DESCRIPTION
COPOLYMER

Technical Field

[0001]

The present disclosure relates to a novel copolymer which is a copolymer of a hydrophobic monomer and a hydrophilic monomer.

[0002]

The present disclosure also relates to an emulsified composition which is emulsified with a water-soluble copolymer.

[0003]

The present disclosure also relates to a skin cleanser containing a water-soluble copolymer.

[0004]

The present disclosure also relates to a sunscreen cosmetic containing a water-soluble copolymer.

[0005]

The present disclosure also relates to a coating film having a sea-island structure in which island particles of an amphipathic copolymer are dispersed in the sea of an aqueous gel and a composition for forming the same.

Background Art

[0006]

Generally, an oil agent exhibits excellent feel of use such as elastic feel and moist feel, and it has been used as a material of cosmetics from long ago. However, the oil agent causes stickiness to lead to deterioration in feel of use when being blended at a high proportion in some cases although it exerts the excellent feel of use described above.

[0007]

Under such circumstances, it has been attempted to

decrease the sticky feel due to the oil agent by devising the composition, structure, and the like of cosmetics. For example, Patent Literature 1 proposes a technique to suppress stickiness by decreasing the emulsified particle diameter in a cosmetic of an emulsified composition.

However, in the technique to suppress stickiness by devising the composition, structure, and the like of cosmetics as described in Patent Literature 1, there is a problem that the dosage form to which the technique can be applied is limited.

[0008]

Meanwhile, novel materials which exhibit both moist feel and feel of use without stickiness have been proposed. For example, Patent Literature 2 discloses a base for cosmetic which contains an alkylene oxide derivative and exhibits both excellent feel and moisture retaining property.

[0009]

In addition, an emulsified composition in which an oil phase component is mixed with an aqueous phase component via an emulsifying agent is widely used as a dosage form of cosmetics. However, general low-molecular emulsifying agents cause problems such as irritation to the skin and stickiness in some cases.

In order to solve such a problem, various emulsification techniques using a high-molecular emulsifying agent have been proposed in recent years.

[0010]

Patent Literature 3 discloses an emulsified composition using hydroxyethylcellulose as an emulsifying agent.

In addition, Patent Literature 4 discloses an emulsified composition using an alkyl-modified carboxyvinyl polymer as an emulsifying agent.

[0011]

In addition, potassium salts of higher fatty acids have been hitherto widely used in skin cleansers such as facial cleansers because of favorable foaming, favorable detergency, refreshing feel after rinsing, and the like thereof. However, in skin cleansers containing potassium salts of higher fatty acids as a main component, there is also a problem that it is difficult to obtain creamy foam quality, the skin is likely to be excessively degreased by washing, and the skin is likely to be tightened after use as the soap scum (scum) remains on the skin although these skin cleansers exhibit such excellent properties.

[0012]

As a method for solving such a problem, concurrent use of higher fatty acids and surfactants such as an acyl taurine salt type surfactant, an acyl isethionate type surfactant, a phosphate type surfactant, and an acyl amino acid type surfactant (for example, Patent Literature 5), blending of additives (for example, silicone compounds, specific glycolipids, raffinose, plant seed mucilage, and various polymer compounds) other than surfactants (for example, Patent Literatures 6 to 12), and the like have been proposed.

In addition, it has also been attempted to improve the above problems by combining an acyl glycine type surfactant with a specific polymer compound without using a potassium salt of a higher fatty acid as a main component (see Patent Literature 13).

[0013]

Furthermore, oil-in-water type emulsified sunscreen cosmetics have a refreshing feel of use and are likely to be continuously used. In order to enhance the ultraviolet protecting effect, an ultraviolet absorber and an ultraviolet scattering agent of a metal oxide powder such as zinc oxide or titanium oxide are used in the oil-in-water type emulsified cosmetic. However, when a large

amount of ultraviolet absorber is blended, there is a problem that discoloration occurs and the feel of use deteriorates as the cosmetic poorly spreads and is sticky. In addition, when a large amount of the metal oxide powder is blended, not only aggregation, settling, and the like of the powder occur with time but there is also a problem that the time dependent stability deteriorates as a decrease in viscosity, emulsion separation, and deposition occur. There is a tendency that the above problems are more likely to arise when these are used concurrently.

[0014]

In order to improve these problems, it has been proposed to concurrently use an ultraviolet absorber such as a dibenzoylmethane derivative and titanium oxide treated with silane and/or silicone (see Patent Literature 14).

In addition, oil-in-water type emulsified cosmetics using water-soluble polymers such as polyacrylic acid amide, xanthan gum, and a (sodium acrylate/acryloyldimethyltaurine) copolymer have been proposed (see Patent Literatures 15 and 16).

[0015]

In addition, a sea-island structure refers to a structure in which two kinds of polymers which are incompatible with each other undergo phase separation and a disperse phase (island phase) containing the other polymer is present on a continuous phase (sea phase) containing one polymer as a point. As described above, the sea-island structure has an ununiform structure in which the phases are separated from each other, and it thus exhibits different properties from a composition having a uniform structure. In order to utilize such properties, researches and developments on the sea-island structure are being actively conducted in the technical fields relating to plastics, rubber, toner, adhesives, and the like.

For example, Patent Literature 17 discloses a tire

coated with a coating mixture having a sea-island structure including a sea phase containing a thermoplastic resin and an island phase containing a polyurethane-based thermoplastic elastomer.

However, it has not been so far attempted to utilize the sea-island structure in the field of cosmetics.

[0016]

Incidentally, Patent Literature 18 discloses an external preparation for skin containing an amphipathic copolymer having a constitutional unit derived from a specific hydrophobic acrylic ester-based monomer and a constitutional unit derived from a specific hydrophilic acrylic monomer.

Citation List

Patent Literature

[0017]

Patent Literature 1: JP 2012-116783 A
Patent Literature 2: Domestic re-publication of PCT international application No. 2006/038724
Patent Literature 3: JP 2011-231049 A
Patent Literature 4: JP 09-019631 A
Patent Literature 5: JP 6-248298 A
Patent Literature 6: JP 10-77206 A
Patent Literature 7: JP 2001-72574 A
Patent Literature 8: JP 2000-178172 A
Patent Literature 9: JP 11-209799 A
Patent Literature 10: JP 2003-73257 A
Patent Literature 11: JP 2007-277140 A
Patent Literature 12: JP 10-183193 A
Patent Literature 13: JP 9-78082 A
Patent Literature 14: JP 9-2929 A
Patent Literature 15: JP 2003-104859 A
Patent Literature 16: JP 2010-215602 A
Patent Literature 17: JP 2013-180652 A

Patent Literature 18: JP 2014-9189 A

Summary of Invention

Technical Problem

[0018]

As described above, an oil agent exhibits a favorable feel of use such as elastic feel, but it also has a problem such as stickiness. Under such circumstances, a novel material exhibiting elastic feel like an oil agent has been demanded.

An object of the present invention is to provide a novel copolymer exhibiting elastic feel. In addition, in a preferred aspect of the present invention, it is a first object to provide a copolymer which hardly causes stickiness but exhibits moist feel.

[0019]

In addition, a polymer emulsifying agent as described above has advantages that the polymer emulsifying agent causes less irritation to the skin and is less sticky when being contained at a low concentration, but it is inferior in the emulsifying power to a conventional low-molecular emulsifying agent. Hence, in order to secure the stability of an emulsified state, it is required to blend a high-molecular emulsifying agent in the emulsified composition at a high proportion and thus to increase the viscosity, but there is a problem of stickiness as a result.

[0020]

In view of such circumstances, it is a second object of the present invention to provide an emulsified composition which exhibits excellent emulsion stability while causing less irritation to the skin and being less sticky.

[0021]

With a recent increase in consumer needs, particularly foam quality and feel after washing are not

sufficiently satisfied by these methods but are desired to be further improved.

[0022]

In view of such circumstances, a third object to be achieved by the present invention is to provide a novel technique to decrease tight feel of the skin after use of a skin cleanser.

In addition, it is a fourth object to provide a technique to decrease tight feel of the skin after use without impairing the advantageous effects inherent in a skin cleanser such as detergency, favorable foaming, favorable foam quality, absence of slimy feel after use, and ease of spreading on the skin.

[0023]

Furthermore, in the technical field of oil-in-water type sunscreen cosmetics, it has been a problem to achieve both the ultraviolet protecting function and the feel of use or emulsion stability. Hitherto, various techniques have been proposed to solve this problem but insufficient.

In view of such circumstances, a fifth object to be achieved by the present invention is to provide an oil-in-water type sunscreen cosmetic exhibiting excellent feel of use such as absence of sticky feel and moisturizing feel and emulsion stability while exhibiting a favorable ultraviolet protecting function.

[0024]

In addition, an object to be achieved by the present invention is to provide a coating film which contains a water-soluble component as a main component and has a sea-island structure and a technique to form the coating film. Another object is to provide a technique to impart a feel like milk containing an oil agent to a coating film containing a water-soluble component as a main component. Preferably, it is a sixth object of the present invention to provide a coating film exhibiting both moisture

retaining property and flexibility and a technique to form the coating film.

Solution to Problem

[0025]

In view of the circumstances to be the background of the first object, the inventors of the present invention have conducted extensive researches in search of an elastic copolymer, and as a result, it has been found out that a copolymer obtained by polymerizing a hydrophobic acrylic ester-based monomer having a polymerizable carboxyl group and two acyl groups having a specific branched structure and a hydrophilic acrylic monomer having a specific structure exhibits solubility, particularly excellent solubility in water and feel with elasticity like an oil agent, thereby completing the present invention. In other words, the present invention is as follows.

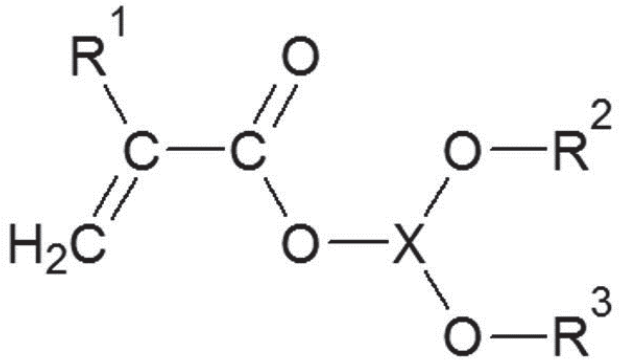
[0026]

A copolymer having one kind or two or more kinds of constitutional units (a) derived from a hydrophobic monomer represented by the following general formula (1) and one kind or two or more kinds of constitutional units (b) derived from a hydrophilic monomer represented by the following general formula (2) as essential constitutional units and a weight average molecular weight of from 20,000 to 110,000.

[0027]

General Formula (1)

[Chemical Formula 1]



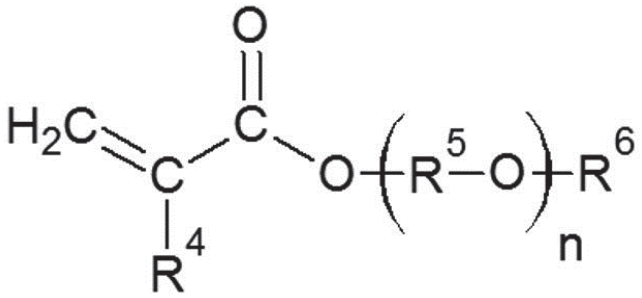
(1)

(In the general formula (1), R1 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R2 and R3 may be the same as or different from each other and represent an acyl group which has from 6 to 22 carbon atoms and a branch but does not contain a ring structure. X represents a group obtained by eliminating an OH group from a trihydric alcohol.)

[0028]

General Formula (2)

[Chemical Formula 2]



(2)

(In the general formula (2), R4 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms, R5 represents an alkylene group which has from 2 to 4 carbon atoms and may have a hydroxyl group, and R6 represents a hydrogen atom, an aromatic hydrocarbon group having from 6 to 10 carbon atoms, an aliphatic hydrocarbon group having from 1 to 14 carbon atoms, or an acyl group having from 1 to 12 carbon atoms. n represents an integer from 6 to 40.)

[0029]

Such a copolymer exhibits elastic feel when being applied to the skin and also exhibits moist feel but does not exhibit stickiness.

[0030]

In a preferred aspect of the present invention, the mass ratio of the constitutional unit (a) to the constitutional unit (b) is from 25 : 75 to 35 : 65.

The copolymer having a mass ratio of the constitutional unit (a) to the constitutional unit (b) in the above range exhibits excellent elastic feel and feel of use without stickiness.

[0031]

In a preferred aspect of the present invention, the molar ratio of the constitutional unit (a) to the constitutional unit (b) is from 35 : 65 to 46 : 54.

The copolymer having a mass ratio of the constitutional unit (a) to the constitutional unit (b) in the above range exhibits excellent elastic feel and feel of use without stickiness.

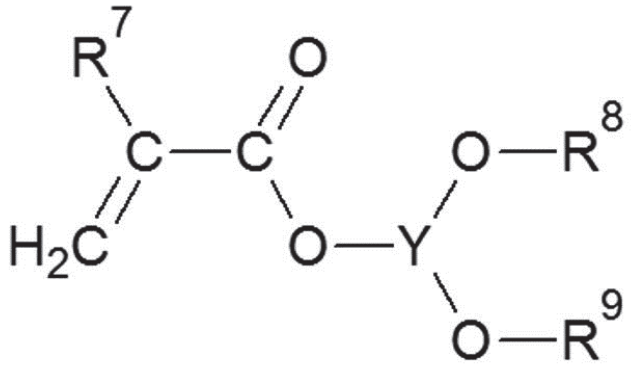
[0032]

In a preferred aspect of the present invention, the hydrophobic monomer is a hydrophobic monomer represented by the following general formula (3).

[0033]

General Formula (3)

[Chemical Formula 3]



(3)

(In the general formula (3), R7 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R8 and R9 may be the same as or different from each other and represent an acyl group which has from 10 to 22 carbon atoms and a branch but does not contain a ring structure or an acyl group which has from 6 to 9 carbon atoms and two or more branches but does not contain a ring structure. Y represents a group obtained by eliminating an OH group from a trihydric alcohol.)

[0034]

By using the above monomer as the hydrophobic monomer, it is possible to obtain a copolymer exhibiting superior feel.

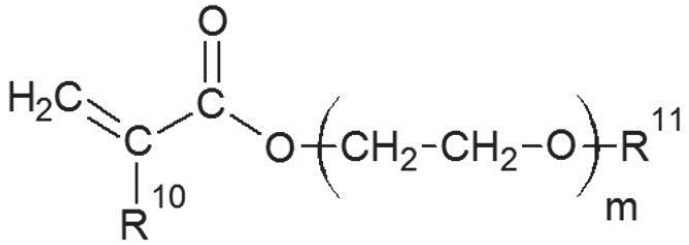
[0035]

In addition, in a preferred aspect of the present invention, the hydrophilic monomer is a hydrophilic monomer represented by the following general formula (4).

[0036]

General Formula (4)

[Chemical Formula 4]



(4)

(In the general formula (4), R10 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R11 represents a hydrogen atom, an aromatic hydrocarbon group having from 6 to 10 carbon atoms, an aliphatic hydrocarbon group having from 1 to 14 carbon atoms, or an acyl group having from 1 to 12 carbon atoms. m represents an integer from 6 to 40.)

[0037]

By using the above monomer as the hydrophilic monomer, it is possible to obtain a copolymer exhibiting superior feel.

[0038]

In a preferred aspect of the present invention, the trihydric alcohol is glycerin, trimethylolpropane, or trimethylolethane.

By adopting such an aspect, it is possible to improve the elastic feel.

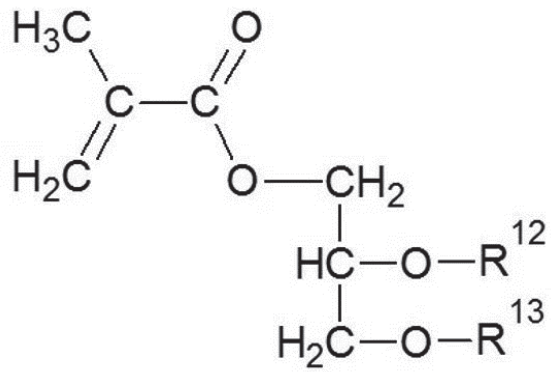
[0039]

The hydrophobic monomer is a compound represented by the following general formula (5).

[0040]

General Formula (5)

[Chemical Formula 5]



(5)

(R12 and R13 in the general formula (5) may be the same as or different from each other and represent an acyl group which has 18 carbon atoms and a branch but does not contain a ring structure.)

[0041]

By using such a hydrophobic monomer, it is possible to improve the elastic feel.

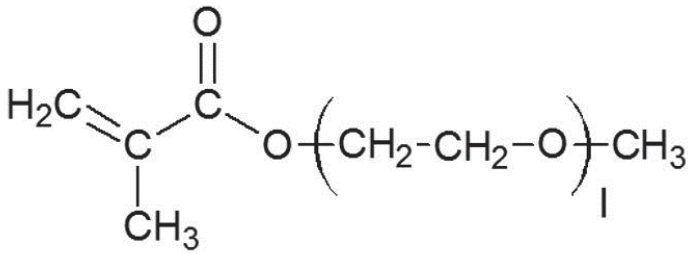
[0042]

In a preferred aspect of the present invention, the hydrophilic monomer is a hydrophilic monomer represented by the following general formula (6).

[0043]

General Formula (6)

[Chemical Formula 6]



(6)

(l in the general formula (6) represents an integer from 6 to 40.)

[0044]

By using such a hydrophilic monomer, it is possible

to improve the elastic feel.

[0045]

The present invention also relates to an external preparation for skin containing the copolymer of the present invention described above. The external preparation for skin exhibits elastic feel after being applied to the skin. It also exhibits excellent moist feel but does not exhibit stickiness.

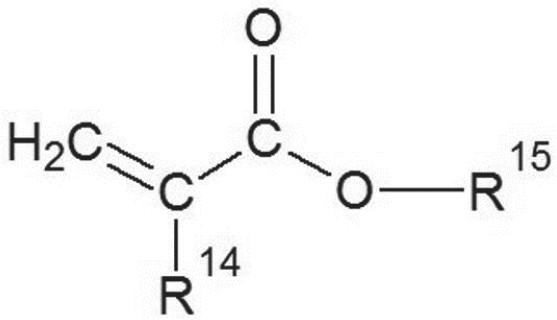
[0046]

The present invention to achieve the second object is an emulsified composition which contains a water-soluble copolymer having one kind or two or more kinds of constitutional units (c) derived from a hydrophobic monomer represented by the general formula (1), the following general formula (7), or the following general formula (8) and one kind or two or more kinds of constitutional units (d) derived from a hydrophilic monomer as essential constitutional units but does not substantially contain an emulsifying agent other than the water-soluble copolymer.

[0047]

General Formula (7)

[Chemical Formula 7]



(7)

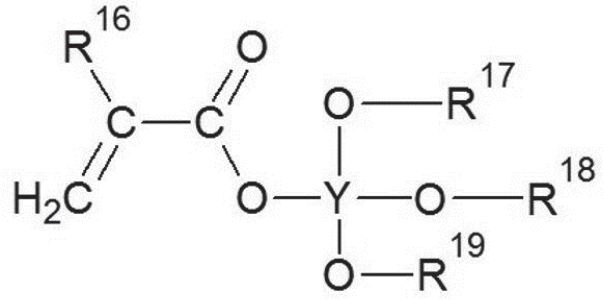
(In the general formula (7), R14 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R15 represents a branched hydrocarbon group which has from 13 to 30 carbon atoms but does not contain a ring structure or

a hydrocarbon group which has from 6 to 12 carbon atoms and two or more branches but does not contain a ring structure.)

[0048]

General Formula (8)

[Chemical Formula 8]



(8)

(In the general formula (8), R16 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R17, R18, and R19 may be the same as or different from one another and represent an acyl group which has from 6 to 22 carbon atoms and a branch but does not contain a ring structure. Y represents a group obtained by eliminating an OH group from a tetrahydric alcohol.)

[0049]

The emulsified composition of the present invention contains the water-soluble copolymer, and it is thus less sticky at the time of use.

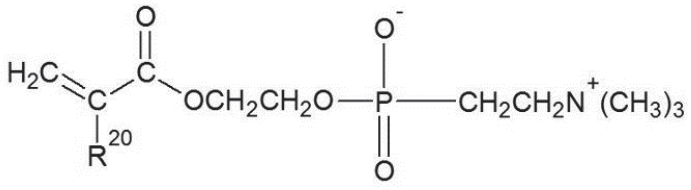
[0050]

In a preferred aspect of the present invention, the hydrophilic monomer is one kind or two or more kinds of hydrophilic monomers selected from the group consisting of a polymerizable carboxylic acid, a hydrophilic monomer represented by the general formula (2), a hydrophilic monomer represented by the following general formula (9), a hydrophilic monomer represented by the following general formula (10), and a hydrophilic monomer represented by the following general formula (11).

[0051]

General Formula (9)

[Chemical Formula 9]



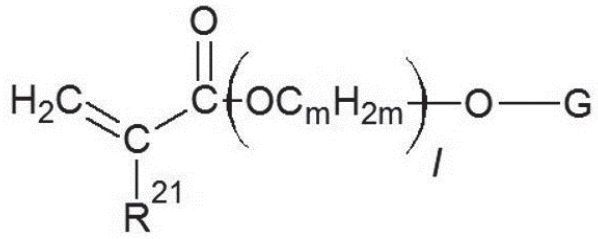
(9)

(R20 in the general formula (9) represents a hydrogen atom or a methyl group.)

[0052]

General Formula (10)

[Chemical Formula 10]



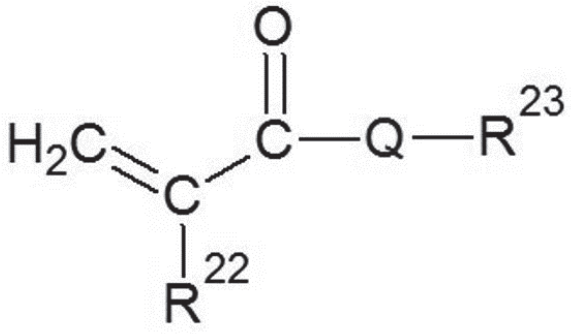
(10)

(In the general formula (10), R21 represents a hydrogen atom or a methyl group and G-O- represents a group obtained by eliminating a hydrogen atom from the hydroxyl group at the position 1 of a reducing sugar. m represents 2 or 3 and l represents an integer from 1 to 5.)

[0053]

General Formula (11)

[Chemical Formula 11]



(11)

(In the general formula (11), R22 represents a hydrogen atom or a methyl group, R23 represents an amino acid residue, a polyamine residue, or an amino alcohol residue, and Q represents an oxygen atom or a group represented by NH.)

[0054]

By containing a water-soluble copolymer containing the constitutional unit (d) derived from such a hydrophilic monomer, it is possible to further decrease stickiness of the emulsified composition of the present invention at the time of use.

[0055]

In a preferred aspect of the present invention, the hydrophobic monomer is a hydrophobic monomer represented by the general formula (1) and the water-soluble monomer is a hydrophilic monomer represented by the general formula (2).

A water-soluble copolymer having constitutional units derived from such a hydrophobic monomer and such a hydrophilic monomer exhibits excellent emulsifying power and an excellent effect of decreasing stickiness of the emulsified composition of the present invention at the time of use.

[0056]

In a preferred aspect of the present invention, the content of the water-soluble copolymer is from 0.5% to 30% by mass.

It is possible to improve the stability of the emulsified composition by setting the content of the water-soluble copolymer to be in the above range.

[0057]

In a preferred aspect of the present invention, the content of an oil phase component is from 0.1% to 70% by mass.

The emulsified composition of the present invention having a content of an oil phase component in the above range exhibits excellent stability.

