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(54) Title: OIL-IN-WATER SILICONE EMULSION COMPOSITION

(57) Abstract: Provided is a silicone emulsion that can be effectively attached to a damaged portion of hair in use for a hair care cosmetic to exert feeling effects, and has excellent storage stability. An oil-in-water emulsion composition for a hair care cosmetic includes : (A) an N-acylamino acid condensate; (B) an organopolysiloxane having no amino group and an amino-modified organopolysiloxane; (C) a polyoxyethylene castor oil and/or a polyoxyethylene hydrogenated castor oil having an addition number of moles of ethylene oxide of 60 or more, and (D) water.



WO 2015/082358 A1

## DESCRIPTION

## OIL-IN-WATER SILICONE EMULSION COMPOSITION

Technical Field

[0001]

5           The present invention relates to an oil-in-water emulsion composition for a hair care cosmetic that contains an organopolysiloxane as an oily component and has excellent storage stability, and more specifically to a hair care cosmetic composition that can uniformly smoothen hair to the tip.

10   Background Art

[0002]

          Conventionally, silicones have been used for a hair care cosmetic such as a shampoo, a conditioner, a hair treatment, a hair rinse, a hair pack, and an out bath treatment to decrease a squeaky  
15   feeling during cleaning and rinsing and impart a smooth feeling including combing properties after drying, and excellent setting properties to hair. Such silicones may be used as one of mixing components for a hair care cosmetic in a mixture with other mixing components. Alternatively, an oil-in-water emulsion that has been  
20   formed from such silicones in advance may be used in a mixture with the other mixing components. This is because it may be difficult to directly mix a silicone that exhibits high effects for hair and has a high viscosity with the other component and the effects of the silicone are further exerted by converting the silicone to  
25   particles with an appropriate particle diameter in advance.

[0003]

For example, Patent Literature 1 proposes a silicone emulsion obtained by emulsification of a mixture of a silicone having a high polymerization degree and a silicone having a low polymerization degree, that is, an emulsion of organopolysiloxane having excellent storage stability even with an average particle diameter of 0.3  $\mu\text{m}$  or more. This emulsion can be used for a hair care cosmetic to decrease a squeaky feeling during cleaning and rinsing, and impart a smooth feeling, combing properties after drying, and excellent setting properties to hair. However, further improvement of effects of imparting a smooth and moist feeling even to hair damaged by coloring, ultraviolet light, heat by a dryer, or the like has been required.

[0004]

Use of a silicone having an amino group as a silicone has been known to impart a smooth and moist feeling to damaged hair. For example, Patent Literature 2 proposes that a mixture of silicones obtained by adding an N-(2-aminoethyl)-3-aminopropyl group-containing polydimethylsiloxane to a polydimethylsiloxane having a low viscosity and a polydimethylsiloxane having a high viscosity is mechanically emulsified with a nonionic surfactant and the obtained emulsion is used for a hair care cosmetic. However, when the silicone having an amino group is mechanically emulsified with a nonionic surfactant, the particle diameter of the emulsion becomes large. Therefore, there is a problem in association with

the stability of the emulsion. In order to form a stable emulsion, a condition needs to be selected so that the viscosity of the emulsion is high, and accordingly further improvement of handleability has been required.

5 Citation List

Patent Literature

[0003]

Patent Literature 1: Japanese Patent Application Laid-Open  
No. 2012-77282

10 Patent Literature 2: Japanese Patent Application Laid-Open  
No. 2006-282518

Summary of Invention

Technical Problem

[0006]

15 It is an object of the present invention to provide a silicone  
emulsion that can be efficiently attached to a portion damaged  
(hereinafter referred to as "damaged portion") by a chemical  
treatment with a hair coloring agent or perm chemicals, heat,  
ultraviolet light, or combing during use for a hair care cosmetic,  
20 to exhibit feeling effects such as uniform soft to the tip and finger  
combing, and has excellent storage stability.

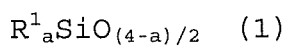
Solution to Problem

[0007]

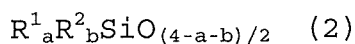
The present inventors have found that the problems can be solved  
25 by an oil-in-water emulsion obtained by emulsifying silicones with

a polyoxyethylene adduct of specific castor oil or hydrogenated castor oil in the presence of N-acylamino acid condensate, whereby the present invention has been completed. Accordingly, the present invention is as follows:

- 5 [1] An oil-in-water emulsion composition for a hair care cosmetic comprising (A) an N-acylamino acid condensate, (B) an organopolysiloxane having an average composition represented by the general formula (1) and an amino-modified organopolysiloxane having an average composition represented by the general formula  
10 (2), (C) a polyoxyethylene castor oil and/or a polyoxyethylene hydrogenated castor oil having an addition number of moles of ethylene oxide of 60 or more, and (D) water,



- (wherein  $R^1$  is a monovalent hydrocarbon group having 1 to 20 carbon  
15 atoms or a hydroxyl group, and  $a$  is 1.8 to 2.2),



- (wherein  $R^1$  is a monovalent hydrocarbon group having 1 to 20 carbon atoms or a hydroxyl group,  $R^2$  is a monovalent hydrocarbon group having at least one, or preferably at least two, amino groups and 1 to  
20 20 carbon atoms,  $a$  and  $b$  are each a natural number,  $a+b$  is 1.8 to 2.2, and  $a/b$  is 15 to 600).

- [2] The emulsion composition as set forth in [1], wherein the organopolysiloxane represented by the general formula (1) in (B) includes (b1) an organopolysiloxane having a high polymerization  
25 degree and (b2) an organopolysiloxane having a low polymerization

degree.

