the component (C) is greater than or equal to the above-described lower limit value, the effect of preventing re-contamination is more easily improved. In a case where the content of the component (C) is lower than or equal to the above-described upper limit value, the liquid stability is more easily improved.

- 25 [0026]

The total content of the components (B) and (C) (hereinafter, also referred to as the total content of (B + C)) with respect to the total mass of the liquid detergent for clothing is preferably 1 to 40 mass%, more preferably 5 to 30 mass%, and particularly preferably 10 to 20 mass%.

5 In a case where the total content of the components (B) and (C) is greater than or equal to the above-described lower limit value, the effect of preventing re-contamination is more easily improved. In a case where the total content of the components (B) and (C) is lower than or equal to the above-described upper limit value, the liquid stability is more easily improved.

10 [0027]

The mass ratio represented by component (A) / [component (B) + component (C)] (hereinafter, also referred to as (A) / ((B) + (C))) is 0.5 to 3.5, preferably 0.5 to 3, and more preferably 1 to 2.5. In a case where the mass ratio thereof is greater than or equal to the above-described lower limit value, the stability of the component (D) is more easily improved. In a case where the mass ratio thereof is lower than or equal to the above-described upper limit value, the effect of preventing re-contamination is more easily improved.

[0028]

The mass ratio represented by the components (B) and (C) (hereinafter, also referred to as (B)/(C)) is 90/10 to 10/90, preferably 90/10 to 60/40, and more preferably 80/20 to 50/50. In a case where the proportion of the component (B) is lower than or equal to the above-described upper limit value, the stability of the component (D) is more easily improved. In a case where the proportion of the component (B) is greater than or equal to the above-described lower limit value, the effect of preventing re-contamination is more easily improved.

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[0029]

The total amount of the components (A) to (C) in the liquid detergent for clothing (hereinafter, also referred to as (A) + (B) + (C)) with respect to the total mass of the liquid detergent for clothing is preferably 30 to 60 mass%, more preferably 35 to 55 mass%, and more preferably 35 to 50 mass%.

In a case where the total amount of the components (A) to (C) is greater than or equal to the above-described lower limit value, the effect of preventing re-contamination is more easily improved. In a case where the total amount of the components (A) to (C) is lower than or equal to the above-described upper limit value, the liquid stability and the enzyme stability are more easily improved.

[0030]

<Component (D)>

The component (D) is an enzyme.

The "enzyme" in the present specification and the scope of claims indicates an enzyme preparation. In the related art, enzymes used for clothing detergent and the like can be used. General examples thereof include protease, amylase, lipase, cellulase, and mannanase.

Examples of protease include Savinase 16L, Savinase Ultra 16L, Savinase Ultra 16XL, Everlase 16L TypeEX, Everlase Ultra 16L, Esperase 8L, Alcalase 2.5L, Alcalase Ultra 2.5L, Liquanase 2.5L, Liquanase Ultra 2.5L, Liquanase Ultra 2.5XL, and Coronase 48L which are trade names and available from Novozymes; and Purafect L, Purafect OX, Properase L, and the like which are trade names and available from Genencor, as protease preparations.

Examples of amylase include Termamyl 300L, Termamyl Ultra 300L, Duramyl 300L, Stainzyme 12L, and Stainzyme Plus 12L which are trade names and available from

Novozymes; Maxamyl which is a trade name and available from Genencor; Pullulanase Amano which is a trade name and available from Amano Enzyme Inc.; and DB-250 which is a trade name and available from SEIKAGAKU CORPORATION, as amylase preparations.

5 Examples of lipase include Lipex 100L and Lipolase 100L which are trade names and available from Novozymes as lipase preparations.

 Examples of cellulase include Celluclean 5000L, Celluclean Classic 400L, and Carzyme 4500L which are trade names and available from Novozymes as cellulase preparations.

10 Examples of mannanase include Mannaway 4L which is a trade name and available from Novozymes as mannanase preparations.

 In the present invention, it is particularly preferable that the component (D) contains at least protease.

 Of the above-described protease preparations, Savinase 16L, Savinase Ultra
15 16L, Savinase Ultra 16L, Savinase Ultra 16XL, Everlase 16L, Everlase Ultra 16L, Liquanase 2.5L, Liquanase Ultra 2.5L, Liquanase Ultra 2.5XL, Coronase 48L, Alcalase 2.5L, and Alcalase Ultra 2.5L which are trade names are preferable, and Everlase 16L, Savinase 16L, Coronase 48L, and Alcalase 2.5L are particularly preferable.

[0031]

20 The component (D) may be one type or may be two or more types.

 The content of the component (D) in the liquid detergent for clothing with respect to the total mass of the liquid detergent for clothing is preferably 0.01 to 3.0 mass%, more preferably 0.05 to 2.0 mass%, and still more preferably 0.1 to 1.5 mass%.

 In a case where the content of the component (D) is greater than or equal to the
25 above-described lower limit value, the effect of blending the component (D) can be

sufficiently obtained. In a case where the content of the component (D) is lower than or equal to the above-described upper limit value, the liquid stability is more easily improved.

In the specification and the scope of claims, the blending amount of enzymes in the liquid detergent for clothing is a blending amount as a preparation, and can be obtained as an amount of enzyme preparation which has been obtained by calculating backward from the amount of raw material used or the amount of enzyme protein in the liquid detergent for clothing through a general method.

[0032]

10 <Component (E)>

Examples of water of component (E) include purified water, distilled water, ion-exchanged water, pure water, ultrapure water, and tap water.

