(19)

Europäisches Patentamt

European Patent Office Office européen des brevets



(11) EP 2 489 722 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

 (43) Date of publication: 22.08.2012 Bulletin 2012/34 (21) Application number: 10823438.6 	(51) Int Cl.: <i>C11D 1/72</i> ^(2006.01) <i>C11D 3/20</i> ^(2006.01) <i>C11D 3/20</i> ^(2006.01) <i>C11D 3/37</i> ^(2006.01)
(22) Date of filing: 14.10.2010	 (86) International application number: PCT/JP2010/068049 (87) International publication number: WO 2011/046170 (21.04.2011 Gazette 2011/16)
 (84) Designated Contracting States: AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR (30) Priority: 15.10.2009 JP 2009238354 	 KONTA Hiroshi Tokyo 130-8644 (JP) KANEKO Yukihiro Tokyo 130-8644 (JP) TERABAYASHI Tsuyoshi Tokyo 130-8644 (JP)
 (71) Applicant: Lion Corporation Tokyo 130-8644 (JP) (72) Inventors: KOBAYASHI Chika Tokyo 130-8644 (JP) 	 (74) Representative: Denjean, Eric Cabinet Laurent & Charras "Le Contemporain" 50, Chemin de la Bruyère 69574 Dardilly Cedex (FR)

(54) LIQUID DETERGENT COMPOSITION

(57) The invention relates to a liquid detergent composition includes: a component (A) which includes a nonionic surfactant represented by the formula R^{1O} (CH₂CH₂O)_nH; a component (B) which includes at least one species of anionic surfactant selected from the group consisting of compounds represented by the formulas $R^{2}CH(SO_{3}M^{1})COOR^{3}$ and $R^{4}CH(SO_{3}M^{2})CONHR^{5}$; and a component (C) which includes at least two species of water-miscible solvents selected from the group consisting of methanol, ethanol, propanol, butanol, ethylene glycol, propylene glycol, butylene glycol, butyl carbitol, phenoxy ethanol, and polyethylene glycol with an average molecular weight of 570 to 3800, wherein the total amount of the component (A) and the component (B) is in the range of 40 to 75 % by mass and the mass ratio of the amount of the component (B) with respect to the total amount of the component (A) and the component (B) satisfies component (B)/(component (A)+component (B)) =1/10 to 6/10. The invention can provide a liquid detergent composition which includes a surfactant at a high concentration and which has superior low-temperature preservation stability and superior low-temperature solubility and sebum detergency during washing.

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

⁵ [0001] The present invention relates to a liquid detergent composition. Priority is claimed on Japanese Patent Application No. 2009-238354, filed October 15, 2009, the amount of which is incorporated herein by reference.

BACKGROUND ART

10

20

25

[0002] Recently, the importance of development of environmentally-friendly products has increased and thus environmentally-friendly products have been required in the field of daily necessities such as clothing detergents. For example, for the purpose of reduction of physical distribution energy and reduction of waste, the size of detergent vessels has decreased. Accordingly, the concentration of a liquid detergent has been required for exhibiting great sebum detergency

¹⁵ with a small amount of detergent. The concentration of a liquid detergent requires that the liquid detergent is not gelated so as not to degrade sebum detergency even when it is diluted with water during washing. Particularly, when the liquid detergent is directly applied to a sebum stain, there is a need for solubility such that the liquid detergent not be attached and not be remained in clothes even at a low temperature (about 15°C) in winter.

[0003] To achieve these requirements, liquid detergent compositions having a nonionic surfactant or an anionic surfactant as a main base are widely used.

For example, Patent Document 1 discloses a liquid detergent composition using both primary alcohol ethoxylate and secondary alcohol ethoxylate to which ethyleneoxide and propyleneoxide are added as a nonionic surfactant.

Patent Document 2 discloses a surfactant composition which can be easily applied to a liquid detergent composition including 35 to 80 % by mass of α -sulfo fatty acid alkyl ester salt as an anionic surfactant and alcohol with a carbon number of 6 to 22.

[0004] Moreover, a liquid detergent composition using primary alcohol ethoxylate as a nonionic surfactant has attracted attention, in that it has great sebum detergency and has low cost and superior versatility.

However, it is generally known that a surfactant is apt to form a high-viscosity higher-order association structure such as hexagonal liquid crystal in a high-concentration region and the primary alcohol ethoxylate forms a high-viscosity liquid crystal phase in a relatively high concentration region when the concentration thereaf is equal to or higher than 40 %

30 crystal phase in a relatively high-concentration region when the concentration thereof is equal to or higher than 40 % by mass. Therefore, since the primary alcohol ethoxylate has a large high-viscosity region, the primary alcohol ethoxylate is apt to increase in viscosity with an increase in concentration and it is thus difficult to obtain a concentrated liquid detergent composition into which 40 % by mass or more of the primary alcohol ethoxylate is mixed.

Moreover, when the liquid detergent composition includes the primary alcohol ethoxylate at a high concentration, the solubility thereof is apt to decrease in a washing bath. Particularly, when the washing is performed with low-temperature water in winter, there is a problem in that gel-like attachments are apt to remain on clothes at the end of washing. **[0005]** Regarding this problem, a method of blending a hydrotropic agent to improve the solubility is known.

However, to obtain a liquid detergent composition which has superior solubility at a higher concentration, it is necessary to cause the primary alcohol ethoxylate and the hydrotropic agent to occupy most of the composition and thus it is not
 possible to satisfactorily blend functional components such as an enzyme or a chelating agent necessary for the detergent.
 [0006] Examples of the liquid detergent composition into which the primary alcohol ethoxylate is mixed include the

following. Patent Document 3 discloses a high-concentration anionic surfactant water-based paste including primary alcohol ethoxylate, 50 to 80 % by mass of an anionic surfactant (such as an α -sulfo fatty acid ester salt), and polyethylene glycol with

an average molecular weight of 200 to 800 so as to contain the anionic surfactant at a high concentration and to suppress
a daily increase in viscosity.
 Batent Decument 4 discloses a clething liquid determent composition including primary cleable otherwlate and polycovy.

Patent Document 4 discloses a clothing liquid detergent composition including primary alcohol ethoxylate and polyoxyalkylene amine so as to exhibit high detergency at a low concentration.

Patent Document 5 discloses a liquid detergent composition using both primary alcohol ethoxylate and an anionic surfactant such as alkyl benzene sulfonate (LAS) or sulfate ester salt of polyoxyethylene alkyl ether (AES).

Patent Documents 6 and 7 disclose a concentrated liquid detergent composition including primary alcohol ethoxylate and an anionic surfactant such as α -sulfo fatty acid derivatives or sulfonation products of polyalkylene glycol monomethyl ether unsaturated fatty acid ester or salts thereof.

55

50

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

5 [0007]

[Patent Document 1] JP-A-11-241092 [Patent Document 2] JP-A-2008-94942 [Patent Document 3] JP-A-2001-288500 [Patent Document 4] JP A 2005 171195

- 10
 [Patent Document 4] JP-A-2005-171195

 [Patent Document 5] JP-A-9-176685
 [Patent Document 6] JP-A-8-269485

 [Patent Document 7] JP-A-9-78092
- 15 DISCLOSURE OF INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008] However, in the liquid detergent composition disclosed in Patent Document 1 or the liquid detergent composition
 using a surfactant composition disclosed in Patent Document 2, the detergency for a sebum stain (sebum detergency) is not satisfactory.

The high-concentration anionic surfactant water-based paste disclosed in Patent Document 3 serves to improve the fluidity when including the anionic surfactant at a high concentration (50 % by mass or more), but does not satisfy preservation stability at a low temperature (at about 5°C), low-temperature solubility (at about 15°C), and sebum deter-

25 gency.

In the clothing liquid detergent composition disclosed in Patent Document 4, the viscosity may increase during preservation at a low temperature.

The liquid detergent composition disclosed in Patent Document 5 contains 30 % by mass or more of LAS or AES and thus cannot be said to be an environmentally-friendly composition.

- In the concentrated liquid detergent composition disclosed in Patent Documents 6 and 7, the synthesis of an anionic surfactant may require a high cost and thus is not satisfactory in cost or versatility. It is also inferior in biodegradability. [0009] The invention is made in consideration of the above-mentioned problems and an object thereof is to provide a liquid detergent composition which includes a surfactant at a high concentration and which has superior low-temperature preservation stability and superior low-temperature solubility and sebum detergency during washing.
- 35

MEANS TO SOLVE THE PROBLEMS

[0010] The inventors actively studied and finally found that it is possible to mix a surfactant at a high concentration without decreasing the low-temperature solubility while suppressing an increase in viscosity by mixing a primary alcohol ethoxylate and a specific anionic surfactant at a specific amount and using two or more species of specific hydrotropic agents. Moreover, since the low-temperature solubility can be retained, the inventors found that it is not necessary to mix the hydrotropic agent at a high concentration and it is possible to satisfactorily mix the functional components such as an enzyme and a chelating agent, and realized the invention.

- [0011] One aspect of the invention relates to a liquid detergent composition including: a component (A): a nonionic surfactant represented by the following formula (1); a component (B): at least one species of anionic surfactant selected from the group consisting of compounds represented by the following formulas (2) and (3); and a component (C): at least two species of water-miscible solvents selected from the group consisting of methanol, ethanol, propanol, butanol, ethylene glycol, propylene glycol, butylene glycol, butyl carbitol, phenoxy ethanol, and polyethylene glycol with an average molecular weight of 570 to 3800, wherein the total amount of the component (A) and the component (B) is in the range
- ⁵⁰ of 40 to 75 % by mass and the mass ratio of the amount of the component (B) with respect to the total amount of the component (A) and the component (B) satisfies component (B)/(component (A)+component (B)) = 1/10 to 6/10.

$$R^{1}O(CH_{2}CH_{2}O)_{n}H$$
 (1)

⁵⁵
$$R^2CH(SO_3M^1)COOR^3$$
 (2)

$$R^{4}CH(SO_{3}M^{2})CONHR^{5}$$
(3)

[0012] In the formulas (1) to (3), R^1 represents a straight-chain alkyl group with a carbon number of 10 to 22, R^2 represents a straight-chain or branched-chain alkyl group with a carbon number of 9 to 14 or a straight-chain or branched-chain alkenyl group with a carbon number of 9 to 16, R^3 represents a straight-chain or branched-chain alkyl group with a carbon number of 1 to 3, R^4 represents a straight-chain or branched-chain or branched-cha

- ⁵ 14 or a straight-chain or branched-chain alkenyl group with a carbon number of 9 to 16, R⁵ represents a hydrogen or a straight-chain or branched-chain alkyl group with a carbon number of 1 to 3 which may have a hydroxyl group, M¹ and M² each identically or differently represents alkali metal, alkaline-earth metal, protonated primary to tertiary amines or ammonium with a total carbon number of 1 to 6 which may have a hydroxyl group, and n represents an average mol number of ethyleneoxide added and is in the range of 5 to 20.
- 10 **[0013]** Another aspect of the invention relates to the liquid detergent composition, wherein the component (C) includes at least ethanol.

[0014] Yet another aspect of the invention relates to the liquid detergent composition, wherein the component (C) includes at least ethanol and polyethylene glycol with an average molecular weight of 570 to 1050.

[0015] Yet another aspect of the invention relates to the liquid detergent composition, wherein the amount of the component (A) is in the range of 20 to 60 % by mass, the amount of the component (B) is in the range of 4 to 45 % by mass, and the amount of the component (C) is in the range of 2 to 20 % by mass.