[3] The emulsion composition as set forth in [1] or [2], wherein (A) is contained in an amount of 0.02 to 1.0% by weight, (B) is contained in an amount of 10 to 60% by weight, (C) is contained in an amount of 1 to 7% by weight, and the rest is water.

[4] A hair care cosmetic composition comprising the emulsion composition as set forth in any one of [1] to [3].

Viscosity was always measured at 25°C and according to the later described Viscosity Measurement Method.

#### Advantageous Effects of Invention

[0008]

When the silicone emulsion of the present invention is mixed in a hair care cosmetic composition, damage repair components of silicones and an N-acylamino acid condensate can be effectively blended to impart feeling effects such as uniform soft to the tip and finger combing to a damaged portion of hair. The emulsion of the present invention exerts synergistic effects of the silicones and the N-acylamino acid condensate used in a hair care cosmetic due to emulsification in the presence of the N-acylamino acid condensate. The comparison of inventive emulsion compositions with emulsions obtained by emulsifying a silicone with only a polyoxyethylene (hydrogenated) castor oil or only with an N-acylamino acid condensate and then mixing each of them in a hair care cosmetic composition, leads to the unexpected effects that

the composition according to the present invention shows excellent feeling-imparting effects to a damaged portion of hair compared to the other emulsions.

[0009]

5           In the emulsion composition of the present invention, since a silicone component is emulsified using polyoxyethylene (hydrogenated) castor oil and an N-acylamino acid condensate, the silicone component has a comparatively small particle diameter and is stably dispersed. Therefore, the emulsion composition has  
10   excellent storage stability. Even when the amount of N-acylamino acid condensate to be used is small, if the amount of polyoxyethylene (hydrogenated) castor oil to be used is decreased, the emulsion also has an effect of maintaining the stability. Therefore, the amount of polyoxyethylene (hydrogenated) castor oil to be used can  
15   be decreased. This leads to an increase in the degree of freedom of the composition of target hair care cosmetics even when the polyoxyethylene (hydrogenated) castor oil is used as a mixing component of the hair care cosmetic.

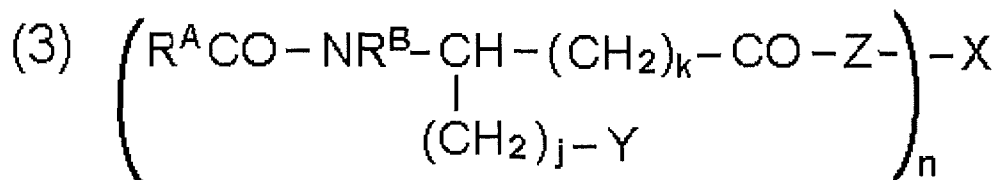
#### Description of Embodiments

20   [0010]

Hereinafter, the present invention is described in detail. The N-acylamino acid condensate as the component (A) of the present invention is a condensate of N-acylated acidic amino acid, which is represented by the following general formula (3).

25   [0011]

[Chemical Formula 1]



[0012]

In the general formula (3),  $R^A$  is a hydrocarbon group having 1 to 23 carbon atoms, and  $R^A CO$  is a long-chain acyl group derived from a saturated or unsaturated fatty acid having 2 to 20 carbon atoms.  $R^A$  is preferably a hydrocarbon group having 7 to 17 carbon atoms, may be a linear, branched, cyclic, or aromatic hydrocarbon chain, and may have a substituent. As  $R^A CO$ -, an acyl group derived from a saturated or unsaturated fatty acid having 8 to 20 carbon atoms is preferably used. Specific examples thereof may include lauric acid, myristic acid, and stearic acid.

[0013]

In the general formula (3),  $R^B$  is a hydrogen atom or a hydrocarbon group having 1 to 3 carbon atoms, and may have a carboxyl group or a sulfonic acid group. Specific examples of the hydrocarbon group having 1 to 3 carbon atoms may include a methyl group, an ethyl group, a propyl group, an isopropyl group, a hydroxymethyl group, a hydroxyethyl group, a hydroxy(iso)propyl group, a dihydroxy(iso)propyl group, a carboxymethyl group, a carboxyethyl group, a carboxypropyl group, and a sulfoethyl group. A hydrogen atom is preferred.

[0014]



In the general formula (3), Y is a carboxyl group, a sulfonic acid group, a sulfate ester group, a phosphate ester group, or a salt thereof. A carboxyl group and a salt thereof are preferred.

[0015]

5           Examples of a basic substance that forms a salt with an acid group of Y may include metal such as alkali metal and an organic basic substance. Examples of alkali metal may include sodium, potassium, and lithium. Examples of alkaline earth metal may include calcium and magnesium. Examples of metal other than the  
10   above-described metal may include aluminum, zinc, iron, cobalt, titanium, zirconium, and a salt of silver. Examples of the organic basic substance may include, but not particularly limited to, an organic amine salt and a basic amino acid salt. Examples of the organic amine salt may include salts of ammonia, monoethanolamine,  
15   diethanolamine, triethanolamine, and triisopropanolamine. Examples of the basic amino acid salt may include salts of arginine and lysine. Other examples thereof may include an ammonium salt and a polyvalent metal salt. In the general formula (3), Y may contain at least one salt optionally selected from the above-described salts.

20   [0016]

In the general formula (3), Z is a linking group varying depending on a compound that condenses an N-acylamino acid derivative, and is -NR'- (wherein R' is a hydrogen atom or a hydrocarbon group having 1 to 10 carbon atoms), -O-, or -S-.