[0058]

The emulsified composition of the present invention is less sticky, and it is thus preferable to form the emulsified composition into a cosmetic.

[0059]

The present invention also relates to an emulsifying agent containing a water-soluble copolymer having one kind or two or more kinds of constitutional units (c) derived from a hydrophobic monomer represented by the general formula (1), (7), or (8) and one kind or two or more kinds of constitutional units (d) derived from a hydrophilic monomer as essential constitutional units.

The emulsifying agent exhibits excellent emulsifying power while being low-irritant.

[0060]

The present invention also relates to a method of producing an emulsified composition, which includes a step of conducting emulsification by using the emulsifying agent described above and is characterized by substantially not using an emulsifying agent other than the emulsifying agent.

According to the method, it is possible to easily produce an emulsified composition without using a conventional emulsifying agent which may cause stickiness and without blending an emulsifying agent at a high proportion.

[0061]

The present invention to achieve the third and fourth objects is a skin cleanser containing a water-soluble copolymer having one kind or two or more kinds of constitutional units (e) derived from a hydrophobic monomer represented by the general formula (1), (7), or (8) and one kind or two or more kinds of constitutional units (f) derived from a hydrophilic monomer as essential constitutional units.

[0062]

The skin cleanser of the present invention realizes a decrease in tight feel after use while being equipped with high-quality foaming and creamy foam quality by containing the water-soluble copolymer described above.

[0063]

In a preferred aspect of the present invention, the hydrophilic monomer is one kind or two or more kinds of hydrophilic monomers selected from the group consisting of a polymerizable carboxylic acid, a hydrophilic monomer represented by the general formula (2), a hydrophilic monomer represented by the general formula (9), a hydrophilic monomer represented by the general formula (10), and a hydrophilic monomer represented by the general formula (11).

[0064]

It is possible to further decrease tight feel after use of the skin cleanser of the present invention by containing the water-soluble copolymer having the constitutional unit (e) derived from such a hydrophilic monomer.

[0065]

In a preferred aspect of the present invention, the hydrophobic monomer is a hydrophobic monomer represented by the general formula (1) and the water-soluble monomer is a hydrophilic monomer represented by the general formula (2).

It is possible to further decrease tight feel after use of the skin cleanser of the present invention by containing a water-soluble copolymer having constitutional units derived from such a hydrophobic monomer and such a hydrophilic monomer.

[0066]

In an embodiment of the present invention, the content of the water-soluble copolymer is from 0.1% to 20% by mass.

It is possible to decrease slimy feel at the time of use of the skin cleanser of the present invention by setting the content of the water-soluble copolymer to be in the above range.

[0067]

It is preferable to apply the present invention to a foaming cleanser.

According to the present invention, it is possible to decrease tight feel of the skin after use without inhibiting foaming and foam quality of the foaming cleanser.

[0068]

It is preferable to apply the present invention to a gel skin cleanser.

According to the present invention, it is possible to decrease the tight feel of the skin after use while improving ease of spreading of the gel skin cleanser on the skin.

[0069]

Skin cleansers containing surfactants exhibit relatively strong detergency and strong tight feel is thus caused after use thereof. Hence, it is preferable to apply the present invention to a skin cleanser in a form containing a surfactant. According to the present invention, it is possible to decrease tight feel of the skin after use of the skin cleanser without impairing or while improving excellent detergency of the surfactant.

[0070]

Skin cleansers containing fatty acid soap favorably foam and exhibit creamy foam quality and excellent detergency but cause strong tight feel after use. Hence, it is preferable to apply the present invention to a skin cleanser in a form containing fatty acid soap. According to the present invention, it is possible to decrease tight feel of the skin after use of the skin cleanser without impairing the advantageous effects of the skin cleanser containing fatty acid soap.

[0071]

In a preferred aspect of the present invention, the ratio of the mass of the water-soluble copolymer contained to the mass of the fatty acid soap contained is from 1 : 500 to 1 : 2, preferably from 1 : 200 to 1 : 3, and more preferably from 1 : 100 to 1 : 5.

It is possible to more effectively decrease tight feel after use of the skin cleanser containing fatty acid soap by setting the content of the water-soluble copolymer to be in the above range.

[0072]

It is also preferable to apply the present invention to a skin cleanser containing a nonionic surfactant.

According to the present invention, it is possible to decrease tight feel of the skin after use of the skin cleanser containing a nonionic surfactant while improving the detergency of the skin cleanser.

[0073]

In a preferred aspect of the present invention, the ratio of the mass of the water-soluble copolymer contained to the mass of the nonionic surfactant contained is from 1 : 20 to 1 : 0.5, preferably from 1 : 15 to 1 : 0.7, and more preferably from 1 : 10 to 1 : 1.

It is possible to more effectively decrease tight feel after use of the skin cleanser by setting the ratio of

the content of the water-soluble copolymer to the content of the nonionic surfactant to be in the above range.

[0074]

The present invention to achieve the fifth object is an oil-in-water type sunscreen cosmetic containing components (A) to (D).

(A) A water-soluble copolymer having one kind or two or more kinds of constitutional units (g) derived from a hydrophobic monomer represented by the general formula (1), (7), or (8) and one kind or two or more kinds of constitutional units (h) derived from a hydrophilic monomer as essential constitutional units

(B) A polyglycerin fatty acid ester obtained by ester condensation of one molecule of polyglycerin having a polymerization degree of 10 with from two to five molecules of a fatty acid having 16 or more carbon atoms

(C) An ionic surfactant

(D) An ultraviolet scattering agent and/or an ultraviolet absorber

[0075]

The sunscreen cosmetic of the present invention exhibits less sticky feel and excellent moisture retaining property while exhibiting an ultraviolet protecting function. The sunscreen cosmetic of the present invention also exhibits emulsion stability.

[0076]

In a preferred aspect of the present invention, the hydrophilic monomer is one kind or two or more kinds of hydrophilic monomers selected from the group consisting of a polymerizable carboxylic acid, a hydrophilic monomer represented by the general formula (2), a hydrophilic monomer represented by the general formula (9), a hydrophilic monomer represented by the general formula (10), and a hydrophilic monomer represented by the general formula (11).

[0077]

By using a water-soluble copolymer containing the constitutional unit (h) derived from such a hydrophilic monomer, it is possible to improve feel of use such as less sticky feel and moisturizing feel.

[0078]

In a preferred aspect of the present invention, the hydrophobic monomer is a hydrophobic monomer represented by the general formula (1) and the hydrophilic monomer is a hydrophilic monomer represented by the general formula (2).

A sunscreen cosmetic containing a water-soluble copolymer having constitutional units derived from such a hydrophobic monomer and such a hydrophilic monomer exhibits superior feel of use.

[0079]

In a preferred aspect of the present invention, the component (C) is an anionic surfactant.

It is possible to further improve emulsion stability by using an anionic surfactant as the ionic surfactant. The sunscreen cosmetic of the present invention using an anionic surfactant also exhibits excellent feel of use.

[0080]

In a preferred aspect of the present invention, the anionic surfactant is sodium acyl lactate.

It is possible to further improve emulsion stability by using sodium acyl lactate as the anionic surfactant. The sunscreen cosmetic of the present invention using sodium acyl lactate also exhibits excellent feel of use.

[0081]

In a preferred aspect of the present invention, the component (B) is polyglyceryl-10 pentastearate.

The sunscreen cosmetic of the present invention containing polyglyceryl-10 pentastearate exhibits excellent emulsion stability and feel of use.

[0082]

In a preferred aspect of the present invention, the component (D) is a water dispersible ultraviolet scattering agent.

The water dispersible ultraviolet scattering agent is uniformly dispersed in the aqueous phase, and a sunscreen cosmetic in such a form exhibits an excellent ultraviolet protecting function.

[0083]

In a preferred aspect of the present invention, the water dispersible ultraviolet scattering agent is an ultraviolet scattering agent of which the surface is treated with sodium polyacrylate.

A sunscreen cosmetic in such a form exhibits an excellent ultraviolet protecting function as the ultraviolet scattering agent is more uniformly dispersed therein.

[0084]

The present invention to achieve the sixth object is

a composition which contains

an amphipathic copolymer having one kind or two or more kinds of constitutional units (i) derived from a hydrophobic monomer and one kind or two or more kinds of constitutional units (j) derived from a hydrophilic monomer as essential constitutional units, a water-soluble polymer and/or any salt thereof, and water,

and forms a coating film having a sea-island structure in which island particles containing the amphipathic copolymer are dispersed in an aqueous gel formed by the water-soluble polymer and/or any salt thereof by evaporation of the water.

[0085]

The coating film has a sea-island structure containing a water-soluble component as a main component and exhibits feel like milk containing an oil agent. According to the composition of the present invention, it

is possible to form a coating film having such a sea-island structure on the skin.

[0086]

In a preferred aspect of the present invention, the average ratio of major axis to minor axis of the island particles is 0.8 or more and the number particle size distribution of the island particles having an average particle diameter of from 1 to 5 μm is 80% or more.

The coating film having such structural features exhibits excellent moisture retaining property and flexibility.

Moreover, it is possible to easily form a coating film exhibiting such excellent properties by applying the composition of the present invention to the skin.

[0087]

In a preferred aspect of the present invention, the water-soluble polymer is one kind or two or more kinds of water-soluble polymers selected from the group consisting of an acrylic acid-based water-soluble polymer, a water-soluble polypeptide, and a water-soluble polysaccharide and/or salts thereof.

By adopting an aspect containing such a water-soluble polymer, it is possible to improve the stability of the composition by improving the water solubility of the components of the composition and suppressing the occurrence of precipitation.

[0088]

In a preferred aspect of the present invention, the water-soluble polymer is one kind or two or more kinds of water-soluble polymers selected from the group consisting of sodium polyacrylate, a (acrylates/(C10-30) alkyl acrylate) crosspolymer, sodium polyglutamate, xanthan gum, and Tremella fuciformis polysaccharide.

It is possible to further improve the stability of the composition by adopting an aspect containing such a

water-soluble polymer.

[0089]

In a preferred aspect of the present invention, the composition contains a polyol which promotes phase separation between the aqueous gel and the amphipathic copolymer and/or a polyol which suppresses the phase separation between the aqueous gel and the amphipathic copolymer.

It is possible to improve uniformity of the coating film by containing such polyols.

[0090]

In a preferred aspect of the present invention, the polyol which promotes the phase separation is a polyol which increases the cloud point of the aqueous solution by being mixed with an aqueous solution of a nonionic surfactant having a polyether chain at the hydrophilic moiety, and the polyol which suppresses the phase separation is a polyol which lowers the cloud point of the aqueous solution by being mixed with an aqueous solution of a nonionic surfactant having a polyether chain at the hydrophilic moiety.

It is possible to improve uniformity of the coating film by containing such polyols.

[0091]

In a preferred aspect of the present invention, the polyol which promotes the phase separation is one kind or two or more kinds of polyols selected from the group consisting of 1,3-butylene glycol and polyethylene glycol.

It is possible to effectively promote the phase separation between the aqueous gel and the amphipathic copolymer and to improve the uniformity of the coating film by using such a polyol.

[0092]

In a preferred aspect of the present invention, the polyol which suppresses the phase separation is one kind or

two or more kinds of polyols selected from the group consisting of glycerin, diglycerin, sorbitol, and maltitol.

It is possible to effectively promote the phase separation between the aqueous gel and the amphipathic copolymer and to improve the uniformity of the coating film by using such a polyol.

[0093]

In a preferred aspect of the present invention, the mass ratio of the total amount of the polyol which promotes the phase separation and the polyol which suppresses the phase separation to the total amount of the amphipathic copolymer and the water-soluble polymer is from 5 : 1 to 20 : 1.

It is possible to improve the uniformity of the coating film by adopting such an aspect.

[0094]

In a preferred aspect of the present invention, the mass ratio of the polyol which promotes the phase separation to the polyol which suppresses the phase separation is from 3.5 : 1 to 1 : 2.5.

It is possible to improve the uniformity of the coating film by adopting such an aspect.

[0095]

In a preferred aspect of the present invention, the content of the amphipathic copolymer is from 0.1% to 5% by mass.

It is possible to obtain a composition capable of forming the coating film which is more flexible and exhibits excellent feel by setting the content of the amphipathic copolymer to be in the above range.

[0096]

In a preferred aspect of the present invention, the content of the oil agent is 1% by mass or less.

It is possible to obtain a composition capable of forming the coating film which is less sticky by adopting

such an aspect.

[0097]

In a preferred aspect of the present invention, one kind or two or more kinds of copolymers selected from the following group E are contained as the amphipathic copolymer.

[0098]

Group E: polyquaternium-51, polyquaternium-61, a (glycerylamidoethyl methacrylate/stearyl methacrylate) copolymer, and an acrylic acid-based amphipathic copolymer containing a constitutional unit (i) derived from a hydrophobic monomer selected from the general formulas (1), (7), and (8)

[0099]

The composition of the present invention containing such an amphipathic copolymer can form the coating film exhibiting stronger milky feel and superior flexibility.

[0100]

In a preferred aspect of the present invention, the acrylic acid-based amphipathic copolymer contains a constitutional unit (j) derived from one kind or two or more kinds of hydrophilic monomers selected from the following group F.

[0101]

Group F: a polymerizable carboxylic acid, a copolymer represented by the general formula (2), a copolymer represented by the general formula (9), a copolymer represented by the general formula (10), and a copolymer represented by the general formula (11).

[0102]

The composition of the present invention containing an amphipathic copolymer having the constitutional unit (j) derived from such a hydrophilic monomer can form the coating film exhibiting superior milky feel and flexibility.

[0103]

In a preferred aspect of the present invention, the acrylic acid-based amphipathic copolymer contains the constitutional unit (i) derived from a hydrophobic monomer represented by the general formula (1) and a constitutional unit (j) derived from a hydrophilic monomer represented by the general formula (2).

According to the composition of the present invention containing such an acrylic acid-based amphipathic copolymer, it is possible to form the coating film exhibiting superior moisture retaining property and flexibility.

[0104]

The present invention also relates to a coating film having a sea-island structure in which island particles containing an amphipathic copolymer are dispersed in an aqueous gel formed by a water-soluble polymer, and in which

the amphipathic copolymer has one kind or two or more kinds of constitutional units (i) derived from a hydrophobic monomer and one kind or two or more kinds of constitutional units (j) derived from a hydrophilic monomer as essential constitutional units.

[0105]

The coating film of the present invention has a sea-island structure containing a water-soluble component as a main component. Moreover, the coating film exhibits feel like milk containing an oil agent even though it contains a water-soluble component as a main component.

[0106]

In a preferred aspect of the present invention, the average ratio of major axis to minor axis of the island particles is 0.8 or more and the number particle size distribution of the island particles having an average particle diameter of from 1 to 5 μm is 80% or more.

The coating film having such structural features exhibits excellent feel like milk containing an oil agent.

[0107]

The present invention also relates to a method of forming the coating film of the present invention described above, which includes

applying a composition containing an amphipathic copolymer having one kind or two or more kinds of constitutional units (i) derived from a hydrophobic monomer and one kind or two or more kinds of constitutional units (j) derived from a hydrophilic monomer as essential constitutional units, a water-soluble polymer and/or any salt thereof, and water to the skin.

According to the method of the present invention, it is possible to easily form the coating film.

[0108]

In addition, in a preferred aspect of the present invention, the composition contains a polyol which promotes the phase separation between the amphipathic copolymer and the aqueous gel and/or a polyol which suppresses the phase separation between the aqueous gel and the amphipathic copolymer.

It is possible to form the coating film exhibiting excellent uniformity by using an aqueous solution containing such polyols.

Advantageous Effects of Invention

[0109]

According to the present invention, it is possible to provide a copolymer and an external preparation for skin which exhibit elastic feel.

[0110]

According to the present invention, it is also possible to provide an emulsified composition which exhibits excellent emulsion stability while causing less irritation to the skin and being less sticky.

[0111]

According to the present invention, it is also

possible to provide a skin cleanser exhibiting decreased tight feel after use.

In addition, in the case of applying the present invention to a skin cleanser containing fatty acid soap, it is possible to decrease tight feel after use without inhibiting high-quality foaming and creamy foam quality.

In addition, even in the case of applying the present invention to a gel skin cleanser, the effect of decreasing tight feel after use is obtained.

[0112]

According to the present invention, it is also possible to provide an oil-in-water type sunscreen cosmetic which exhibits excellent feel of use such as absence of sticky feel and moisturizing feel and emulsion stability while exhibiting a favorable ultraviolet protecting function.

[0113]

According to the present invention, it is also possible to provide a coating film which has a sea-island structure and contains a water-soluble component as a main component and a technique to form the coating film. The coating film exhibits feel like milk containing an oil agent even though it contains a water-soluble component as a main component.

In addition, in a preferred aspect of the present invention, it is possible to provide a coating film which is not sticky and a technique to form the coating film.

Brief Description of Drawings

[0114]

Fig. 1 is a bar graph which illustrates the evaluation results of gel cosmetics containing a copolymer of Example 1 and Comparative Example 1.

Fig. 2 illustrates a three-component system phase diagram in which the blending ratio among a (glyceryl

diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer, squalane, and water in Examples 9 to 31 is plotted.

Fig. 3 is a three-component system phase diagram in which the blending ratio among a (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer, caprylic/capric triglyceride, and water in Examples 32 to 62 is plotted.

Fig. 4 illustrates a three-component system phase diagram in which the blending ratio among a (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer, dimethicone, and water in Examples 63 to 89 is plotted.

Fig. 5 illustrates a three-component system phase diagram of 1,3-butylene glycol, glycerin, and the total amount of xanthan gum and a (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer contained in Examples 104 to 124.

Fig. 6 illustrates photomicrographs of the compositions of Examples 105, 106, 108, 111, 113, 114, 115, 119, 120, 122, and 123.

Fig. 7 is pie charts which illustrate the results on the feel evaluation of the composition of Example 104 in Test Example 7.

Description of Embodiments

[0115]

The copolymer of the present invention to achieve the first object has one kind or two or more kinds of constitutional units (a) derived from a hydrophobic monomer represented by the general formula (1) and one kind or two or more kinds of constitutional units (b) derived from a hydrophilic monomer represented by the general formula (2) as essential constitutional units.

Incidentally, in the present invention, the

"constitutional unit derived from a monomer" refers to a constitutional unit formed by cleavage of a carbon-carbon unsaturated bond of the corresponding monomer by a polymerization reaction.

Hereinafter, the hydrophobic monomer represented by the general formula (1) and the hydrophilic monomer represented by the general formula (2) will be described.

[0116]

<1> Hydrophobic monomer

The copolymer of the present invention contains one kind or two or more kinds of constitutional units derived from a hydrophobic monomer represented by the general formula (1) (hereinafter simply referred to as the "constitutional unit (1)" in some cases) as an essential constitutional unit.

[0117]

Here, examples of the alkyl group represented by R1 may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R1 is preferably a hydrogen atom or a methyl group.

[0118]

In addition, examples of the acyl group which is represented by R2 and R3, has from 6 to 22 carbon atoms and a branch, but does not contain a ring structure may include a 2-methylpentanoyl group, a 3-methylpentanoyl group, a 4-methylpentanoyl group, a 2-ethylbutanoyl group, a 2-ethylbutanoyl group, a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2-methylhexanoyl group, a 4-methylhexanoyl group, a 5-methylhexanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2-methylheptanoyl group, a 2-ethylhexyl group, a 2-propylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl group, a 2-methyloctanoyl group, a 3,3,5-trimethylhexanoyl group, a 2-methylnonanoyl group, a

4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-diethylhexanoyl group, a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group, a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0119]

In a more preferred embodiment of the present invention, the hydrophobic monomer represented by the general formula (1) is a hydrophobic monomer represented by the general formula (3).

[0120]

Examples of such an acyl group which is represented by R8 and R9, has from 10 to 22 carbon atoms and a branch, but does not contain a ring structure in a preferred embodiment may include a 2-methylnonanoyl group, a 4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-

diethylhexanoyl group), a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group), a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0121]

In addition, examples of the acyl group which is represented by R8 and R9, has from 6 to 9 carbon atoms and two or more branches, but does not contain a ring structure in a preferred embodiment may include a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl group, and a 3,5,5-trimethylhexanoyl group.

[0122]

The number of carbon atoms in the acyl group of R8 and R9 in the general formula (3) is preferably from 12 to 22, more preferably from 14 to 20, and still more preferably from 16 to 20.

In addition, the number of carbon atoms in the main chain of the acyl group of R8 and R9 in the general formula

(3) is preferably from 9 to 21, more preferably from 12 to 20, and still more preferably from 16 to 18.

In addition, the number of branches in the acyl group of R8 and R9 in the general formula (3) is preferably from 1 to 3, more preferably from 1 or 2, and still more preferably 1.

Furthermore, in the acyl groups of R8 and R9 in the general formula (3), it is more preferable as the position number of the carbon atom in the main chain to which a branched chain is bonded is higher. Specifically, the branched chain is bonded preferably to the 1st to 3rd carbon atom, more preferably to the 1st or 2nd carbon atom, and still more preferably to the 1st carbon atom from the carbon atom at the end of the main chain.

[0123]

Specific examples of R8 and R9 may suitably include a 10-methylundecanoyl group, a 10-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 16-methylheptadecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0124]

The group which is represented by X or Y in the general formulas (1) and (3) and derived from a trihydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a trihydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a trihydric alcohol selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

[0125]

In a preferred aspect of the present invention, it is

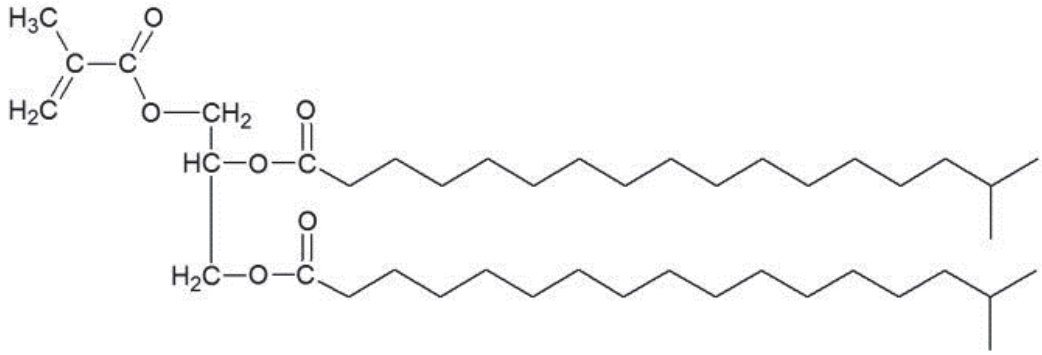
preferable to use a monomer represented by the general formula (5) as the hydrophobic monomer.

[0126]

Examples of the hydrophobic monomer represented by the general formula (5) may include compounds represented by the following formulas (12) to (14). Preferably, a compound which is represented by the following formula (12) and in which a branched chain is attached to the terminal of an acyl group is used.