[0016] Yet another aspect of the invention relates to the liquid detergent composition, wherein the mass ratio of the amount of the component (B) with respect to the total amount of the component (A) and the component (B) satisfies component (B)/(component (A)+component (B)) = 2/10 to 5/10.

EFFECT OF THE INVENTION

[0017] The liquid detergent composition according to the invention includes a surfactant at a high concentration and has superior low-temperature preservation stability and superior low-temperature solubility and sebum detergency during washing.

EMBODIMENTS OF THE INVENTION

[0018] Hereinafter, the invention will be described in detail. A liquid detergent composition according to the invention includes components (A) to (C) described below.

<Component (A)>

[0019] A component (A) is a nonionic surfactant represented by the following formula (1)

35

40

15

20

25

 $R^{1}O(CH_{2}CH_{2}O)_{n}H$ (1)

[0020] In the formula (1), R¹ represents a straight-chain alkyl group with a carbon number of 10 to 22. Since the alkyl group has a straight-chain shape, detergency is enhanced. Since the carbon number of the alkyl group is equal to or greater than 10, sebum detergency is enhanced. Since the carbon number of the alkyl group is equal to or less than 22, low-temperature preservation stability and low-temperature solubility during washing is improved.

The carbon number of the alkyl group is preferably in the range of 10 to 20 and more preferably in the range of 10 to 18. R¹ originates from alcohol (R¹-OH) which is a source material. Examples of the alcohol include primary higher alcohol, higher fatty acid, and higher fatty acid amide.

⁴⁵ Specific examples of the alkyl group of R¹ include decyl, undecyl, dodecyl, tridecyl, tetradecyl, hexadecyl, stearyl, and icosyl.

[0021] n represents an average mol number of ethyleneoxide added. n is in the range of 5 to 20, preferably in the range of 8 to 18, and more preferably in the range of 10 to 16. When n is in the above-mentioned range, the sebum detergency is enhanced.

- ⁵⁰ **[0022]** In the component (A), the mol number distribution of ethyleneoxide added is not particularly limited. The added mol number distribution varies depending on the reaction method of producing the component (A). For example, when ethyleneoxide is added to a hydrophobic material using a general alkali catalyst such as sodium hydroxide or potassium hydroxide, a relatively wide distribution is apt to be obtained. Moreover, when ethyleneoxide is added to a hydrophobic material using a specific alkoxylating catalyst such as magnesium oxide to which metal ions such as Al³⁺, Ga³⁺, In³⁺,
- 55 TI³⁺, Co³⁺, Sc³⁺, La³⁺, and Mn²⁺ described in JP-B-6-15038 are added, a relatively narrow distribution is apt to be obtained. [0023] Specific examples of the component (A) include components obtained by adding ethyleneoxide to natural alcohol such as product name "CO-1214" or "CO-1270" made by P & G Co. so that the average added mol number was 12 moles or 15 moles.

The examples of the component (A) may be used alone or in combination of two or more species.

<Component (B)>

⁵ **[0024]** A component (B) is at least one species of anionic surfactant selected from the group consisting of compounds represented by the following formulas (2) and (3).

 $R^{2}CH(SO_{3}M^{1})COOR^{3}$ (2)

10

15

 $R^4CH(SO_3M^2)CONHR^5$ (3)

[0025] In the formula (2), R² represents a straight-chain or branched-chain alkyl group with a carbon number of 9 to 14 or a straight-chain or branched-chain alkenyl group with a carbon number of 9 to 16. Since the carbon number of the alkyl group is equal to or greater than 9, the sebum detergency is enhanced. When the carbon number is equal to or less than 14, the precipitation in the preservation at a low temperature can be suppressed.

- From the viewpoint of an increase in sebum detergency or prevention of viscosity at a low temperature, the carbon number of the alkyl group is preferably in the range of 10 to 14 and more preferably in the range of 10 to 12. On the other hand, the carbon number of the alkenyl group is preferably in the range of 10 to 16 and more preferably in the range of 10 to 12.
- 20 [0026] R³ represents a straight-chain or branched-chain alkyl group with a carbon number of 1 to 3. Since the carbon number of the alkyl group is equal to or greater than 1, the precipitation at a low temperature can be suppressed. Since the carbon number is equal to or less than 3, the low-temperature solubility during washing is improved. The carbon number of the alkyl group is preferably in the range of 1 to 2.
- [0027] M¹ represents a counter ion and forms a water-soluble salt along with R²CH(COOR³)SO₃⁻. Examples thereof include alkali metal, alkaline-earth metal, protonated primary to tertiary amines or ammonium with a total carbon number of 1 to 6 which may have a hydroxyl group. The alkali metal and the alkaline-earth metal can be present as cations and the number of atoms coupled to R²CH(COOR³)SO₃⁻ varies depending on the valence of the cations.

Examples of the alkali metal include sodium and potassium. Examples of the alkaline-earth metal include calcium.

The protonated primary to tertiary amines with a total carbon number of 1 to 6 may have a hydroxyl group or may not have a hydroxyl group. From the viewpoint of improvement of the low-temperature solubility at a low temperature, it is preferable that they have a hydroxyl group. Examples of the primary to tertiary amines include alkanolamine. Specific examples thereof include monoethanolamine, diethanolamine, and triethanolamine.

Sodium, monoethanolamine, and triethanolamine can be preferably used as M^1 .

[0028] Examples of the compound represented by the formula (2) include α -sulfo fatty acid ester salt (MES). Specific examples thereof include α -sulfolauric methyl ester monoethanolamine salt, α -sulfolauric methyl ester sodium salt, and α -sulfopalmitic methyl ester monoethanolamine salt.

The compounds represented by the formula (2) may be used alone or in combination of two or more species thereof. **[0029]** On the other hand, in the formula (3), R^4 represents a straight-chain or branched-chain alkyl group with a carbon number of 9 to 14 or a straight-chain or branched-chain alkenyl group with a carbon number of 9 to 16. Since

- 40 the carbon number of the alkyl group is equal to or greater than 9, the sebum detergency is enhanced. When the carbon number is equal to or less than 14, the precipitation in the preservation at a low temperature can be suppressed. From the viewpoint of prevention of an increase in sebum detergency or viscosity at a low temperature, the carbon number of the alkyl group is preferably in the range of 10 to 14 and more preferably in the range of 12 to 14. On the other hand, the carbon number of the alkenyl group is preferably in the range of 10 to 16 and more preferably in the
- other hand, the carbon number of the alkenyl group is preferably in the range of 10 to 16 and more preferably in the
 range of 12 to 16.
 R² and R⁴ may be identical to or different from each other.
 Specific examples of the alkyl group of R² include nonyl, secondary nonyl, decyl, secondary decyl, undecyl, secondary

undecyl, dodecyl, secondary dodecyl, tridecyl, isotridecyl, secondary tridecyl, tetradecyl, and secondary tetradecyl. Specific examples of the alkenyl group of R² include nonenyl, decenyl, undecenyl, dodecenyl, and tetradecenyl.

- 50 Specific examples of the alkyl group of R⁴ include nonyl, secondary nonyl, decyl, secondary decyl, undecyl, secondary tridecyl, secondary tridecyl, secondary tetradecyl. Specific examples of the alkenyl group of R⁴ include nonenyl, decenyl, undecenyl, dodecenyl, and tetradecenyl. [0030] R⁵ represents hydrogen or a straight-chain or branched-chain alkyl group with a carbon number of 1 to 3 which may have a hydroxyl group. Since the carbon number of the alkyl group is equal to or greater than 1, the precipitation
- at a low temperature can be suppressed. Since the carbon number is equal to or less than 3, the low-temperature solubility during washing is improved.

The carbon number of the alkyl group is preferably in the range of 2 to 3.

The alkyl group may have one or more hydroxyl groups or may not. From the viewpoint of improvement of the low-

temperature solubility at a low temperature, it is preferable that the alkyl group have a hydroxyl group. The straight-chain alkyl group is more excellent in low-temperature preservation stability than the branched-chain alkyl group.

[0031] M² represents a counter ion and forms a water-soluble salt along with R⁴CH(COOR⁵)SO₃⁻. Examples thereof include alkali metal, alkaline-earth metal, protonated primary to tertiary amines or ammonium with a total carbon number of 1 to 6 which may have a hydroxyl group. The alkali metal and the alkaline-earth metal can be present as cations and

the number of atoms coupled to R⁴CH(COOR⁵)SO₃⁻ varies depending on the valence of the cations. Examples of the alkali metal include sodium and potassium. Examples of the alkaline-earth metal include calcium. The protonated primary to tertiary amines with a total carbon number of 1 to 6 may or may not have a hydroxyl group. From the viewpoint of improvement of the low-temperature solubility at a low temperature, it is preferable that they have

5

- ¹⁰ a hydroxyl group. Examples of the primary to tertiary amines include alkanolamine. Specific examples thereof include monoethanolamine, diethanolamine, triethanolamine and the like. Sodium, monoethanolamine, and triethanolamine can be preferably used as M². M¹ and M² may be identical to or different from each other.
- [0032] Examples of the compound represented by the formula (3) include derivatives of α-sulfo fatty acid ester salt.
 15 Specific examples thereof include α-sulfolauric monoethanolamide sodium salt and α-sulfolauric isopropanolamide sodium salt.

The compounds represented by the formula (3) may be used alone or in combination of two or more species thereof. [0033] As the component (B), the compounds represented by the formula (2) may be used, the compounds represented by the formula (2) may be used to act the us

- by the formula (3) may be used, or they may be used together, but the compounds represented by the formula (3) can be preferably used. The compounds represented by the formula (3) are more bulky in molecular structure than the compounds represented by the formula (2) (that is, the steric hindrance is larger). As the steric hindrance becomes larger, the formation of a liquid crystal phase is more apt to be prevented. Accordingly, it is possible to suppress the increase in viscosity even when a surfactant is included with a high concentration.
- [0034] The component (A) is blended into the liquid detergent composition according to the invention for the purpose of imparting detergency (particularly, sebum detergency). On the other hand, the component (B) has a function of preventing the formation of a liquid crystal phase, and is superior in water solubility because it is a salt. Therefore, in the liquid detergent composition according to the invention, since the increase in viscosity is suppressed by using the component (A) and the component (B) together, the liquid detergent composition can include the surfactant at a high concentration and is thus superior in sebum detergency. In addition, since the liquid detergent composition is not easily
- 30 gelated in spite of the dilution with water during washing, it is possible to effectively exhibit excellent sebum detergency. Here, when the liquid detergent composition includes the component (A) but does not include the component (B) and the liquid detergent composition is input to a washing machine, gelation may be caused and the liquid detergent composition may not be easily dissolved in water, thereby not exhibiting satisfactory sebum detergency.
- When the liquid detergent composition does not include the component (A) but includes the component (B) at a high concentration, precipitates insoluble in water can be easily generated, thereby degrading the low-temperature preservation stability or the low-temperature solubility. The degradation in solubility is remarkable particularly when low-temperature water is used in winter or the like.

[0035] The amount of the component (A) is preferably in the range of 20 to 60 % by mass with respect to 100 % by mass of the liquid detergent composition, more preferably in the range of 25 to 55 % by mass, and still more preferably in the range of 25 to 55 % by mass.