25           In the general formula (3), j and k are each any of 0, 1, and

2, and are not 0 at the same time. Specific examples of an amino acid constituting the N-acylamino acid may include glutamic acid and aspartic acid. Glutamic acid is preferred.

[0017]

5 In the general formula (3), X is a group that condenses the N-acylamino acid derivative in parentheses of the general formula (3), and a compound having at least two functional groups that contribute to a condensation reaction with a carboxyl group of the N-acylamino acid derivative and a molecular weight of 1,000,000  
10 or less. The functional groups that contribute to the condensation reaction are preferably at least one selected from a hydroxyl group, an amino group, and a thiol group. Specific examples of the compound used for condensation of the N-acylamino acid derivative may include amino acids having two amino groups or an amino group and a hydroxy  
15 group or a thiol group, such as arginine, lysine, tyrosine, and tryptophan; compounds having an amino group and a hydroxyl group in the molecule, such as aminopropanol, aminophenol, and glucosamine; compounds having a thiol group and a hydroxyl group in the molecule, such as mercaptopropanediol; compounds having a  
20 thiol group and an amino group, such as aminothiophenol; proteins, peptides, and hydrolysates thereof; and polyhydroxyl compounds. Among them, a condensate with an amino acid is preferred, and lysine is preferred. Specific examples of the condensate of an N-acylglutamic acid derivative with lysine may include sodium  
25 dilaureamidoglutamide lysine, which is available from Asahi Kasei

Chemicals Corporation as Pellicer (registered trademark).

[0018]

When the amount of the component (A) in the present invention is 0.01% by weight or more in the oil-in-water emulsion, the stabilization effect of the emulsion of the present invention is excellent together with the effects of the component (C). The upper limit of the amount of the component (A) contained is not particularly limited, and is usually 1% by weight or less. When the amount of the component (A) to be used is large, a sticky feeling may be obtained during use in a hair care cosmetic. The amount of the component (A) contained is more preferably 0.02 to 0.5% by weight.

[0019]

The component (B) of the present invention is a mixture of an organopolysiloxane having no amino group and an average composition represented by the general formula (1) and an amino-modified organopolysiloxane having an average composition represented by the general formula (2). The organopolysiloxanes are components of imparting a smooth feeling and combing properties to hair in an aqueous emulsion.

In the general formula (1):  $R^1_a SiO_{(4-a)/2}$ ,

$R^1$  may be the same or different in the molecule, and is selected from an unsubstituted monovalent hydrocarbon group having 1 to 20 carbon atoms, a hydrogen atom, and a hydroxyl group. Examples of the unsubstituted monovalent hydrocarbon group may include an alkyl group such as a methyl group, an ethyl group, a propyl group, a

butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, a dodecyl group, a tetradecyl group, a hexadecyl group, and an octadecyl group; a cycloalkyl group such as a cyclopentyl group and a cyclohexyl group; an aryl group such as a phenyl group; and an aralkyl group such as a 2-phenylethyl group and a 2-phenylpropyl group. Among them, a methyl group and/or a phenyl group are preferred, and it is particularly preferable that 50% by mole or more of the unsubstituted monovalent hydrocarbon group be a methyl group.

10 [0020]

In the general formula (1), a, which represents an average number of  $R^1$  to be bonded to the silicon atom of the siloxane, is 1.8 to 2.2. The molecular structure of the organopolysiloxane having an average composition represented by the general formula (1) may have not only a linear chain but also a branched structure, and preferably has a linear chain structure. The organopolysiloxane of the present invention can be produced by a method known to those skilled in the art. Specific examples of preferred

organopolysiloxane, or silicone may include a

20 trimethylsiloxy-terminated dimethyl silicone, a

hydroxy-terminated dimethyl silicone, a

trimethylsiloxy-terminated phenylmethyl silicone, a

methylhydrogensiloxane, and an alkyl aralkyl-modified silicone.

As the organopolysiloxane having no amino group of the component

25 (B) of the present invention, a trimethylsiloxy-terminated dimethyl

silicone and/or a hydroxy-terminated dimethyl silicone are preferably used.

[0021]

The viscosity of organopolysiloxane represented by the general formula (1) at 25°C is  $1 \times 10^3$  to  $5 \times 10^4$  mPa·s. When the viscosity of the component (A) at 25°C is less than  $1 \times 10^3$  mPa·s, adhesion of organopolysiloxane to hair and feeling are not sufficiently imparted. When the viscosity is more than  $5 \times 10^4$  mPa·s, emulsification is difficult, and a stable emulsion cannot be obtained. The viscosity at 25°C is preferably  $5 \times 10^3$  to  $5 \times 10^4$  mPa·s, and more preferably  $1 \times 10^4$  to  $3 \times 10^4$  mPa·s.

The organopolysiloxane represented by the general formula (1) may be a mixture of at least two organopolysiloxanes having different viscosities as an organopolysiloxane having a high viscosity (b1) and an organopolysiloxane having a low viscosity (b2) as long as the viscosity falls within the above range. The mixture is rather preferred since the adhesion to hair is improved. This is because the mixture contains a larger amount of the organopolysiloxane component having a high degree of polymerization and a high viscosity as compared with the use of organopolysiloxane having a single molecular weight distribution.

[0022]

When the mixture of organopolysiloxanes represented by the general formula (1) is used, the viscosity of the component (b1) having a high viscosity at 25°C is  $1 \times 10^4$  to  $5 \times 10^6$  mPa·s. When

the viscosity of the component (b1) at 25°C is less than  $1 \times 10^4$  mPa·s, the adhesion of organopolysiloxane to hair and feeling are not sufficiently imparted. When the viscosity is more than  $5 \times 10^6$  mPa·s, emulsification is made difficult, and a stable emulsion cannot be obtained. The viscosity at 25°C is preferably  $1 \times 10^4$  to  $1 \times 10^6$  mPa·s, and more preferably  $1 \times 10^5$  to  $1 \times 10^6$  mPa·s.