The component (E) may be one type or may be two or more types.

The content of the component (E) in the liquid detergent for clothing with respect to the total mass of the liquid detergent for clothing is preferably 10 to 50 mass%, more preferably 15 to 50 mass%, and particularly preferably 20 to 45 mass%.

In a case where the content of the component (E) is within the range, stabilization of the component (D) can be sufficiently achieved while maintaining the washing performance.

20 In particular, in a case where the content of the component (E) is within the range of 20 to 45 mass%, the component (A) is contained in the liquid detergent for clothing at a high concentration. Therefore, it is possible to use the liquid detergent for clothing as a concentrated type detergent and to reduce turbidity and separation of the liquid detergent for clothing due to the component (D).

25 The content of the component (E) means the total moisture content in the liquid

detergent for clothing, and is denoted as a sum of the amount to be blended with water alone and the amount of water in a solution when raw materials (each components) are blended as the solution.

The total content of the components (A) to (E) does not exceed 100 mass% with
5 respect to the total mass of the liquid detergent for clothing.

[0033]

<Optional Components>

The liquid detergent for clothing of the present invention may contain components other than the components (A) to (E) within the scope not impairing the
10 effect of the present invention as necessary. As the other components, it is possible to blend components commonly used in a liquid detergent for clothing, and examples thereof include components shown below.

[0034]

(Other Nonionic Surfactants)

15 The other nonionic surfactants are not particularly limited as long as the component (A) is excluded.

Examples thereof include alkylene oxide adducts of fatty acid alkyl esters, primary alcohols having 12 to 14 carbon atoms, alkylphenols, higher fatty acids (having 10 to 15 carbon atoms), and higher amines (having 10 to 15 carbon atoms);
20 polyoxyethylene polyoxypropylene block copolymers, fatty acid alkanolamines, fatty acid alkanolamides, polyhydric alcohol fatty acid esters (with 3 to 10 hydroxyl groups) or alkylene oxide adducts thereof, polyhydric alcohol fatty acid ethers (with 3 to 10 hydroxyl groups), alkyl amine oxides, alkenyl amine oxide, alkylene oxide adducts of hardened castor oil, sugar fatty acid esters, N-alkyl polyhydroxy fatty acid amides, and
25 alkyl glucoside.

The blending amount of the other nonionic surfactants is preferably 1 to 20 mass% with respect to the total mass of the liquid detergent for clothing.

In particular, it is preferable to use the component (A) in combination with primary alcohol ethoxylate obtained by adding ethylene oxide to a primary alcohol. In a case where the component (A) and the primary alcohol ethoxylate are used in combination, the mass ratio (component (A)) / (primary alcohol ethoxylate) of the component (A) and the primary alcohol ethoxylate is preferably 3/7 to 10/1, more preferably 5/5 to 10/1, and still more preferably 7/3 to 9/1.

[0035]

10 (Other Anionic Surfactants)

The other anionic surfactants are not particularly limited as long as the components (B) and (C) are excluded. Examples of the other anionic surfactants include α -olefin sulfonate; alkyl ether sulfate ester salts or alkenyl ether sulfate ester salts, alkanesulfonate having an alkyl group, and α -sulfofatty acid ester salts. Examples of these salts include alkali metal salts of sodium, potassium and the like, alkaline earth metal salts of magnesium and the like, and alkanolamine salts of monoethanolamine, diethanolamine, and the like.

Among them, α -olefin sulfonate having 10 to 20 carbon atoms is preferable as α -olefin sulfonate.

20 Alkyl sulfate ester salts having an overall carbon number of 10 to 20 are preferable as alkyl sulfate ester salts.

Secondary alkanesulfonate with an alkyl group having 10 to 20 carbon atoms and preferably 14 to 17 carbon atoms is particularly preferable as alkanesulfonate.

α -sulfofatty acid ester salts having an overall carbon number of 10 to 20 are

preferable as α -sulfofatty acid ester salts.

Examples of other anionic surfactants include carboxylic acid type anionic surfactants such as higher fatty acids (having 10 to 15 carbon atoms, for example, coconut fatty acids) or salts thereof, alkyl ether carboxylate, polyoxyalkylene ether
5 carboxylate, alkyl (or alkenyl) amido ether carboxylate, and acylaminocarboxylate; and phosphate ester type anionic surfactants such as alkyl phosphate ester salts, polyoxyalkylene alkyl phosphate ester salts, polyoxyalkylene alkyl phenyl phosphate ester salts, and glycerin fatty acid ester monophosphate ester salts. Examples of these salts include alkali metal salts of sodium, potassium and the like, alkaline earth metal
10 salts of magnesium and the like, and alkanolamine salts of monoethanolamine, diethanolamine, and the like.

The blending amount of the other anionic surfactants is preferably 1 to 5 mass% with respect to the total mass of the liquid detergent for clothing.

[0036]

15 (Cationic Surfactant)

Examples of the cationic surfactant include a cationic surfactant such as an alkyltrimethylammonium salt, a dialkyldimethylammonium salt, an alkylbenzyltrimethylammonium salt, and an alkylpyridinium salt. Examples of these salts include alkali metal salts of sodium, potassium and the like, alkaline earth metal
20 salts of magnesium and the like, and alkanolamine salts of monoethanolamine, diethanolamine, and the like.

The blending amount of the cationic surfactants is preferably 1 to 5 mass% with respect to the total mass of the liquid detergent for clothing.