[0127]

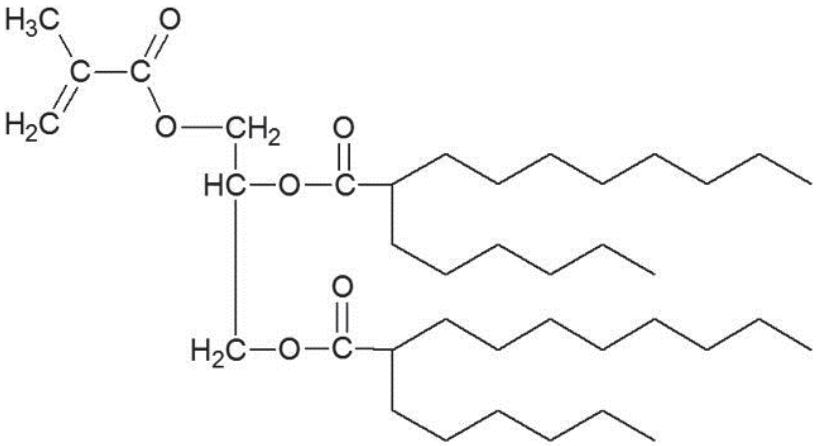
[Chemical Formula 12]



Formula (12)

[0128]

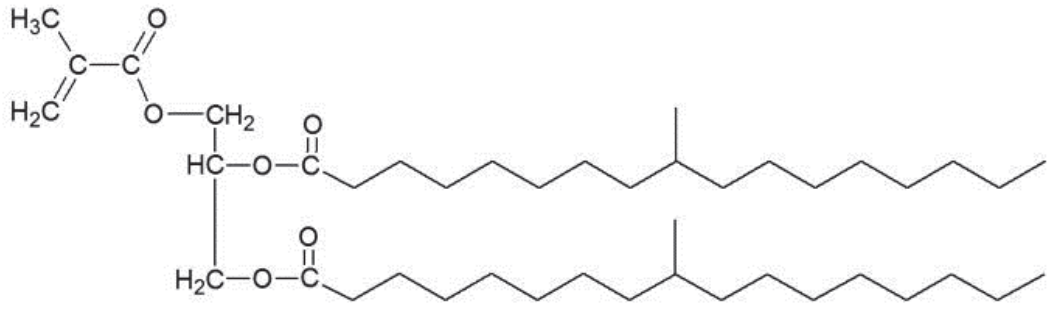
[Chemical Formula 13]



Formula (13)

[0129]

[Chemical Formula 14]



Formula (14)

[0130]

The hydrophobic monomer which constitutes the copolymer of the present invention and is represented by the general formula (1) can be synthesized, for example, by the following method.

a) A trihydric alcohol is ketalized. Examples of the specific synthesis method may include the method described in Production Example 1 of JP 2009-136749 A.

b) A (meth)acrylic acid ester of ketal is synthesized by transesterification of the ketalized trihydric alcohol that is synthesized in a) with a (meth)acrylic acid alkyl ester, and a reaction for removal of ketone of the (meth)acrylic acid ester of ketal thus obtained is conducted to synthesize a mono(meth)acrylic acid ester of the trihydric alcohol. Examples of the specific synthesis method may include the method described in Example 1 of JP 2004-18389 A.

c) The mono(meth)acrylic acid ester of the trihydric alcohol obtained in b) is reacted with a carboxylic acid having a predetermined branched structure or an anhydride or chloride thereof to obtain a hydrophobic monomer represented by the general formula (1).

[0131]

Incidentally, as the ketalized trihydric alcohol, there are also commercially available products, and it is also possible to obtain the ester of a trihydric alcohol of the present invention through the above steps b) and c) by

utilizing such a commercially available product. Examples of such a commercially available product may include (S)-(+)-2,2-dimethyl-1,3-dioxalane-4-methanol, (R)-(+)-2,2-dimethyl-1,3-dioxalane-4-methanol (all manufactured by Tokyo Chemical Industry Co., Ltd.). Furthermore, as the mono(meth)acrylic acid ester of a trihydric alcohol as well, there are commercially available products, and it is also possible to obtain the ester of a trihydric alcohol of the present invention through the step c) by utilizing such a commercially available product. Examples of such a commercially available product may include "BLEMMER GLM" (glycerol monomethacrylate) manufactured by NOF CORPORATION).

[0132]

In the copolymer of the present invention, the proportion of the constitutional unit (a) in the entire constitutional units is preferably from 1% to 40% by mass and more preferably from 5% to 35% by mass.

It is possible to improve the elasticity of the copolymer of the present invention by setting the proportion of the constitutional unit (a) to be in the above range.

[0133]

<2> Hydrophilic monomer

The copolymer of the present invention contains one kind or two or more kinds of constitutional units derived from a hydrophilic monomer represented by the general formula (2) as an essential constitutional unit.

[0134]

Examples of the alkyl group represented by R4 in the general formula (2) may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R4 is preferably a hydrogen atom or a methyl group.

[0135]

In addition, examples of the alkylene group represented by R5 may include an ethylene group, a propylene group, an isopropylene group, a 2-hydroxypropylene group, a 1-hydroxy-2-methylethylene group, and a 2-hydroxy-1-methylethylene group, and an ethylene group or a propylene group is preferable and an ethylene group is more preferable among these.

[0136]

In addition, among the groups represented by R6, examples of the aromatic group having from 6 to 10 carbon atoms may include a phenyl group, a benzyl group, a methylphenyl group, and an ethylphenyl group; examples of the aliphatic hydrocarbon group having from 1 to 14 carbon atoms may suitably include a methyl group, an ethyl group, a butyl group, a tertiary butyl group, a hexyl group, a cyclohexyl group, an octyl group, a 2-ethylhexyl group, and a lauryl group; and examples of the acyl group having from 1 to 12 carbon atoms may suitably include a formyl group, an acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a valeryl group, and a lauroyl group. Among these, the group represented by R5 is preferably an aliphatic hydrocarbon group having from 1 to 14 carbon atoms and more preferably an alkyl group having from 1 to 12 carbon atoms.

[0137]

Furthermore, n in the general formula (2) is a numerical range of from 6 to 40.

[0138]

Specific examples of the monomer in which R5 is a propylene group among the monomers represented by the general formula (2) may include polypropylene glycol (9) monoacrylate, polypropylene glycol (13) monoacrylate, polypropylene glycol (9) monomethacrylate, and polypropylene glycol (13) monomethacrylate. Incidentally, the numbers in the parentheses denote N. A large number of

these polymers are commercially available. Specific examples of these commercially available products may include "BLEMMER" AP-400, AP-550, AP-800, PP-500, and PP-800 (trade name, all manufactured by NOF CORPORATION).

[0139]

Specific examples of the monomer in which R5 is an ethylene group among the monomers represented by the general formula (2) may include polyethylene glycol (10) monoacrylate, polyethylene glycol (8) monomethacrylate, polyethylene glycol (23) monoacrylate, polyethylene glycol (23) monomethacrylate, methoxypolyethylene glycol (9) acrylate, methoxypolyethylene glycol (9) methacrylate, methoxy polyethylene glycol (23) methacrylate, oleyloxypolyethylene glycol (18) methacrylate, lauroxypolyethylene glycol (18) acrylate, lauroyloxypolyethylene glycol (10) methacrylate, and stearoxypolyethylene glycol (30) monomethacrylate.

[0140]

In a preferred embodiment of the present invention, the monomer represented by the general formula (6) is used as the hydrophilic monomer.

[0141]

l in the general formula (6) is preferably from 6 to 30 and more preferably from 8 to 30.

[0142]

The hydrophilic monomers described above can be obtained at a high yield by an esterification reaction of the corresponding polyethylene glycol, polyethylene glycol monoether, and polyethylene glycol monoester with a chloride or anhydride of acrylic acid or methacrylic acid. There are also already a large number of commercially available products, and it is also possible to utilize such commercially available products. Specific examples of such commercially available products may include BLEMMER AE-400, PE-350, AME-400, PME-400, PME-1000, ALE-800, and PSE-1300,

(trade name, all manufactured by NOF CORPORATION) and the like.

[0143]

The constitutional unit which is contained in the copolymer of the present invention and derived from a hydrophilic monomer may be only one kind, but two or more kinds of constitutional units may be contained in combination as long as the conditions described above are satisfied.

[0144]

In the copolymer of the present invention, the proportion of the constitutional unit (b) derived from a hydrophilic monomer in the entire constitutional units is from 30% to 95% by mass and preferably from 40% to 90% by mass.

It is possible to improve the elastic feel of the copolymer of the present invention by setting the proportion of the constitutional unit (b) to be in the above range.

[0145]

<3> Other arbitrary constitutional units

In addition to the constitutional unit 1 and the constitutional unit 2, the copolymer of the present invention can contain a unit derived from a monomer to be usually used in a copolymer as an arbitrary constitutional unit in a range in which the effect of the invention is not impaired. Examples of such an arbitrary constitutional unit may include a constitutional unit derived from a monomer such as a (meth)acrylic acid amide such as acrylic acid amide, methacrylic acid amide, acrylic acid monoalkylamide, or methacrylic acid monoalkylamide, a (meth)acrylic acid alkyl ester such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl

(meth)acrylate, n-dodecyl methacrylate, stearyl (meth)acrylate, or isostearyl (meth)acrylate, a cyclic alkyl ester of (meth)acrylic acid such as cyclohexyl (meth)acrylate, a (meth)acrylic acid hydroxyalkyl ester such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, or 4-hydroxybutyl (meth)acrylate, a (meth)acrylic acid aryl ester such as benzyl (meth)acrylate, a (meth)acrylic acid alkoxyalkyl ester such as methoxymethyl (meth)acrylate or methoxyethyl (meth)acrylate, vinyl acetate, vinyl pyrrolidone, styrene, α-methylstyrene, or acrylonitrile. Most of these monomers are commercially available.

[0146]

<4> Copolymer of present invention

The copolymer of the present invention is a copolymer containing the constitutional unit (a) and the constitutional unit (b) in the backbone. In addition, the copolymer of the present invention is usually a random copolymer in which the constitutional units are randomly bonded to one another, but it may be a block copolymer or a graft copolymer.

[0147]

The copolymer of the present invention has a weight average molecular weight of from 20,000 to 110,000. The copolymer of the present invention exhibits elastic feel by setting the weight average molecular weight thereof to be in the above range.

The weight average molecular weight of the copolymer of the present invention is more preferably from 20,000 to 80,000, more preferably from 30,000 to 80,000, more preferably from 40,000 to 70,000, still more preferably from 50,000 to 70,000, and still more preferably from 57,000 to 66,000.

Incidentally, the weight average molecular weight here refers to the weight average molecular weight in terms

of polystyrene measured by GPC.

[0148]

The method of producing the copolymer of the present invention is not particularly limited, but the copolymer can be obtained by, for example, a method in which the monomers from which the respective constitutional units are derived are mixed in a solvent and the polymerization reaction of the mixture is conducted according to a method to be usually used for polymerization of an acrylic monomer.

Here, the weight average molecular weight of the copolymer can be adjusted by changing the reaction time and reaction temperature of the polymerization reaction. Specifically, the weight average molecular weight can be decreased by shortening the reaction time.

[0149]

In addition, it is preferable that the copolymer of the present invention is soluble in water since it is easy to handle the copolymer upon utilization. The term "copolymer" as used herein is defined as a copolymer of which a 20% by mass aqueous solution has a transmittance of 90% or more at 25°C. In order to obtain such a polymer, it is particularly preferable to use a polymerization method in which the radical polymerization of the monomer mixture is conducted in a mixed solvent of an aqueous solution with an aqueous solvent miscible with water at an arbitrary proportion at 25°C among the polymerization methods. In addition, a polymerization method in which a buffer solution is used instead of water is still more preferable since the amount of residual monomer after the polymerization reaction is small. The aqueous solution which exhibits a buffering action and is used in this method is not particularly limited as long as it is a usually used buffer solution, but specific examples thereof may include a potassium chloride-hydrochloric acid solution, a potassium hydrogen phthalate-hydrochloric acid solution,

a potassium dihydrogen phosphate-disodium hydrogen phosphate solution, a potassium hydrogen citrate-citric acid solution, and a sodium carbonate-sodium hydrogen carbonate solution. In addition, the buffer solution may be formed when the initiator is added to an aqueous solution of a salt, acid, or base which forms a buffer solution with an ion of the initiator. Furthermore, specific examples of the aqueous solvent which is miscible with water at an arbitrary proportion at 25°C and used in this method may include alcohols having from 1 to 3 carbon atoms such as methyl alcohol, ethyl alcohol, n-propyl alcohol, and isopropyl alcohol, ketones such as acetone and methyl ethyl ketone, diols such as ethylene glycol, polyethylene glycol, propylene glycol, and 1,3 butylene glycol, ethylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether and ethylene glycol monoethyl ether, and tetrahydrofuran. Among these aqueous solvents, alcohols having from 1 to 3 carbon atoms, such as methanol, ethanol, n-propanol, and isopropanol, are particularly preferable since the polymerization reaction is likely to proceed.

[0150]

In the present invention, the mass ratio of the constitutional unit (a) constituting the copolymer to the constitutional unit (b) constituting the copolymer is preferably from 5 : 95 to 50 : 50, more preferably from 10 : 90 to 45 : 55, still more preferably from 20 : 80 to 40 : 60, and still more preferably from 25 : 75 to 35 : 65.

[0151]

In addition, the molar ratio of the constitutional unit (a) constituting the copolymer to the constitutional unit (b) constituting the copolymer is preferably from 8 : 92 to 62 : 38, more preferably from 15 : 85 to 57 : 43, still more preferably from 29 : 71 to 52 : 48, and still more preferably from 35 : 65 to 46 : 54.

It is possible to further improve the elastic feel by setting the mass ratio and molar ratio of the constitutional unit (a) to the constitutional unit (b) in the copolymer to be in the above ranges.

[0152]

<5> External preparation for skin containing copolymer of present invention

The external preparation for skin containing the copolymer of the present invention hardly causes stickiness while exhibiting elastic feel.

The content of the copolymer of the present invention in the external preparation for skin is preferably from 0.5% to 30% by mass and more preferably from 1% to 25% by mass.

[0153]

Examples of the external preparation for skin of the present invention may suitably include external medicines such as ointment and cosmetics. Furthermore, examples of the cosmetics may include skincare products such as cream, milky lotion, skin lotion, beauty essence, and sunscreen cosmetics, makeup products such as under makeup products, foundation, eye color, and mascara, skin cleansers such as a facial cleanser, and hair cosmetics such as hear tonic, hair liquid, and hair spray.

[0154]

The external preparation for skin of the present invention can contain a component to be usually used in an external preparation for skin as an arbitrary component in a range in which the effect of the present invention is not impaired. Specific examples of the arbitrary component may preferably include oils and waxes such as macadamia nut oil, avocado oil, corn oil, olive oil, rapeseed oil, sesame oil, castor oil, safflower oil, cottonseed oil, jojoba oil, coconut oil, palm oil, liquid lanolin, hardened coconut oil, hardened oil, vegetable wax, hardened castor oil, beeswax, candelilla wax, carnauba wax, insects wax, lanolin, reduced

lanolin, hard lanolin, and jojoba wax, hydrocarbons such as liquid paraffin, squalane, pristane, ozokerite, paraffin, ceresin, petroleum jelly, and microcrystalline wax, higher fatty acids such as oleic acid, isostearic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, and undecylenic acid, higher alcohols such as cetyl alcohol, stearyl alcohol, isostearyl alcohol, behenyl alcohol, octyldodecanol, myristyl alcohol, and cetostearyl alcohol, synthetic ester oils such as cetyl isooctanoate, isopropyl myristate, hexyldecyl isostearate, diisopropyl adipate, di-2-ethylhexyl sebacate, cetyl lactate, diisostearyl malate, ethylene glycol di-2-ethylhexanoate, neopentyl glycol dicaprate, glycerin di-2-heptylundecanoate, glycerin tri-2-ethylhexanoate, trimethylolpropane tri-2-ethylhexanoate, trimethylolpropane triisostearate, and pentaneerythritol tetra-2-ethylhexanoate, oil agents such as silicone oils such as chain polysiloxanes such as dimethylpolysiloxane, methylphenylpolysiloxane, and diphenylpolysiloxane, cyclic polysiloxanes such as octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and dodecamethylcyclohexanesiloxane, and modified polysiloxanes such as amino-modified polysiloxane, polyether-modified polysiloxane, alkyl-modified polysiloxane, and fluorine-modified polysiloxane, anionic surfactants such as fatty acid soap (sodium laurate, sodium palmitate, and the like), potassium lauryl sulfate, and triethanolamine alkyl ether sulfate, cationic surfactants such as stearyl trimethyl ammonium chloride, benzalkonium chloride, and lauryl amine oxide, amphoteric surfactants such as imidazoline-based amphoteric surfactants (2-cocoyl-2-imidazolinium hydroxide-1-carboxyethyloxy disodium salt and the like.), betaine-based surfactants (alkylbetaine, amidobetaine, sulfobetaine, and the like), and acyl methyl taurine, nonionic surfactants such as sorbitan fatty acid esters (sorbitan monostearate, sorbitan sesquioleate, and

the like), glycerin fatty acids (glyceryl monostearate and the like), propylene glycol fatty acid esters (propylene glycol monostearate and the like), hardened castor oil derivatives, POE sorbitan fatty acid esters (POE sorbitan monooleate, polyoxyethylene sorbitan monostearate, and the like), POE sorbitol fatty acid esters (POE-sorbitol monolaurate and the like), POE glycerin fatty acid esters (POE-glycerin monoisostearate and the like), POE fatty acid esters (polyethylene glycol monooleate, POE distearate, and the like), POE alkyl ethers (POE 2-octyl dodecyl ether and the like), POE alkyl phenyl ethers (POE nonyl phenyl ether and the like), Pluronic type nonionic surfactants, POE · POP alkyl ethers (POE · POP 2-decyltetradecyl ether and the like), Tetronics, POE castor oil · hardened castor oil derivatives (POE castor oil, POE hardened castor oil, and the like), sucrose fatty acid esters, and alkyl glucosides, polyhydric alcohols such as polyethylene glycol, glycerin, 1,3-butylene glycol, erythritol, sorbitol, xylitol, maltitol, propylene glycol, dipropylene glycol, diglycerin, isoprene glycol, 1,2-pentanediol, 2,4-hexylene glycol, 1,2-hexanediol, and 1,2-octanediol, moisturizing components such as sodium pyrrolidone carboxylate, lactic acid, and sodium lactate, thickeners such as guar gum, quince seed, carrageenan, galactan, gum arabic, pectin, mannan, starch, xanthan gum, curdlan, methylcellulose, hydroxyethylcellulose, carboxymethylcellulose, methylhydroxypropylcellulose, chondroitin sulfate, dermatan sulfate, glycogen, heparan sulfate, hyaluronic acid, sodium hyaluronate, tragacanth gum, keratan sulfate, chondroitin, mucoitin sulfate, hydroxyethyl guar gum, carboxymethyl guar gum, dextran, keratosulfate, locust bean gum, succinoglucan, caloninic acid, chitin, chitosan, carboxymethyl chitin, agar, polyvinyl alcohol, polyvinyl pyrrolidone, carboxyvinyl polymer, sodium polyacrylate, polyethylene glycol, and bentonite, lower alcohols such as ethanol and

isopropanol, ultraviolet absorbers such as hexyl diethylaminohydroxybenzoylbenzoate, t-butyl methoxybenzoylmethane, a p-aminobenzoic acid-based ultraviolet absorber, an anthranilic acid-based ultraviolet absorber, a salicylic acid-based ultraviolet absorber, and a cinnamic acid-based ultraviolet absorber, and vitamins such as vitamin A or any derivative thereof, vitamin B family such as vitamin B6 hydrochloride, vitamin B6 tripalmitate, vitamin B6 dioctanoate, vitamin B2 or any derivative thereof, vitamin B12, and vitamin B15 or any derivative thereof, vitamin E family such as α-tocopherol, β-tocopherol, γ-tocopherol, and vitamin E acetate, vitamin D family, vitamin H, pantothenic acid, pantethine, and pyrroloquinoline quinone.

[0155]

The external preparation for skin of the present invention can be prepared by treating the essential components and arbitrary components by a conventional method.

[0156]

In addition, the emulsified composition of the present invention to achieve the second object is characterized by containing a water-soluble copolymer which has a constitutional unit (c) derived from a hydrophobic monomer and a constitutional unit (d) derived from a hydrophilic monomer. Hereinafter, the hydrophobic monomer, the hydrophilic monomer, and the water-soluble copolymer which is a copolymer thereof will be described in the section <1>.

[0157]

<1> Water-soluble copolymer

[1] Hydrophobic monomer

In the present invention, a water-soluble copolymer containing one kind or two or more kinds of constitutional units derived from a hydrophobic monomer represented by the

general formula (1), (7), or (8) (hereinafter simply referred to as the "constitutional unit (7)" or the like in some cases) as an essential constitutional unit is used.

Incidentally, in the present invention, the "constitutional unit derived from a monomer" refers to a constitutional unit formed by cleavage of a carbon-carbon unsaturated bond of the corresponding monomer by a polymerization reaction.

Hereinafter, the hydrophobic monomer represented by the general formula (1), (7), or (8) will be described.

[0158]

(1-1) Hydrophobic monomer represented by general formula (7)

In the general formula (7), R14 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R15 represents a branched hydrocarbon group which has from 13 to 30 carbon atoms but does not contain a ring structure or a hydrocarbon group which has from 6 to 12 carbon atoms and two or more branches but does not contain a ring structure.

Here, examples of the alkyl group represented by R14 may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R14 is preferably a hydrogen atom or a methyl group.

[0159]

In addition, examples of the branched hydrocarbon group which is represented by R15, has from 13 to 30 carbon atoms, but does not contain a ring structure may include a 1-methyldodecanyl group, an 11-methyldodecanyl group, a 3-ethylundecanyl group, 3-ethyl-4,5,6-trimethyloctyl group, a 1-methyltridecanyl group, a 1-hexyloctyl group, a 2-butyldecanyl group, a 2-hexyloctyl group, a 4-ethyl-1-isobutyloctyl group, a 1-methylpentadecanyl group, a 2-hexyldecanyl group, a 2-octyldecanyl group, a 2-hexyldodecanyl group, a 16-methylheptadecanyl group, a 9-

methylheptadecanyl group, a 7-methyl-2-(3-methylhexyl)decanyl group, a 3,7,11,15-tetramethylhexadecanyl group, a 2-octyldodecanyl group, a 2-decyltetradecanyl group, and a 2-dodecylhexadecanyl group.

[0160]

In addition, examples of the hydrocarbon group which is represented by R15, has from 6 to 12 carbon atoms and two or more branches, but does not contain a ring structure may include a 2,2-dimethylbutyl group, a 2,3-dimethylbutyl group, a 3,3-dimethylbutyl group, a 1,3-dimethylbutyl group, a 1,2,2-trimethylpropyl group, a 1,1-dimethylpentanyl group, a 1-isopropylbutyl group, a 1-isopropyl-2-methylpropyl group, a 1,1-diethylpropyl group, a 1-ethyl-1-isopropylpropyl group, a 2-ethyl-4-methylpentyl group, a 1-propyl-2,2-dimethylpropyl group, a 1,1,2-trimethylpentyl group, a 1-isopropyl-3-methylbutyl group, a 1,2-dimethyl-1-ethylbutyl group, a 1,3-dimethyl-1-ethylbutyl group, a 1-ethyl-1-isopropylpropyl group, a 1,1-dimethylhexyl group, a 1-methyl-1-ethylpentyl group, a 1-methyl-1-propylbutyl group, a 1,4-dimethylhexyl group, a 1-ethyl-3-methylpentyl group, a 1,5-dimethylhexyl group, a 1-ethyl-6-methylheptyl group, a 1,1,3,3-tetramethylbutyl group, a 1,2-dimethyl-1-isopropylpropyl group, a 3-methyl-1-(2,2-dimethylethyl)butyl group, a 1-isopropylhexyl group, a 3.5.5-trimethylhexyl group, a 2-isopropyl-5-methylhexyl group, a 1,5-dimethyl-1-ethylhexyl group, a 3,7-dimethyloctyl group, a 2,4,5-trimethylheptyl group, a 2,4,6-trimethylheptyl group, and a 3,5-dimethyl-1-(2,2-dimethylethyl)hexyl group.

[0161]

(1-2) Hydrophobic monomer represented by general formula (1) or (8)

In the general formulas (1) and (8), R1 and R16 represent a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R2, R3, R17, R18, and R19 may be the

same as or different from one another and represent an acyl group which has from 6 to 22 carbon atoms and a branch but does not contain a ring structure. X represents a group obtained by eliminating an OH group from a trihydric alcohol.