[0023]

When the mixture of organopolysiloxanes represented by the general formula (1) is used, the viscosity of the component (b2) having a low viscosity at 25°C is 0.5 mPa·s or more and ~~less than~~  $1 \times 10^4$  mPa·s or less. The viscosity of the component (b1) having a low viscosity is set so that the viscosity of the mixture of the component (b1) with the component (b2) is  $1 \times 10^3$  to  $5 \times 10^4$  mPa·s, and is preferably 10 to 50 mPa·s.

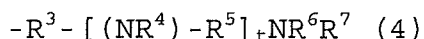
[0024]

In the general formula (2):  $R^1_a R^2_b SiO_{(4-a-b)/2}$ , which represents the average component of the amino-modified organopolysiloxane as another component in the component (B) of the present invention,

$R^1$  may be the same or different in the molecule, and is an unsubstituted hydrocarbon group having 1 to 20 carbon atoms or a hydroxyl group, which may be the same groups as those shown in  $R^1$  in the general formula (1).  $R^1$  may partially contain an alkoxy group having 1 to 3 carbon atoms.

[0025]

$R^2$  in the general formula (2) is a hydrocarbon group having one or preferably at least two amino groups, which is represented by the following general formula (4).



In the general formula (4),  $R^3$  and  $R^5$  are each a divalent C1 to C18 hydrocarbon residue,  $R^4$ ,  $R^6$ , and  $R^7$  are each a hydrogen atom or an unsubstituted C1 to C10 alkyl group, and  $t$  represents an integer of 0 or 1 to 6.

[0026]

Examples of the divalent C1 to C18 hydrocarbon residues  $R^3$  and  $R^5$  may include a methylene group, an ethylene group, an n-propylene group, an iso-propylene group, an n-butylene group, an iso-butylene group, a t-butylene group, an n-pentylene group, an iso-pentylene group, a hexylene group such as an n-hexylene group, a heptylene group such as an n-heptylene group, an octylene group such as an n-octylene group and an iso-octylene group, a 2,2,4-trimethylpentylene group, a nonylene group such as a n-nonylene group, a decylene group, a dodecylene group such as an n-dodecylene group, and an octadecylene group. Examples of alkyl groups as  $R^4$ ,  $R^6$ , and  $R^7$  are C1 to C10 alkyl groups among those exemplified by  $R^1$ .

[0027]

Preferred examples of  $R^2$  may include  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}(\text{CH}_3)$ ,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$ ,  $-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}(\text{CH}_3)$ ,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$ ,

-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH(CH<sub>2</sub>CH<sub>3</sub>),

-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, and

-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH(cyclo-C<sub>6</sub>H<sub>11</sub>). For cosmetics, it is

preferable that R<sup>2</sup> be -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>,

5 and more preferably -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>.

[0028]

In the general formula (2), a and b are each a natural number showing an average number of substituents R<sup>1</sup> and R<sup>2</sup>, respectively, that are bonded to the silicon of the amino-modified

10 polyorganosiloxane, and a+b is 1.8 to 2.2. The molecular structure of the organopolysiloxane may have not only a linear chain structure but also a branched structure, and preferably has a linear chain structure.

[0029]

15 The ratio of the average number a of R<sup>1</sup> having no amino group to the average number b of R<sup>2</sup> having at least one amino group is 15 to 600, which is an index of the ratio of a siloxane unit having no amino group to a siloxane unit having an amino group. As a value that shows the entire amount of amino groups in the amino-modified

20 organopolysiloxane, an amine number represented by the volume (mL) of 1 N hydrochloric acid necessary for neutralization of 1 g of the siloxane is also used. The amine number changes depending on the number of amino groups in the molecule of the amino-modified polyorganosiloxane and the molecular weight thereof. The amine

25 number of the amino-modified organopolysiloxane of the present



invention needs to be 0.1 to 3.0, and preferably 0.15 to 2.0.

When the amine number is less than 0.1, an adsorption ability to the surface of hair decreases. When the amine number is more than 3.0, the number of amino group as a hydrophilic group is too large, and therefore the adsorption to hair is difficult.

[0030]

The viscosity of the amino-modified organopolysiloxane (B) of the present invention at 25°C is 100 to 10,000 mPa·s, and preferably 200 to 2,000 mPa·s. When the viscosity is less than 100 mPa·s, a sufficient conditioning effect to hair is not obtained. When it is more than 10,000 mPa·s, uniform combing properties to the tip and setting properties cannot be imparted to hair. The viscosity of the whole component (B) that is the mixture of the organopolysiloxane having no amino group represented by the general formula (1) and the amino-modified organopolysiloxane at 25°C is  $1 \times 10^3$  to  $5 \times 10^4$  mPa·s, and preferably  $5 \times 10^3$  to  $5 \times 10^4$  mPa·s. The viscosity of the amino-modified organopolysiloxane needs to be selected so that the viscosity of the whole component (B) falls within this range.