[0037]

25 (Amphoteric Surfactant)

Examples of the amphoteric surfactant include an alkylbetaine type amphoteric surfactant, an alkylamidobetain type amphoteric surfactant, an imidazoline type amphoteric surfactant, an alkylaminosulfone type amphoteric surfactant, an alkylaminocarboxylic acid type amphoteric surfactant, an alkylamidocarboxylic acid type amphoteric surfactant, an amide amino acid type amphoteric surfactant, and a phosphoric acid type amphoteric surfactant.

The blending amount of the amphoteric surfactants is preferably 1 to 5 mass% with respect to the total mass of the liquid detergent for clothing.

[0038]

10 The total amount of the surfactants in the liquid detergent for clothing (that is, a sum of components (A) to (C) and the surfactants as optional components) with respect to the total mass of the liquid detergent for clothing is preferably 30 to 60 mass% and more preferably 35 to 55 mass%.

15 In a case where the total amount of the surfactants is greater than or equal to the above-described lower limit value, the effect of preventing re-contamination is more easily improved. In a case where the total amount of the surfactants is lower than or equal to the above-described upper limit value, the liquid stability and the enzyme stability are more easily improved.

[0039]

20 The liquid detergent for clothing of the present application may contain a water-miscible organic solvent such as ethanol, an alkaline agent such as monoethanolamine, an antioxidant such as dibutylhydroxytoluene, a preservative such as sodium benzoate, an enzyme stabilizer such as calcium chloride or sodium lactate, a perfume, and a pigment.

25 [0040]

The liquid detergent for clothing of the present invention preferably has a pH of 4 to 9 at 25 °C, and more preferably a pH of 6 to 9 at 25 °C. In a case where the pH is within such a range, the storage stability of the liquid detergent for clothing can be favorably maintained.

5 The pH of the liquid detergent for clothing can be controlled through blending of a pH adjusting agent as necessary. The pH adjusting agent is optional as long as the effect of the present invention is not impaired. However, sulfuric acid, sodium hydroxide, potassium hydroxide, alkanolamine, and the like are preferable from the viewpoint of the stability of the component (D).

10 The pH is a value measured at 25°C according to JIS Z8802: 2011.

[0041]

The liquid detergent for clothing of the present invention is produced through a well-known production method in the related art. An example thereof includes a method in which the above-described components (A) to (D) are added to the component
15 (E), optional components are added thereto as necessary, and the components are mixed with each other.

[0042]

The method for using the liquid detergent for clothing of the present invention can be prepared by, for example, a method for putting a liquid detergent for clothing into
20 water together with washing objects during washing and a method for immersing washing objects in an aqueous detergent solution prepared by dissolving a liquid detergent for clothing in water in advance. In addition, usual washing may be performed after directly applying a liquid detergent for clothing to washing objects and allowing the washing objects to stand for a certain period of time (application washing).

25 [0043]

As described above, the liquid detergent for clothing of the present invention contains the components (A) to (E), and the mass ratio of component (A) / [component (B) + component (C)] is within a specific range, and the mass ratio of component (B) / component (C) is within a specific range. Therefore, the liquid detergent for clothing of the present invention has excellent liquid stability, an excellent effect of preventing re-contamination, and excellent enzyme stability.

[0044]

It is preferable that the liquid detergent for clothing of the present invention contains the components (A) to (E) and the component (A) is a nonionic surfactant represented by Formula (I).

It is preferable that the liquid detergent for clothing of the present invention contains components (A) to (E), and the component (A) is polyoxyethylene fatty acid alkyl ester.

It is preferable that the liquid detergent for clothing of the present invention contains the components (A) to (E) and the component (A) is polyoxyethylene fatty acid methyl ester.

It is preferable that the liquid detergent for clothing of the present invention contains the components (A) to (E) and the component (D) is protease.

[Examples]

[0045]

Hereinafter, the present invention will be described below in more detail using examples, but the present invention is not limited to these examples. In the examples, "%" indicates "mass%" unless otherwise specified.

The composition of the liquid detergent for clothing of each example is shown in Tables 1 and 2.

The raw materials used in this example are as follows.

[0046]

<Component (A): Nonionic Surfactant>

· A-1 which is obtained by adding 15 mol of ethylene oxide to polyoxyethylene
 5 fatty acid methyl ester (MEE) and coconut fatty acid methyl (a mixture of methyl laurate
 / methyl myristate = 8/2 by mass ratio) using an alkoxylation catalyst. In General
 Formula (I), R^1 is an alkyl group having 11 carbon atoms and an alkyl group having 13
 carbon atoms, R^2 is a methyl group, s is 15, t is 0, and u is 0. A-1 is synthesized
 through the following synthesis method.

10 [Synthesis Method of A-1]

A-1 was synthesized through the synthesis method disclosed in Japanese
 Unexamined Patent Application, First Publication No. 2000-144179.

Aluminum-magnesium hydroxide (KYOWAAD 300 (trade name) manufactured
 by Kyowa Chemical Industry Co., Ltd.) having a composition of $2.5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot w\text{H}_2\text{O}$
 15 was calcined at 600°C for 1 hour in a nitrogen atmosphere to obtain calcined
 aluminum-magnesium hydroxide (unmodified) catalyst. 2.2 g of calcined
 aluminum-magnesium hydroxide (unmodified) catalyst, 2.9 mL of 0.5N potassium
 hydroxide-ethanol solution, 280 g of a lauric acid methyl ester, and 70 g of a myristic
 acid methyl ester were put into a 4L autoclave to modify the catalyst in the autoclave.
 20 Subsequently, the air in the autoclave was substituted with nitrogen. Then, 1,052 g of
 ethylene oxide was introduced into the autoclave while maintaining the temperature at
 180°C and the pressure at 0.3 MPa. The mixture was reacted while being stirred.