[0162]

Here, examples of the alkyl group represented by R1 and R16 may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R1 is preferably a hydrogen atom or a methyl group.

[0163]

In addition, examples of the acyl group which is represented by R2, R3, R17, R18, and R19, has from 6 to 22 carbon atoms and a branch, but does not contain a ring structure may include a 2-methylpentanoyl group, a 3-methylpentanoyl group, a 4-methylpentanoyl group, a 2-ethylbutanoyl group, a 2-ethylbutanoyl group, a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2-methylhexanoyl group, a 4-methylhexanoyl group, a 5-methylhexanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2-methylheptanoyl group, a 2-ethylhexyl group, a 2-propylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl group, a 2-methyloctanoyl group, a 3,3,5-trimethylhexanoyl group, a 2-methylnonanoyl group, a 4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-diethylhexanoyl group, a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group, a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-

trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0164]

In addition, in a preferred embodiment of the present invention, in the general formulas (1) and (8), R2, R3, R17, R18, and R19 may be the same as or different from one another and represent an acyl group which has from 10 to 22 carbon atoms and a branch but does not contain a ring structure or an acyl group which has from 6 to 9 carbon atoms and two or more branches but does not contain a ring structure.

[0165]

Examples of such an acyl group which is represented by R2, R3, R17, R18, and R19, has from 10 to 22 carbon atoms and a branch, but does not contain a ring structure in a preferred embodiment may include a 2-methylnonanoyl group, a 4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-diethylhexanoyl group), a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group), a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-

butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0166]

In addition, examples of the acyl group which is represented by R2, R3, R17, R18, and R19, has from 6 to 9 carbon atoms and two or more branches, but does not contain a ring structure in a preferred embodiment may include a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl group, and a 3,5,5-trimethylhexanoyl group.

[0167]

The group which is represented by X in the general formula (1) and derived from a trihydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a trihydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a trihydric alcohol selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

[0168]

In addition, the group which is represented by Y in the general formula (8) and derived from a tetrahydric

alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a tetrahydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a tetrahydric alcohol selected from the group consisting of diglycerin, pentaerythritol, erythritol, D-threitol, and L-threitol.

[0169]

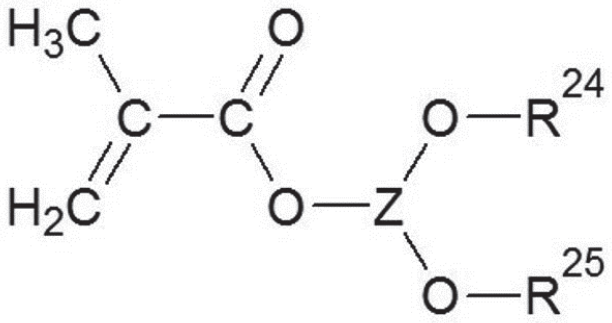
In the present invention, it is particularly preferable to use a water-soluble copolymer containing the constitutional unit (1).

In addition, in a more preferred embodiment of the present invention, the hydrophobic monomer represented by the general formula (1) is a hydrophobic monomer represented by the following general formula (15).

[0170]

General Formula (15)

[Chemical Formula 15]



(15)

(In the general formula (15), R24 and R25 may be the same as or different from each other and represent an acyl group which has from 16 to 22 carbon atoms and a branch but does not contain a ring structure. Z represents a group obtained by eliminating an OH group from a trihydric alcohol.)

[0171]

The number of carbon atoms in the acyl group of R24

and R25 in the general formula (15) is from 12 to 22, more preferably from 14 to 20, and still more preferably from 16 to 20.

In addition, the number of carbon atoms in the main chain of the acyl group of R24 and R25 in the general formula (15) is preferably from 9 to 21, more preferably from 12 to 20, and still more preferably from 16 to 18.

In addition, the number of branches in the acyl group of R24 and R25 in the general formula (15) is preferably from 1 to 3, more preferably 1 or 2, and still more preferably 1.

Furthermore, in the acyl group of R24 and R25 in the general formula (15), it is more preferable as the position number of the carbon atom in the main chain to which a branched chain is bonded is higher. Specifically, the branched chain is bonded preferably to the 1st to 3rd carbon atom, more preferably to the 1st or 2nd carbon atom, and still more preferably to the 1st carbon atom from the carbon atom at the end of the main chain.

[0172]

Specific examples of R24 and R25 may suitably include a 10-methylundecanoyl group, a 10-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 16-methylheptadecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0173]

The group which is represented by Z in the general formula (15) and derived from a trihydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a trihydric alcohol, but examples thereof may suitably include a group obtained by

eliminating an OH group from a trihydric alcohol selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

[0174]

[2] Hydrophilic Monomer

As the hydrophilic monomer in the present invention, it is possible to use a polymerizable carboxylic acid and compounds represented by the general formulas (2), (9), (10), and (11).

[0175]

(2-1) Polymerizable carboxylic acid

In the present invention, specific examples of the polymerizable carboxylic acid or any salt thereof may include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid, and sodium salts, potassium salts, ammonium salts, and amine salts thereof. Among these, acrylic acid, methacrylic acid, and salts thereof are particularly preferable because of high polymerizability thereof. In the case of introducing a constitutional unit derived from a salt of a polymerizable carboxylic acid into the water-soluble copolymer of the present invention, the polymerizable carboxylic acid may be converted into a salt in advance and the salt may be subjected to a polymerization reaction or a constitutional unit derived from a polymerizable carboxylic acid may be introduced into a water-soluble copolymer by a polymerization reaction and then neutralized with a base into a salt.

[0176]

(2-2) Hydrophilic monomer represented by general formula (2)

In the general formula (2), R4 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms, R5 represents an alkylene group which has from 2 to 4 carbon atoms and may have a hydroxyl group, and R6 represents a hydrogen atom, an aromatic hydrocarbon group having from 6

to 10 carbon atoms, an aliphatic hydrocarbon group having from 1 to 14 carbon atoms, or an acyl group having from 1 to 12 carbon atoms. n represents an integer from 6 to 40.

[0177]

Examples of the alkyl group represented by R4 in the general formula (2) may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R4 is preferably a hydrogen atom or a methyl group.

[0178]

In addition, examples of the alkylene group represented by R5 may include an ethylene group, a propylene group, an isopropylene group, a 2-hydroxypropylene group, a 1-hydroxy-2-methylethylene group, and a 2-hydroxy-1-methylethylene group, and an ethylene group or a propylene group is preferable and an ethylene group is more preferable among these.

[0179]

In addition, among the groups represented by R6, examples of the aromatic group having from 6 to 10 carbon atoms may include a phenyl group, a benzyl group, a methylphenyl group, and an ethylphenyl group; examples of the aliphatic hydrocarbon group having from 1 to 14 carbon atoms may suitably include a methyl group, an ethyl group, a butyl group, a tertiary butyl group, a hexyl group, a cyclohexyl group, an octyl group, a 2-ethylhexyl group, and a lauryl group; and examples of the acyl group having from 1 to 12 carbon atoms may suitably include a formyl group, an acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a valeryl group, and a lauroyl group. Among these, the group represented by R5 is preferably an aliphatic hydrocarbon group having from 1 to 14 carbon atoms and more preferably an alkyl group having from 1 to 12 carbon atoms.

[0180]

Furthermore, n in the general formula (2) is a numerical range of from 6 to 40.

[0181]

Specific examples of the monomer in which R5 is a propylene group among the monomers represented by the general formula (2) may include polypropylene glycol (9) monoacrylate, polypropylene glycol (13) monoacrylate, polypropylene glycol (9) monomethacrylate, and polypropylene glycol (13) monomethacrylate. Incidentally, the numbers in the parentheses denote N. A large number of these polymers are commercially available. Specific examples of these commercially available products may include "BLEMMER" AP-400, AP-550, AP-800, PP-500, and PP-800 (trade name, all manufactured by NOF CORPORATION).

[0182]

Specific examples of the monomer in which R5 is an ethylene group among the monomers represented by the general formula (2) may include polyethylene glycol (10) monoacrylate, polyethylene glycol (8) monomethacrylate, polyethylene glycol (23) monoacrylate, polyethylene glycol (23) monomethacrylate, methoxypolyethylene glycol (9) acrylate, methoxypolyethylene glycol (9) methacrylate, methoxy polyethylene glycol (23) methacrylate, oleyloxypolyethylene glycol (18) methacrylate, lauroxypolyethylene glycol (18) acrylate, lauroyloxypolyethylene glycol (10) methacrylate, and stearoxypolyethylene glycol (30) monomethacrylate.

[0183]

The hydrophilic monomers described above can be obtained at a high yield by an esterification reaction of the corresponding polyethylene glycol, polyethylene glycol monoether, and polyethylene glycol monoester with a chloride or anhydride of acrylic acid or methacrylic acid. There are also already a large number of commercially available products, and it is also possible to use such

commercially available products. Specific examples of such commercially available products may include BLEMMER AE-400, PE-350, AME-400, PME-400, PME-1000, ALE-800, and PSE-1300, (trade name, all manufactured by NOF CORPORATION) and the like.

[0184]

(2-3) Hydrophilic monomer represented by general formula (9)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (9) may be used.

[0185]

Specific examples of the hydrophilic monomer represented by the general formula (9) may include 2-acryloyloxyethyl phosphorylcholine (APC) and 2-methacryloyloxyethyl phosphorylcholine (MPC). These monomers can be synthesized, for example, by the following method described in Polymer Journal, Vol22, No. 5.

<Synthesis method>

After 2-bromoethyl phosphoryl dichloride is reacted with 2-hydroxyethyl methacrylate or 2-hydroxyethyl acrylate to obtain 2-methacryloyloxyethyl-2'-bromoethyl phosphate or 2-acryloyloxyethyl-2'-bromoethyl phosphate, this compound is reacted with triethylamine in methanol.

[0186]

(2-4) Hydrophilic monomer represented by general formula (10)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (10) may be used.

[0187]

In the hydrophilic monomer represented by the general formula (10), specific examples of the reducing sugar of the group which is represented by G-O- and obtained by eliminating a hydrogen atom from the hydroxyl group at the position 1 of a reducing sugar may include one kind or two

or more kinds selected from the group consisting of monosaccharides such as glucose, mannose, galactose, arabinose, xylose, and ribose, disaccharides such as maltose, lactose, and cellobiose, trisaccharides such as maltotriose, and oligosaccharides such as maltooligosaccharide, and among these, one kind or two or more kinds selected from the group consisting of glucose, galactose, arabinose, xylose, ribose, maltose, and lactose cellobiose are preferable and glucose is particularly preferable. In addition, as the monomer represented by the general formula (10), glucosyloxyethyl methacrylate (hereinafter abbreviated as GEMA) or glucosyloxyethyl acrylate (hereinafter abbreviated as GEA) are preferable.

[0188]

(2-5) Hydrophilic monomer represented by general formula (11)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (11) may be used.

[0189]

In the monomer represented by the general formula (11), the amino acid in the amino acid residue represented by R23 is not particularly limited as long as it is a usually known amino acid, and specific examples thereof may include glycine, alanine, glutamine, lysine, and arginine. Among these, a lysine residue is particularly preferable since the water-soluble copolymer to be obtained exhibits an excellent effect of recovering the skin barrier.

[0190]

In addition, the polyamine in the polyamine residue represented by R23 means an amine having two or more amino groups which may be substituted with an alkyl group in the same molecule, and specific examples thereof may include a diamine, a triamine, a tetraamine, or amines in which hydrogen atoms of these amino groups are substituted with

alkyl groups. Among these, a diamine is preferable since the feel of use of the external preparation for skin containing the water-soluble copolymer to be obtained is particularly excellent, and particularly preferred specific examples thereof may include ethylenediamine, 1,4-diamino-n-butane, and 1,6-diamino-n-hexane from the viewpoint of availability of starting materials for synthesis.

[0191]

Furthermore, the amino alcohol in the amino alcohol residue represented by R23 means a compound having an amino group which may be substituted with an alkyl group and an alcoholic hydroxyl group in the same molecule. The amino alcohol is not particularly limited as long as it is usually known, and specific examples thereof may include ethanolamine and triethylaminoethanol.

[0192]

The salt of the monomer represented by the general formula (11) is not particularly limited, but specific examples thereof may include a sodium salt, a potassium salt, an ammonium salt, and an amine salt obtained by neutralizing the acid moiety with a base and a hydrochloride, a sulfate, a nitrate, a phosphate, a citrate, an oxalate, and a carbonate obtained by neutralizing the amino group moiety with an acid. In the case of introducing a constitutional unit derived from a salt of the monomer represented by the general formula (11) into the water-soluble copolymer of the present invention, the monomer represented by the general formula (11) may be converted into a salt in advance and the salt may be subjected to a polymerization reaction or a constitutional unit derived from the monomer represented by the general formula (11) may be introduced into a water-soluble copolymer by a polymerization reaction and then neutralized into a salt.

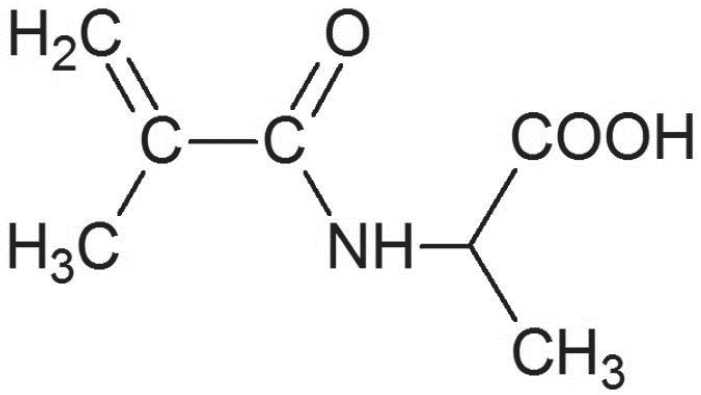
[0193]

Specific examples of the monomer represented by the general formula (11) and any salt thereof may suitably include compounds 1 to 11 having the following structures and salts thereof.

[0194]

Compound 1

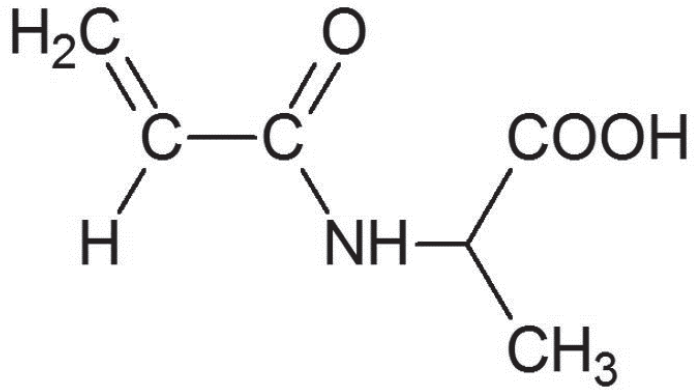
[Chemical Formula 16]



[0195]

Compound 2

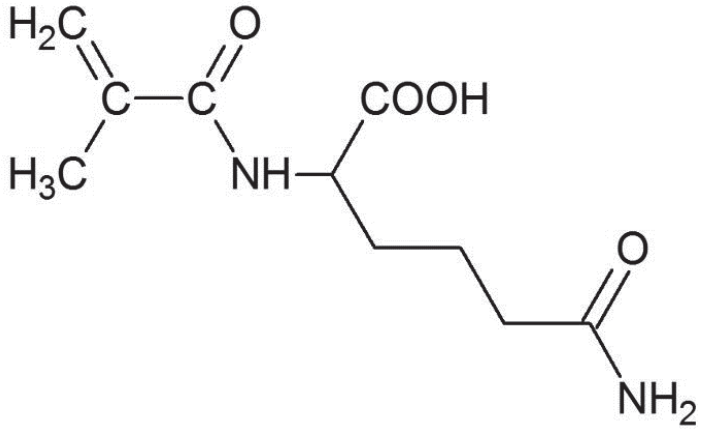
[Chemical Formula 17]



[0196]

Compound 3

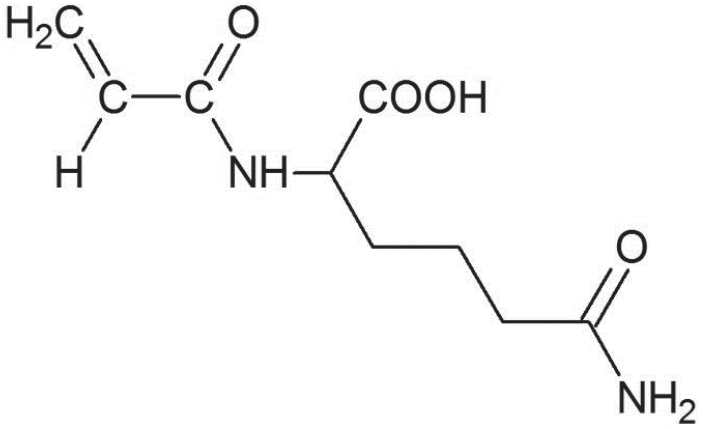
[Chemical Formula 18]



[0197]

Compound 4

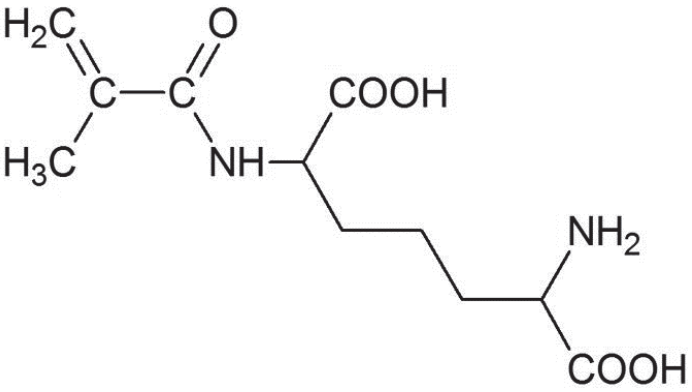
[Chemical Formula 19]



[0198]

Compound 5

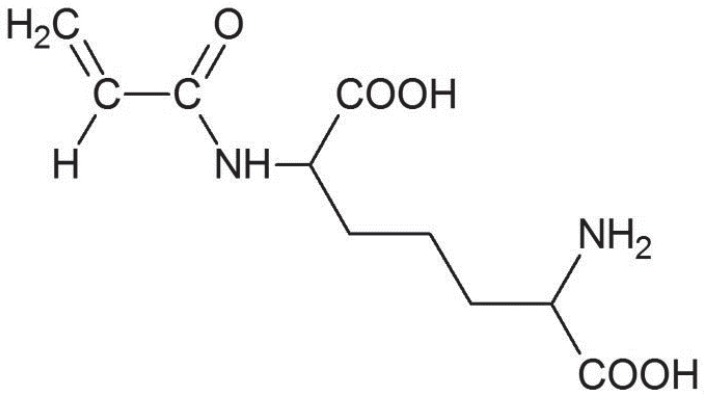
[Chemical Formula 20]



[0199]

Compound 6

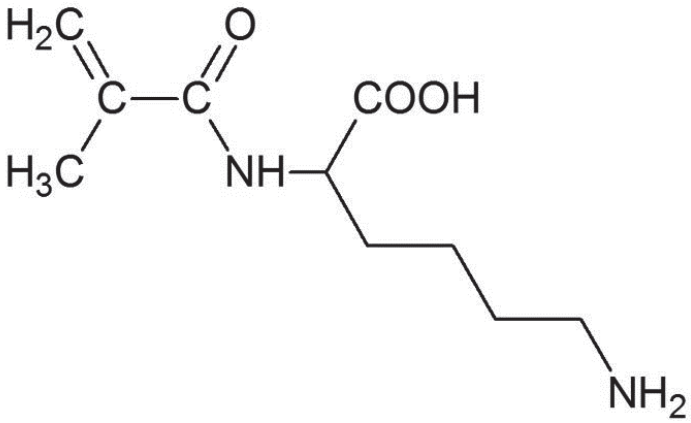
[Chemical Formula 21]



[0200]

Compound 7

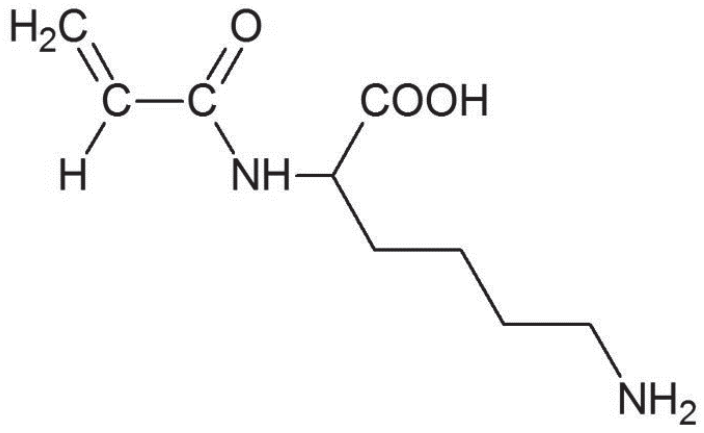
[Chemical Formula 22]



[0201]

Compound 8

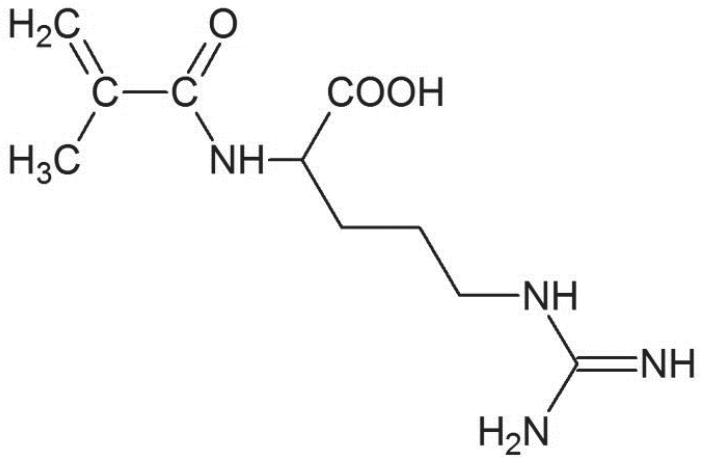
[Chemical Formula 23]



[0202]

Compound 9

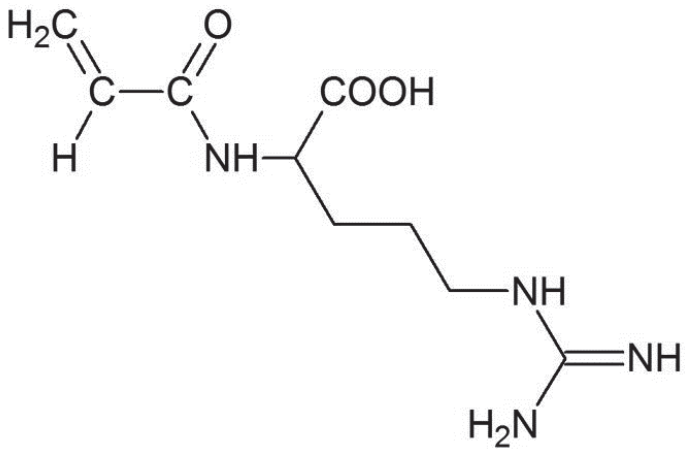
[Chemical Formula 24]



[0203]

Compound 10

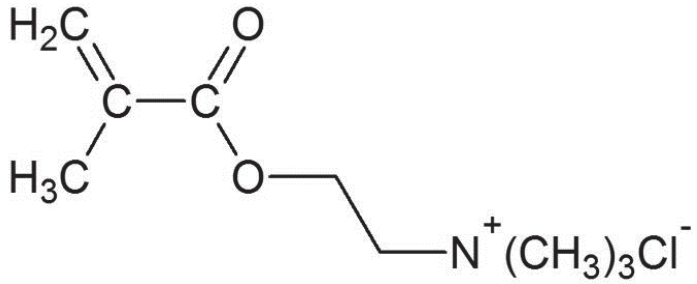
[Chemical Formula 25]



[0204]

Compound 11

[Chemical Formula 26]

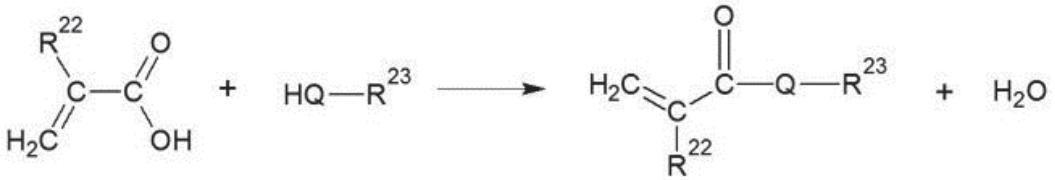


[0205]

The hydrophilic monomer represented by the general formula (11) can be synthesized, for example, by an esterification reaction or an amidation reaction using (meth)acrylic acid or (meth)acrylic acid chloride as presented in the following reaction formulas (1) and (2).