[0031]

The amino-modified organopolysiloxane used as the component (B) of the present invention is generally known as an amino-modified silicone oil, and can be produced by a method well known to those skilled in the art. A typical method for synthesizing an amino-modified silicone oil is as follows. Specifically,

introduction of an aminoalkyl group into a silicon atom is usually performed in a state of silane, and aminoalkylsilane is first produced. The aminoalkylsilane is hydrolyzed to produce an amino group-containing siloxane oligomer or an amino group-containing disiloxane. The amino group-containing siloxane oligomer or the amino group-containing disiloxane and a linear oligomer or a cyclic oligomer of dimethylsiloxane are subjected to a reequilibration reaction of Si-O bond in the presence of an alkaline catalyst to produce an amino-modified silicone oil. When hexamethyldisiloxane is used in the reequilibration reaction, an amino-modified silicone oil terminated with a trimethylsilyl group can be obtained. When the mass ratio of oligomers or disiloxanes to be used for production is adjusted, an amino-modified silicone oil having specific kinematic viscosity and amine number can be obtained. When the kinematic viscosity and the amine number fall within the scope of the present invention, the amino-modified silicone oil may be used alone or a mixture of two or more kinds thereof may be used.

[0032]

The amount of the component (B) contained in the emulsion of the present invention is 10 to 60% by weight. When it is less than 10% by weight, effects of imparting a smooth feeling and combing properties to hair are not sufficiently obtained. When it is more than 60% by weight, the viscosity of the aqueous emulsion is high and the handleability deteriorates. The amount contained is more preferably 30 to 50% by weight. The weight ratio of the

amino-modified organopolysiloxane represented by the general formula (2) to the organopolysiloxane represented by the general formula (1) is preferably 1/20 to 2/1, and more preferably 1/15 to 1/2. When it is less than 1/20, sufficient combing properties and setting properties after drying cannot be sufficiently imparted to hair. When it is more than 2/1, that is, the ratio of the amino-modified organopolysiloxane becomes high, the stability of the emulsion decreases and sufficient feeling effects cannot be imparted to hair.

10 [0033]

The component (C) of the present invention is a polyoxyethylene hydrogenated castor oil and/or a polyoxyethylene castor oil, and is a component that functions as a surfactant in emulsification of the component (B). In the present invention, the polyoxyethylene hydrogenated castor oil or the polyoxyethylene castor oil needs to have an addition number of moles of ethylene oxide of 60 or more. When the polyoxyethylene hydrogenated castor oil or the polyoxyethylene castor oil having an addition number of moles of ethylene oxide less than 60 is added, the particle diameter of the emulsion increases if the addition amount thereof is the same as that when the polyoxyethylene hydrogenated castor oil or the polyoxyethylene castor oil having an addition number of moles of ethylene oxide of 60 or more is used. Therefore, this is not preferred in terms of storage stability of the emulsion. There is a problem in which the amount of surfactants to be added must be further

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increased.

[0034]

The amount of the component (C) contained in the emulsion of the present invention is 1 to 7% by weight. When the amount is less than 1% by weight, emulsification is made difficult. When it is more than 7% by weight, the viscosity of the aqueous emulsion composition is high and the handleability deteriorates. The amount is more preferably 3 to 5% by weight.

[0035]

The water (D) in the present invention is not particularly limited, but ion exchanged water is preferably used. The pH thereof is preferably 2 to 12, and particularly preferably 4 to 10. Use of mineral water is not recommended. However, when mineral water is used, it is desirable that mineral water be used in combination with a metal deactivator, or the like. The amount of water to be added in emulsification in the emulsion of the present invention corresponds to an amount of 40 to 90% by weight, and preferably 40 to 60% by weight. The emulsion of the present invention is stably diluted with water, and can be further diluted after preparation of the emulsion. The amount of water in a diluted emulsion is not particularly limited.

[0036]

The emulsion composition of the present invention may contain other components acceptable as mixing components of a hair care cosmetic without impairing the object of the present invention.

Examples of the other components may include an antiseptic such as a quaternary ammonium-containing compound and phenoxyethanol, various surfactants, a thickener such as guar gum and xanthan gum, and a perfume.

5 [0037]

A method for producing the emulsion composition of the present invention is not particularly limited, and the emulsion composition can be produced by a known method. The above-described components can be mixed and emulsified with an ordinarily mixer suitable for the production of an emulsion, such as a homogenizer, a colloid mill, a homomixer, and a high-speed rotor/stator mixer, to produce the emulsion. The emulsification can be performed by a method of mixing and stirring all the components (A) to (D) to prepare an oil-in-water emulsion, or a method in which the component (B) and a small amount of water (D), and all or a part of the surfactant (C), and the N-acylamino acid condensate (A) are stirred to prepare a water-in-oil emulsion, and the residual water and surfactant are added and stirred to prepare an oil-in-water emulsion. In terms of ease in adjustment of emulsion particle diameter and stability of the emulsion, the method of first preparing a water-in-oil emulsion and then preparing an oil-in-water emulsion is preferred.

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Examples

[0038]

Hereinafter, Examples of the present invention will be described in detail, but the present invention is not limited to

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the following Examples. A storage stability test method and a particle diameter measurement method with respect to emulsions in Examples, and a conditioner preparation method, a hair sample preparation method, a hair feeling evaluation test method, and a Bereck Softness test method with respect to conditioners using the emulsions are as follows. All values of viscosity were measured at 25°C.

[0039]

< Storage Stability Test Method >

A prepared emulsion was placed in a 50-mL glass bottle, and allowed to stand at 40°C. After one month, the presence or absence of creaming, separation, and oil floating on a liquid surface was visually confirmed. Evaluation criteria are as follows.

AA: There are no creaming, separation, and oil floating on a liquid surface.

A: The concentration distribution of emulsion is visually observed.

B: Creaming proceeds and the aqueous phase is separated, but after shaking, the state returns to the original emulsion.

C: Oil floats on a liquid surface; The emulsion is destroyed and an oil content floats.