The obtained reaction liquid was cooled to 80°C, 159 g of water and 5 g of
 activated clay and 5 g of diatomaceous earth as filter aids were added thereto and mixed

therewith. The catalyst was filtered off to obtain A-1.

The narrow ratio of A-1 is 30 mass%.

[0047]

· A-2 which is obtained by adding 15 mol of ethylene oxide to MEE and coconut
 5 fatty acid methyl (a mixture of methyl laurate / methyl myristate = 8/2 by mass ratio)
 using an alkoxylation catalyst. In General Formula (I), R^1 is an alkyl group having 11
 carbon atoms and an alkyl group having 13 carbon atoms, R^2 is a methyl group, s is 15, t
 is 0, and u is 0. A-2 is synthesized through the following synthesis method.

[Synthesis Method of A-2]

10 A-2 was synthesized according to the following synthesis method.

137 g of 2-ethylhexanol (a primary reagent manufactured by KANTO
 KAGAKU) and 41.7 g of calcium acetate monohydrate (special grade reagent
 manufactured by KANTO KAGAKU) were placed in a 500 mL beaker and mixed with
 each other using a paddle stirring blade at room temperature (25°C) to obtain a dispersion
 15 (dispersion step). 20.9 g of sulfuric acid (special grade reagent manufactured by
 KANTO KAGAKU) was added thereto using a dropping funnel over 10 minutes while
 stirring the dispersion, and the mixture was mixed (mixing step). In the mixing step,
 heat is generated by adding sulfuric acid. Therefore, the beaker was cooled by being
 bathed to control the reaction temperature to 30°C to 50°C. After sulfuric acid was
 20 added, the mixture was further stirred for 2 hours while maintaining the temperature at
 50°C (catalyst-aging step) to obtain an alkoxylation catalyst.

12.5 g of the above-described alkoxylation catalyst, 462 g of methyl laurate
 (PASTEL M12 manufactured by Lion Chemical Co., Ltd) and 166 g of methyl myristate
 (PASTEL M14 manufactured by Lion Chemical Co., Ltd) were placed and stirred in an

autoclave. The air of the autoclave was substituted with nitrogen while stirring, the temperature was raised to 100°C, and dehydration was carried out for 30 minutes under a decompressed condition of lower than or equal to 1.3 kPa. Next, the temperature was raised to 160°C, and 1,876 g of ethylene oxide (15 times the total molar amount of methyl laurate and methyl myristate) was introduced and stirred under the condition of 0.1 to 0.5 MPa (addition reaction step). The mixture was further stirred at an addition reaction temperature for 0.5 hours (aging step), and then cooled to 80°C to obtain 2,516 g of a crude reaction product (fatty acid methyl ester ethoxylate (MEE), average addition molar number of EO = 15). The product obtained by removing the catalyst through filtration of the crude reaction product was regarded as A-2.

The narrow ratio of A-2 is 30 mass%.

· A-3: SOFTANOL which is obtained by adding 7 mol of ethylene oxide to a secondary alcohol having 12 to 14 carbon atoms. SOFTANOL 70 (trade name) is manufactured by NIPPON SHOKUBAI CO., LTD. In General Formula (II), R³ is a branched alkyl group having 12 to 14 carbon atoms, v is 7, w is 0, and x is 0.

[0048]

<Component (B): Polyoxyalkylene Alkyl Ether Sulfuric Acid or Salt thereof>

· B-1: AES which is polyoxyalkylene alkyl ether sulfate (a mixture of sodium polyoxyethylene lauryl ether sulfate and sodium polyoxyethylene myristyl ether sulfate with an average addition molar number of EO of 1). R⁴ is a linear alkyl group having 12 and 14 carbon atoms, m is 1.0, n is 0, and M is sodium in General Formula (IV). The ratio of a compound (component (b0)), in which m is 0 and n is 0, with respect to B-1 is 43 mass%.

[Preparation Example of B-1]

400 g of an alcohol (a mixture of an alcohol having 12 carbon atoms and an alcohol having 14 carbon atoms at a mass ratio of 75/25), of which the trade name is CO1270 and is manufactured by P&G, as a raw material alcohol and 0.8 g of a potassium hydroxide catalyst as a reaction catalyst were put into a 4L autoclave. After substituting
 5 the air in the autoclave with nitrogen, the temperature was raised while stirring the mixture. Subsequently, 91 g of ethylene oxide was introduced while maintaining the temperature at 180°C and the pressure at 0.3 MPa or less and the mixture was reacted to obtain alcohol ethoxylate.

The average addition molar number of ethylene oxide in the obtained alcohol
 10 ethoxylate was analyzed using GC-5890 which is a gas chromatograph mass spectrometer manufactured by Hewlett-Packard, a hydrogen flame ionization detector (FID), and Ultra-1 (manufactured by HP Development Company, L.P., L 25 m × ϕ 0.2 mm × T 0.11 μ m) as a column, and as a result, was 1.0. In addition, the amount of the compound (which finally becomes the component (b0)) to which ethylene oxide was not
 15 added was 43 mass% with respect to the obtained whole alcohol ethoxylate.