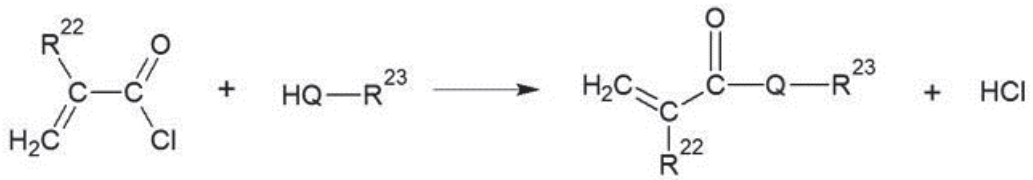
Reaction formula (1)

[Chemical Formula 27]



Reaction formula (2)

[Chemical Formula 28]



(In the reaction formulas, R22 represents a hydrogen atom or a methyl group and R23 represents an amino acid residue, a polyamine residue, or an amino alcohol residue. Q represents an oxygen atom or a group represented by NH.)

[0206]

As described above, in the present invention, it is possible to use the general formulas (2), (9), (10), and (11) as the hydrophilic polymer.

In a preferred embodiment of the present invention, the water-soluble copolymer contains a constitutional unit (2) derived from the general formula (2).

[0207]

[3] Water-soluble copolymer

In the present invention, it is possible to preferably use a water-soluble copolymer having the constitutional unit (1) and the constitutional unit (2). In addition, a water-soluble copolymer having the constitutional unit (15) and the constitutional unit (2) is more preferably used.

Among such water-soluble copolymers, a (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer is particularly preferably used.

By containing such a water-soluble copolymer, an emulsified composition which is low-irritant and less sticky and exhibits excellent emulsion stability is obtained.

[0208]

The (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer mainly contains a constitutional unit (c) derived from a hydrophobic monomer

in which R24 and R25 are a 16-methylheptadecanoyl group among the hydrophobic monomers represented by the general formula (15) as the constitutional unit (c).

The (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer also mainly contains a constitutional unit (d) derived from a hydrophilic monomer in which R4 is a methyl group, R5 is an ethylene group, R6 is a methyl group, and n is 23 among the hydrophilic monomers represented by the general formula (2) as the constitutional unit (d).

[0209]

Generally, a highly hydrophobic surfactant is suitable for the formation of a water-in-oil type emulsified composition and a highly hydrophilic surfactant is suitable for the formation of an oil-in-water type emulsified composition. In the same manner, the water-soluble copolymer of the present invention is suitable for the formation of a water-in-oil type emulsified composition in a case in which the proportion of the hydrophobic constitutional unit (c) is high and the water-soluble copolymer is suitable for the formation of an oil-in-water type emulsified composition in a case in which the proportion of the hydrophilic constitutional unit (d) is high.

In this manner, it is possible to adjust the emulsified form of the emulsified composition to be formed by appropriately adjusting the proportions and ratios of the constitutional unit (c) and the constitutional unit (d).

[0210]

In the present invention, the proportion of the constitutional unit (c) in the entire constitutional units in the water-soluble copolymer is preferably from 1% to 50% by mass, more preferably from 20% to 50% by mass and from 30% to 40% by mass.

It is possible to provide an oil-in-water type

emulsified composition exhibiting further decreased sticky feel by setting the proportion of the constitutional unit (c) in the water-soluble copolymer to be in the above range.

[0211]

In the present invention, the proportion of the constitutional unit (d) in the entire constitutional units in the water-soluble copolymer is preferably from 50% to 99% by mass, more preferably from 50% to 80% by mass and from 60% to 70% by mass.

It is possible to provide an oil-in-water type emulsified composition exhibiting further decreased sticky feel by setting the proportion of the constitutional unit (d) in the water-soluble copolymer to be in the above range.

[0212]

In the present invention, the mass ratio of the constitutional unit (c) constituting the water-soluble copolymer to the constitutional unit (d) constituting the water-soluble copolymer is preferably from 10 : 90 to 50 : 50, more preferably from 20 : 80 to 50 : 50, and still more preferably from 30 : 70 to 40 : 60.

[0213]

In addition, the molar ratio of the constitutional unit (c) constituting the water-soluble copolymer to the constitutional unit (d) constituting the water-soluble copolymer is preferably from 15 : 85 to 62 : 38, more preferably from 29 : 71 to 62 : 38, and still more preferably from 41 : 59 to 52 : 48.

It is possible to obtain a water-soluble copolymer which is suitable for the formation of an oil-in-water type emulsified composition and exhibits excellent emulsifying power by setting the mass ratio and molar ratio of the constitutional unit (c) to the constitutional unit (d) in the water-soluble copolymer to be in the above ranges.

[0214]

In the present invention, the average molecular

weight of the water-soluble copolymer is preferably from 20,000 to 110,000, more preferably from 20,000 to 80,000, more preferably from 30,000 to 80,000, more preferably from 40,000 to 70,000, still more preferably from 50,000 to 70,000, and still more preferably from 57,000 to 66,000.

Incidentally, the average molecular weight here refers to the weight average molecular weight in terms of polystyrene measured by GPC.

[0215]

<2> Emulsified composition

The emulsified composition of the present invention is characterized by substantially not containing an emulsifying agent other than the water-soluble copolymer described above.

Here, the term "substantially not containing an emulsifying agent other than the water-soluble copolymer described above" means that the content of an emulsifying agent other than the water-soluble copolymer described above is 0.3% by mass or less, preferably 0.1% by mass or less, still more preferably 0.01% by mass or less, and still more preferably 0.001% by mass or less. In addition, it is particularly preferable that an emulsifying agent other than the water-soluble copolymer described above is not contained.

[0216]

The content of the water-soluble copolymer described above in the emulsified composition is preferably from 0.1% to 50% by mass and more preferably from 0.5% to 30% by mass.

It is possible to further improve the emulsion stability of the emulsified composition by setting the content of the water-soluble copolymer described above to be in the above range.

[0217]

The contents of the aqueous phase and the oil phase in the emulsified composition of the present invention can

be appropriately adjusted by changing the ratio of the constitutional unit (c) to the constitutional unit (d) in the water-soluble copolymer.

Hereinafter, the contents of the oil phase and the aqueous phase and the like in the case of using the water-soluble copolymer containing the constitutional unit (c) and the constitutional unit (d) at a ratio suitable for the formation of the oil-in-water type emulsified composition described above will be described.

Incidentally, in the present disclosure, the description will be made on the assumption that the water-soluble copolymer of the present invention is not contained in the oil phase and the oil phase component and the aqueous phase and the aqueous phase component.

[0218]

The content of the oil phase component in the emulsified composition of the present invention is preferably from 0.01% to 80% by mass and more preferably from 0.1% to 70% by mass.

It is possible to improve the emulsion stability of the emulsified composition by setting the content of the oil phase component to be in the above range.

Incidentally, the oil phase component is an oil agent and a lipophilic component and refers to a component to be contained in the oil phase in the emulsified composition.

[0219]

In the emulsified composition of the present invention, the mass ratio of the water-soluble copolymer described above to the oil phase component is preferably from 1 : 100 to 1 : 0.2 and more preferably from 1 : 70 to 1 : 0.3.

It is possible to improve the emulsion stability of the emulsified composition by setting the mass ratio of the water-soluble copolymer to the oil phase component to be in the above range.

[0220]

In the emulsified composition of the present invention, the mass ratio of the oil phase to the aqueous phase is preferably from 0.1 : 99.9 to 80 : 20 and more preferably from 1 : 99 to 65 : 35.

It is possible to form a stable oil-in-water type emulsified composition by setting the mass ratio of the oil phase to the aqueous phase to be in the above range.

[0221]

The components to be contained in the oil phase and aqueous phase are not particularly limited.

Examples of the oil agent constituting the oil phase may include liquid oils and fats, solid oils and fats, waxes, hydrocarbon oils, higher fatty acids, higher alcohols, synthetic ester oils, and silicone oils.

[0222]

Examples of liquid oils and fats may include avocado oil, camellia oil, turtle oil, macadamia nut oil, corn oil, mink oil, olive oil, rapeseed oil, egg yolk oil, sesame oil, persic oil, wheat germ oil, sasanqua oil, castor oil, linseed oil, safflower oil, cottonseed oil, eno oil, meadowfoam oil, soybean oil, peanut oil, tea seed oil, kaya oil, rice bran oil, Paulownia tomentosa oil, Japanese Paulownia tomentosa oil, jojoba oil, germ oil, triglycerin, glyceryl trioctanoate, and glyceryl triisopalmitate.

[0223]

Examples of solid oils and fats may include cocoa butter, coconut oil, horse fat, hardened coconut oil, palm oil, beef tallow, mutton tallow, hardened beef tallow, palm kernel oil, lard, beef bone fat, vegetable kernel oil, hardened oil, neat's-foot oil, vegetable wax, and hardened castor oil.

[0224]

Examples of waxes may include beeswax, candelilla wax, cotton wax, carnauba wax, bayberry wax, insects wax,

spermaceti, montan wax, barn wax, lanolin, kapok wax, lanolin acetate, liquid lanolin, sugarcane wax, isopropyl lanolin fatty acid, hexyl laurate, reduced lanolin, jojoba wax, hard lanolin, shellac wax, POE lanolin alcohol ether, POE lanolin alcohol acetate, POE cholesterol ether, lanolin fatty acid polyethylene glycol, and POE hydrogenated lanolin alcohol ether.

[0225]

Examples of hydrocarbon oils may include liquid paraffin, ozokerite, pristane, paraffin, ceresin, squalene, petroleum jelly, and microcrystalline wax.

[0226]

Examples of higher fatty acids may include lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, 12-hydroxystearic acid, undecylenic acid, and tall oil fatty acid.

[0227]

Examples of higher alcohols may include cetyl alcohol, stearyl alcohol, behenyl alcohol, batyl alcohol, myristyl alcohol, and cetostearyl alcohol.

[0228]

Examples of synthetic ester oils may include isopropyl myristate, cetyl octanoate, octyl dodecyl myristate, isopropyl palmitate, butyl stearate, hexyl laurate, myristyl myristate, decyl oleate, hexyldecyl dimethyloctanoate, cetyl lactate, myristyl lactate, lanolin acetate, isocetyl stearate, isocetyl isostearate, sucrose stearate, sucrose oleate, cholesteryl 12-hydroxystearate, ethylene glycol di-2-ethylhexylate, dipentaerythritol fatty acid ester, N-alkyl glycol monoisostearate, neopentyl glycol dicaprate, diisostearyl malate, glyceryl di-2-heptylundecanoate, trimethylolpropane tri-2-ethylhexylate, trimethylolpropane triisostearate, pentane erythritol tetra-2-ethylhexylate, glyceryl tri-2-ethylhexylate, trimethylolpropane triisostearate, cetyl 2-ethylhexanoate,

2-ethylhexyl palmitate, glyceryl trimyristate, glyceride tri-2-heptylundecanoate, methyl ester of castor oil fatty acid, oleic acid oil, cetostearyl alcohol, acetoglyceride, 2-heptylundecyl palmitate, cetyl palmitate, diisobutyl adipate, 2-octyldodecyl ester N-lauroyl-L-glutamate, di-2-heptylundecyl adipate, ethyl laurate, di-2-ethylhexyl sebacate, 2-hexyldecyl myristate, 2-hexyldecyl palmitate, 2-hexyldecyl adipate, diisopropyl sebacate, 2-ethylhexyl succinate, ethyl acetate, butyl acetate, amyl acetate, and triethyl citrate.

[0229]

Examples of silicone oils may include chain polysiloxanes such as dimethylpolysiloxane, methylphenylpolysiloxane, and methylhydrogenpolysiloxane and cyclic polysiloxanes such as decamethylpolysiloxane, dodecamethylpolysiloxane, and tetramethyltetrahydrogenpolysiloxane.

[0230]

It is possible to use one kind or two or more kinds of oil agents.

[0231]

Arbitrary additives to be usually blended in cosmetics may be blended in the emulsified composition of the present invention in a range in which the effect of the present invention is not impaired. Examples of such additives may include moisturizing agents such as polyethylene glycol, glycerin, 1,3-butylene glycol, erythritol, sorbitol, xylitol, and maltitol; lower alcohols such as ethanol; antioxidants such as butylated hydroxytoluene, tocopherol, and phytin; antibacterial agents such as benzoic acid, salicylic acid, sorbic acid, an alkyl ester of parahydroxybenzoic acid, and hexachlorophene; benzoic acid-based ultraviolet absorbers such as para-aminobenzoic acid (hereinafter abbreviated as "PABA"), PABA monoglycerin ester, N,N-dipropoxyPABA ethyl

ester, N,N-diethoxyPABA ethyl ester, N,N-dimethylPABA methyl ester, N,N-dimethylPABA ethyl ester, N,N-dimethylPABA butyl ester, and N,N-dimethylPABA 2-ethylhexyl ester; anthranilic acid-based ultraviolet absorbers such as homomenthyl-N-acetyl anthranilate; salicylic acid-based ultraviolet absorbers such as amyl salicylate, menthyl salicylate, homomenthyl salicylate, octyl salicylate, phenyl salicylate, benzyl salicylate, and p-isopropanolphenyl salicylate; cinnamic acid-based ultraviolet absorbers such as octyl cinnamate, ethyl-4-isopropyl cinnamate, methyl-2,5-diisopropyl cinnamate, ethyl-2,4-diisopropyl cinnamate, methyl-2,4-diisopropyl cinnamate, propyl-p-methoxycinnamate, isopropyl-p-methoxycinnamate, isoamyl-p-methoxycinnamate, octyl-p-methoxycinnamate (2-ethylhexyl-p-methoxycinnamate), 2-ethoxyethyl-p-methoxycinnamate, cyclohexyl-p-methoxycinnamate, ethyl-α-cyano-β-phenylcinnamate, 2-ethylhexyl-α-cyano-β-phenylcinnamate, and glyceryl mono-2-ethylhexanoyl-di-p-methoxycinnamate; silicone-based cinnamic acid ultraviolet absorbers such as [3-bis(trimethylsiloxy)methylsilyl-1-methylpropyl]-3,4,5-trimethoxycinnamate, [3-bis(trimethylsiloxy)methylsilyl-3-methylpropyl]-3,4,5-trimethoxycinnamate, [3-bis(trimethylsiloxy)methylsilylpropyl]-3,4,5-trimethoxycinnamate, [3-bis(trimethylsiloxy)methylsilylbutyl]-3,4,5-trimethoxycinnamate, [3-tris(trimethylsiloxy)silylbutyl]-3,4,5-trimethoxycinnamate, [3-tris(trimethylsiloxy)silylbutyl]-3,4,5-trimethoxycinnamate, and [3-tris(trimethylsiloxy)silyl-1-methylpropyl]-3,4-dimethoxycinnamate; benzophenone-based ultraviolet absorbers such as 2,4-dihydroxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-

methylbenzophenone, 2-hydroxy-4-methoxybenzophenone-5-sulfonate, 4-phenylbenzophenone, 2-ethylhexyl-4'-phenyl-benzophenone-2-carboxylate, 2-hydroxy-4-n-octoxybenzophenone, and 4-hydroxy-3-carboxybenzophenone; ultraviolet absorbers such as 3-(4'-methylbenzylidene)-d,l-camphor, 3-benzylidene-d,l-camphor, ethyl ester of urocanic acid, 2-phenyl-5-methylbenzoxazole, 2,2'-hydroxy-5-methylphenylbenzotriazole, 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, dibenzalazine, dianisoylmethane, 4-methoxy-4'-t-butyldibenzoylmethane, and 5-(3,3'-dimethyl-2-norbornylidene)-3-pentan-2-one; organic acids such as acyl sarcosinic acid (for example, sodium lauroyl sarcosinate), glutathione, citric acid, malic acid, tartaric acid, and lactic acid; vitamins such as vitamin A and any derivative thereof, vitamin B family such as vitamin B6 hydrochloride, vitamin B6 tripalmitate, vitamin B6 dioctanoate, vitamin B2 and any derivative thereof, vitamin B12, and vitamin B15 and any derivative thereof, vitamin E family such as α-tocopherol, β-tocopherol, γ-tocopherol, and vitamin E acetate, vitamin D family, vitamin H, pantothenic acid, pantethine, nicotinic acid amide, and benzyl nicotinate; various kinds of medicines such as γ-oryzanol, allantoin, glycyrrhizic acid (salt), glycyrrhetinic acid and any derivative thereof, tranexamic acid and any derivative thereof [as a tranexamic acid derivative, a dimer of tranexamic acid (for example, trans-4-(trans-aminomethylcyclohexanecarbonyl)aminomethylcyclohexane carboxylic acid hydrochloride), an ester of tranexamic acid with hydroquinone (for example, 4'-hydroxyphenyl ester of trans-4-aminomethylcyclohexane carboxylic acid), an ester of tranexamic acid with gentisic acid (for example, 2-(trans-4-aminomethylcyclohexylcarbonyloxy)-5-hydroxybenzoic acid and any salt thereof), and an amide of tranexamic acid

(for example, trans-4-aminomethylcolohexanecarboxylic acid methylamide and any salt thereof, trans-4-(P-methoxybenzoyl)aminomethylcyclohexane carboxylic acid and any salt thereof, and trans-4-guanidinomethylcyclohexane carboxylic acid and any salt thereof)], saponins such as hinokitiol, bisabolol, eucalyptol, thymol, inositol, Saikosaponin, ginseng saponin, Luffa cylindrica saponin, and Sapindus mukurossi saponin, pantothenyl ethyl ether, ethinyl estradiol, tranexamic acid, arbutin, cepharanthine, placenta extract; extracts of plants such as Rumex japonicus, Sophora flavescens, Nuphar japonicum, Citrus sinensis, Salvia officinalis, Achillea alpina, Malva sylvestris, Swertia japonica, thyme, Angelica acutiloba, Picea jezoensis var. hondoensis, Betula, Equisetum arvense, Luffa cylindrica, Aesculus hippocastanum, Saxifraga stolonifera, Arnica montana, Lilium, Artemisia indica var. maximowiczii, Paeonia lactiflora, Aloe, Gardenia jasminoides, and Chamaecyparis pisifera; coloring matters; porous and/or water-absorbing powders (for example, starches obtained from corn, potatoes, and the like and powders of anhydrous silicic acid, talc, kaolin, magnesium aluminum silicate, calcium alginate, and the like); neutralizing agents; preservatives; perfumes; and pigments.

[0232]

The emulsified composition of the present invention can be produced by respectively preparing an aqueous phase component containing the water-soluble copolymer described above and an oil phase component and stirring and mixing these by a conventional method.

[0233]

The emulsified composition of the present invention is low-irritant and less sticky, and it is thus preferably used as a cosmetic such as milky lotion, cream, essence liquid, sunscreen, or liquid foundation, an external preparation for skin, a quasi-drug, and a pharmaceutical.

[0234]

<3> Emulsifying agent

The present invention also relates to an emulsifying agent which contains the water-soluble copolymer described above. The description on the water-soluble copolymer and the emulsified composition can be applied to the emulsifying agent of the present invention.

[0235]

<4> Method of producing emulsified composition

The present invention also relates to a method of producing an emulsified composition using the emulsifying agent of the present invention described above. The method of the present invention is characterized by not using an emulsifying agent other than the emulsifying agent of the present invention. The description on the water-soluble copolymer and the emulsified composition can be applied to the production method of the present invention.

[0236]

The skin cleanser of the present invention to achieve the third and fourth objects is characterized by containing a water-soluble copolymer having a constitutional unit (e) derived from a hydrophobic monomer and a constitutional unit (f) derived from a hydrophilic monomer. Hereinafter, the hydrophobic monomer, the hydrophilic monomer, and the water-soluble copolymer which is a copolymer thereof will be described in the section <1>.

[0237]

<1> Water-soluble copolymer

[1] Hydrophobic monomer

In the present invention, a water-soluble copolymer containing one kind or two or more kinds of constitutional units derived from a hydrophobic monomer represented by the general formula (1), (7), or (8) (hereinafter simply referred to as the "constitutional unit (7)" or the like in some cases) as an essential constitutional unit is used.

Incidentally, in the present invention, the "constitutional unit derived from a monomer" refers to a constitutional unit formed by cleavage of a carbon-carbon unsaturated bond of the corresponding monomer by a polymerization reaction.

Hereinafter, the hydrophobic monomer represented by the general formula (1), (7), or (8) will be described.

[0238]

(1-1) Hydrophobic monomer represented by general formula (7)

In the general formula (7), R14 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R15 represents a branched hydrocarbon group which has from 13 to 30 carbon atoms but does not contain a ring structure or a hydrocarbon group which has from 6 to 12 carbon atoms and two or more branches but does not contain a ring structure.

Here, examples of the alkyl group represented by R14 may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R14 is preferably a hydrogen atom or a methyl group.

[0239]

In addition, examples of the branched hydrocarbon group which is represented by R15, has from 13 to 30 carbon atoms, but does not contain a ring structure may include a 1-methyldodecanyl group, an 11-methyldodecanyl group, a 3-ethylundecanyl group, 3-ethyl-4,5,6-trimethyloctyl group, a 1-methyltridecanyl group, a 1-hexyloctyl group, a 2-butyldecanyl group, a 2-hexyloctyl group, a 4-ethyl-1-isobutyloctyl group, a 1-methylpentadecanyl group, a 2-hexyldecanyl group, a 2-octyldecanyl group, a 2-hexyldodecanyl group, a 16-methylheptadecanyl group, a 9-methylheptadecanyl group, a 7-methyl-2-(3-methylhexyl)decanyl group, a 3,7,11,15-tetramethylhexadecanyl group, a 2-octyldodecanyl group, a

2-decyltetradecanyl group, and a 2-dodecylhexadecanyl group.

[0240]

In addition, examples of the hydrocarbon group which is represented by R15, has from 6 to 12 carbon atoms and two or more branches, but does not contain a ring structure may include a 2,2-dimethylbutyl group, a 2,3-dimethylbutyl group, a 3,3-dimethylbutyl group, a 1,3-dimethylbutyl group, a 1,2,2-trimethylpropyl group, a 1,1-dimethylpentanyl group, a 1-isopropylbutyl group, a 1-isopropyl-2-methylpropyl group, a 1,1-diethylpropyl group, a 1-ethyl-1-isopropylpropyl group, a 2-ethyl-4-methylpentyl group, a 1-propyl-2,2-dimethylpropyl group, a 1,1,2-trimethylpentyl group, a 1-isopropyl-3-methylbutyl group, a 1,2-dimethyl-1-ethylbutyl group, a 1,3-dimethyl-1-ethylbutyl group, a 1-ethyl-1-isopropylpropyl group, a 1,1-dimethylhexyl group, a 1-methyl-1-ethylpentyl group, a 1-methyl-1-propylbutyl group, a 1,4-dimethylhexyl group, a 1-ethyl-3-methylpentyl group, a 1,5-dimethylhexyl group, a 1-ethyl-6-methylheptyl group, a 1,1,3,3-tetramethylbutyl group, a 1,2-dimethyl-1-isopropylpropyl group, a 3-methyl-1-(2,2-dimethylethyl)butyl group, a 1-isopropylhexyl group, a 3.5.5-trimethylhexyl group, a 2-isopropyl-5-methylhexyl group, a 1,5-dimethyl-1-ethylhexyl group, a 3,7-dimethyloctyl group, a 2,4,5-trimethylheptyl group, a 2,4,6-trimethylheptyl group, and a 3,5-dimethyl-1-(2,2-dimethylethyl)hexyl group.