[0040]

< Viscosity Measurement Method >

The viscosity for 0.5 mL of emulsion sample was measured at 25°C with a Cone/Plate viscometer BROOKFIELD DV-II Pro VISCOMETER CPE 52 (manufactured by Brookfield Engineering). The shear rate

during measurement was  $5 \text{ sec}^{-1}$ .

< Particle Diameter Measurement Method >

The particle diameter of an emulsion was measured with Zetasizer Nano ZS90 (dynamic light scattering method, manufactured by Malvern Instruments Ltd.). The obtained particle diameter was an average particle diameter (Z-average).

[0041]

< Preparation of Sample for Evaluation >

[Pretreatment]

10       An untreated Asian hair bundle (length: 200 mm, width: 18 mm, and weight: about 3 g (available from Kerling International Haarfabrik GmbH)) was used. The hair bundle was immersed in a mixed solvent (acetone / isopropyl alcohol / ethanol / water) all day and night to remove grease. The hair bundle was cleaned with a  
15       surfactant and then air dried. The dried hair bundle was bleached with a commercially available bleaching agent by an ordinary method. Subsequently, the hair bundle was cleaned with a surfactant (5% Alscope LS25B aqueous solution) and then dried. By the  
above-described treatment, a damaged hair bundle was prepared.

20       [Conditioner Treatment]

A conditioner (0.5 g/g hair) of Table 1 was applied to hair of the pretreated hair bundle over about 2 minutes, and rinsed off for 1 minute. This operation was repeated two times, and the hair bundle was air dried.

25       [0042]

## &lt; Sensory Evaluation &gt;

The feeling of the hair bundle sample treated with the conditioner was evaluated as finger combing. The sensory about good finger combing was evaluated by passing the finger through the hair bundle sample treated with the conditioner of Table 1 from the top to the down of the hair bundle. The evaluation was performed by comparison of one to one. A case in which smoother texture is uniform to the tip is expressed as A, and another case is expressed as C. The evaluation was performed by 8 subjects. A total score of 0 or more and less than 2 is evaluated as C, a total score of 2 or more and less than 4 is evaluated as B, a total score of 4 or more and less than 6 is evaluated as A, and a total score of 6 or more and less than 8 is evaluated as AA.

[0043]

## 15 &lt; Bereck Softness Test &gt;

This test method was performed in accordance with the following Literature 1. In this test, a hair bundle sample alternatively passed through a plurality of metal bars arranged in parallel was pulled up at a constant rate, and a force  $\Delta J$  ( $J \cdot g^{-1}$ ) applied to the metal bars at this time was measured with a tensile test machine INSTRON (registered trademark) 3343 (manufactured by Instron Corporation). In the measurement, dried hair before and after treatment with a conditioner was used. A rate of change before and after the treatment was calculated from the formula 2 using the hair before the treatment as a standard. As  $\Delta J$  (%) is larger, the soft before and after the



treatment with a conditioner is improved. As it is smaller, improvement of the soft is evaluated to be low.

$$\Delta J (\%) = ((\Delta J_{\text{untreated}} - \Delta J_{\text{treated}}) / \Delta J_{\text{untreated}}) \times 100 \quad (2)$$

(Wherein  $\Delta J_{\text{treated}}$  is an average value after the treatment with a conditioner, and  $\Delta J_{\text{untreated}}$  is an average value before the treatment with a conditioner.)

Literature 1: "A novel device for measuring hair stiffness and lubricity;" K. ABRAHAM VAYNBERG and M. NALL, J. Cosmet. Sci., 60, 135-141 (March/April 2009)

[0044]

< Example 1 >

As the components (B), 20.0 parts by weight of trimethylsilyl-terminated dimethylpolysiloxane having a viscosity of  $3.0 \times 10^5$  mPa·s, 20.0 parts by weight of trimethylsilyl-terminated dimethylpolysiloxane having a viscosity of 10.0 mPa·s (the viscosity of the mixture of two trimethylsilyl-terminated dimethylpolysiloxane was  $1.7 \times 10^4$  mPa·s), and 5.0 parts by weight of N-(2-aminoethyl)-3-aminopropyl group-containing dimethylpolysiloxane (amodimethicone) having a viscosity of 1,000 mPa·s and an amine number of 0.6 were mixed to obtain 45 parts by weight of an organopolysiloxane mixture having a viscosity of  $1.4 \times 10^4$  mPa·s. In the organopolysiloxane mixture, 5 parts by weight of polyoxyethylene hydrogenated castor oil having an addition number of moles of ethylene oxide of 100 moles as the component (C), 0.1 parts by weight of 30% aqueous solution of sodium

dilaureamidoglutamide lysine (Pellicer (registered trademark) available from Asahi Kasei Chemicals Corporation) as the component (A), 1.0 part by weight of phenoxyethanol, and 43.9 parts by weight of purified water were stirred at room temperature and 3,000 rpm for 20 minutes with ULTRA-TURRAX T 50 basic shaft generator G45G manufactured by IKA, to prepare an aqueous emulsion of Example 1. The viscosity and the particle diameter of the prepared emulsion were measured in accordance with the measurement methods described above, and the storage stability was evaluated in accordance with the storage stability test method. Subsequently, a hair conditioner composition having a composition shown in a composition ratio A of Table 1 was prepared, and the properties were evaluated in accordance with the methods and the criteria. The results of the evaluations are shown in Table 2.