- 40 in the range of 30 to 45 % by mass. When the amount of the component (A) is equal to or greater than 20 % by mass, superior sebum detergency can be imparted to the liquid detergent composition. On the other hand, when the amount of the component (A) is equal to or less than 60 % by mass, it is possible to maintain good solubility and low-temperature preservation stability of the liquid detergent composition.
- On the other hand, the amount of the component (B) is preferably in the range of 4 to 45 % by mass with respect to 100 % by mass of the liquid detergent composition, more preferably in the range of 9 to 40 % by mass, and still more preferably in the range of 10 to 35 % by mass. When the amount of the component (B) is equal to or greater than 4 % by mass, it is possible to suppress the increase in viscosity at a low temperature and thus to impart the preservation stability (particularly, low-temperature preservation stability) and the solubility to the liquid detergent composition. On the other hand, when the amount of the component (B) is equal to or less than 45 % by mass, it is possible to maintain good sebum detergency of the liquid detergent composition.
- [0036] In the liquid detergent composition according to the invention, the total amount of the component (A) and the component (B) is in the range of 40 to 75 % by mass with respect to 100 % by mass of the liquid detergent composition. The total amount is preferably in the range of 45 to 70 % by mass and more preferably in the range of 50 to 65 % by mass. When the total amount is equal to or greater than 40 % by mass, it is possible to impart the sebum detergency
- ⁵⁵ to the liquid detergent composition and thus to satisfactorily exhibit the function of a concentrated liquid detergent. On the other hand, when the total amount is equal to or less than 75 % by mass, it is possible to maintain good lowtemperature preservation stability of the liquid detergent composition.

[0037] The mass ratio of the amount of the component (B) with respect to the total amount of the component (A) and

the component (B) satisfies component (B)/(component (A)+component (B)) = 1/10 to 6/10, preferably 2/10 to 5/10, and more preferably 2/10 to 4/10. When the mass ratio of the amount of the component (B) to the total amount of the component (A) and the component (B) is in the above-mentioned range, it is possible to impart the low-temperature preservation stability, the low-temperature solubility, and the sebum detergency to the liquid detergent composition.

⁵ When the ratio of the component (B) is excessively low, the low-temperature solubility of the liquid detergent composition is lowered. On the other hand, when the ratio of the component (B) is excessively high, the sebum detergency of the liquid detergent composition is lowered.

The mass ratio of the amount of the component (B) to the total amount of the component (A) and the component (B) is in the above-mentioned range but the total amount of the component (A) and the component (B) is greater than 75 % by mass, the fluidity or the low-temperature fluidity may be lowered.

<Component (C)>

10

[0038] A component (C) includes at least two species of water-miscible solvents selected from the group consisting of methanol, ethanol, propanol, butanol, ethylene glycol, propylene glycol, butylene glycol, butyl carbitol, phenoxy ethanol, and polyethylene glycol with an average molecular weight of 570 to 3800.

The component (C) serves as a hydrotropic agent imparting the low-temperature preservation stability and the lowtemperature solubility to the liquid detergent composition. However, when one species of solvent described above is used alone, the liquid detergent composition is not easily soluble in water. When it is intended to enhance the solubility

20 of the liquid detergent composition, the ratio of the component (C) has only to be raised, but the ratio of the surfactant may be lowered as much, or it is difficult to blend the functional components such as an enzyme or a chelating agent as much.

However, in the invention, since two or more species of solvents are together used as the component (C), it is possible to impart the solubility to the liquid detergent composition without raising the ratio of the component (C) more than

- necessary. In addition, since it is not necessary to raise the ratio of the component (C), it is possible to blend a satisfactory amount of functional components without lowering the ratio of the surfactant.
 [0039] The combination of solvents used as the component (C) is not particularly limited, but it is preferable that at least ethanol be used from the viewpoint that it is easy to prevent the formation of a liquid crystal phase and it is easy.
- least ethanol be used from the viewpoint that it is easy to prevent the formation of a liquid crystal phase and it is easy to prevent microorganisms from reproducing. By using ethanol, it is possible to further enhance the low-temperature solubility or the low-temperature preservation stability.
 Moreover, preferably, one or meta-analysis of methanol, ethanol, prepared, butanol, and phenomy ethanol which are an analysis.
- Moreover, preferably, one or more species of methanol, ethanol, propanol, butanol, and phenoxy ethanol which are classified into monohydric alcohol and one or more species of ethylene glycol, propylene glycol, butylene glycol, butyle carbitol, and polyethylene glycol which are classified into polyhydric alcohol can be combined for use. Among the monohydric alcohols, phenoxy ethanol can be preferably used in addition to ethanol.
- On the other hand, among the polyhydric alcohols, ethylene glycol, polyethylene glycol, and propylene glycol can be preferably used. From the viewpoint that the increase in viscosity is suppressed to further enhance the low-temperature solubility or the low-temperature preservation stability of the liquid detergent composition and to stably dissolve optional components to be described later, polyethylene glycol with an average molecular weight of 570 to 3800 can be more preferably used. Among the polyethylene glycols with an average molecular weight of 570 to 3800, the average molecular weight is more preferably in the range of 570 to 1050 and still more preferably in the range of 950 to 1050.
- ⁴⁰ weight is more preferably in the range of 570 to 1050 and still more preferably in the range of 950 to 1050. [0040] The average molecular weight means the average molecular weight described in Japanese Standards of Quasidrug Ingredients 2006. Examples of polyethylene glycol with an average molecular weight of 570 to 3800 include Polyethylene Glycol 600 (with an average molecular weight of 570 to 630), Polyethylene Glycol 1000 (with an average molecular weight of 950 to 1050), Polyethylene Glycol 2000 (with an average molecular weight of 1850 to 2150), and
- ⁴⁵ Polyethylene Glycol 4000 (with an average molecular weight of 2600 to 3800). In some products, for example, like Polyethylene Glycol #1000, # may be interposed between polyethylene glycol and a numerical value. As the component (C), the combination of ethanol and polyethylene glycol with an average molecular weight of 570 to 1050 can be preferably used and the combination of ethanol and polyethylene glycol with an average molecular weight of 950 to 1050 can be more preferably used.
- ⁵⁰ **[0041]** The amount of the component (C) is preferably in the range of 2 to 20 % by mass with respect to 100 % by mass of the liquid detergent composition and more preferably in the range of 2 to 15 % by mass. When the amount of the component (C) is equal to or greater than 2 % by mass, the low-temperature preservation stability and the low-temperature solubility can be imparted to the liquid detergent composition. On the other hand, when the amount of the component (C) is equal to or less than 20 % by mass, a satisfactory amount of optional components can be blended
- ⁵⁵ into the liquid detergent composition. When ethanol is used as the component (C), the amount thereof is preferably in the range of 3 to 10 % by mass with respect to 100 % by mass of the liquid detergent composition. When polyethylene glycol is used as the component (C), the amount thereof is preferably in the range of 2 to 8 % by mass with respect to 100 % by mass of the liquid detergent.

composition.

<Optional Components>

- ⁵ **[0042]** The liquid detergent composition according to the invention includes components (A) to (C) described above as essential components, and may include only components (A) to (C) or may further include water, other surfactants other than components (A) to (B), and other components if necessary without damaging the advantageous effect of the invention.
- 10 (Water)

20

[0043] It is preferable that the liquid detergent composition according to the invention include water, from the viewpoint of easy preparation, preservation stability, and solubility in water.

The amount of water is preferably in the range of 15 to 50 % by mass with respect to 100 % by mass of the liquid detergent composition and more preferably in the range of 20 to 45 % by mass.

(Other Surfactants)

[0044] Examples of the other surfactants include nonionic surfactants other than the component (A), anionic surfactants other than the component (B), cationic surfactants, and amphoteric surfactants.

- Examples of the nonionic surfactants other than the component (A) include alkylphenol, alkyleneoxide adduct of higher fatty acid, higher amine, or the like, polyoxyethylene polyoxypropylene block copolymer, fatty acid alkanolamine, fatty acid alkanolamide, polyhydric alcohol fatty acid ester or alkyleneoxide adduct thereof, polyhydric alcohol fatty acid ester, alkyl (or alkenyl)amine oxide, alkyleneoxide adduct of hydrogenated castor oil, saccharide fatty acid ester, N-alkylpolyhydroxy fatty acid amide, and alkyl glycoside.
- 20 hydroxy fatty acid amide, and alkyl glycoside.
 [0045] Examples of the anionic surfactant other than the component (B) include carboxylic acid type anionic surfactants such as straight-chain alkyl benzene sulfuric acid or salt thereof, α-olefin sulfonate, straight-chain or branched-chain alkyl ester sulfonate, alkyl ether ester sulfonate or alkenyl ether ester sulfonate, alkane sulfonate having an alkyl group, higher fatty acid salt, alkyl ether carboxylate, polyoxyalkylene ether carboxylate, alkyl (or alkenyl)amide ether carboxylate, polyoxyalkylene
- ³⁰ and acylamino carboxylate, and ester phosphate type anionic surfactants such as alkyl ester phosphate, polyoxyalkylene alkyl ester phosphate, polyoxyalkylene alkyl phenyl ester phosphate, and glycerin fatty acid ester monoester phosphate. [0046] Examples of the cationic surfactant include anionic surfactants such as alkyltrimethylammonium salt, dialkyld-imethylammonium salt, alkylbenzyl dimethylammonium salt, and alkylpyridinium salt.
- Examples of the amphoteric surfactant include amphoteric surfactants such as alky betaine type, alkylamide betaine type, imidazoline type, alkylamino sulfone type, alkylamino carboxylate type, alkylamide carboxylate type, amideamino acid type, and phosphate type.

(Other Components)

- 40 [0047] From the viewpoint of improvement of the detergency, the liquid detergent composition according to the invention can include an enzyme typically used in clothing liquid detergent compositions. Examples of the enzyme include commercially-available lipase (lipase preparation) such as Production Names "Liquanase", "Savinase", "Alcalase", "Everlase", "Kannase", and "Esperaze", made by Novozymes Inc.; Product Name "API 21" made by Showa Denko K.K.; product Names "Maxtaze", "Maxacal", "Purafect", "Maxapem", and "Properase" made
- ⁴⁵ by Genencor International Inc.; Product Name "KAP" made by Kao Corporation; Product Names "Protease K-14" and "Protease K-16" described in JP-A-5-25492; Product Names "Termamyl", "Duramyl", "Stainzyme", and "Promozyme 200L" made by Novozymes Inc.; Product Name "Maxamyl" made by Genencor International Inc.; Product Name "Pullulanaseamano" made by Amano Enzyme Inc.; Product Name "DB-250 (Pullulanase originating from Aerobacter Aerogenes ATCC9621: crude or crystallized product) made by Seikagaku Corporation; Product Names "Lipolase", "Lipolase
- ⁵⁰ Ultra", "Lipex", and "Lipex 100L" made by Novozymes Inc.; and Product Name "Liposome" made by Showa Denko K.K. [0048] The amount of the enzyme is preferably in the range of 0.1 to 3 % by mass with respect to 100 % by mass of the liquid detergent composition. When the amount of the enzyme is equal to or greater than 0.1 % by mass, the detergency for various stains (particularly, the detergency for oily stains such as a sebum stain) is improved. When the amount of the enzyme is equal to or less than 3 % by mass, the detergency for various stains can be easily obtained, which is economically advantageous.
- which is economically advantageous.
 [0049] Moreover, the liquid detergent composition according to the invention may have a viscosity reducer such as paratoluene sulfonic acid, benzoate (which also serves as an antiseptic agent), and urea and a solubilizer, for example, by 0.01 to 15 % by mass.

The liquid detergent composition according to the invention may include a metal ion scavenger such as a malonic acid, a succinic acid, a malic acid, a diglycol acid, a tartaric acid, and a citric acid, for example, by 0. 1 to 20 % by mass. The liquid detergent composition according to the invention may include an antioxidant such as butylhydroxy toluene,

distyrenated cresol, sodium sulfite, and sodium hydrogen sulfite, for example, by 0.01 to 2 % by mass.