[0241]

(1-2) Hydrophobic monomer represented by general formula (1) or (8)

In the general formulas (1) and (8), R1 and R16 represent a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R2, R3, R17, R18, and R19 may be the same as or different from one another and represent an acyl group which has from 6 to 22 carbon atoms and a branch but does not contain a ring structure. X represents a group

obtained by eliminating an OH group from a trihydric alcohol.

[0242]

Here, examples of the alkyl group represented by R1 and R16 may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R1 is preferably a hydrogen atom or a methyl group.

[0243]

In addition, examples of the acyl group which is represented by R2, R3, R17, R18, and R19, has from 6 to 22 carbon atoms and a branch, but does not contain a ring structure may include a 2-methylpentanoyl group, a 3-methylpentanoyl group, a 4-methylpentanoyl group, a 2-ethylbutanoyl group, a 2-ethylbutanoyl group, a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2-methylhexanoyl group, a 4-methylhexanoyl group, a 5-methylhexanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2-methylheptanoyl group, a 2-ethylhexyl group, a 2-propylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl group, a 2-methyloctanoyl group, a 3,3,5-trimethylhexanoyl group, a 2-methylnonanoyl group, a 4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-diethylhexanoyl group, a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group, a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-

methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0244]

In addition, in a preferred embodiment of the present invention, in the general formulas (1) and (8), R2, R3, R17, R18, and R19 may be the same as or different from one another and represent an acyl group which has from 10 to 22 carbon atoms and a branch but does not contain a ring structure or an acyl group which has from 6 to 9 carbon atoms and two or more branches but does not contain a ring structure.

[0245]

Examples of such an acyl group which is represented by R2, R3, R17, R18, and R19, has from 10 to 22 carbon atoms and a branch, but does not contain a ring structure in a preferred embodiment may include a 2-methylnonanoyl group, a 4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-diethylhexanoyl group), a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group), a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl

group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0246]

In addition, examples of the acyl group which is represented by R2, R3, R17, R18, and R19, has from 6 to 9 carbon atoms and two or more branches, but does not contain a ring structure in a preferred embodiment may include a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl group, and a 3,5,5-trimethylhexanoyl group.

[0247]

The group which is represented by X in the general formula (1) and derived from a trihydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a trihydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a trihydric alcohol selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

[0248]

In addition, the group which is represented by Y in the general formula (8) and derived from a tetrahydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a tetrahydric alcohol, but examples thereof may suitably

include a group obtained by eliminating an OH group from a tetrahydric alcohol selected from the group consisting of diglycerin, pentaerythritol, erythritol, D-threitol, and L-threitol.

[0249]

In the present invention, it is particularly preferable to use a water-soluble copolymer containing the constitutional unit (1).

In addition, in a more preferred embodiment of the present invention, the hydrophobic monomer represented by the general formula (1) is a hydrophobic monomer represented by the general formula (15).

[0250]

The number of carbon atoms in the acyl group of R24 and R25 in the general formula (15) is from 12 to 22, more preferably from 14 to 20, and still more preferably from 16 to 20.

In addition, the number of carbon atoms in the main chain of the acyl group of R24 and R25 in the general formula (15) is preferably from 9 to 21, more preferably from 12 to 20, and still more preferably from 16 to 18.

In addition, the number of branches in the acyl group of R24 and R25 in the general formula (15) is preferably from 1 to 3, more preferably 1 or 2, and still more preferably 1.

Furthermore, in the acyl group of R24 and R25 in the general formula (15), it is more preferable as the position number of the carbon atom in the main chain to which a branched chain is bonded is higher. Specifically, the branched chain is bonded preferably to the 1st to 3rd carbon atom, more preferably to the 1st or 2nd carbon atom, and still more preferably to the 1st carbon atom from the carbon atom at the end of the main chain.

[0251]

Specific examples of R24 and R25 may suitably include

a 10-methylundecanoyl group, a 10-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 16-methylheptadecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0252]

The group which is represented by Z in the general formula (15) and derived from a trihydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a trihydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a trihydric alcohol selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

[0253]

[2] Hydrophilic Monomer

As the hydrophilic monomer in the present invention, it is possible to use a polymerizable carboxylic acid and compounds represented by the general formulas (2), (9), (10), and (11).

[0254]

(2-1) Polymerizable carboxylic acid

In the present invention, specific examples of the polymerizable carboxylic acid or any salt thereof may include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid, and sodium salts, potassium salts, ammonium salts, and amine salts thereof. Among these, acrylic acid, methacrylic acid, and salts thereof are particularly preferable because of high polymerizability. In the case of introducing a constitutional unit derived from a salt of a polymerizable carboxylic acid into the water-soluble copolymer of the

present invention, the polymerizable carboxylic acid may be converted into a salt in advance and the salt may be subjected to a polymerization reaction or a constitutional unit derived from a polymerizable carboxylic acid may be introduced into a water-soluble copolymer by a polymerization reaction and then neutralized with a base into a salt.

[0255]

(2-2) Hydrophilic monomer represented by general formula (2)

In the general formula (2), R4 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms, R5 represents an alkylene group which has from 2 to 4 carbon atoms and may have a hydroxyl group, and R6 represents a hydrogen atom, an aromatic hydrocarbon group having from 6 to 10 carbon atoms, an aliphatic hydrocarbon group having from 1 to 14 carbon atoms, or an acyl group having from 1 to 12 carbon atoms. n represents an integer from 6 to 40.

[0256]

Examples of the alkyl group represented by R4 in the general formula (2) may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R4 is preferably a hydrogen atom or a methyl group.

[0257]

In addition, examples of the alkylene group represented by R5 may include an ethylene group, a propylene group, an isopropylene group, a 2-hydroxypropylene group, a 1-hydroxy-2-methylethylene group, and a 2-hydroxy-1-methylethylene group, and an ethylene group or a propylene group is preferable and an ethylene group is more preferable among these.

[0258]

In addition, among the groups represented by R6, examples of the aromatic group having from 6 to 10 carbon atoms may include a phenyl group, a benzyl group, a

methylphenyl group, and an ethylphenyl group; examples of the aliphatic hydrocarbon group having from 1 to 14 carbon atoms may suitably include a methyl group, an ethyl group, a butyl group, a tertiary butyl group, a hexyl group, a cyclohexyl group, an octyl group, a 2-ethylhexyl group, and a lauryl group; and examples of the acyl group having from 1 to 12 carbon atoms may suitably include a formyl group, an acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a valeryl group, and a lauroyl group. Among these, the group represented by R5 is preferably an aliphatic hydrocarbon group having from 1 to 14 carbon atoms and more preferably an alkyl group having from 1 to 12 carbon atoms.

[0259]

Furthermore, n in the general formula (2) is a numerical range of from 6 to 40.

[0260]

Specific examples of the monomer in which R5 is a propylene group among the monomers represented by the general formula (2) may include polypropylene glycol (9) monoacrylate, polypropylene glycol (13) monoacrylate, polypropylene glycol (9) monomethacrylate, and polypropylene glycol (13) monomethacrylate. Incidentally, the numbers in the parentheses denote N. A large number of these polymers are commercially available. Specific examples of these commercially available products may include "BLEMMER" AP-400, AP-550, AP-800, PP-500, and PP-800 (trade name, all manufactured by NOF CORPORATION).

[0261]

Specific examples of the monomer in which R5 is an ethylene group among the monomers represented by the general formula (2) may include polyethylene glycol (10) monoacrylate, polyethylene glycol (8) monomethacrylate, polyethylene glycol (23) monoacrylate, polyethylene glycol (23) monomethacrylate, methoxypolyethylene glycol (9)

acrylate, methoxypolyethylene glycol (9) methacrylate, methoxy polyethylene glycol (23) methacrylate, oleyloxypolyethylene glycol (18) methacrylate, lauroxypolyethylene glycol (18) acrylate, lauroyloxypolyethylene glycol (10) methacrylate, and stearoxypolyethylene glycol (30) monomethacrylate.

[0262]

The hydrophilic monomers described above can be obtained at a high yield by an esterification reaction of the corresponding polyethylene glycol, polyethylene glycol monoether, and polyethylene glycol monoester with a chloride or anhydride of acrylic acid or methacrylic acid. There are also already a large number of commercially available products, and it is also possible to use such commercially available products. Specific examples of such commercially available products may include BLEMMER AE-400, PE-350, AME-400, PME-400, PME-1000, ALE-800, and PSE-1300, (trade name, all manufactured by NOF CORPORATION) and the like.

[0263]

(2-3) Hydrophilic monomer represented by general formula (9)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (9) may be used.

[0264]

Specific examples of the hydrophilic monomer represented by the general formula (9) may include 2-acryloyloxyethyl phosphorylcholine (APC) and 2-methacryloyloxyethyl phosphorylcholine (MPC). These monomers can be synthesized, for example, by the following method described in Polymer Journal, Vol22, No. 5.

<Synthesis method>

After 2-bromoethyl phosphoryl dichloride is reacted with 2-hydroxyethyl methacrylate or 2-hydroxyethyl acrylate to obtain 2-methacryloyloxyethyl-2'-bromoethyl phosphate or

2-acryloyloxyethyl-2'-bromoethyl phosphate, this compound is reacted with triethylamine in methanol.

[0265]

(2-4) Hydrophilic monomer represented by general formula (10)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (10) may be used.

[0266]

In the hydrophilic monomer represented by the general formula (10), specific examples of the reducing sugar of the group which is represented by G-O- and obtained by eliminating a hydrogen atom from the hydroxyl group at the position 1 of a reducing sugar may include one kind or two or more kinds selected from the group consisting of monosaccharides such as glucose, mannose, galactose, arabinose, xylose, and ribose, disaccharides such as maltose, lactose, and cellobiose, trisaccharides such as maltotriose, and oligosaccharides such as maltooligosaccharide, and among these, one kind or two or more kinds selected from the group consisting of glucose, galactose, arabinose, xylose, ribose, maltose, and lactose cellobiose are preferable and glucose is particularly preferable. In addition, as the monomer represented by the general formula (10), glucosyloxyethyl methacrylate (hereinafter abbreviated as GEMA) or glucosyloxyethyl acrylate (hereinafter abbreviated as GEA) are preferable.

[0267]

In the monomer represented by the general formula (11), the amino acid in the amino acid residue represented by R23 is not particularly limited as long as it is a usually known amino acid, and specific examples thereof may include glycine, alanine, glutamine, lysine, and arginine. Among these, a lysine residue is particularly preferable since the water-soluble copolymer to be obtained exhibits

an excellent effect of recovering the skin barrier.

[0268]

In addition, the polyamine in the polyamine residue represented by R23 means an amine having two or more amino groups which may be substituted with an alkyl group in the same molecule, and specific examples thereof may include a diamine, a triamine, a tetraamine, or amines in which hydrogen atoms of these amino groups are substituted with alkyl groups. Among these, a diamine is preferable since the feel of use of the external preparation for skin containing the water-soluble copolymer to be obtained is particularly excellent, and particularly preferred specific examples thereof may include ethylenediamine, 1,4-diamino-n-butane, and 1,6-diamino-n-hexane from the viewpoint of availability of starting materials for synthesis.

[0269]

Furthermore, the amino alcohol in the amino alcohol residue represented by R23 means a compound having an amino group which may be substituted with an alkyl group and an alcoholic hydroxyl group in the same molecule. The amino alcohol is not particularly limited as long as it is usually known, and specific examples thereof may include ethanolamine and triethylaminoethanol.

[0270]

The salt of the monomer represented by the general formula (11) is not particularly limited, but specific examples thereof may include a sodium salt, a potassium salt, an ammonium salt, and an amine salt obtained by neutralizing the acid moiety with a base and a hydrochloride, a sulfate, a nitrate, a phosphate, a citrate, an oxalate, and a carbonate obtained by neutralizing the amino group moiety with an acid. In the case of introducing a constitutional unit derived from a salt of the monomer represented by the general formula (11) into the water-soluble copolymer of the present invention, the

monomer represented by the general formula (11) may be converted into a salt in advance and the salt may be subjected to a polymerization reaction or a constitutional unit derived from the monomer represented by the general formula (11) may be introduced into a water-soluble copolymer by a polymerization reaction and then neutralized into a salt.

[0271]

Specific examples of the monomer represented by the general formula (11) and any salt thereof may suitably include the compounds 1 to 11 described above and salts thereof.

[0272]

The hydrophilic monomer represented by the general formula (11) can be synthesized, for example, by an esterification reaction or an amidation reaction using (meth)acrylic acid or (meth)acrylic acid chloride as presented in the reaction formulas (1) and (2).

[0273]

As described above, in the present invention, it is possible to use the general formulas (2), (9), (10), and (11) as the hydrophilic polymer.

In a preferred embodiment of the present invention, the water-soluble copolymer contains the constitutional unit (2) derived from the general formula (2).

[0274]

[3] Water-soluble copolymer

In the present invention, it is possible to preferably use a water-soluble copolymer having the constitutional unit (1) and the constitutional unit (2). In addition, a water-soluble copolymer having the constitutional unit (15) and the constitutional unit (2) is more preferably used.

Among such water-soluble copolymers, a (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate)

copolymer is particularly preferably used.

By containing such a water-soluble copolymer, it is possible to provide a skin cleanser causing less tight feel after use.

[0275]

The (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer mainly contains a constitutional unit (e) derived from a hydrophobic monomer in which R24 and R25 are a 16-methylheptadecanoyl group among the hydrophobic monomers represented by the general formula (15) as the constitutional unit (e).

The (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer also mainly contains a constitutional unit (f) derived from a hydrophilic monomer in which R4 is a methyl group, R5 is an ethylene group, R6 is a methyl group, and n is 23 among the hydrophilic monomers represented by the general formula (2) as the constitutional unit (f).

[0276]

In the present invention, the proportion of the constitutional unit (e) in the entire constitutional units in the water-soluble copolymer is preferably from 1% to 60% by mass, more preferably from 10% to 50% by mass and from 20% to 40% by mass.

It is possible to provide a skin cleanser causing further decreased tight feel after use by setting the proportion of the constitutional unit (e) in the water-soluble copolymer to be in the above range.

[0277]

In the present invention, the proportion of the constitutional unit (f) in the entire constitutional units in the water-soluble copolymer is preferably from 40% to 99% by mass, more preferably from 50% to 90% by mass and from 60% to 80% by mass.

It is possible to provide a skin cleanser causing

further decreased tight feel after use by setting the proportion of the constitutional unit (f) in the water-soluble copolymer to be in the above range.

[0278]

In the present invention, the mass ratio of the constitutional unit (e) constituting the water-soluble copolymer to the constitutional unit (f) constituting the water-soluble copolymer is preferably from 1 : 99 to 60 : 40, more preferably from 10 : 90 to 50 : 50, and still more preferably from 20 : 80 to 40 : 60.

[0279]

In addition, the molar ratio of the constitutional unit (e) constituting the water-soluble copolymer to the constitutional unit (f) constituting the water-soluble copolymer is preferably from 1 : 99 to 71 : 29, more preferably from 15 : 85 to 62 : 38, still more preferably from 29 : 71 to 52 : 48, and still more preferably from 35 : 65 to 45 : 55.

It is possible to obtain a water-soluble copolymer exhibiting a superior effect of decreasing tight feel by setting the mass ratio and molar ratio of the constitutional unit (e) to the constitutional unit (f) in the water-soluble copolymer to be in the above ranges.

[0280]

In the present invention, the average molecular weight of the water-soluble copolymer is preferably from 20,000 to 110,000, more preferably from 20,000 to 80,000, more preferably from 30,000 to 80,000, more preferably from 40,000 to 70,000, still more preferably from 50,000 to 70,000, and still more preferably from 57,000 to 66,000.

Incidentally, the average molecular weight here refers to the weight average molecular weight in terms of polystyrene measured by GPC.

[0281]

<2> Skin cleanser

[1] Dosage form

A skin cleanser is a composition containing a cleansing component and is used for the purpose of removing dirt of the skin such as sebum. In this manner, the skin cleanser has the action of removing sebum present on the skin and it thus has a problem of causing tight feel of the skin after use.

The skin cleanser of the present invention is characterized by containing the water-soluble copolymer described above. According to the present invention, it is possible to decrease tight feel of the skin after use without inhibiting or while improving the detergency inherent in the skin cleanser.

[0282]

As the dosage form of the skin cleanser of the present invention, a dosage form to be usually used for a skin cleanser can be applied without particular limitation. The usual skin cleanser includes a solid skin cleanser, a powdery skin cleanser, a creamy skin cleanser, a liquid skin cleanser, and a gel skin cleanser, but the present invention can be applied to any dosage form.

[0283]

The content of the water-soluble copolymer described above in the skin cleanser of which the dosage form is a liquid such as a creamy form, a liquid form, or a gel form is preferably from 0.1% to 20% by mass, more preferably from 0.5% to 10% by mass, and still more preferably from 1% to 3% by mass.

By setting the content of the water-soluble copolymer described above to be in the above range, it is possible to further decrease tight feel of the skin after use without inhibiting the detergency inherent in the skin cleanser.

[0284]

The skin cleanser can be divided into those that are allowed to foam before use and those that are not allowed

to foam before use. It is possible to decrease tight feel of the skin after use without inhibiting the detergency inherent in the skin cleanser even if the present invention is applied to either type of skin cleanser.

[0285]

In the skin cleanser to be allowed to foam before use, the content of the water-soluble copolymer described above is preferably 0.1% by mass or more, more preferably 0.5% by mass or more, still more preferably 0.8% by mass or more, and still more preferably 1% by mass or more from the viewpoint of improving favorable foaming.

In addition, the content of the water-soluble copolymer described above is preferably 20% by mass or less, more preferably 10% by mass or less, still more preferably 3% by mass or more, and still more preferably 1% by mass or less from the viewpoint of decreasing slimy feel of the skin after use.

Examples of the skin cleanser to be allowed to foam before use may preferably include a creamy skin cleanser.

[0286]

In the skin cleanser not to be allowed to foam before use, the content of the water-soluble copolymer described above is preferably from 0.1% to 10% by mass, more preferably from 0.5% to 5% by mass, still more preferably from 0.6% to 3% by mass, and still more preferably from 0.7% to 2% by mass from the viewpoint of improving ease of spreading on the skin.

Examples of the skin cleanser not to be allowed to foam before use may preferably include a gel skin cleanser.

[0287]

(2) Skin cleanser containing surfactant

Skin cleansers containing a surfactant as a cleansing component exhibit strong detergency but have a problem of causing strong tight feel of the skin after use. Hence, it is preferable to apply the present invention to a skin

cleanser containing a surfactant.

[0288]

The surfactant that can be contained in the skin cleanser of the present invention is not particularly limited as long as it is usually used in a skin cleanser, and it is possible to use either of an ionic surfactant or a nonionic surfactant.

[0289]

As the ionic surfactant, any of an anionic surfactant, a cationic surfactant, an amphoteric surfactant, or a nonionic surfactant can be used.

[0290]

Examples of the anionic surfactant may preferably include fatty acid soap such as a fatty acid sodium salt, a fatty acid potassium salt, or a fatty acid triethanolamine salt, a salt of an alkyl sulfate which may have a polyoxyethylene group, such as sodium lauryl sulfate, potassium lauryl sulfate, or triethanolamine lauryl sulfate which may have a polyoxyethylene group, a salt of an alkyl phosphate which may have a polyoxyethylene group, such as sodium lauryl phosphate, potassium lauryl phosphate, or triethanolamine lauryl phosphate which may have a polyoxyethylene group, and a salt of an alkyl sulfosuccinate.

[0291]

Examples of the anionic surfactant may preferably include an alkyl trimethyl ammonium salt, an alkyl pyridinium salt, a distearyl dimethyl ammonium chloride dialkyl dimethyl ammonium salt, poly(N,N'-dimethyl-3,5-methylenepiperidinium) chloride, an alkyl quaternary ammonium salt, an alkyl dimethyl benzyl ammonium salt, an alkyl isoquinolinium salt, a dialkyl moriphonium salt, a POE-alkylamine, an alkylamine salt, a polyamine fatty acid derivative, an amyl alcohol fatty acid derivative, benzalkonium chloride, and benzethonium chloride.

[0292]

Examples of the amphoteric surfactant, examples of the amphoteric surfactant may include an imidazoline-based amphoteric surfactant and a betaine-based surfactant.

[0293]

Examples of the nonionic surfactant may preferably include a glycerin fatty acid ester, a polyglycerin fatty acid ester, a polyoxyethylene glycerin fatty acid ester, a sorbitan fatty acid ester, a polyoxyethylene sorbitan fatty acid ester, a polyoxyethylene sorbitol fatty acid ester, a polyoxyethylene alkyl phenyl ether, a polyoxyethylene lanolin · lanolin alcohol · beeswax derivative, polyoxyethylene castor oil · hardened castor oil, polyoxyethylene sterol · hydrogenated sterol, a polyoxyethylene alkyl ether, a polyoxyethylene polyoxypropylene alkyl ether, a polyoxyethylene fatty acid ester, a polyoxyethylene alkyl ether fatty acid ester, a polyoxyethylene hardened castor oil fatty acid ester, a polyoxyethylene trimethylolpropane fatty acid ester, a polyethylene glycol fatty acid ester, a sucrose fatty acid ester, a polyoxyethylene polyoxypropylene block copolymer, and organo-modified silicone.

[0294]

The content of these surfactants is not particularly limited and can be appropriately set depending on the kind of surfactant.

Hereinafter, the skin cleanser in a form containing fatty acid soap, a form containing a nonionic surfactant, and a gel form will be described more specifically.

[0295]

(2-1) Skin cleanser containing fatty acid soap

By applying the present invention to a skin cleanser containing fatty acid soap, it is possible to decrease tight feel of the skin after use without impairing high-quality foaming and creamy foam quality of the skin

cleanser.

[0296]

The form of the skin cleanser containing fatty acid soap may be any of a solid form, a liquid form, or a creamy form, but it is preferable that the skin cleanser is in a liquid or creamy form. It is particularly preferable that the skin cleanser is in a creamy form to be allowed to foam before use.

[0297]

The fatty acid constituting the fatty acid soap is not particularly limited as long as it can be applied to a skin cleanser, and it may be saturated or unsaturated and is preferably a fatty acid having from 8 to 24 carbon atoms, particularly from 10 to 22 carbon atoms. Specific examples of preferred fatty acids may include lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, oleic acid, hydroxystearic acid, hydroxydecenoic acid, coconut oil fatty acid, reduced coconut oil fatty acid, beef tallow fatty acid, reduced beef tallow fatty acid, and palm kernel fatty acid. Among these fatty acids, it is preferable to contain one kind or two or more kinds selected from myristic acid, palmitic acid, and stearic acid from the viewpoint of foaming, safety, and stability, and it is particularly preferable to use three kinds of myristic acid, palmitic acid, and stearic acid. Examples of an alkali agent to form a salt with these higher fatty acids may include an alkali metal salt such as sodium or potassium, an ammonium salt, an alkanolamine salt such as a monoethanolamine salt, a diethanolamine salt, a triethanolamine salt, 2-amino-2-methylpropanol, or 2-amino-2-methylpropanediol, and a basic amino acid salt such as lysine or arginine.