[0045]

< Example 2 >

An aqueous emulsion of Example 2 and a conditioner composition were prepared in the same manner as in Example 1 except that 5 parts by weight of polyoxyethylene hydrogenated castor oil having an addition number of moles of ethylene oxide of 200 moles was used as the component (C). The viscosity and the particle diameter of the prepared emulsion were measured in accordance with the measurement methods described above, and the storage stability was evaluated in accordance with the storage stability test method. Subsequently, a hair conditioner composition with formulation A

shown in Table 1 was prepared, and the properties were evaluated in accordance with the methods and the criteria described above. The results of the evaluations are shown in Table 2.

[0046]

5 < Example 3 >

An aqueous emulsion of Example 3 and a conditioner composition were prepared in the same manner as in Example 1 except that 4 parts by weight of polyoxyethylene hydrogenated castor oil having an addition number of moles of ethylene oxide of 200 moles was used  
10 as the component (C). The viscosity and the particle diameter of the prepared emulsion were measured in accordance with the measurement methods described above, and the storage stability was evaluated in accordance with the storage stability test method. Subsequently, a hair conditioner composition having a composition  
15 shown in the formulation A of Table 1 was prepared, and the properties were evaluated in accordance with the methods and the criteria. The results of the evaluations are shown in Table 2.

[0047]

< Comparative Example 1 >

20 An aqueous emulsion of Comparative Example 1 and a conditioner were prepared in the same manner as in Example 1 except that the 30% aqueous solution of sodium dilaureamidoglutamide lysine was not used as the component (A). The viscosity and the particle diameter of the prepared emulsion were measured in accordance with the  
25 measurement methods described above, and the storage stability was

evaluated in accordance with the storage stability test method. Subsequently, a mixing composition B of Table 1 in which 0.0044% of 30% aqueous solution of sodium dilaureamidoglutamide lysine was added to the formulation A of Table 1 (0.0044% corresponds to the amount of 30% aqueous solution of sodium dilaureamidoglutamide lysine contained in the silicone emulsion of the formulation A) was used as a hair conditioner composition for evaluation. The properties were evaluated in accordance with the methods and the criteria. The results of the evaluations are shown in Table 2.

10 [0048]

< Comparative Example 2 >

An aqueous emulsion of Comparative Example 2 and a conditioner composition were prepared in the same manner as in Example 1 except that 5 parts by weight of polyoxyethylene hydrogenated castor oil having an addition number of moles of ethylene oxide of 40 moles was used as the component (C). The viscosity and the particle diameter of the prepared emulsion were measured in accordance with the measurement methods described above, and the storage stability was evaluated in accordance with the storage stability test method. Subsequently, a hair conditioner composition having a composition shown in the formulation A of Table 1 was prepared, and the properties were evaluated in accordance with the methods and the criteria. The results of the evaluations are shown in Table 2.

[0049]

25 < Comparative Example 3 >

An aqueous emulsion of Comparative Example 3 and a conditioner composition were prepared in the same manner as in Example 1 except that 5 parts by weight of polyoxyethylene tridecyl ether was used instead of the component (C). The viscosity and the particle diameter of the prepared emulsion were measured in accordance with the measurement methods described above, and the storage stability was evaluated in accordance with the storage stability test method. Subsequently, a hair conditioner composition having a composition shown in the formulation A of Table 1 was prepared, and the properties were evaluated in accordance with the methods and the criteria. The results of the evaluations are shown in Table 2.

[0050]

Table 1

COMPONENT		FORMULATION A (% by weight)	FORMULATION B (% by weight)
A	HYDROXYETHYL CELLULOSE	1.2	1.2
	WATER	86.5	86.5
B	CETYL ALCOHOL	1	1
	STEARYL ALCOHOL	3	3
	BEHENTRIMONIUM CHLORIDE	1.8	1.8
	STEARAMIDOPROPYL DIMETHYLAMINE	0.5	0.5
C	POLYSORBATE 80	1	1
D	CITRIC ACID	0.2	0.2
	ETHYLENEDIAMINETETRAACETIC ACID	0.2	0.2
E	SILICONE EMULSION	4.4	4.4
F	30% AQUEOUS SOLUTION OF PELLICER	-	0.0044
G	ANTISEPTIC	0.1	0.1
TOTAL		100	100

[0051]

Table 2

	COMPONENT COMPOSITION		EXAMPLE			COMPARATIVE EXAMPLE		
			1	2	3	1	2	3
SILICONE EMULSION	COMPONENT A	30% AQUEOUS SOLUTION OF PELLICER	0.1	0.1	0.1	-	0.1	0.1
	COMPONENT B	DIMETHYL POLYSILOXANE (LOW)	20	20	20	20	20	20
		DIMETHYL POLYSILOXANE (HIGH)	20	20	20	20	20	20
		AMODIMETHICONE	5	5	5	5	5	5
	COMPONENT C	HYDROGENATED CASTOR OIL PEG-40	-	-	-	-	5	-
		HYDROGENATED CASTOR OIL PEG-100	5	-	-	-	-	-
		HYDROGENATED CASTOR OIL PEG-200	-	5	4	5	-	-
		POLYOXYETHYLENE TRIDECYL ETHER	-	-	-	-	-	5
	COMPONENT D	PURIFIED WATER	BALANCE	BALANCE	BALANCE	BALANCE	BALANCE	BALANCE
	EVALUATION	STORAGE STABILITY	AA	AA	AA	AA	B	A
VISCOSITY (25°C) (mPa.s)		65	37	37	206	402	579	
AVERAGE PARTICLE DIAMETER (nm)		446	473	460	445	1080	458	
CONDITIONER	ADDITION OF 30% AQUEOUS SOLUTION OF PELLICER TO CONDITIONER COMPOSITION		-	-	-	DONE	-	-
	EVALUATION	SENSORY EVALUATION	AA	AA	AA	B	C	B
		BERECK SOFTNESS (%)	27	28	27	24	23	19

## INDUSTRIAL APPLICABILITY

[0052]

5 The emulsion composition of the present invention can impart a smooth feeling and combing properties to a damaged portion of hair, has an appropriate emulsion particle diameter, and is stably stored over a long period of time. Therefore, the emulsion composition is useful as a raw material for a hair care cosmetic

such as a shampoo, a conditioner, a hair treatment, a hair rinse, a hair pack, and an out bath treatment.