Next, 237 g of alcohol ethoxylate obtained above was placed in a 500 mL flask equipped with a stirrer, and air was substituted with nitrogen. Then, 96 g of liquid sulfuric anhydride (SULFAN) was slowly added dropwise while maintaining the reaction temperature at 40°C. After completion of the dropwise addition, the mixture was
 20 continuously stirred for 1 hour (sulfation reaction) to obtain polyoxyethylene alkyl ether sulfuric acid. Next, the polyoxyethylene alkyl ether sulfuric acid was neutralized with an aqueous solution of sodium hydroxide to obtain B-1.

· B-2: AEPS which is a monoethanolamine salt of polyoxyethylene polyoxypropane-1,2-diyl alkyl ether sulfate ester. R^4 is a linear alkyl group having 12

carbon atoms, m is 2.0, n is 1.0, and M is monoethanolamine in General Formula (IV).

[Synthesis Method of AEPS]

640 g of a linear primary alcohol having 12 carbon atoms [trade name: 1-dodecanol (molecular weight of 186.33) manufactured by Tokyo Chemical Industry Co., Ltd., purity > 99%] and 1.0 g of KOH, were put into an autoclave equipped with a stirrer, a temperature controller, and an automatic introduction device. Dehydration was carried out at 110°C and 1.3 kPa for 30 minutes. After the dehydration, air was substituted with nitrogen, and the temperature was raised to 120°C. Then, 199 g of propane-1,2-diyl oxide was put thereinto. Next, after addition reaction and aging were performed at 120°C, the temperature was raised to 145°C, and 303 g of ethylene oxide was put thereinto. Next, after addition reaction and aging were performed at 145°C, the temperature was cooled to 80°C, and unreacted ethylene oxide was removed at 4.0 kPa. After the removal of unreacted ethylene oxide, 1.0 g of acetic acid was added to the autoclave and the mixture was stirred at 80°C for 30 minutes. Then, the resultant was drawn out to obtain alkoxylate in which the alkyl group was a dodecyl group, the average addition molar number of PO was 1.0, and the average addition molar number of EO of 2.0.

The obtained alkoxylate was sulfated with a descending thin film reactor using SO₃ gas. The obtained sulfated product was neutralized with monoethanolamine to obtain a composition containing a monoethanolamine salt of polyoxyethylene polyoxypropane-1,2-diyl alkyl ether sulfate ester (AEPS).

· B-3: AES which is polyoxyalkylene alkyl ether sulfate (sodium polyoxyethylene lauryl ether sulfate with an average addition molar number of EO of 2) of which the trade name is CINOLINE SPE-1250 manufactured by New Japan Chemical

Co., Ltd. R^4 is an alkyl group having 12 carbon atoms, m is 2.0, n is 0, and M is sodium in General Formula (IV).

[0049]

<Component (C): Linear Alkylbenzene Sulfonic Acid or Salt thereof>

5 · C-1: LAS which is linear alkylbenzene sulfonic acid of which the trade name is LIPON LH-200 manufactured by Lion Corporation.

 · C-2: SAS which is secondary sodium alkanesulfonate having 14 to 17 carbon atoms of which the trade name is "HOSTAPUR SAS 30A" manufactured by Clariant.

[0050]

10 <Component (D): Enzyme>

 · D-1: CORONASE and CORONASE 48L (trade names) manufactured by Novozymes.

 · D-2: ALCALASE and ALCALASE 2.5L (trade names) manufactured by Novozymes.

15 · D-3: EVERLASE and EVERLASE 16L (trade names) manufactured by Novozymes.

[0051]

<Component (E): Water>

 · E-1: Water and distilled water which is manufactured by KANTO KAGAKU.

20 [0052]

<Other Optional Components>

 · EP NONION: A nonionic surfactant obtained by performing block addition of 8 mol of ethylene oxide, 2 mol of propylene oxide, and 8 mol of ethylene oxide in this order to a natural alcohol (primary alcohol having 12 carbon atoms / primary alcohol

having 14 carbon atoms = 7/3 by a mass ratio).

· LMAO: Polyoxyethylene alkyl ether obtained by adding 15 mol of ethylene oxide to a natural alcohol having 12 and 14 carbon atoms (primary alcohol).

[Synthesis Method of LMAO]

5 861.2 g of CO-1214 (trade name, a natural alcohol having 12 and 14 carbon atoms) manufactured by Procter & Gamble Company and 2.0 g of a 30 mass% NaOH aqueous solution were put into a pressure-resistant reaction container, and the air in the reaction container was substituted with nitrogen. Next, after dehydration was performed for 30 minutes at a temperature of 100°C and a pressure of lower than or equal to 2.0 kPa, the temperature was raised to 160°C. Next, 760.6 g of ethylene oxide (gaseous form) was gradually added to the reaction solution while stirring the reaction solution. At this time, ethylene oxide was added thereto using a blow-in tube while controlling the addition rate so that the reaction temperature did not exceed 180°C.

15 After completion of the addition of ethylene oxide, aging was carried out at a temperature of 180°C and a pressure of lower than or equal to 0.3 MPa for 30 minutes. Then, unreacted ethylene oxide was distilled off at a temperature of 180°C and a pressure of lower than or equal to 6.0 kPa for 10 minutes.

20 Next, after the temperature was cooled to be lower than or equal to 100°C, a 70 mass% p-toluenesulfonic acid was added thereto for neutralization so as to control the pH of a 1 mass% aqueous solution of the reaction product to about 7, and LMAO was obtained.

· MEA: Monoethanolamine (alkali agent) of which the trade name is "MONOETHANOLAMINE" manufactured by NIPPON SHOKUBAI CO., LTD.

· Coconut fatty acid: An anionic surfactant of which the trade name is

"COCONUT FATTY ACID" (NOF CORPORATION).