[0298]

The content of the fatty acid contained in the skin cleanser is not particularly limited. In the case of

preparing a creamy skin cleanser, the content of the fatty acid can be set to preferably from 10% to 70% by mass, more preferably from 20% to 60% by mass, and still more preferably from 30% to 50% by mass.

[0299]

From the viewpoint of decreasing tight feel after use of the skin cleanser, the ratio of the mass of the above-described water-soluble copolymer contained to the mass of the fatty acid contained is preferably from 1 : 500 to 1 : 2, more preferably from 1 : 200 to 1 : 3, and still more preferably from 1 : 100 to 1 : 5.

In addition, from the viewpoint of improving favorable foaming, the ratio of the mass of the above-described water-soluble copolymer contained to the mass of the fatty acid contained is set to preferably from 1 : 200 to 1 : 2, more preferably from 1 : 100 to 1 : 5, and still more preferably from 1 : 50 to 1 : 10.

In addition, from the viewpoint of decreasing slimy feel of the skin after use, the ratio of the mass of the above-described water-soluble copolymer contained to the mass of the fatty acid contained is set to preferably from 1 : 500 to 1 : 10, more preferably from 1 : 200 to 1 : 20, and still more preferably from 1 : 100 to 1 : 50.

[0300]

(2-2) Skin cleanser containing nonionic surfactant

It is possible to effectively decrease tight feel of the skin after use even in the case of applying the present invention to a skin cleanser containing a nonionic surfactant. As the nonionic surfactant, those described above can be used without limitation.

[0301]

In the form containing a nonionic surfactant, the content of the water-soluble copolymer described above is preferably 0.1% by mass or more, more preferably 0.5% by mass or more, and still more preferably 1% by mass or more

from the viewpoint of decreasing tight feel after use.

In addition, from the viewpoint of improving the detergency, the content of the water-soluble copolymer described above is preferably 0.5% by mass or more, more preferably 1% by mass or more, still more preferably 2% by mass or more, and still more preferably 3% by mass or more.

[0302]

From the viewpoint of decreasing tight feel after use of the skin cleanser, the ratio of the mass of the above-described water-soluble copolymer contained to the mass of the nonionic surfactant contained is set to preferably from 1 : 20 to 1 : 0.5, more preferably from 1 : 10 to 1 : 0.7, and still more preferably from 1 : 5 to 1 : 1.

In addition, from the viewpoint of improving the detergency, the ratio of the mass of the above-described water-soluble copolymer contained to the mass of the nonionic surfactant contained is set to preferably from 1 : 10 to 1 : 0.5, more preferably from 1 : 5 to 1 : 0.5, more preferably from 1 : 3 to 1 : 0.6, and still more preferably from 1 : 1.5 to 1 : 0.7.

[0303]

In addition, in the case of producing a gel skin cleanser containing a nonionic surfactant, the ratio of the mass of the above-described water-soluble copolymer contained to the mass of the nonionic surfactant contained is set to preferably from 1 : 15 to 1 : 0.7, more preferably from 1 : 10 to 1 : 1, and still more preferably from 1 : 7 to 1 : 3 from the viewpoint of improving ease of spreading on the skin at the time of use.

[0304]

[3] Others

The skin cleanser of the present invention can contain arbitrary components to be usually used in an external preparation for skin in addition to the components described above. Examples of such arbitrary components may

include oils and waxes such as macadamia nut oil, avocado oil, corn oil, olive oil, rapeseed oil, sesame oil, castor oil, safflower oil, cottonseed oil, jojoba oil, coconut oil, palm oil, liquid lanolin, hardened coconut oil, hardened oil, vegetable wax, hardened castor oil, beeswax, candelilla wax, carnauba wax, insects wax, lanolin, reduced lanolin, hard lanolin, and jojoba wax; hydrocarbons such as liquid paraffin, squalane, pristane, ozokerite, paraffin, ceresin, petroleum jelly, and microcrystalline wax; higher fatty acids such as oleic acid, isostearic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, and undecylenic acid; higher alcohols such as cetyl alcohol, stearyl alcohol, isostearyl alcohol, behenyl alcohol, octyldodecanol, myristyl alcohol, and cetostearyl alcohol; synthetic ester oils such as cetyl isooctanoate, isopropyl myristate, hexyldecyl isostearate, cetyl lactate, diisostearyl malate, ethylene glycol di-2-ethylhexanoate, neopentyl glycol dicaprate, glycerin di-2-heptylundecanoate, glycerin tri-2-ethylhexanoate, trimethylolpropane tri-2-ethylhexanoate, trimethylolpropane triisostearate, and pentaneerythritol tetra-2-ethylhexanoate; oil agents such as silicone oils such as chain polysiloxanes such as dimethylpolysiloxane, methylphenylpolysiloxane, and diphenylpolysiloxane, cyclic polysiloxanes such as octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and dodecamethylcyclohexanesiloxane, and modified polysiloxanes such as amino-modified polysiloxane, polyether-modified polysiloxane, alkyl-modified polysiloxane, and fluorine-modified polysiloxane; polyhydric alcohols such as polyethylene glycol, glycerin, 1,3-butylene glycol, erythritol, sorbitol, xylitol, maltitol, propylene glycol, dipropylene glycol, diglycerin, isoprene glycol, 1,2-pentanediol, 2,4-hexanediol, 1,2-hexanediol, and 1,2-octanediol; moisturizing components such as sodium pyrrolidone carboxylate, lactic acid, and

sodium lactate; powders such as mica, talc, kaolin, synthetic mica, calcium carbonate, magnesium carbonate, anhydrous silicic acid (silica), aluminum oxide, and barium sulfate which may have a treated surface; inorganic pigments such as red iron oxide, yellow iron oxide, black iron oxide, cobalt oxide, ultramarine blue, iron blue, titanium oxide, and zinc oxide which may have a treated surface; pearlescent agents such as titanium mica, fish phosphorus foil, and bismuth oxychloride which may have a treated surface; organic coloring matters such as Red No. 202, Red No. 228, Red No. 226, Yellow No. 4, Blue No. 404, Yellow No. 5, Red No. 505, Red No. 230, Red No. 223, Orange No. 201, Red No. 213, Yellow No. 204, Yellow No. 203, Blue No. 1, Green No. 201, Purple No. 201, and Red No. 204 which may be laked; organic powders such as polymethyl methacrylate, nylon powder, and organopolysiloxane elastomer; ultraviolet absorbers such as a p-aminobenzoic acid-based ultraviolet absorber, an anthranilic acid-based ultraviolet absorber, a salicylic acid-based ultraviolet absorber, a cinnamic acid-based ultraviolet absorber, a benzophenone-based ultraviolet absorber, a saccharide-based ultraviolet absorber, 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole, and 4-methoxy-4'-t-butyldibenzoylmethane; lower alcohols such as ethanol and isopropanol; vitamins such as vitamin A or any derivative thereof, vitamin B family such as vitamin B6 hydrochloride, vitamin B6 tripalmitate, vitamin B6 dioctanoate, vitamin B2 or any derivative thereof, vitamin B12, and vitamin B15 or any derivative thereof, vitamin E family such as α-tocopherol, β-tocopherol, γ-tocopherol, and vitamin E acetate, vitamin D family, vitamin H, pantothenic acid, pantethine, and pyrroloquinoline quinone; an antibacterial agent such as phenoxyethanol.

[0305]

The skin cleanser of the present invention can be

produced by treating the respective components described above by a conventional method.

[0306]

The present invention is preferably applied to a facial cleanser. According to the present invention, it is possible to provide a facial cleanser which hardly causes tight feel of the skin after face washing.

[0307]

The sunscreen cosmetic of the present invention to achieve the fifth object is characterized by containing the four components [1] to [4] as essential components. Hereinafter, the components [1] to [4] will be described in detail.

[0308]

<1> Component (A) · · · water-soluble copolymer

[1] Hydrophobic monomer

The component (A) is a water-soluble copolymer containing one kind or two or more kinds of constitutional units derived from a hydrophobic monomer represented by the general formula (1), (7), or (8) (hereinafter simply referred to as the "constitutional unit (7)" or the like in some cases) as an essential constitutional unit.

Incidentally, in the present invention, the "constitutional unit derived from a monomer" refers to a constitutional unit formed by cleavage of a carbon-carbon unsaturated bond of the corresponding monomer by a polymerization reaction.

Hereinafter, the hydrophobic monomer represented by the general formula (1), (7), or (8) will be described.

[0309]

(1-1) Hydrophobic monomer represented by general formula (7)

In the general formula (7), R14 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R15 represents a branched hydrocarbon group which has from 13 to 30 carbon atoms but does not contain a ring structure

or a hydrocarbon group which has from 6 to 12 carbon atoms and two or more branches but does not contain a ring structure.

Here, examples of the alkyl group represented by R14 may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R14 is preferably a hydrogen atom or a methyl group.

[0310]

In addition, examples of the branched hydrocarbon group which is represented by R15, has from 13 to 30 carbon atoms, but does not contain a ring structure may include a 1-methyldodecanyl group, an 11-methyldodecanyl group, a 3-ethylundecanyl group, 3-ethyl-4,5,6-trimethyloctyl group, a 1-methyltridecanyl group, a 1-hexyloctyl group, a 2-butyldecanyl group, a 2-hexyloctyl group, a 4-ethyl-1-isobutyloctyl group, a 1-methylpentadecanyl group, a 2-hexyldecanyl group, a 2-octyldecanyl group, a 2-hexyldodecanyl group, a 16-methylheptadecanyl group, a 9-methylheptadecanyl group, a 7-methyl-2-(3-methylhexyl)decanyl group, a 3,7,11,15-tetramethylhexadecanyl group, a 2-octyldodecanyl group, a 2-decyltetradecanyl group, and a 2-dodecylhexadecanyl group.

[0311]

In addition, examples of the hydrocarbon group which is represented by R15, has from 6 to 12 carbon atoms and two or more branches, but does not contain a ring structure may include a 2,2-dimethylbutyl group, a 2,3-dimethylbutyl group, a 3,3-dimethylbutyl group, a 1,3-dimethylbutyl group, a 1,2,2-trimethylpropyl group, a 1,1-dimethylpentanyl group, a 1-isopropylbutyl group, a 1-isopropyl-2-methylpropyl group, a 1,1-diethylpropyl group, a 1-ethyl-1-isopropylpropyl group, a 2-ethyl-4-methylpentyl group, a 1-propyl-2,2-dimethylpropyl group, a 1,1,2-trimethylpentyl group, a 1-isopropyl-3-methylbutyl group, a 1,2-dimethyl-1-

ethylbutyl group, a 1,3-dimethyl-1-ethylbutyl group, a 1-ethyl-1-isopropylpropyl group, a 1,1-dimethylhexyl group, a 1-methyl-1-ethylpentyl group, a 1-methyl-1-propylbutyl group, a 1,4-dimethylhexyl group, a 1-ethyl-3-methylpentyl group, a 1,5-dimethylhexyl group, a 1-ethyl-6-methylheptyl group, a 1,1,3,3-tetramethylbutyl group, a 1,2-dimethyl-1-isopropylpropyl group, a 3-methyl-1-(2,2-dimethylethyl)butyl group, a 1-isopropylhexyl group, a 3.5.5-trimethylhexyl group, a 2-isopropyl-5-methylhexyl group, a 1,5-dimethyl-1-ethylhexyl group, a 3,7-dimethyloctyl group, a 2,4,5-trimethylheptyl group, a 2,4,6-trimethylheptyl group, and a 3,5-dimethyl-1-(2,2-dimethylethyl)hexyl group.

[0312]

(1-2) Hydrophobic monomer represented by general formula (1) or (8)

In the general formulas (1) and (8), R1 and R16 represent a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R2, R3, R17, R18, and R19 may be the same as or different from one another and represent an acyl group which has from 6 to 22 carbon atoms and a branch but does not contain a ring structure. X represents a group obtained by eliminating an OH group from a trihydric alcohol.

[0313]

Here, examples of the alkyl group represented by R1 and R16 may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R1 is preferably a hydrogen atom or a methyl group.

[0314]

In addition, examples of the acyl group which is represented by R2, R3, R17, R18, and R19, has from 6 to 22 carbon atoms and a branch, but does not contain a ring structure may include a 2-methylpentanoyl group, a 3-

methylpentanoyl group, a 4-methylpentanoyl group, a 2-ethylbutanoyl group, a 2-ethylbutanoyl group, a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2-methylhexanoyl group, a 4-methylhexanoyl group, a 5-methylhexanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2-methylheptanoyl group, a 2-ethylhexyl group, a 2-propylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl group, a 2-methyloctanoyl group, a 3,3,5-trimethylhexanoyl group, a 2-methylnonanoyl group, a 4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-diethylhexanoyl group, a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group, a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0315]

In addition, in a preferred embodiment of the present invention, in the general formulas (1) and (8), R2, R3, R17,

R18, and R19 may be the same as or different from one another and represent an acyl group which has from 10 to 22 carbon atoms and a branch but does not contain a ring structure or an acyl group which has from 6 to 9 carbon atoms and two or more branches but does not contain a ring structure.

[0316]

Examples of such an acyl group which is represented by R2, R3, R17, R18, and R19, has from 10 to 22 carbon atoms and a branch, but does not contain a ring structure in a preferred embodiment may include a 2-methylnonanoyl group, a 4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-diethylhexanoyl group), a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group), a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0317]

In addition, examples of the acyl group which is

represented by R2, R3, R17, R18, and R19, has from 6 to 9 carbon atoms and two or more branches, but does not contain a ring structure in a preferred embodiment may include a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl group, and a 3,5,5-trimethylhexanoyl group.

[0318]

The group which is represented by X in the general formula (1) and derived from a trihydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a trihydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a trihydric alcohol selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

[0319]

In addition, the group which is represented by Y in the general formula (8) and derived from a tetrahydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a tetrahydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a tetrahydric alcohol selected from the group consisting of diglycerin, pentaerythritol, erythritol, D-threitol, and L-threitol.

[0320]

In the present invention, it is particularly preferable to use a water-soluble copolymer containing the constitutional unit (1).

In addition, in a more preferred embodiment of the present invention, the hydrophobic monomer represented by the general formula (1) is a hydrophobic monomer represented by the general formula (15).

[0321]

R24 and R25 in the general formula (15) are preferably an acyl group which has from 10 to 22 carbon atoms and a branch but does not contain a ring structure.

The number of carbon atoms in the acyl group of R24 and R25 in the general formula (15) is from 12 to 22, more preferably from 14 to 20, and still more preferably from 16 to 20.

In addition, the number of carbon atoms in the main chain of the acyl group of R24 and R25 in the general formula (15) is preferably from 9 to 21, more preferably from 12 to 20, and still more preferably from 16 to 18.

In addition, the number of branches in the acyl group of R24 and R25 in the general formula (15) is preferably from 1 to 3, more preferably 1 or 2, and still more preferably 1.

Furthermore, in the acyl group of R24 and R25 in the general formula (15), it is more preferable as the position number of the carbon atom in the main chain to which a branched chain is bonded is higher. Specifically, the branched chain is bonded preferably to the 1st to 3rd carbon atom, more preferably to the 1st or 2nd carbon atom, and still more preferably to the 1st carbon atom from the carbon atom at the end of the main chain.

[0322]

Specific examples of R24 and R25 may suitably include a 10-methylundecanoyl group, a 10-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 16-methylheptadecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0323]

The group which is represented by Z in the general

formula (15) and derived from a trihydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a trihydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a trihydric alcohol selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

[0324]

[2] Hydrophilic Monomer

As the hydrophilic monomer constituting the water-soluble copolymer of the component (A), it is possible to use a polymerizable carboxylic acid and compounds represented by the general formulas (2), (9), (10), and (11).

[0325]

(2-1) Polymerizable carboxylic acid

In the present invention, specific examples of the polymerizable carboxylic acid or any salt thereof may include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid, and sodium salts, potassium salts, ammonium salts, and amine salts thereof. Among these, acrylic acid, methacrylic acid, and salts thereof are particularly preferable because of high polymerizability. In the case of introducing a constitutional unit derived from a salt of a polymerizable carboxylic acid into the water-soluble copolymer of the present invention, the polymerizable carboxylic acid may be converted into a salt in advance and the salt may be subjected to a polymerization reaction or a constitutional unit derived from a polymerizable carboxylic acid may be introduced into a water-soluble copolymer by a polymerization reaction and then neutralized with a base into a salt.

[0326]

(2-2) Hydrophilic monomer represented by general formula (2)

In the general formula (2), R4 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms, R5 represents an alkylene group which has from 2 to 4 carbon atoms and may have a hydroxyl group, and R6 represents a hydrogen atom, an aromatic hydrocarbon group having from 6 to 10 carbon atoms, an aliphatic hydrocarbon group having from 1 to 14 carbon atoms, or an acyl group having from 1 to 12 carbon atoms. n represents an integer from 6 to 40.

[0327]

Examples of the alkyl group represented by R4 in the general formula (2) may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R4 is preferably a hydrogen atom or a methyl group.

[0328]

In addition, examples of the alkylene group represented by R5 may include an ethylene group, a propylene group, an isopropylene group, a 2-hydroxypropylene group, a 1-hydroxy-2-methylethylene group, and a 2-hydroxy-1-methylethylene group, and an ethylene group or a propylene group is preferable and an ethylene group is more preferable among these.

[0329]

In addition, among the groups represented by R6, examples of the aromatic group having from 6 to 10 carbon atoms may include a phenyl group, a benzyl group, a methylphenyl group, and an ethylphenyl group; examples of the aliphatic hydrocarbon group having from 1 to 14 carbon atoms may suitably include a methyl group, an ethyl group, a butyl group, a tertiary butyl group, a hexyl group, a cyclohexyl group, an octyl group, a 2-ethylhexyl group, and a lauryl group; and examples of the acyl group having from 1 to 12 carbon atoms may suitably include a formyl group, an acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a valeryl group, and a lauroyl group.

Among these, the group represented by R5 is preferably an aliphatic hydrocarbon group having from 1 to 14 carbon atoms and more preferably an alkyl group having from 1 to 12 carbon atoms.

[0330]

Furthermore, n in the general formula (2) is a numerical range of from 6 to 40.

[0331]

Specific examples of the monomer in which R5 is a propylene group among the monomers represented by the general formula (2) may include polypropylene glycol (9) monoacrylate, polypropylene glycol (13) monoacrylate, polypropylene glycol (9) monomethacrylate, and polypropylene glycol (13) monomethacrylate. Incidentally, the numbers in the parentheses denote N. A large number of these polymers are commercially available. Specific examples of these commercially available products may include "BLEMMER" AP-400, AP-550, AP-800, PP-500, and PP-800 (trade name, all manufactured by NOF CORPORATION).

[0332]

Specific examples of the monomer in which R5 is an ethylene group among the monomers represented by the general formula (2) may include polyethylene glycol (10) monoacrylate, polyethylene glycol (8) monomethacrylate, polyethylene glycol (23) monoacrylate, polyethylene glycol (23) monomethacrylate, methoxypolyethylene glycol (9) acrylate, methoxypolyethylene glycol (9) methacrylate, methoxy polyethylene glycol (23) methacrylate, oleyloxypolyethylene glycol (18) methacrylate, lauroxypolyethylene glycol (18) acrylate, lauroyloxypolyethylene glycol (10) methacrylate, and stearoxypolyethylene glycol (30) monomethacrylate.

[0333]

The hydrophilic monomers described above can be obtained at a high yield by an esterification reaction of

the corresponding polyethylene glycol, polyethylene glycol monoether, and polyethylene glycol monoester with a chloride or anhydride of acrylic acid or methacrylic acid. There are also already a large number of commercially available products, and it is also possible to use such commercially available products. Specific examples of such commercially available products may include BLEMMER AE-400, PE-350, AME-400, PME-400, PME-1000, ALE-800, and PSE-1300, (trade name, all manufactured by NOF CORPORATION) and the like.

[0334]

(2-3) Hydrophilic monomer represented by general formula (9)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (9) may be used.

[0335]

Specific examples of the hydrophilic monomer represented by the general formula (9) may include 2-acryloyloxyethyl phosphorylcholine (APC) and 2-methacryloyloxyethyl phosphorylcholine (MPC). These monomers can be synthesized, for example, by the following method described in Polymer Journal, Vol22, No. 5.

<Synthesis method>

After 2-bromoethyl phosphoryl dichloride is reacted with 2-hydroxyethyl methacrylate or 2-hydroxyethyl acrylate to obtain 2-methacryloyloxyethyl-2'-bromoethyl phosphate or 2-acryloyloxyethyl-2'-bromoethyl phosphate, this compound is reacted with triethylamine in methanol.

[0336]

(2-4) Hydrophilic monomer represented by general formula (10)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (10) may be used.

[0337]

In the hydrophilic monomer represented by the general formula (10), specific examples of the reducing sugar of the group which is represented by G-O- and obtained by eliminating a hydrogen atom from the hydroxyl group at the position 1 of a reducing sugar may include one kind or two or more kinds selected from the group consisting of monosaccharides such as glucose, mannose, galactose, arabinose, xylose, and ribose, disaccharides such as maltose, lactose, and cellobiose, trisaccharides such as maltotriose, and oligosaccharides such as maltooligosaccharide, and among these, one kind or two or more kinds selected from the group consisting of glucose, galactose, arabinose, xylose, ribose, maltose, lactose cellobiose are preferable and glucose is particularly preferable. In addition, as the monomer represented by the general formula (10), glucosyloxyethyl methacrylate (hereinafter abbreviated as GEMA) or glucosyloxyethyl acrylate (hereinafter abbreviated as GEA) are preferable.

[0338]

(2-5) Hydrophilic monomer represented by general formula (11)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (11) may be used.

[0339]

In the monomer represented by the general formula (11), the amino acid in the amino acid residue represented by R23 is not particularly limited as long as it is a usually known amino acid, and specific examples thereof may include glycine, alanine, glutamine, lysine, and arginine. Among these, a lysine residue is particularly preferable since the water-soluble copolymer to be obtained exhibits an excellent effect of recovering the skin barrier.

[0340]

In addition, the polyamine in the polyamine residue

represented by R23 means an amine having two or more amino groups which may be substituted with an alkyl group in the same molecule, and specific examples thereof may include a diamine, a triamine, a tetraamine, or amines in which hydrogen atoms of these amino groups are substituted with alkyl groups. Among these, a diamine is preferable since the feel of use of the external preparation for skin containing the water-soluble copolymer to be obtained is particularly excellent, and particularly preferred specific examples thereof may include ethylenediamine, 1,4-diamino-n-butane, and 1,6-diamino-n-hexane from the viewpoint of availability of starting materials for synthesis.

[0341]

Furthermore, the amino alcohol in the amino alcohol residue represented by R23 means a compound having an amino group which may be substituted with an alkyl group and an alcoholic hydroxyl group in the same molecule. The amino alcohol is not particularly limited as long as it is usually known, and specific examples thereof may include ethanolamine and triethylaminoethanol.

[0342]

The salt of the monomer represented by the general formula (11) is not particularly limited, but specific examples thereof may include a sodium salt, a potassium salt, an ammonium salt, and an amine salt obtained by neutralizing the acid moiety with a base and a hydrochloride, a sulfate, a nitrate, a phosphate, a citrate, an oxalate, and a carbonate obtained by neutralizing the amino group moiety with an acid. In the case of introducing a constitutional unit derived from a salt of the monomer represented by the general formula (11) into the water-soluble copolymer of the present invention, the monomer represented by the general formula (11) may be converted into a salt in advance and the salt may be subjected to a polymerization reaction or a constitutional

unit derived from the monomer represented by the general formula (11) may be introduced into a water-soluble copolymer by a polymerization reaction and then neutralized into a salt.

[0343]

Specific examples of the monomer represented by the general formula (11) and any salt thereof may include the compounds 1 to 11 and salts thereof.