⁵ Moreover, the liquid detergent composition according to the invention may include an antiseptic agent such as Product Name "Kathon CG" made by Rohm and Haas Co., for example, by 0.001 to 1 % by mass.

[0050] The liquid detergent composition according to the invention may include a flexibilizer or a texture improver, an alkali builder such as alkanolamine, a pH control agent, a hydrotropic agent other than the component (C), a fluorescent agent, a migration-proofing agent, an anti-soil redeposition agent, a pearl agent, and a soil-release agent, for the purpose of improvement of the detergency or stability.

- Examples of the flexibilizer include long-chain aliphatic amide alkyl tertiary amines such as caprylic dimethylaminopropylamide, caprylic dimethylaminopropylamide, lauric dimethylaminopropylamide, myristic dimethylaminopropylamide, palmitic dimethylaminopropylamide, stearic dimethylaminopropylamide, behenic dimethylaminopropylamide, and oleic dimethylaminopropylamide or salts thereof; palmitic diethanolaminopropylamide; and stearic diethanolaminopropyla-
- ¹⁵ mide. For example, the liquid detergent composition according to the invention may include stearic dimethylaminopropylamide by 1 to 5 % by mass.
 Examples of the texture improver include polyether-modified silicones such as Product Names "CF1188HV", "SH3748", "SH3794", "SH3772M", "SH3775M", "SF8410", "SH8700", "BY22-008", "BY22-012", "SILWET L-7001", "SILWET L-
- 7002", "SILWET L-7602", "SILWET L-7604", "SILWET FZ-2104", "SILWET FZ-2120", "SILWET FZ-2161", "SILWET FZ-2161", "SILWET FZ-2162", "SILWET FZ-2164", "SILWET FZ-2171", "ABN SILWET FZ-F1-009-01", "ABN SILWET FZ-F1-009-02", "ABN SILWET FZ-F1-009-03", "ABN SILWET FZ-F1-009-05", "ABN SILWET FZ-F1-009-09", "ABN SILWET FZ-F1-009-11", "ABN SILWET FZ-F1-009-13", "ABN SILWET FZ-F1-009-54", and "ABN SILWET FZ-22-22" made by Dow Coming Toray Co., Ltd.; Product Names "X-20-8010 B", "KF352A", "KF6008", "KF615A", "KF6012", "KF6016", and "KF6017"
- made by Shin-Etsu Chemical Co., Ltd.; and Product Names "TSF4450", "TSF4452", and "TSF4445" made by GE Toshiba
 Silicones Co., Ltd. The polyether-modified silicones may be included by 0.1 to 3 % by mass in the liquid detergent composition.

[0051] In addition, the liquid detergent composition according to the invention may include an aromatizer, a colorant or an emulsifier, and a natural material for the purpose of improvement in added value of products.

A representative example of the aromatizer is a perfume composition described in JP-A-2002-146399. A preferable blending amount thereof is in the range of 0.1 to 1 % by mass.

General-purpose paints or pigments such as "Acid Red 138", "Polar Red RLS", "Acid Yellow 203", "Acid Blue 9", "Blue No. 1", "Blue No. 205", "Green No. 3", and "Turquoise P-GR" (all of which are product names) can be included, for example, by 0.00005 to 0.005 % by mass as the colorant.

Examples of the emulsifier include polystyrene emulsion and polyvinyl acetate emulsion. An emulsion with a solid content
 of 30 to 50 % by mass can be typically suitably used. Specifically, Product Name "Saibinol RPX-196 PE-3 with solid content of 40 % by mass" made by Saiden Chemical Industry Co., Ltd. can be added thereto by 0.01 to 0.5 % by mass. Examples of an extract of the natural material include plants such as Maackia amurensis, Arctostaphylos uva-ursi), Echinacea, Scutellaria baicalensis, Phellodendron amurense, Coptis japonica, allspice, oregano, Styphnolobiumjaponicum, Matricaria chamomilla L., Lonicera japonica, Sophora flavescens, Schizonepeta tenuifolia, cinnamon, laurel, Mag-

- ⁴⁰ nolia hypoleuca, burdock, comfrey, Torilis japonica seed, great burnet, Paeonia lactiflora, ginger, Solidago altissima, Sambucus nigra, common sage, European mistletoe, Atractylodes lancea, thyme, Anemarrhena asphodeloides, clove tree, Citrus unshiu, tea tree, barberry, Houttuynia cordata, Nandina domestica Thunb, Boswellia carterii Birdw, Angelica dahurica, Aglaophenia whiteleggei, Saposhnikovia seseloides, Psoralea corylifolia L, Humulus lupulus, Dalbergia cochinchinensis, mountain grape, Millettia, Melissa officinalis Linn, Iris domestica, Mosla japonica, eucalyptus, lavender,
- ⁴⁵ rose, rosemary, Aspidistra elatior, Cryptomeria japonica, Abies balsamea, Dictamnus albus, Kochia scoparia, Polygonum aviculare, Gentiana macrophylla, Liquidambar formosana, Adenophora triphylla var, Trapa japonica, Cayratia japonica, Glycyrrhiza, and Hypericum perforatum. These can be included, for example, by 0 to 0.5 % by mass.

<Physical Properties>

50

10

[0052] In the liquid detergent composition according to the invention, the pH is preferably in the range of 4 to 9 at 25° C and more preferably in the range of 4 to 8. When the pH is in this range, it is possible to maintain good temporal stability in spite of preservation of the liquid detergent composition for a long period of time.

The pH of the liquid detergent composition can be adjusted by the use of the pH control agent. Examples of the pH control agent include inorganic acids such as a hydrochloric acid, a sulfuric acid, a phosphoric acid; organic acids such as polyvalent carboxylic acids and hydroxyl carboxylic acids; sodium hydroxide; potassium hydroxide; alkanolamine; and ammonia. Among these, the sulfuric acid, the sodium hydroxide, the potassium hydroxide, and the alkanolamine can be preferably used from the viewpoint of temporal stability of the liquid detergent composition. The pH control agents

can be used alone or in combination of two or more species.

The inorganic acid (preferably the hydrochloric acid or the sulfuric acid) or the potassium hydroxide can be added thereto for fine adjustment of the pH of the liquid detergent composition.

In the invention, the pH (the pH at 25°C) of the liquid detergent composition is a value measured through the use of a pH meter (product name "HM-30G", made by DKK-Toa Corporation).

[0053] In the liquid detergent composition according to the invention, the viscosity at 25°C is preferably in the range of 40 to 150 mPa·s and more preferably in the range of 50 to 130 mPa·s.

Particularly, in the concentrated liquid detergent, the pickup cup is small and thus the picked-up quantity (used quantity) is small. Accordingly, when the liquid detergent does not have appropriate viscosity, it is difficult to measure a desired

- 10 quantity of the liquid detergent. However, when the viscosity is equal to or greater than 40 mPa·s, appropriate viscosity can be maintained and thus the convenience for use is good, thereby easily measuring an appropriate quantity. On the other hand, when the viscosity is equal to or less than 150 mPa·s, it is possible to suppress the gelation in inputting the liquid detergent composition to a detergent inlet of a washing machine at a low temperature.
 [0054] The viscosity of the liquid detergent composition is measured as follows.
- ¹⁵ First, a measurement sample is heated to 25°C in a constant-temperature bath set to 25°C. Then, the measurement sample heated to 25°C is set into a B-type viscometer (product name "viscometer Model DVM-B", made by Tokyo Keiki Inc.), rotation thereof is started at a rotation speed of 60 rpm/min by the use of rotor Nos. 2 to 4, and the viscosity is measured under the measuring condition of a measuring time of 60 seconds.
- 20 <Production of Liquid Detergent Composition>

5

[0055] The liquid detergent composition according to the invention can be produced by the use of usual methods. For example, the liquid detergent composition can be produced by blending components (A) to (C) and optional components if necessary. At this time, water can be preferably added thereto.

- ²⁵ **[0056]** The obtained liquid detergent composition according to the invention can be used in the same way as typically used clothing liquid detergents. That is, examples thereof include a method of inputting the liquid detergent composition according to the invention (the product of the invention) to water along with the laundry during washing, a method of directly applying the product of the invention to oil stains or sebum stains, and a method of dissolving the product of the invention in water and immersing clothes therein. In addition, a method of applying the product of the invention to the
- 30 laundry, appropriately leaving the laundry, and then performing a typical washing operation using a usual detergent can be also preferably used.

[0057] As described above, the liquid detergent composition according to the invention includes the components (A) to (C). The component (A) is a nonionic surfactant which is obtained by processing an environmentally-friendly surfactant source material, that is, the fat and oil material, and which is superior in biodegradability (particularly, sebum detergency)

- ³⁵ and is excellent in cost and source supply. On the other hand, the component (B) is an anionic surfactant having a function of preventing the formation of a liquid crystal phase which can be more easily formed when the concentration of the surfactant becomes higher. Accordingly, since the increase in viscosity is suppressed by using both the component (A) and the component (B) as the surfactant, the liquid detergent composition can include the surfactant at a high concentration and thus is superior in sebum detergency. Since the liquid detergent composition is not easily gelated in
- 40 diluting the liquid detergent composition with water during washing, it is possible to effectively exhibiting superior sebum detergency.

[0058] Since it includes the component (C), the liquid detergent composition according to the invention has superior low-temperature preservation stability and low-temperature solubility.

The liquid detergent has viscosity. Accordingly when the low-temperature preservation stability is not sufficient, the viscosity unnecessarily increases and it is difficult to measure the liquid detergent in picking up the liquid detergent from the vessel. This tendency is marked in winter.

However, since the liquid detergent composition according to the invention is superior in low-temperature preservation stability, appropriate viscosity can be maintained at a low temperature in winter and thus the liquid detergent composition can be easily handled.

⁵⁰ Particularly, in winter, the residual component of the detergent may be attached to clothes. However, since the liquid detergent composition according to the invention is superior in low-temperature solubility, the non-dissolved residual component of the detergent is not easily attached to clothes.

[EXAMPLES]

55

[0059] Hereinafter, the invention will be specifically described with reference to examples, but the invention is not limited to the examples.

<<Used Materials>>

[0060] The following compounds were used as the component (A).

a-1: material in which ethyleneoxide is added to natural alcohol "CO-1270" (alcohol with a carbon number of 12/alcohol with a carbon number of 14=70 % by mass/30 % by mass, with a straight chain ratio of 100% and an intermediate chain branching ratio of 0%) made by P & G Co. so that the average added mol number be 15 mol (with a purity of 90%) a-2: material in which ethyleneoxide is added to natural alcohol "CO-1214" (alcohol with a carbon number of 12/alcohol with a carbon number of 14=71 % by mass/29 % by mass, with a straight chain ratio of 100% and an intermediate chain branching ratio of 0%) made by P & G Co. so that the average added mol number be 15 mol (with a purity of 90%) a-3: material in which ethyleneoxide is added to natural alcohol "CO-1270" made by P & G Co. so that the average added mol number be 15 mol (with a purity of 90%) a-3: material in which ethyleneoxide is added to natural alcohol "CO-1270" made by P & G Co. so that the average added mol number be 12 mol (with a purity of 90%)

a-4: material in which ethyleneoxide is added to natural alcohol "CO-1214" made by P & G Co. so that the average added mol number be 9 mol (with a purity of 90%)

15

[0061] a-1 to a-4 were synthesized as follows.