· BHT: Dibutylhydroxytoluene (antioxidant) of which the trade name is

"SUMILZER BHT-R" manufactured by Sumitomo Chemical Co., Ltd.

· Ethanol: A water-miscible organic solvent of which the trade name is "95%

5 SPECIFIC SYNTHETIC ALCOHOL" manufactured by Japan Alcohol Trading CO., LTD.

· Sodium benzoate: A preservative of which the trade name is "SODIUM BENZOATE", (TOAGOSEI CO., LTD.).

· Calcium chloride: An enzyme stabilizer of which the trade name is

10 "CALCIUM CHLORIDE" (KANTO KAGAKU).

· Sodium Lactate: An enzyme stabilizer of which the trade name is "SODIUM LACTATE" (KANTO KAGAKU).

· Sokalan HP 20: A re-contamination preventing agent of which the trade name is "Sokalan HP 20" (BASF).

15 · Perfume: A flavoring agent which is a perfume composition A disclosed in Tables 11 to 18 of Japanese Unexamined Patent Application, First Publication No. 2002-146399.

· Colorant: A coloring agent of which the trade name is "Green No. 3" manufactured by Kishi Kasei Co., LTD.

20 [0053]

<Examples 1 to 16 and Comparative Examples 1 to 5>

Components (A) to (D) were added to a component (E) in accordance with the compositions shown in Tables 1 and 2, and mixed with optional components to obtain liquid detergents for clothing of each example.

The compositions (blending components, content (mass%)) of the liquid detergents for clothing obtained in each example are shown in Tables 1 and 2. Unless otherwise specified, mass% indicates pureness.

In the tables, in a case where there are blanks in blending components, the
5 blending components are not blended.

[0054]

<Evaluation Method for Liquid Detergent for Clothing>

Regarding the liquid detergents for clothing of each example, the enzyme stability, the effect of preventing re-contamination, and the liquid stability were evaluated
10 as follows.

The evaluation results are shown in Tables 1 and 2.

[0055]

<Evaluation of Enzyme Stability>

(Measurement of Protease Activity)

15 Milk casein (Casein, Bovine Milk, Carbohydrate and Fatty Acid Free / Calbiochem (registered trademark)) was dissolved in 1N sodium hydroxide (a 1 mol/L sodium hydroxide solution (1N) manufactured by KANTO KAGAKU), the pH was set to 10.5, and the resultant was diluted with an aqueous solution of 0.05 M boric acid (boric acid (special grade) manufactured by KANTO KAGAKU) so that the concentration of
20 milk casein becomes 0.6%, to obtain a protease substrate.

A solution obtained by diluting 1 g of the obtained each liquid detergent for clothing by 25 times with calcium chloride (CALCIUM CHLORIDE (special grade) manufactured by KANTO KAGAKU) 3° DH hard water was used as a sample solution.

5 g of the above-described protease substrate was added to 1 g of the sample
25 solution, and the mixture was stirred with a vortex mixer for 10 seconds. Then, the

mixture was allowed to stand at 37°C for 30 minutes to proceed the enzymatic reaction. Thereafter, 5 g of a 0.44 M aqueous solution of trichloroacetic acid (TCA (special grade) manufactured by KKANTO KAGAKU) as an enzymatic reaction terminator was added to the solution, and the mixture was stirred with a vortex mixer for 10 seconds.

- 5 Thereafter, this solution was allowed to stand at 20°C for 30 minutes, and an unreacted substrate to be deposited was removed with a 0.45 μ m filter to collect the filtrate.

 The absorbance (absorbance α) of the collected filtrate at a wavelength of 275 nm was measured using an ultraviolet visible light spectrophotometer UV-160 manufactured by Shimadzu Corporation. This shows that the amount of tyrosine
10 (produced by protease degrading the protease substrate) becomes larger in the filtrate as the absorbance α increases.

 5 g of TCA as an enzymatic reaction terminator was separately added to 1 g of each sample solution in order to eliminate the influence of absorption of components other than target components, and the mixture was stirred for 10 seconds with a vortex
15 mixer. Then, 5 g of a protease substrate was added thereto and the mixture was stirred for 10 seconds with the vortex mixer. An unreacted substrate was removed with a 0.45 μ m filter to collect the filtrate. Thereafter, the absorbance (absorbance β) of the filtrate at a wavelength of 275 nm was measured using UV-160.

[0056]

- 20 (Evaluation of Storage Stability of Protease Activity)

 After preparation, the protease activities of a liquid detergent for clothing (product stored at 35°C) stored for 4 weeks at 35°C and a liquid detergent for clothing (product stored at 4°C) stored for 4 weeks at 4°C were measured. From these measurement results, the residual ratio (%) of protease activity was obtained by the

following equation.

Absorbance values of each sample at 275 nm substituted into the following equation was used while excluding absorbance values at 600 nm which has been measured at the same time, in order to exclude scattered light such as air bubbles from absorbance.

$$\text{Protease activity residual ratio} = (\text{absorbance } \alpha \text{ of product stored at } 35^{\circ}\text{C} - \text{absorbance } \beta \text{ of product stored at } 35^{\circ}\text{C}) / (\text{absorbance } \alpha \text{ of product stored at } 4^{\circ}\text{C} - \text{absorbance } \beta \text{ of product stored at } 4^{\circ}\text{C}) \times 100$$

The storage stability of the protease activity was evaluated from the obtained protease activity residual ratio (%) according to the following evaluation criteria.

A: Greater than or equal to 80%.