## CLAIMS

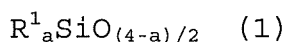
1. An oil-in-water emulsion composition for a hair care cosmetic, comprising:

(A) an N-acylamino acid condensate;

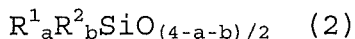
(B) an organopolysiloxane having an average composition represented by the general formula (1) and an amino-modified organopolysiloxane having an average composition represented by the general formula (2);

(C) a polyoxyethylene castor oil and/or a polyoxyethylene hydrogenated castor oil having an addition number of moles of ethylene oxide of 60 or more; and

(D) water,



(wherein  $R^1$  is a monovalent hydrocarbon group having 1 to 20 carbon atoms or a hydroxyl group, and  $a$  is 1.8 to 2.2),



(wherein  $R^1$  is a monovalent hydrocarbon group having 1 to 20 carbon atoms or a hydroxyl group,  $R^2$  is a monovalent hydrocarbon group having at least one amino group and 1 to 20 carbon atoms,  $a$  and  $b$  are each a natural number,  $a+b$  is 1.8 to 2.2, and  $a/b$  is 15 to 600).

2. The emulsion composition according to claim 1, wherein the organopolysiloxane represented by the general formula (1) in (B) comprises (b1) an organopolysiloxane having a high polymerization degree and (b2) an organopolysiloxane having a low polymerization degree.



3. The emulsion composition according to claim 1 or 2, wherein (A) is contained in an amount of 0.02 to 1.0% by weight, (B) is contained in an amount of 10 to 60% by weight, (C) is contained in an amount of 1 to 7% by weight, and the rest is water.

5 4. A hair care cosmetic composition comprising the emulsion composition according to any one of claims 1 to 3.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2014/075987

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. A61K8/44 A61Q5/12 A61K8/891 A61K8/898 A61K8/92 A61K8/06 ADD. According to International Patent Classification (IPC) or to both national classification and IPC														
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) A61K A61Q Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data														
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>           JP 2006 111549 A (NIPPON NSC LTD)            27 April 2006 (2006-04-27)            abstract            page 31; table 7            paragraph [0097]            paragraphs [0110] - [0112]            -----         </td> <td style="text-align: center; vertical-align: top;">1,2,4</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>           JP 2008 290987 A (SHISEIDO CO LTD)            4 December 2008 (2008-12-04)            abstract            page 18, paragraph 0069; example 13            paragraph [0083]            -----         </td> <td style="text-align: center; vertical-align: top;">1-4</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>           US 2013/171222 A1 (IGARASHI KENJI [JP] ET AL)            4 July 2013 (2013-07-04)            the whole document            -----  <div style="text-align: right;">-/-</div> </td> <td style="text-align: center; vertical-align: top;">1-4</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	JP 2006 111549 A (NIPPON NSC LTD) 27 April 2006 (2006-04-27) abstract page 31; table 7 paragraph [0097] paragraphs [0110] - [0112] -----	1,2,4	X	JP 2008 290987 A (SHISEIDO CO LTD) 4 December 2008 (2008-12-04) abstract page 18, paragraph 0069; example 13 paragraph [0083] -----	1-4	A	US 2013/171222 A1 (IGARASHI KENJI [JP] ET AL) 4 July 2013 (2013-07-04) the whole document ----- <div style="text-align: right;">-/-</div>	1-4
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X	JP 2006 111549 A (NIPPON NSC LTD) 27 April 2006 (2006-04-27) abstract page 31; table 7 paragraph [0097] paragraphs [0110] - [0112] -----	1,2,4												
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A	US 2013/171222 A1 (IGARASHI KENJI [JP] ET AL) 4 July 2013 (2013-07-04) the whole document ----- <div style="text-align: right;">-/-</div>	1-4												
<div style="display: flex; justify-content: space-between;"> <div> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.         </div> <div> <input checked="" type="checkbox"/> See patent family annex.         </div> </div>														
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>														
Date of the actual completion of the international search  <div style="text-align: center; font-size: 1.2em;">4 February 2015</div>		Date of mailing of the international search report  <div style="text-align: center; font-size: 1.2em;">05/03/2015</div>												
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center; font-size: 1.2em;">Durand-Oral, Ilknur</div>												

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/075987

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010/055060 A1 (YOSHIDA NAOYUKI [JP] ET AL) 4 March 2010 (2010-03-04) the whole document -----	1-4

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/075987

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2006111549 A	27-04-2006	JP 4832746 B2 JP 2006111549 A	07-12-2011 27-04-2006
JP 2008290987 A	04-12-2008	NONE	
US 2013171222 A1	04-07-2013	CN 103096867 A EP 2613757 A2 JP 2012077282 A KR 20130049205 A US 2013171222 A1 WO 2012031903 A2	08-05-2013 17-07-2013 19-04-2012 13-05-2013 04-07-2013 15-03-2012
US 2010055060 A1	04-03-2010	EP 2116224 A1 JP 2014129383 A US 2010055060 A1 WO 2008066193 A1	11-11-2009 10-07-2014 04-03-2010 05-06-2008