(Synthesis of a-1)

- 20 [0062] 224.4 g of natural alcohol "CO-1270" made by P & G Co. as source alcohol and 2.0 g of 30 % by mass aqueous sodium hydroxide were input to a pressure-resistance reaction vessel and the inside of the vessel was replaced with nitrogen. The resultant was dewatered for 30 minutes while maintaining the inside of the vessel at a temperature of 100°C and a pressure of 1.5 to 2.0 kPa and then the temperature was raised to 160°C. 760.4 g of ethyleneoxide (gaseous state) was slowly added to the natural alcohol while stirring the natural alcohol and adjusting the adding rate by the use
- of a blowing tube so that the reaction temperature not be higher than 180°C. After the adding of ethyleneoxide was ended, the resultant was aged for 30 minutes while maintaining the inside of the vessel at a temperature of 180°C and a pressure of 0.2 to 0.3 MPa, then the pressure in the vessel was lowered to 5.5 to 6.0 kPa, and non-reacted ethyleneoxide was distilled away for 10 minutes.
- Subsequently, the temperature in the vessel was lowered to 80°C to 100°C, and then 70 % by mass p-toluenesulfonic acid was added thereto to neutralize the resultant so that the pH of the 1 % by mass aqueous solution of the reactant was about 7, whereby a-1 was obtained.

(Synthesis of a-2)

³⁵ **[0063]** a-2 was obtained in the same way as obtaining a-1, except that 224.4 g of natural alcohol "CO-1214" made by P & G Co. was used as source alcohol and the amount of ethyleneoxide was changed to 760.6 g.

(Synthesis of a-3)

⁴⁰ **[0064]** a-3 was obtained in the same way as obtaining a-1, except that the amount of ethyleneoxide was changed to 610.2 g.

(Synthesis of a-4)

50

45 [0065] a-4 was obtained in the same way as obtaining a-1, except that 224.4 g of natural alcohol "CO-1214" made by P & G Co. was used as source alcohol and the amount of ethyleneoxide was changed to 457.2 g.
 [0066] The following compounds were used as the nonionic surfactant other than the component (A). The nonionic

[0066] The following compounds were used as the nonionic surfactant other than the component (A). The nonionic surfactant was defined as "component (A')".

a-5: polyoxyethylene lauryl ether, EO (ethyleneoxide)-average 3 mol adduct (product name "EMALEX 703", made by Nihon Emulsion Co., Ltd.) (with a purity of 100%)

a-6: polyoxyethylene lauryl ether, EO-average 25 mol adduct (product name "EMALEX 725", made by Nihon Emulsion Co., Ltd.) (with a purity of 100%)

a-7: $C_{12}H_{25}O(CH_2CH_2O)_{10}(CH_2CH(CH_3)O)H$, (with a purity of 100%).

- a-8: $C_{14}H_{29}O(CH_2CH_2O)_7(CH_2CH(CH_3)O)(CH_2CH_2O)_3H$, (with a purity of 100%).
- ⁵⁵ a-9: polyoxyethylene (15) beef tallow alkylamine (composition of beef tallow alkylamine: 1 % by mass of an alkyl group with a carbon number of 12, 3 % by mass of an alkyl group with a carbon number of 14, 31 % by mass of an alkyl group with a carbon number of 16, 20 % by mass of an alkyl group with a carbon number of 18, 1 % by mass of an alkyl group with a carbon number of 20, and 44 % by mass of an alkenyl group with a carbon number of 18), EO-average 15 mol

adduct (product name "Ethomeen T/25", made by Lion Akzo Co., Ltd.) (with a purity of 100%) **[0067]** a-7 and a-8 were synthesized as follows.

(Synthesis of a-7)

5

40

50

[0068] 1026 g of alcohol "Conol 20P" made by New Japan Chemical Co., Ltd. as source alcohol was input to a pressureresistance reaction vessel and the inside of the vessel was replaced with nitrogen. The alcohol was dewatered for 30 minutes while maintaining the inside of the vessel at a temperature of 100°C and a pressure of 1.5 to 2.0 kPa, and then the temperature was raised to 140°C. 2063 g of ethyleneoxide (gaseous state) was slowly added to the alcohol while stirring the alcohol and adjusting the adding rate by the use of a blowing tube so that the reaction temperature not be

10 stirring the alcohol and adjusting the adding rate by the use of a blowing tube so that the reaction temperature not be higher than 180°C.

After the adding of ethyleneoxide was ended, the resultant was aged for 30 minutes while maintaining the inside of the vessel at a temperature of 180°C and a pressure of 0.2 to 0.3 MPa, then the pressure in the vessel was lowered to 5.5 to 6.0 kPa, and non-reacted ethyleneoxide was distilled away for 10 minutes.

- ¹⁵ The temperature in the vessel was lowered to 80°C to 100°C, then 1231 g of the crude product was taken out of the vessel, and the temperature in the vessel was raised to 120°C. 173 g of propyleneoxide (gaseous state) was slowly added to the reactant while stirring the residual reactant and adjusting the adding rate by the use of a blowing tube so that the reaction temperature not be higher than 125°C.
- After the adding of propyleneoxide was ended, the resultant was aged for 2 hours while maintaining the inside of the vessel at a temperature of 120°C and a pressure of 0.25 to 0.30 MPa, then the pressure in the vessel was lowered to
- 5.5 to 6.0 kPa, and non-reacted propyleneoxide was distilled away for 10 minutes, whereby a-7 was obtained.

(Synthesis of a-8)

- [0069] 1004 g of alcohol "Conol 1495" made by New Japan Chemical Co., Ltd. as source alcohol and 10.0 g of potassium hydroxide were input to a pressure-resistance reaction vessel and the inside of the vessel was replaced with nitrogen. The alcohol was dewatered for 30 minutes while maintaining the inside of the vessel at a temperature of 100°C and a pressure of 1.5 to 2.0 kPa, and then the temperature was raised to 140°C. 1444 g of ethyleneoxide (gaseous state) was slowly added to the alcohol while stirring the alcohol and adjusting the adding rate by the use of a blowing
- 30 tube so that the reaction temperature not be higher than 180°C. After the adding of ethyleneoxide was ended, the resultant was aged for 30 minutes while maintaining the inside of the vessel at a temperature of 180°C and a pressure of 0.2 to 0.3 MPa, then the pressure in the vessel was lowered to 5.5 to 6.0 kPa, and non-reacted ethyleneoxide was distilled away for 10 minutes.
- The temperature in the vessel was lowered to 80°C to 100°C, then 1463 g of the crude product was taken out of the vessel, and the temperature in the vessel was raised to 120°C. 110 g of propyleneoxide (gaseous state) was slowly added to the reactant while stirring the residual reactant and adjusting the adding rate by the use of a blowing tube so that the reaction temperature not be higher than 125°C. After the adding of propyleneoxide was ended, the resultant was aged for 2 hours while maintaining the inside of the

After the adding of propyleneoxide was ended, the resultant was aged for 2 hours while maintaining the inside of the vessel at a temperature of 120°C and a pressure of 0.2 to 0.3 MPa, then the pressure in the vessel was lowered to 5.5 to 6.0 kPa, and non-reacted propyleneoxide was distilled away for 10 minutes.

- Then, the temperature in the vessel was raised to 140°C, and 251 g of ethyleneoxide (gaseous state) was slowly added to the reactant while stirring the reactant and adjusting the adding rate by the use of a blowing tube so that the reaction temperature not be higher than 180°C.
- After the adding of ethyleneoxide was ended, the resultant was aged for 30 minutes while maintaining the inside of the vessel at a temperature of 180°C and a pressure of 0.2 to 0.3 MPa, then the pressure in the vessel was lowered to 5.5 to 6.0 kPa, and non-reacted ethyleneoxide was distilled away for 10 minutes, whereby a-8 was obtained.

[0070] The following compounds were used as the component (B).

b-1: C₁₀H₂₁CH(SO₃NH₃CH₂CH₂OH)COOCH₃ (with a purity of 100%)

b-2: $C_{10}H_{21}CH(SO_3Na)COOCH_3$ (with a purity of 100%)

b-3: C₁₄H₂₉CH(SO₃NH₃CH₂CH₂OH)COOCH₃ (with a purity of 100%)

b-4: C₁₀H₂₁CH(SO₃Na)CONHCH₂CH₂OH (with a purity of 100%)

b-5: C₁₀H₂₁CH(SO₃Na)CONHCH₂CH(OH)CH₃, (with a purity of 100%)

55 **[0071]** b-1 to b-5 were synthesized as follows.

(Synthesis of b-1)

5

[0072] 54 g (0.25 mol) of laurate methylester and 540 g of carbon tetrachloride were put into a 1 L four-necked flask mounted with a thermometer, a stirrer, a dropping funnel, and a drying calcium chloride tube, and 24 g (0.3 mol) of sulfuric anhydride was added dropwise therein while maintaining the reaction temperature at a temperature of 10°C to 15°C. After the dropwise addition was ended, the resultant was stirred to reflux for 3 hours.

Subsequently, the reaction solvent (carbon tetrachloride) was distilled away in a water bath of 50°C by the use of an evaporator, 500 mL of methanol was added thereto, and then the resultant was stirred to reflux for 20 minutes. Thereafter, the pH of the reactant solution was adjusted to 7 with 0.5 mol/L aqueous monoethanolamine. Then, the reaction solvent

- 10 (methanol) was distilled away under depressurization. At this time, since the resultant was foamed, isopropanol was added thereto and water was distilled away while boiling the resultant together. The residue (crude product) was heated to a temperature of 50°C to 60°C and was dissolved in a mixed solution (with a volume ratio of ethanol/water=9/1) of ethanol and water to remove the insoluble components. Then, the solution was cooled to 5°C for recrystallization, and the precipitates were filtrated and were dried in vacuum, whereby 58 g of α -sulfo
- 15 laurate methyl ester monoethanolamine salt (b-1) was obtained. Here, b-1 is a compound corresponding to the formula (2).

(Synthesis of b-2)

[0073] α -sulfo laurate methyl ester sodium salt (b-2) was obtained in the same way as obtaining b-1, except that the 20 pH of the reactant solution was adjusted to 7 using 20 % by mass aqueous sodium hydroxide instead of 0.5 mol/L aqueous monoethanolamine. Here, b-2 is a compound corresponding to the formula (2).

(Synthesis of b-3)

25 [0074] α-sulfo palmitate methyl ester monoethanolamine salt (b-3) was obtained in the same way as obtaining b-1, except that 68 g (0.25 mol) of palmitate methyl ester was used instead of 54 g (0.25 mol) of laurate methyl ester. Here, b-3 is a compound corresponding to the formula (2).

(Synthesis of b-4)

30 [0075] 20 g (63.2 mmol) of α -sulfo laurate methyl ester sodium salt and 150 mL of toluene were put into a 300 mL one-necked flask mounted with a Dean-Stark apparatus and a stirrer, and the resultant was made to reflow and was dewatered.

Thereafter, the inside of the flask was cooled to room temperature, the Dean-Stark apparatus was detached therefrom, 35 and a Dimroth condenser pipe was attached thereto. 4.05 g (66.4 mmol) of 2-aminoethanol and 342 mg (6.3 mmol) of sodium methoxide were added to the reactant solution and the resultant was stirred at 90°C for 4 hours. Thereafter, the resultant was cooled to room temperature, 1.3 mL of 5 N aqueous hydrochloric acid was added thereto, and the resultant was boiled along with isopropanol to completely distill away the solvent (toluene), whereby a solid crude product was obtained.