B: Greater than or equal to 70% and less than 80%.

C: Greater than or equal to 60% and less than 70%.

D: Less than 60%.

The evaluation results are shown in each of the columns of the enzyme stability (enzyme residual ratio) and the enzyme stability (stability).

[0057]

<Evaluation of Effect of Preventing Re-Contamination>

A washing treatment was conducted by repeating a washing step, rinsing step, and drying step, shown below, three times in this order using the liquid detergents of each example.

[0058]

Washing Step:

The following cotton cloth, polyester (PE) cloth, artificially contaminated wet type cloth, and an undershirt were used as washing objects.

Cotton cloth: Five 5 cm x 5 cm cotton knitted fabrics (manufactured by Tanigashira Shoten) as cloth determined as having been re-contaminated.

Polyester (PE) cloth: Five 5 cm x 5 cm sheets of POLYESTER TROPICAL (manufactured by Tanigashira Shoten) as cloth determined as having been
5 re-contaminated.

Artificially contaminated wet type cloth: 20 sheets of contaminated cloth (cloth to which stains having a composition of an oleic acid of 28.3%, triolein of 15.6%, cholesterol oleate of 12.2%, liquid paraffin of 2.5%, squalene of 2.5%, cholesterol of 1.6%, gelatin of 7.0%, mud of 29.8%, carbon black of 0.5% (mass ratio)) manufactured
10 by Cleaning Science Association of Japan.

Undershirt: A finely cut (about 3 cm × 3 cm) undershirt (LL size, manufactured by DVD).

900 mL of 3° DH hard water at 25°C was placed in a Terg-o-tometer (manufactured by UNITED STATES TESTING CO., INC.), 0.6 g of a liquid detergent
15 was added thereto, and then, the washing objects were placed therein. Thereafter, 3° DH hard water was added thereto to adjust the bath ratio to be 20 times, and then, the washing objects were washed at 120 rpm, 25°C for 10 minutes.

[0059]

Rinsing Step:

20 The washing objects which have been washed were dehydrated for 1 minute. Then, 900 mL of 3° DH hard water at 25°C was placed therein and rinsed at 120 rpm, 25°C for 3 minutes. This operation (dehydration and rinsing) was repeated twice. In the second operation, rinsing was carried out by adding a predetermined amount of softening agent to 900 mL of 3° DH hard water at 25°C. HANG-TO-DRY-INDOORS

SOFLAN (manufactured by Lion Corporation) was used as a softening agent.

[0060]

Drying Step:

The washing objects which have been rinsed were dehydrated for 1 minute.

- 5 Then, only the cloth sheets determined as having been re-contaminated (cotton cloth and PE cloth) were taken out, caught in filter paper, and dried with an iron.

[0061]

- The reflectances (Z values) of the cloth sheets determined as having been re-contaminated before and after washing treatment were measured, and ΔZ was obtained
10 from the following equation using the reflectometer (spectroscopic color difference meter SE 2000 manufactured by NIPPON DENSHOKU INDUSTRIES Co., LTD).

$$\Delta Z = (Z \text{ value before washing treatment}) - (Z \text{ value after washing treatment})$$

- Regarding ΔZ of five cloth sheets determined as having been re-contaminated of each of the cotton cloth and the PE cloth, each average value of of the cloth sheets was
15 determined. The effect of preventing re-contamination of the cotton cloth and the PE cloth using the liquid detergent was evaluated according to the following criteria using this average value as an index. In the following criteria, A and B are set to have been passed. Evaluation results are shown in Tables 1 and 2.

[0062]

- 20 <Criteria for Cotton Cloth>

A: ΔZ is less than 5.

B: ΔZ is greater than or equal to 5 and less than 7.

C: ΔZ is greater than or equal to 7 and less than 9.

D: ΔZ is greater than or equal to 9.

- 25 [0063]

<Criteria for PE Cloth>

A: ΔZ is less than 3.

B: ΔZ is greater than or equal to 3 and less than 4.

C: ΔZ is greater than or equal to 4 and less than 5.

5 D: ΔZ is greater than or equal to 5.

[0064]

<Evaluation of Liquid Stability>

A transparent glass bottle (wide mouth standard bottle, PS-No. 11) was filled with 100 mL of a liquid detergent for clothing, and a lid was closed and sealed. The
10 transparent glass bottle was allowed to stand for 7 days in a constant-temperature tank at 5°C (or 25°C) in this state and stored.

After such storage, the appearance of the liquid was visually observed, and the appearance stability of the liquid detergent for clothing was evaluated according to the following evaluation criteria.

15 (Evaluation Criteria)

A: There is no precipitated substance recognized at the bottom of the glass bottle, and the liquid has fluidity.

B: There is no precipitated substance recognized at the bottom of the glass bottle, and gelation is partially recognized. However, when the glass bottle is allowed
20 to stand at room temperature for 3 hours, no gelled portion is observed and the whole liquid has fluidity.

C: There is a precipitated substance recognized at the bottom of the glass bottle. However, when the glass bottle is gently shaken, the precipitated substance disappears (dissolves).

25 D: There is a precipitated substance recognized at the bottom of the glass bottle.

Even if the glass bottle is gently shaken, the precipitated substance does not disappear or is gelled or turbid immediately after production of a liquid detergent for clothing.

The evaluation results are shown in each of the columns of the room-temperature stability (25°C) and the low-temperature stability (5°C) in Tables 1

5 and 2.