- 40 The obtained crude product was heated to a temperature of 50°C to 60°C and was dissolved in a mixed solution (with a volume ratio of methanol/water=9/1) of methanol and water, the resultant was recrystallized at -20°C, and the precipitates were filtrated. The residue was heated to a temperature of 50°C to 60°C and was dissolved in a mixed solution of methanol and water, the resultant was recrystallized at -20°C, and the precipitates were filtrated and dried in vacuum, whereby 15.44 g of b-4 was obtained.
- 45 The obtained b-4 (15 mg) was dissolved in 0.5 mL of heavy water and the resultant was subjected to measurement at a measuring temperature of 25°C by the use of ¹H-NMR (270 MHz, product name "FT NMR SYSTEM JNM-EX270", made by Jeol Datum Ltd.). With reference to the peak of the heavy water of 4.75 ppm, the chemical shift was $\delta 0.73$ (br, 3H), δ1.15 (br, 16H), δ1.88 (br, 2H), δ3.24 (m, 1H), δ3.33 (m, 1H), and δ3.58 (br, 3H). As a result, it could be seen that the obtained b-4 was α-sulfo laurate monoethanolamide sodium salt. Here, b-4 is a compound corresponding to the 50 formula (3).

(Synthesis of b-5)

[0076] A solid crude product was obtained in the same way as obtaining b-4, except that 4.98 g (66.4 mmol) of 3-55 amino-2-propanol was used instead of 4.05 g (66.4 mmol) of 2-aminoethanol.

The obtained crude product was extracted with a mixed solution (with a volume ratio of chloroform/methanol/water=1/1/8) of chloroform, methanol, and water, the water layer was separated, the resultant was boiled along with isopropanol and was depressurized to distill away the solvent (mixed solution), and the resultant was dried in vacuum, whereby 18.9 g of b-5 was obtained.

The obtained b-5 (15 mg) was dissolved in 0.5 mL of heavy water and the resultant was subjected to measurement at a measuring temperature of 25°C by the use of ¹H-NMR (270 MHz, product name "FT NMR SYSTEM JNM-EX270", made by Jeol Datum Ltd.). With reference to the peak of the heavy water of 4.75 ppm, the chemical shift was $\delta 0.71$ (br,

⁵ 3H), δ 1.05-1.15 (m+br, 19H), δ 1.87 (br, 2H), δ 3.18 (br, 2H), δ 3.60 (br, 1H), and δ 3.82 (br, 1H). As a result, it could be seen that the obtained b-5 was α-sulfo laurate isopropanolamide sodium salt. Here, b-5 is a compound corresponding to the formula (3).

[0077] The following compounds were used as the anionic surfactant other than the component (B). The anionic surfactant was defined as "component (B')".

¹⁰ b-6: polyoxyethylene alkyl ether sodium sulfate (AES) (ethyleneoxide was added to alcohol "Neodol 23", made by Shell Chemicals Limited) (mixture in which a mass ratio of alcohol with a carbon number of 12 and alcohol with a carbon number of 13 is 1:1, with a branching ratio of 20%) so that the average added mol number was 2 mol (with a purity of 66.3%) [0078] b-6 was synthesized as follows.

400 g of "Neodol 23" made by Shell Chemicals Limited as source alcohol and 0.8 g of potassium hydroxide as a catalyst

- ¹⁵ were put into a 4 L autoclave, the inside of the autoclave was replaced with nitrogen, and the temperature was raised while stirring the resultant. Thereafter, 272 g of ethyleneoxide was added while maintaining the inside of the autoclave at a temperature of 180°C and a pressure of 0.3 MPa, whereby the reactant (alcohol ethoxylate) in which an average added mol number of ethyleneoxide is 2 was obtained.
- Subsequently, 280 g of the obtained alcohol ethoxylate was put into 500 mL flask mounted with a stirrer, the inside of the flask was replaced with nitrogen, 67 g of liquid sulfuric anhydride (sulfane) was slowly added dropwise therein while maintaining the reaction temperature at 40°C. After the dropwise addition was ended, the resultant was continuously stirred for 1 hour (sulfation reaction), whereby polyoxyethylene alkyl ether sulfuric acid was obtained. By neutralizing the obtained resultant with aqueous sodium hydroxide, polyoxyethylene alkyl ether sodium sulfate (b-6) was obtained. **[0079]** The following compounds were used as the component (C).
- 25

40

c-1: ethanol (product name "Specific Alcohol 95% Synthesized", made by Japan Alcohol Trading Co., Ltd.) (with a purity of 95%)

c-2: propylene glycol (made by BASF Co., Ltd.) (with a purity of 100%)

- c-3: methanol (made by Junsei Chemical Co., Ltd.) (with a purity of 100%)
- ³⁰ c-4: butanol (product name "1-Butanol", made by Tokyo Chemical Industry Co., Ltd.) (with a purity of 100%)
 c-5: phenoxyethanol (product name "Ethylene Glycol Monophenylether", made by Tokyo Chemical Industry Co., Ltd.) (with a purity of 100%)

c-6: butyl carbitol (product name "Diethylene Glycol Monobutyl Glycol", made by Tokyo Chemical Industry Co., Ltd.) (with a purity of 100%)

³⁵ c-7: propanol (product name, "1-Propanol", made by Tokyo Chemical Industry Co., Ltd.) (with a purity of 100%)
 c-8: ethylene glycol (made by Tokyo Chemical Industry Co., Ltd.) (with a purity of 100%)
 c-8: ethylene glycol (made by Tokyo Chemical Industry Co., Ltd.) (with a purity of 100%)

c-9: butylene glycol (product name "1,3-Butanediol", made by Tokyo Chemical Industry Co., Ltd.) (with a purity of 100%)

- c-10: polyethylene glycol (product name "PEG#1000-L60", made by Lion Corporation, with an average molecular weight of 950 to 1050) (with a purity of 60%)
 - c-11: polyethylene glycol (product name "PEG#600", made by Lion Corporation, with an average molecular weight of 570 to 630) (with a purity of 60%)

[0080] The following reagents were used as the optional components.

⁴⁵ Sodium benzoate: product name "Sodium Benzoate", made by Toa Gosei Co., Ltd. (with a purity of 100%) Citric acid: product name "Liquid Citric Acid", made by Ipposha Oil Industries Co., Ltd. (with a purity of 50%) Palmitic acid: product name "NAA-160", made by NOF Corporation (with a purity of 100%) Paratoluenesulfonic acid: product name "PTS Acid", made by Kyowa Hakko Kirin Co., Ltd. (with a purity of 70%) Liquanase: product name "Liquanase Ultra 2.5XL", made by Novozymes Inc. (with a purity of 100%)

 Dibutylhydroxy toluene: product name "Sumilzer BHT-R", made by Sumitomo Chemical Co., Ltd. (with a purity of 100%) Monoethanolamine: made by Nippon Shokubai Co., Ltd. (with a purity of 75%)
 Perfume: perfume composition A described in Tables 11 to 18 of JP-A-2002-146399 (with a purity of 100%)
 Green No. 3 (pigment): product name "Green No. 3", made by Taketombo Co., Ltd. (with a purity of 100%)
 [0081] Blending quantities of the components used for preparation of the liquid detergent composition are shown in

55 Table 1. The values in Table 1 are quantities reduced to purity. The "balance" means the amount of water blended to the liquid detergent composition when the total amount of all the components included in the liquid detergent composition is adjusted to 100 % by mass.

[0082]

	liquid detergent composition	blended amount(% by mass)
	component (A)	blended amounts described in Table 2 to 5
	component (B)	blended amounts described in Table 2 to 5
	component (C)	blended amounts described in Table 2 to 5
	sodium benzoate	1.8
	citric acid	0.3
	palmitic acid	0.1
	paratoluenesulfonic acid	1.0
	Liquanase	0.5
optional component	dibutylhydroxy toluene	0.05
op liendi component	monoethanol amine	1.0
	perfume	0.4
	Green No. 3	0.0003
	pH control agent (sodium hydroxide or sulfuric acid)	appropriate amount
	purified water	balance
	Total	100
	optional component	Iiquid detergent composition Iiquid detergent composition component (A) component (B) component (C) sodium benzoate citric acid palmitic acid paratoluenesulfonic acid Liquanase dibutylhydroxy toluene Green No. 3 pH control agent (sodium hydroxide or sulfuric acid) purified water

[Table 1]

<<Measurement and Evaluation>>

30

50

<Measurement of Viscosity>

[0083] A beaker containing 100 g of the liquid detergent composition was put into a constant-temperature bath of 25°C and was heated for 1 hour. The heated liquid detergent composition was set to a B-type viscometer (product name "Viscometer Model DVM-B", made by Tokyo Keiki Inc.), rotation thereof was started at a rotation speed of 60 rpm/min by the use of rotor No. 2 or 3, and the viscosity was measured under the measuring condition of a measuring time of 60 seconds. In Comparative Example 3, rotation was started at a rotation speed of 60 rpm/min by the use of rotor No. 4 and the viscosity was measured under the measuring time of 60 seconds.

40 <Evaluation of Initial Appearance>

[0084] The appearance when the beaker containing 100 g of the liquid detergent composition was obliquely inclined was observed with the naked eye and the initial appearance was evaluated on the basis of the following criteria. A: There is fluidity.

B: There is no fluidity.

<Evaluation of Low-temperature Preservation Stability>

[0085] 100 mL of the liquid detergent composition was put into a transparent glass bottle (wide-mouthed standard bottle PS-No. 11), and the bottle was covered and sealed with a lid. In this state, the bottle was left at room temperature (25°C) for 1 month and this resultant was set as a room-temperature preserved sample.

100 mL of the liquid detergent composition was put into a transparent glass bottle, and the bottle was covered and sealed with a lid. In this state, the bottle was left in a constant-temperature bath for 1 month. Thereafter, the liquid detergent composition was taken out from the constant-temperature bath and was left at room temperature (25°C) for 1 hour. The liquid appearance and the liquid viscosity of the resultant contents were observed with the naked eye and the lowtemperature preservation stability was evaluated on the basis of the following criteria.

A: The appearance was transparent and uniform and the liquid viscosity was identical to that of the room-temperature preserved sample.

B: The appearance was transparent and uniform, no precipitate was recognized, and the liquid viscosity was slightly higher that of the room-temperature preserved sample, which was allowable.

C: The precipitate and/or the increase in viscosity were recognized.

5 < Evaluation of Low-temperature Solubility>

[0086] 300 mL of ion-exchange water at 15°C was put into a 500 mL beaker, and 0.1 g of the liquid detergent composition was added dropwise therein by the use of a dropping pipette while stirring the ion-exchange water at a rotation speed of 500 rpm/min by the use of a magnetic stirrer (made by Mitamura Kogyo Inc.). The time (dissolution time) until the liquid detergent composition was completely dissolved was measured and the low-temperature solubility was evaluated

- 10 liquid detergent composition was cor on the basis of the following criteria.
 - A: The dissolution time was less than 50 seconds.
 - B: The dissolution time was equal to or more than 50 seconds and less than 100 seconds.
 - C: The dissolution time was equal to or more than 100 seconds.
- 15

20

30

35

<Evaluation of Sebum Detergency>

[0087] 10 pieces obtained by cutting a cotton cloth sheet (woven cotton fabric, No. 100 yarn count) and scraping a sebum stain on a face in a size of 20 cm square and 4 pieces ofT shirts (cotton 100%, made by B.V.D. Co., Ltd.) which are commercially available were input into an electrical washing machine ("CW-C30A1 Type", made by Mitsubishi Electric

Corporation).