[0065]

[Table 1]

		Example								
		1	2	3	4	5	6	7	8	9
Liquid detergent for clothing (mass%)	Component (A)	30			30	30	30	38	38	38
	A-1									
	A-2		30							
	A-3			30						
	Component (B)	10	10	10	10	10	10	6	6	6
	B-1									
	B-2									
	B-3									
	Component (C)	10	10	10	10	10	10	6	6	6
	C-1									
	C-2									
	Component (D)	0.5	0.5	0.5	0.3	0.5	0.5	0.5	0.5	0.5
	D-1									
	D-2									
	D-3									
	Component (E)	36.4495	36.4495	36.4495	36.3495	36.4495	35.4395	36.4495	36.4495	36.4495
	E-1									
	Optional components									
	EP Nonion									
	LMAO									
	MEA	1	1	1	1	1	1	1	1	1
	Coconut fatty acid	3	3	3	3	3	3	3	3	3
	BHT	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
	Ethanol	8	8	8	8	8	8	8	8	8
	Sodium benzoate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Calcium chloride						0.01			
	Sodium lactate						1			
	Sokalan HP20									
Evaluation	Perfume	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Colorant	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
	Total	100	100	100	100	100	100	100	100	100
	Content of (B+C)	20	20	20	20	20	20	12	12	12
	(A)+(B)+(C)	50	50	50	50	50	50	50	50	50
	Content of surfactant	53	53	53	53	53	53	53	53	53
	(A)/((B)+(C))	1.5	1.5	1.5	1.5	1.5	1.5	3.17	3.17	3.17
	(B)/(C)	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50	50/50
	Residual activity ratio (%)	90	86	83	87	88	95	80	88	83
	Enzyme stability	A	A	A	A	A	A	A	A	A
	Stability	A	A	A	A	A	A	A	A	A
	Cotton cloth ΔZ	2.5	3.5	4.5	3.5	3.5	3.5	4	4.5	4
	Determination	A	A	A	A	A	A	A	A	A
	PE Cloth ΔZ	1	1.5	2.5	1.5	2	2	2	2.5	2.5
	Determination	A	A	A	A	A	A	A	A	A
Liquid stability	Room-temperature stability (25°C)	A	A	A	A	A	A	A	A	A
	Low-temperature stability (5°C)	A	A	A	A	A	A	A	A	A

[0066]

[Table 2]

		Example										Comparative Example																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																															
		10	11	12	13	14	15	16	1	2	3	4	5																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														
Liquid detergent for clothing (mass%)	Component (A)	A-1	20	30	30		25																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				

[0067]

From the results shown in Tables 1 and 2, the liquid detergents for clothing of Examples 1 to 16 to which the present invention was applied all had excellent enzyme stability, effect of preventing re-contamination, and liquid stability.

5 On the other hand, in a liquid detergent for clothing (Comparative Example 1) which did not contain the component (C), sufficient low-temperature stability could not be obtained.

In liquid detergents for clothing (Comparative Examples 2 and 3) which did not contain the component (B), sufficient enzyme stability could not be obtained.

10 In a liquid detergent for clothing (Comparative Example 4) in which (B) / (C) was outside the scope of the invention of the present application, sufficient liquid stability could not be obtained.

In a liquid detergent for clothing (Comparative Example 5) in which (A) / ((B) + (C)) was outside the scope of the invention of the present application, sufficient effect of
15 preventing re-contamination could not be obtained.

From the above results, it was confirmed that the liquid detergents for clothing to which the present invention was applied had excellent liquid stability, and the effect of preventing re-contamination and the enzyme stability were also favorable.

Industrial Applicability

20 [0068]

The liquid detergent for clothing of the present invention has liquid stability, an excellent effect of preventing re-contamination, and excellent enzyme stability.

CLAIMS

1. A liquid detergent for clothing, comprising:

a component (A);

5 a component (B);

a component (C);

a component (D); and

a component (E),

wherein the mass ratio represented by component (A) / [component (B) +

10 component (C)] is 0.5 to 3.5,

wherein the mass ratio represented by component (B) / component (C) is 90/10

to 10/90,

wherein the component (A) is a nonionic surfactant represented by General

Formula (I) or (II),

15 $R^1-C(=O)O-[(EO)_s/(PO)_t]-(EO)_u-R^2 \cdots (I)$

$R^3-O-[(EO)_v/(PO)_w]-(EO)_x-H \cdots (II)$

(in Formula (I), R^1 is a hydrocarbon group having 7 to 22 carbon atoms, R^2 is an

alkyl group having 1 to 6 carbon atoms, s represents an average repeating number of EO

which is 6 to 20, t represents an average repeating number of PO which is 0 to 6, u

20 represents an average repeating number of EO which is 0 to 20, EO represents an

oxyethylene group, and PO represents an oxypropylene group, and

in Formula (II), R^3 is a branched hydrocarbon having 7 to 22 carbon atoms,

carbon atom bonded to oxygen atom is a secondary carbon atom, v represents an average

repeating number of EO which is 3 to 20, w represents an average repeating number of

25 PO which is 0 to 6, x represents an average repeating number of EO which is 0 to 20, EO

represents an oxyethylene group, and PO represents an oxypropylene group)

wherein the component (B) is polyoxyalkylene alkyl ether sulfuric acid or a salt thereof,

wherein the component (C) is linear alkylbenzene sulfonic acid or a salt thereof,

5 wherein the component (D) is an enzyme, and

wherein the component (E) is water.

2. The liquid detergent for clothing according to claim 1,

wherein the content of the component (E) is 10 to 50 mass% with respect to the

10 total mass of the liquid detergent for clothing.