Then, 10 mL of the liquid detergent composition was input into about 30 L of tap water of 25°C, and a washing operation of sequentially carrying out washing (for 10 minutes) using a standard water flow, dewatering (for 1 minute), rinsing using a standard water flow (repeated twice), and dewatering (for 1 minute) was performed.

A cotton cloth piece not having a sebum stain was defined as a non-stained cloth piece, a cotton cloth piece not subjected to the washing operation was defined as a stained cloth piece, and a cotton cloth piece having been subjected to the washing operation was defined as a washed cloth piece.

The reflectance of the non-stained cloth piece, the stained cloth piece, and the washed cloth piece was measured by the use of a spectral color-difference meter ("SE2000", made by Nippon Denshoku Industries Co., Ltd.) and the deterging rates thereof were calculated using Expression (I).

Deterging rate (%)={(K/S of stained cloth-K/S of washed cloth)/(K/S of stained cloth-K/S of non-stained cloth)} \times 100 ... (I) In Expression (I) "K/S" represent (1-R/100)²/(2R/100) (where R represents the reflectance (%) of the non-stained cloth, the stained cloth, or the washed cloth).

[0088] The deterging rates (%) of 10 pieces of stained cloth were calculated and the sebum detergency was evaluated using the average value thereof on the basis of the following criteria.

- A: The average value of the deterging rates was equal to or more than 70%.
- B: The average value of the deterging rates was equal to or more than 50% and less than 70%.
- C: The average value of the deterging rates was less than 50%.
- 40 << Examples 1 to 48 and Comparative Examples 1 to 14>>

[0089] Various components were put into a 500 mL beaker on the basis of the blending compositions shown in Tables 2 to 5 and were sufficiently stirred with a magnetic stirrer (made by Mitanura Kogyo Inc.). Subsequently, optional components (excluding purified water) were added thereto in accordance with the blending amounts shown in Table 1, then

⁴⁵ purified water was added thereto so that the total amount was 98 % by mass while stirring the resultant, and the resultant was further stirred. An appropriate amount of pH control agent (sodium hydroxide or sulfuric acid) was added thereto so that the pH at 25°C was 7.0, and then purified water was added thereto so that the total amount was 100 % by mass, whereby liquid detergent compositions were obtained.

The obtained liquid detergent compositions were measured and evaluated. The results are shown in Tables 2 to 5.

⁵⁰ The unit of the blending amounts in Tables 2 to 5 is % by mass and all the components are expressed in amounts reduced to purity.
[0090]

55

55	

ы

[Table 2]

			Examples														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
component (A)	a-1	45	40	30	20	45	40	30	20	24	36	45	24	36	45	30	30
	a-2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	a-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	a-4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
component (B)	b-1	5	10	20	30	-	-	-	-	16	24	30	-	-	-	-	-
	b-2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20	-
	b-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20
	b-4	-	-	-	-	5	10	20	30	-	-	-	16	24	30	-	-
	b-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
component (C)	c-1	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	c-2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-10	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
(A)+(B) [% by mass]		50	50	50	50	50	50	50	50	40	60	75	40	60	75	50	50
(B)/{(A)+(B)}		1/10	2/10	4/10	6/10	1/10	2/10	4/10	6/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10
viscosity [mPa·s]		120	112	105	98	113	99	86	75	125	128	135	102	95	115	109	112

55	50	45	40	35	30	25	20	15	10	5

						``	,										
			Examples														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
evaluation	initial appearance	Α	Α	Α	Α	Α	Α	Α	А	А	А	Α	Α	Α	Α	А	Α
	low-temperature preservation stability	В	В	В	В	В	В	А	A	В	В	В	А	А	А	В	В
	low-temperature solubility	В	Α	Α	Α	В	Α	Α	А	В	В	В	В	Α	В	Α	Α
	sebum detergency	Α	Α	Α	В	Α	Α	Α	В	В	А	Α	В	Α	Α	А	В

	[0091]		
5			
10			
15			
20			
25			
30			
35			
40			
45			
50			
55			

ъ

ab	le	31	

						[Ta	ble 3]										
									Exan	nples							
		17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
component (A)	a-1	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
	a-2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	a-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	a-4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
component (B)	b-1	-	20	20	-	20	20	20	20	20	20	20	20	-	-	-	-
	b-2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	b-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	b-4	-	-	-	20	-	-	-	-	-	-	-	-	20	20	20	20
	b-5	20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
component (C)	c-1	10	3	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	c-2	-	-	-	-	5	-	-	-	-	-	-	-	5	-	-	-
	c-3	-	-	-	-	-	5	-	-	-	-	-	-	-	5	-	-
	c-4	-	-	-	-	-	-	5	-	-	-	-	-	-	-	5	-
	c-5	-	-	-	-	-	-	-	5	-	-	-	-	-	-	-	5
	c-6	-	-	-	-	-	-	-	-	5	-	-	-	-	-	-	-
	c-7	-	-	-	-	-	-	-	-	-	5	-	-	-	-	-	-
	c-8	-	-	-	-	-	-	-	-	-	-	5	-	-	-	-	-
	c-9	-	-	-	-	-	-	-	-	-	-	-	5	-	-	-	-
	c-10	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
(A)+(B) [% by mass]		50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
(B)/{(A)+(B)}		4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10
viscosity [mPa·s]		103	137	129	115	110	102	98	99	111	108	105	115	105	95	90	96

55	50	45	40	35	30	25	20	15	10	S

			Examples														
		17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
evaluation	initial appearance	Α	А	А	Α	Α	А	Α	А	А	А	Α	А	А	А	А	А
	low-temperature preservation stability	В	В	В	В	В	В	В	В	В	В	В	В	A	A	A	А
	solubility low-temperature	А	В	В	А	Α	А	А	А	А	А	А	А	А	А	А	А
	sebum detergency	Α	А	А	Α	Α	А	Α	А	А	А	Α	А	А	А	А	А

(continued)

	[0092]		
5			
10			
15			
20			
25			
30			
35			
40			
45			
50			
55			

ы

[Table 4]

											Exa	nples								
		33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51
	a-1	30	30	30	30	30	30	30	30	30	30	30	30	30	-	-	-	-	-	-
component (A)	a-2	-	-	-	-	-	-	-	-	-	-	-	-	-	30	-	-	30	-	-
component (A)	a-3	-	-	-	-	I	-	-	-	-	-	-	-	-	-	30	-	-	30	-
	a-4	-	-	-	-	I	-	-	-	-	-	-	-	-	-	-	30	-	-	30
	b-1	-	-	-	-	20	20	20	-	-	-	-	-	-	20	20	20	-	-	-
	b-2	-	-	-	-	I	-	-	-	-	-	-	-	-	-	1	-	-	-	-
component (B)	b-3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	b-4	20	20	20	20	-	-	-	20	20	20	20	20	20	-	-	-	20	20	20
	b-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-1	5	5	5	5	-	5	-	-	5	-	10	10	10	10	10	10	10	10	10
	c-2	-	-	-	-	5	5	-	5	-	-	-	-	-	-	-	-	-	-	-
	c-3	-	-	-	-	I	-	-	-	-	-	-	-	-	-	1	-	-	-	-
	c-4	-	-	-	-	I	-	-	5	5	-	-	-	-	-	I	-	-	-	-
	c-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
component (C)	c-6	5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-7	-	5	-	-	I	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	c-8	-	-	5	-	5	-	10	-	-	10	-	-	-	-	-	-	-	-	-
	c-9	-	-	-	5	I	-	-	-	-	-	-	-	-	-	1	-	-	-	-
	c-10	2	2	2	2	-	-	2	-	-	2	5	8	-	2	2	2	2	2	2
	c-11	-	-	-	-	-	-	-	-	-	-	-	-	2	-	-	-	-	-	-
(A)+(B) [% by ma	ass]	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
(B)/{(A)+(B)}		4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10	4/10

55 50 50 30 22 10 5 55 50 35 30 25 10 5	55	50	45	40	35	30	25	20	15	10	S
---	----	----	----	----	----	----	----	----	----	----	---

											Exar	nples								
		33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51
viscos	ity [mPa·s]	105	100	95	108	135	120	140	125	128	102	102	123	88	120	132	135	114	120	115
	initial appearance	A	A	А	A	A	A	A	А	А	А	А	А	А	А	А	А	А	А	А
Evaluation	low- temperature preservation stability	A	A	A	A	В	В	В	В	В	A	A	A	В	В	В	В	A	A	A
	low- temperature solubility	A	A	A	A	В	A	В	А	В	В	A	A	А	А	В	В	A	A	В
	sebum detergency	A	A	А	A	A	А	A	А	А	А	А	А	А	А	В	В	А	В	В

(continued)

	[0093]		
5			
10			
15			
20			
25			
30			
35			
40			
45			
50			
55			

	55	50	45	40	35	30	25	20	15	10	თ
--	----	----	----	----	----	----	----	----	----	----	---

[Table 5]

			-				[1ab									
								Cor	mparative E	xamples						
			1	2	3	4	5	6	7	8	9	10	11	12	13	14
component	(A)	a-1	50	-	30	30	-	-	30	30	30	30	21	48	48	15
component	(A')	a-5	-	-	-	-	30	-	-	-	-	-	-	-	-	-
		a-6	-	-	-	-	-	30	-	-	-	-	-	-	-	-
		a-7	-	-	-	-	-	-	-	20	-	-	-	-	-	-
		a-8	-	-	-	-	-	-	-	-	20	-	-	-	-	-
		a-9	-	-	-	-	-	-	-	-	-	20	-	-	-	-
component	(B)	b-1	-	50	20	20	20	20	-	-	-	-	14	32	2.5	35
component	(B')	b-6	-	-	-	-	-	-	20	-	-	-	-	-	-	-
component	(C)	c-1	10	10	-	10	10	10	10	10	10	10	10	10	10	10
		c-10	2	2	2	2	2	2	2	2	2	2	2	2	2	2
(A)+(B) [% I	oy mass]	•	50	50	50	50	50(*1)	50(*1)	50(*2)	50(*3)	50(*3)	50(*3)	35	80	50.5	50
(B)/{(A)+(B)	}		0/10	10/10	4/10	4/10	4/10(*4)	4/10(*4)	4/10(*5)	0/10	0/10	0/10	4/10	4/10	0.5/10	7/10
viscosity [m	Pa·s]		1233	320	2252	280	230	211	289	310	285	1184	115	1106	135	103
evaluation	initial appe	arance	В	Α	В	Α	А	А	А	Α	Α	В	Α	В	А	А
	low-temper preservation		С	С	С	С	В	С	С	С	С	С	В	С	С	С
	low-temper solubility	rature	С	С	С	С	С	С	С	С	С	С	В	С	С	В
	sebum det	ergency	С	С	С	С	С	С	С	В	В	С	С	В	В	С
*2:(A)+(B') [

[0094] As can be apparently seen from Tables 2 to 4, the liquid detergent compositions obtained in the examples could include surfactants with high concentrations without enhancing the viscosity thereof. The liquid detergent compositions had superior low-temperature preservation stability and had superior low-temperature solubility and sebum detergency during washing.

- ⁵ Particularly, in the comparison result of Examples 1 to 8, the sebum detergency was apt to be improved as the ratio of the component (A) in the surfactants increased, and the low-temperature solubility was apt to be improved as the ratio of the component (B) increased. When the compounds represented by the formula (3) were used as the component (B), the increase in viscosity was further suppressed and thus the low-temperature preservation stability was superior, compared the case where the compounds represented by the formula (2) were used.
- In the comparison result of Examples 9 to 14, as the concentration of the surfactant (that is, the total amount of the component (A) and the component (B)) in the liquid detergent composition increased, the sebum detergency was apt to be improved. When the compounds represented by the formula (3) were used as the component (B), the low-temperature preservation stability was superior.
- [0095] In the comparison result of Examples 7 and 15, when the compounds represented by the formula (3) were used as the component (B), the low-temperature preservation stability was superior, compared with the case where the compounds represented by the formula (2) were used as the component (B).
 In the comparison result of Examples 2 and 16, when the component (B).
 - In the comparison result of Examples 3 and 16, when the carbon number of R² of the compounds represented by the formula (2) as the component (B) was 10, the sebum detergency was superior.
- In the comparison result of Examples 7 and 17, when the compound CH_2CH_2OH of which R^5 is a straight-chain shape among the compounds represented by the formula (3) was used as the component (B), the low-temperature preservation stability was superior, compared with the case where the compound $CH_2CH(OH)CH_3$ having a branched-chain shape was used.

In the comparison result of Example3 with Examples 18 and 19, the low-temperature solubility in Example 3 including a larger amount of ethanol was superior.

²⁵ In the comparison result of Examples 7 and 20, the low-temperature preservation stability in Example 7 including a larger amount of ethanol was superior.

In the comparison result of Examples 21 to 36, when the compounds represented by the formula (3) were used as the component (B), the low-temperature preservation stability was superior. When two species of solvents were used as the component (C) and when three species of solvents were used, the same tendency was exhibited.

³⁰ In the comparison result of Examples 3 and 7 with Examples 21 to 36 and Examples 37 to 42, when solvents other than ethanol and/or polyethylene glycol were used as the component (C), there was a tendency that the viscosity increases and the low-temperature solubility or the low-temperature preservation stability decreases.

In the comparison result of Example 7 with Examples 43 and 44, when the amount of polyethylene glycol as the component (C) was in the range of 2 to 8 % by mass, both the low-temperature solubility and the low-temperature preservation stability were superior.

In the comparison result of Examples 7 and 45, when polyethylene glycol 1000 with an average molecular weight 950 to 1050 was used as the component (C), the low-temperature preservation stability was superior, compared with the case where polyethylene glycol 600 which is polyethylene glycol with an average molecular weight of 570 to 630 was used. In the comparison result of Examples 3 and 7 with Examples 46 to 51, when the compounds (a-1 and a-2) of which the

- ⁴⁰ average added mol number (n) of which ethyleneoxide was 15 was used as the component (A), the low-temperature solubility and the sebum detergency were superior, compared with the case where the compounds (a-3 and a-4) with n=12 and n=9 were used. When the compounds represented by the formula (3) were used as the component (B), the low-temperature preservation stability was superior.
- [0096] On the other hand, as can be apparently seen from Table 5, in Comparative Example 1 not including a component
 (B), there was no fluidity and the initial appearance was not good. In addition, the viscosity was apt to easily increase and the low-temperature preservation stability and the low-temperature solubility were inferior. Particularly, the gelation was caused by inputting the liquid detergent composition and thus the liquid detergent composition was hardly dissolved in water, thereby degrading the sebum detergency.
- In Comparative Example 2 not including a component (A), the sebum detergency was inferior. Since the component (B)
 ⁵⁰ was included with a high concentration, precipitates insoluble in water were generated and the low-temperature preservation stability and the low-temperature solubility were inferior.
 In Comparative Examples 3 and 4 including a species of solvent as the component (C), the low-temperature preservation stability, the low-temperature solubility, and the sebum detergency were inferior. Particularly, in Comparative Example 3 not including ethanol, the initial appearance was not good.
- ⁵⁵ In Comparative Examples 5 and 6 including the component (A') instead of the component (A), the increase in viscosity at room temperature was suppressed thanks to the component (B), but the gelation was easily generated by the dilution with water, and the low-temperature solubility and the sebum detergency were inferior. Particularly, in Comparative Example 6 including a-6 instead of the component (A), the increase in viscosity could be easily caused at a low temperature

and thus the low-temperature preservation stability was inferior.

In Comparative Example 7 including the component (B') instead of the component (B), the viscosity was apt to easily increase and the low-temperature preservation stability and the low-temperature solubility were inferior. Particularly, the gelation was caused by inputting the liquid detergent composition and thus the liquid detergent composition was hardly dissolved in water, thereby degrading the sebum detergency.

- In Comparative Examples 8 to 10 not including a component (B) but including the component (A') instead, the viscosity was apt to easily increase and the low-temperature preservation stability and the low-temperature solubility were inferior. In Comparative Example 11 in which the total amount of the component (A) and the component (B) was 35 % by mass, the sebum detergency was inferior.
- In Comparative Example 12 in which the total amount of the component (A) and the component (B) was 80 % by mass, the viscosity was apt to easily increase and the low-temperature preservation stability was inferior. The initial appearance was not good and the low-temperature solubility was inferior.

In Comparative Example 13 in which the mass ratio of the amount of the component (B) to the total amount of the component (A) and the component (B) was 0.5/10, the low-temperature preservation stability and the low-temperature solubility were inferior.

In Comparative Example 14 in which the mass ratio of the amount of the component (B) to the total amount of the component (A) and the component (B) was 7/10, the low-temperature preservation stability and the sebum detergency were inferior.

20 INDUSTRIAL APPLICABILITY

[0097] Since the liquid detergent composition according to the invention includes a surfactant at a high concentration and has superior low-temperature preservation stability and superior low-temperature solubility and sebum detergency during washing, it is applicable to a clothing detergent or the like.

25

5

15

Claims

- 1. A liquid detergent composition comprising:
- 30

35

a component (A): a nonionic surfactant represented by a following formula (1); a component (B): at least one species of anionic surfactant selected from the group consisting of compounds represented by a following formulas (2) and (3); and

a component (C): at least two species of water-miscible solvents selected from the group consisting of methanol, ethanol, propanol, butanol, ethylene glycol, propylene glycol, butylene glycol, butyl carbitol, phenoxy ethanol, and polyethylene glycol with an average molecular weight of 570 to 3800,

wherein a total amount of the component (A) and the component (B) is in a range of 40 to 75 % by mass and a mass ratio of the amount of the component (B) with respect to the total amount of the component (A) and the component (B) satisfies component (B)/(component (A)+component (B)) = 1/10 to 6/10:

40

R ¹ O(CH ₂ CH ₂ O) _n H	(1)
--	-----

 $R^{2}CH(SO_{3}M^{1})COOR^{3}$ (2)

 $^{45} R^{4}CH(SO_{3}M^{2})CONHR^{5}$ (3)

(In the formulas (1) to (3), R¹ represents a straight-chain alkyl group with a carbon number of 10 to 22, R² represents a straight-chain or branched-chain alkyl group with a carbon number of 9 to 14 or a straight-chain or branched-chain alkenyl group with a carbon number of 9 to 16, R³ represents a straight-chain or branched-chain alkyl group with a carbon number of 1 to 3, R⁴ represents a straight-chain or branched-chain alkyl group with a carbon number of 9 to 16, R³ represents a straight-chain or branched-chain alkyl group with a carbon number of 9 to 14 or a straight-chain or branched-chain alkenyl group with a carbon number of 9 to 14 or a straight-chain or branched-chain alkenyl group with a carbon number of 9 to 16, R⁵ represents a hydrogen or a straight-chain or branched-chain alkyl group with a carbon number of 1 to 3 which may have a hydroxyl group, M¹ and M² each identically or differently represents alkali metal, alkaline-earth metal, protonated primary to tertiary amines or ammonium with a total carbon number of 1 to 6 which may have a hydroxyl group, and n represents an average mol number of ethyleneoxide added and is in the range of 5 to 20.).

2. The liquid detergent composition according to Claim 1, wherein the component (C) comprises at least ethanol.

- **3.** The liquid detergent composition according to Claim 1 or 2, wherein the component (C) comprises at least ethanol and polyethylene glycol with an average molecular weight of 570 to 1050.
- 4. The liquid detergent composition according to any one of Claims 1 to 3, wherein an amount of the component (A) is in a range of 20 to 60 % by mass, an amount of the component (B) is in a range of 4 to 45 % by mass, and an amount of the component (C) is in a range of 2 to 20 % by mass.

5

10

The liquid detergent composition according to any one of Claims 1 to 4, wherein the mass ratio of the amount of the component (B) with respect to the total amount of the component (A) and the component (B) satisfies component (B)/(component (A)+component (B)) = 2/10 to 5/10.

15			
20			
25			
30			
35			
40			
45			
50			
55			

	INTERNATIONAL SEARCH REPORT		al application No. /JP2010/068049
C11D1/72(CATION OF SUBJECT MATTER 2006.01)i, C11D1/28(2006.01)i, i, C11D17/08(2006.01)i		
According to Int	ternational Patent Classification (IPC) or to both nationa	l classification and IPC	
B. FIELDS SE			
	nentation searched (classification system followed by cla C11D1/68, C11D1/28, C11D3/20,		3
Jitsuyo		nt that such documents are include tsuyo Shinan Toroku Ko roku Jitsuyo Shinan Ko	ho 1996-2011
CAplus	pase consulted during the international search (name of c (STN) , REGISTRY(STN) , JSTPlus(J 0(JDreamII)		
C. DOCUMEN	NTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where ap	propriate, of the relevant passages	Relevant to claim No.
A	JP 2009-144106 A (Lion Corp. 02 July 2009 (02.07.2009), claims; paragraphs [0024] to (Family: none)		1-5
A	CN 101434764 A (CHINA PETROC 20 May 2009 (20.05.2009), pages 2, 5 to 11; examples 4, (Family: none)		1-5
A	JP 63-86798 A (Kao Corp.), 18 April 1988 (18.04.1988), claims; pages 7 to 8 & GB 2197338 A & & PH & HK 32691 A	24938 A	1-5
× Further do	ocuments are listed in the continuation of Box C.	See patent family annex.	
 "A" document c to be of par "E" earlier appli filing date "L" document v cited to est special reas "O" document n "P" document p the priority 	egories of cited documents: lefining the general state of the art which is not considered ticular relevance ication or patent but published on or after the international which may throw doubts on priority claim(s) or which is ablish the publication date of another citation or other on (as specified) eferring to an oral disclosure, use, exhibition or other means ublished prior to the international filing date but later than date claimed	date and not in conflict with the the principle or theory underlyi "X" document of particular relevan considered novel or cannot b step when the document is take "Y" document of particular relevan considered to involve an inv	ce; the claimed invention cannot be e considered to involve an inventive en alone ce; the claimed invention cannot be ventive step when the document is ier such documents, such combination ed in the art patent family
07 Jan	uary, 2011 (07.01.11)	18 January, 201	
	ng address of the ISA/ se Patent Office	Authorized officer	
Facsimile No.	10 (second sheet) (July 2009)	Telephone No.	

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT	JP2010/068049				
Category* Citation of document, with indication, where appropriate, of the relevant passages A JP 2008-94942 A (Lion Corp.), 24 April 2008 (24.04.2008), claims; paragraphs [0002] to [0003], [0042] to [0062] (Family: none)	Relevant to claim No. 1-5				

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- JP 2009238354 A [0001]
- JP 11241092 A [0007]
- JP 2008094942 A [0007]
- JP 2001288500 A [0007]
- JP 2005171195 A [0007]
- JP 9176685 A [0007]

- JP 8269485 A [0007]
- JP 9078092 A [0007]
- JP 6015038 B [0022]
- JP 5025492 A [0047]
- JP 2002146399 A [0051] [0080]