[0344]

The hydrophilic monomer represented by the general formula (11) can be synthesized, for example, by an esterification reaction or an amidation reaction using (meth)acrylic acid or (meth)acrylic acid chloride as presented in the reaction formulas (1) and (2).

[0345]

As described above, in the present invention, it is possible to use the general formulas (2), (9), (10), and (11) as the hydrophilic polymer.

In a preferred embodiment of the present invention, the water-soluble copolymer contains the constitutional unit 2 derived from the general formula (2).

[0346]

[3] Water-soluble copolymer

In the present invention, it is possible to preferably use a water-soluble copolymer having the constitutional unit (1) and the constitutional unit (2). In addition, a water-soluble copolymer having the constitutional unit (15) and the constitutional unit (2) is more preferably used.

Among such water-soluble copolymers, a (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer is particularly preferably used.

By containing such a water-soluble copolymer, an emulsified composition which is low-irritant and less sticky and exhibits excellent emulsion stability is

obtained.

[0347]

The (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer mainly contains a constitutional unit (g) derived from a hydrophobic monomer in which R24 and R25 are a 16-methylheptadecanoyl group among the hydrophobic monomers represented by the general formula (15) as the constitutional unit (g).

The (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer also mainly contains a constitutional unit (h) derived from a hydrophilic monomer in which R4 is a methyl group, R5 is an ethylene group, R6 is a methyl group, and n is 23 among the hydrophilic monomers represented by the general formula (2) as the constitutional unit (h).

[0348]

In the present invention, the proportion of the constitutional unit (g) in the entire constitutional units in the water-soluble copolymer is preferably from 1% to 50% by mass, more preferably from 5% to 40% by mass and from 10% to 30% by mass.

It is possible to provide a sunscreen cosmetic exhibiting excellent moisturizing feel and further decreased sticky feel by setting the proportion of the constitutional unit (g) in the water-soluble copolymer to be in the above range.

[0349]

In the present invention, the proportion of the constitutional unit (h) in the entire constitutional units in the water-soluble copolymer is preferably from 50% to 99% by mass, more preferably from 60% to 95% by mass and from 70% to 90% by mass.

It is possible to provide a sunscreen cosmetic exhibiting excellent moisturizing feel and further decreased sticky feel by setting the proportion of the

constitutional unit (h) in the water-soluble copolymer to be in the above range.

[0350]

In the present invention, the mass ratio of the constitutional unit (g) constituting the water-soluble copolymer to the constitutional unit (h) constituting the water-soluble copolymer is preferably from 5 : 95 to 50 : 50, more preferably from 10 : 90 to 45 : 55, still more preferably from 20 : 80 to 40 : 60, and still more preferably from 25 : 75 to 35 : 65.

[0351]

In addition, the molar ratio of the constitutional unit (g) constituting the water-soluble copolymer to the constitutional unit (h) constituting the water-soluble copolymer is preferably from 8 : 92 to 62 : 38, more preferably from 15 : 85 to 57 : 43, still more preferably from 29 : 71 to 52 : 48, and still more preferably from 35 : 65 to 46 : 54.

It is possible to further improve the feel of use of the sunscreen cosmetic by setting the mass ratio and molar ratio of the constitutional unit (g) to the constitutional unit (h) in the water-soluble copolymer to be in the above ranges.

[0352]

In the present invention, the average molecular weight of the water-soluble copolymer is preferably from 20,000 to 110,000, more preferably from 20,000 to 80,000, more preferably from 30,000 to 80,000, more preferably from 40,000 to 70,000, still more preferably from 50,000 to 70,000, and still more preferably from 57,000 to 66,000.

[0353]

The content of the water-soluble copolymer described above is not particularly limited, but it is usually from 0.001% to 15% by mass and preferably from 0.01% to 10% by mass.

[0354]

<2> Component (B) · · · polyglycerin fatty acid ester

The sunscreen cosmetic of the present invention is characterized by containing a polyglycerin fatty acid ester obtained by ester condensation of one molecule of polyglycerin having a polymerization degree of 10 with from two to five molecules of a fatty acid having 16 or more carbon atoms as the component (B).

[0355]

The fatty acid which has 16 or more carbon atoms and constitutes the polyglycerin fatty acid ester of the component (B) may have a branched chain and may be saturated or unsaturated.

Examples thereof may preferably include oleic acid and isostearic acid.

In addition, the number of molecules of the fatty acid to be ester-bonded to one molecule of polyglycerin may be from 2 to 5 and is preferably 5 molecules.

In the present invention, polyglyceryl-10 pentastearate is particularly preferably used as the component (B).

[0356]

The content of the polyglycerin fatty acid ester of the component (B) can be usually set to from 0.1% to 10% by mass.

In addition, from the viewpoint of improving the emulsion stability, the content of the component (B) is 0.3% by mass or more, more preferably 0.5% by mass, and still more preferably 0.7% by mass or more.

Furthermore, from the viewpoint of suppressing stickiness, the content of the component (B) is preferably 7% by mass or less, more preferably 5% by mass or less, and still more preferably 3% by mass or less.

[0357]

<3> Component (C) · · · ionic surfactant

The sunscreen cosmetic of the present invention contains an ionic surfactant as the component (C). The ionic surfactant is not particularly limited as long as it is used in cosmetics, and any of an anionic surfactant, a cationic surfactant, or an amphoteric surfactant can be used.

[0358]

Examples of the anionic surfactant may preferably include fatty acid soap such as a fatty acid sodium, a fatty acid potassium, or a fatty acid triethanolamine, an a salt of an alkyl sulfate which may have a polyoxyethylene group, such as sodium lauryl sulfate, potassium lauryl sulfate, or triethanolamine lauryl sulfate which may have a polyoxyethylene group, a salt of an acyl lactic acid, a salt of an alkyl phosphate which may have a polyoxyethylene group, such as sodium lauryl phosphate, potassium lauryl phosphate, or triethanolamine lauryl phosphate which may have a polyoxyethylene group, and a salt of an alkyl sulfosuccinate.

[0359]

Examples of the cationic surfactant may preferably include an alkyl trimethyl ammonium salt, an alkyl pyridinium salt, a distearyl dimethyl ammonium chloride dialkyl dimethyl ammonium salt, poly(N,N'-dimethyl-3,5-methylenepiperidinium) chloride, an alkyl quaternary ammonium salt, an alkyl dimethyl benzyl ammonium salt, an alkyl isoquinolinium salt, a dialkyl moriphonium salt, a POE-alkylamine, an alkylamine salt, a polyamine fatty acid derivative, an amyl alcohol fatty acid derivative, benzalkonium chloride, and benzethonium chloride.

[0360]

Examples of the amphoteric surfactant, examples of the amphoteric surfactant may include an imidazoline-based amphoteric surfactant and a betaine-based surfactant.

[0361]

As the component (C), it is preferable to use an anionic surfactant and it is still more preferable to use a salt of an acyl lactic acid among these surfactants.

[0362]

As the salt of an acyl lactic acid, a sodium salt is preferable, and specific examples thereof may preferably include sodium lauroyl lactylate, sodium isostearoyl lactate, and sodium stearoyl lactylate.

[0363]

The content of the ionic surfactant is not particularly limited, and it is usually from 0.01% to 2.0% by mass and more preferably from 0.1% to 1% by mass.

In addition, from the viewpoint of improving emulsion stability, the content of the ionic surfactant is preferably 0.05% by mass or more, more preferably 0.07% by mass or more, and still more preferably 0.1% by mass or more.

Furthermore, from the viewpoint of suppressing stickiness, the content of the ionic surfactant is preferably 1.5% by mass or less, more preferably 1% by mass or less, and still more preferably 0.5% by mass or less.

[0364]

<4> Component (D) · · · ultraviolet scattering agent/ultraviolet absorber

The sunscreen cosmetic of the present invention contains an ultraviolet scattering agent and/or an ultraviolet absorber as the component (D).

[0365]

The ultraviolet scattering agent refers to micro metal oxide exhibiting an ultraviolet scattering action, and the kind thereof is not particularly limited as long as it can be blended in an emulsified cosmetic. Examples of the metal oxide may include titanium dioxide, zinc oxide, zirconium oxide, and cerium oxide.

[0366]

The content of the ultraviolet scattering agent is not particularly limited, and it is usually from 0.01% to 20% by mass, more preferably from 0.1% to 15% by mass, and still more preferably from 1% to 10% by mass.

[0367]

The ultraviolet scattering agent has a particle diameter so as to be called fine particles in the technical field, and for example, it has a primary particle diameter measured by electron microscopic observation of usually 5 nm or more and preferably 10 nm or more and usually 100 nm or less and preferably 80 nm or less.

As the ultraviolet scattering agent to be used in the present invention, it is preferable to contain at least one kind selected from the group consisting of micro titanium dioxide and micro zinc oxide since these exhibit an excellent ultraviolet scattering effect.

[0368]

The ultraviolet scattering agent to be used in the present invention can be prepared by a conventional method in which a salt of the corresponding metal is thermally decomposed in a gas phase, but it is also possible to use a commercially available product as it is since there are a large number of commercially available products. As such commercially available products, specifically, examples of micro titanium dioxide may include "MTY-110M3S" (manufactured by TAYCA CORPORATION), "MTY-02" (manufactured by TAYCA CORPORATION), "MT-100TV" (manufactured by TAYCA CORPORATION), "MT-500HSA" (manufactured by TAYCA CORPORATION), "MT-100T" (manufactured by TAYCA CORPORATION), "MT-01" (manufactured by TAYCA CORPORATION), "MT-10EX" (manufactured by TAYCA CORPORATION), "MT-05" (manufactured by TAYCA CORPORATION), "MT-100Z" (manufactured by TAYCA CORPORATION), "MT-150EX" (manufactured by TAYCA CORPORATION), "MT-100AQ" (manufactured by TAYCA CORPORATION), "MT-100WP" (manufactured by TAYCA

CORPORATION), "MT-100SA" (manufactured by TAYCA CORPORATION), "MT-500B" (manufactured by TAYCA CORPORATION), "MT-500SA" (manufactured by TAYCA CORPORATION), "MT-600B" (manufactured by TAYCA CORPORATION), "MT-500SAS" (manufactured by TAYCA CORPORATION), "TIPAQUE CR-50" (manufactured by ISHIHARA SANGYO KAISHA, LTD.), "TIPAQUE TTO-M-1" (manufactured by ISHIHARA SANGYO KAISHA, LTD.), "TIPAQUE TTO-V4" (manufactured by ISHIHARA SANGYO KAISHA, LTD.), "ST-455" (manufactured by Titan Kogyo, Ltd.), "STT-65C-S" (manufactured by Titan Kogyo, Ltd.), "STT-30 EHS" (manufactured by Titan Kogyo, Ltd.), and "Bayer titanium R-KB-1" (manufactured by Bayer).

[0369]

In addition, examples of micro zinc oxide may include "MZ-300" (manufactured by TAYCA CORPORATION), "MZY-303S" (manufactured by TAYCA CORPORATION), "MZ-306X" (manufactured by TAYCA CORPORATION), "MZ-500" (manufactured by TAYCA CORPORATION), "MZY-505S" (manufactured by TAYCA CORPORATION), "MZ-506X" (manufactured by TAYCA CORPORATION), "MZ-510 HPSX" (manufactured by TAYCA CORPORATION), "WSX-MZ-700" (manufactured by TAYCA CORPORATION), "SAMT-UFZO-450" (manufactured by Miyoshi Kasei, Inc.), "SAMT-UFZO-500" (manufactured by Miyoshi Kasei, Inc.), "FZO-50" (manufactured by ISHIHARA SANGYO KAISHA, LTD.), "Maxlight ZS-032" (manufactured by SHOWA DENKO K.K.), and "Maxlight ZS-032D" (manufactured by SHOWA DENKO K.K.).

[0370]

In the present invention, it is preferable that the surface of the ultraviolet scattering agent is coated with an inorganic compound such as silica or alumina or an organic compound such as sodium polyacrylate, fatty acid metal soap, or silicone.

[0371]

It is preferable that the ultraviolet scattering agent is dispersible in water. A water-dispersible

ultraviolet scattering agent is uniformly dispersed in the aqueous phase, and the sunscreen cosmetic of the present invention in such a form thus exhibits an excellent ultraviolet protecting function.

[0372]

Examples of the water-dispersible ultraviolet scattering agent may preferably include an ultraviolet scattering agent of which the surface is coated with a hydrophilic compound.

As such a water-dispersible ultraviolet scattering agent, an ultraviolet scattering agent of which the surface is treated with sodium polyacrylate is preferable. The sunscreen cosmetic of the present invention containing an ultraviolet scattering agent of which the surface is treated with sodium polyacrylate as the component (D) exhibits excellent dispersibility and an excellent ultraviolet protecting function.

[0373]

The ultraviolet absorber is not particularly limited as long as it is an ultraviolet absorber which can be usually blended in an emulsified cosmetic, but it is preferable to contain a UV-A absorber which absorbs ultraviolet rays having a wavelength of from 320 to 400 nm (region A) and a UV-B absorber which absorbs ultraviolet rays having a wavelength of from 290 to 320 nm (region B) in order to absorb ultraviolet rays in a wide wavelength region.

The content of the ultraviolet absorber is not particularly limited, and it is usually 0.01% by mass or more, preferably 0.1% by mass or more, and more preferably 1% by mass or more and usually 20% by mass or less, preferably 15% by mass or less, and more preferably 10% by mass or less.

[0374]

Examples of the UV-A absorber may include compounds

such as 2-hydroxy-4-methoxybenzophenone, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-ethylhexyl dimethoxybenzylidene dioxoimidazolidine propionate, bis(resulcinyl)triazine, methylenebisbenzotriazolyl tetramethylbutylphenol, diethylamino hydroxybenzoyl hexyl benzoate, and t-butyl methoxydibenzoylmethane. Among these, diethylamino hydroxybenzoyl hexyl benzoate and t-butyl methoxydibenzoylmethane are particularly preferable because of excellent ultraviolet absorbing ability thereof. As these compounds, there are commercially available products, and the commercially available products can be thus used as they are. Specific examples of the commercially available products may include "Uvinal A Plus Granular" (diethylamino hydroxybenzoyl hexyl benzoate, manufactured by BASF) and "PARSOL 1789" (t-butyl methoxybenzoylmethane, manufactured by DSM Nutritional Products, LLC).

[0375]

The content of the UV-A absorber is usually 0.01% by mass or more and preferably 0.1% by mass or more and usually 5% by mass or less and preferably 3% by mass or less.

[0376]

Specific examples of the UV-B absorber may include compounds such as 2-ethylhexyl p-methoxycinnamate, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, dimethicone diethyl benzalmalonate, 2,4,6-trianilino-p-(carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine, 2-hydroxy-4-methoxybenzophenone, homomenthyl salicylate, and octyl salicylate. As these compounds, there are commercially available products, and the commercially available products can be thus used as they are. Specific examples of the commercially available products may include "Uvinal MC 80" (2-ethylhexyl p-methoxycinnamate, manufactured by BASF), "Uvinal T150" (2,4,6-trianilino-p-(carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine, manufactured by BASF), "Uvinal M40"

(2-hydroxy-4-methoxybenzophenone, manufactured by BASF), "PARSOL SLX" (dimethico diethyl benzalmalonate, manufactured by DSM Nutritional Products, LLC), "PARSOL 340" (2-ethylhexyl 2-cyano-3,3-diphenylacrylate, manufactured by DSM Nutritional Products, LLC), "PARSOL HMS" (homomenthyl salicylate, manufactured by DSM Nutritional Products, LLC), and "PARSOL EMS" (octyl salicylate, manufactured by DSM Nutritional Products, LLC).

[0377]

The content of the UV-B absorber is usually 0.1% by mass or more and preferably 0.5% by mass or more and usually 10% by mass or less and preferably 7% by mass or less.

[0378]

<5> Other compositions

The components to be contained in the oil phase and the aqueous phase are not particularly limited.

Examples of the oil agent constituting the oil phase may include liquid oils and fats, solid oils and fats, waxes, hydrocarbon oils, higher fatty acids, higher alcohols, synthetic ester oils, and silicone oils.

[0379]

Examples of liquid oils and fats may include avocado oil, camellia oil, turtle oil, macadamia nut oil, corn oil, mink oil, olive oil, rapeseed oil, egg yolk oil, sesame oil, persic oil, wheat germ oil, sasanqua oil, castor oil, linseed oil, safflower oil, cottonseed oil, eno oil, meadowfoam oil, soybean oil, peanut oil, tea seed oil, kaya oil, rice bran oil, Paulownia tomentosa oil, Japanese Paulownia tomentosa oil, jojoba oil, germ oil, triglycerin, glyceryl trioctanoate, and glyceryl triisopalmitate.

[0380]

Examples of solid oils and fats may include cocoa butter, coconut oil, horse fat, hardened coconut oil, palm oil, beef tallow, mutton tallow, hardened beef tallow, palm

kernel oil, lard, beef bone fat, vegetable kernel oil, hardened oil, neat's-foot oil, vegetable wax, and hardened castor oil.

[0381]

Examples of waxes may include beeswax, candelilla wax, cotton wax, carnauba wax, bayberry wax, insects wax, spermaceti, montan wax, barn wax, lanolin, kapok wax, lanolin acetate, liquid lanolin, sugarcane wax, isopropyl lanolin fatty acid, hexyl laurate, reduced lanolin, jojoba wax, hard lanolin, shellac wax, POE lanolin alcohol ether, POE lanolin alcohol acetate, POE cholesterol ether, lanolin fatty acid polyethylene glycol, and POE hydrogenated lanolin alcohol ether.

[0382]

Examples of hydrocarbon oils may include liquid paraffin, ozokerite, pristane, paraffin, ceresin, squalene, petroleum jelly, and microcrystalline wax.

[0383]

Examples of higher fatty acids may include lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, 12-hydroxystearic acid, undecylenic acid, and tall oil fatty acid.

[0384]

Examples of higher alcohols may include cetyl alcohol, stearyl alcohol, behenyl alcohol, batyl alcohol, myristyl alcohol, and cetostearyl alcohol.

[0385]

Examples of synthetic ester oils may include isopropyl myristate, cetyl octanoate, octyl dodecyl myristate, isopropyl palmitate, butyl stearate, hexyl laurate, myristyl myristate, decyl oleate, hexyldecyl dimethyloctanoate, cetyl lactate, myristyl lactate, lanolin acetate, isocetyl stearate, isocetyl isostearate, sucrose stearate, sucrose oleate, cholesteryl 12-hydroxystearate, ethylene glycol di-2-ethylhexylate, dipentaerythritol fatty

acid ester, N-alkyl glycol monoisostearate, neopentyl glycol dicaprate, diisostearyl malate, glyceryl di-2-heptylundecanoate, trimethylolpropane tri-2-ethylhexylate, trimethylolpropane triisostearate, pentane erythritol tetra-2-ethylhexylate, glyceryl tri-2-ethylhexylate, trimethylolpropane triisostearate, cetyl 2-ethylhexanoate, 2-ethylhexyl palmitate, glyceryl trimyristate, glyceride tri-2-heptylundecanoate, methyl ester of castor oil fatty acid, oleic acid oil, cetostearyl alcohol, acetoglyceride, 2-heptylundecyl palmitate, cetyl palmitate, diisobutyl adipate, 2-octyldodecyl N-lauroyl-L-glutamate, di-2-heptylundecyl adipate, ethyl laurate, di-2-ethylhexyl sebacate, 2-hexyldecyl myristate, 2-hexyldecyl palmitate, 2-hexyldecyl adipate, diisopropyl sebacate, 2-ethylhexyl succinate, ethyl acetate, butyl acetate, amyl acetate, and triethyl citrate.

[0386]

Examples of silicone oils may include chain polysiloxanes such as dimethylpolysiloxane, methylphenylpolysiloxane, and methylhydrogenpolysiloxane and cyclic polysiloxanes such as decamethylpolysiloxane, dodecamethylpolysiloxane, and tetramethyltetrahydrogenpolysiloxane.

[0387]

It is possible to use one kind or two or more kinds of oil agents.

[0388]

Arbitrary additives to be usually blended in cosmetics may be blended in the sunscreen cosmetic of the present invention in a range in which the effect of the present invention is not impaired. Examples of such additives may include moisturizing agents such as polyethylene glycol, glycerin, 1,3-butylene glycol, erythritol, sorbitol, xylitol, and maltitol; lower alcohols such as ethanol; antioxidants such as butylated

hydroxytoluene, tocopherol, and phytin; antibacterial agents such as benzoic acid, salicylic acid, sorbic acid, an alkyl ester of parahydroxybenzoic acid, and hexachlorophene; organic acids such as acyl sarcosinic acid (for example, sodium lauroyl sarcosinate), glutathione, citric acid, malic acid, tartaric acid, and lactic acid; vitamins such as vitamin A and any derivative thereof, vitamin B family such as vitamin B6 hydrochloride, vitamin B6 tripalmitate, vitamin B6 dioctanoate, vitamin B2 and any derivative thereof, vitamin B12, and vitamin B15 and any derivative thereof, vitamin E family such as α-tocopherol, β-tocopherol, γ-tocopherol, and vitamin E acetate, vitamin D family, vitamin H, pantothenic acid, pantethine, nicotinic acid amide, and benzyl nicotinate; various kinds of medicines such as γ-oryzanol, allantoin, glycyrrhizic acid (salt), glycyrrhetinic acid and any derivative thereof, tranexamic acid and any derivative thereof [as a tranexamic acid derivative, a dimer of tranexamic acid (for example, trans-4-(trans-aminomethylcyclohexanecarbonyl)aminomethylcyclohexane carboxylic acid hydrochloride), an ester of tranexamic acid with hydroquinone (for example, 4'-hydroxyphenyl ester of trans-4-aminomethylcyclohexane carboxylic acid), an ester of tranexamic acid with gentisic acid (for example, 2-(trans-4-aminomethylcyclohexylcarbonyloxy)-5-hydroxybenzoic acid and any salt thereof), and an amide of tranexamic acid (for example, trans-4-aminomethylcolohexanecarboxylic acid methylamide and any salt thereof, trans-4-(P-methoxybenzoyl)aminomethylcyclohexane carboxylic acid and any salt thereof, and trans-4-guanidinomethylcyclohexane carboxylic acid and any salt thereof)], saponins such as hinokitiol, bisabolol, eucalyptol, thymol, inositol, Saikosaponin, ginseng saponin, Luffa cylindrica saponin, and Sapindus mukurossi saponin, pantothenyl ethyl ether, ethinyl estradiol, tranexamic acid, arbutin, cepharanthine,

and placenta extract; extracts of plants such as Rumex japonicus, Sophora flavescens, Nuphar japonicum, Citrus sinensis, Salvia officinalis, Achillea alpina, Malva sylvestris, Swertia japonica, thyme, Angelica acutiloba, Picea jezoensis var. hondoensis, Betula, Equisetum arvense, Luffa cylindrica, Aesculus hippocastanum, Saxifraga stolonifera, Arnica montana, Lilium, Artemisia indica var. maximowiczii, Paeonia lactiflora, Aloe, Gardenia jasminoides, and Chamaecyparis pisifera; coloring matters; porous and/or water-absorbing powders (for example, starches obtained from corn, potatoes, and the like and powders of anhydrous silicic acid, talc, kaolin, magnesium aluminum silicate, calcium alginate, and the like); neutralizing agents; preservatives; perfumes; and pigments.

[0389]

The sunscreen cosmetic of the present invention can be produced, for example, by the following method.

The oil agent, the component (B), and other oil phase components are mixed together, heated, and dissolved to prepare a mixture of oil phase components. The ultraviolet scattering agent is added to the mixture and dispersed by using a disper in the case of containing an ultraviolet scattering agent (component (D)).

Next, the water phase components and the component (C) are mixed and heated, and the mixture of the oil phase components is added to this mixture and emulsified by using a homogenizer. After emulsification, the component (A) and, if necessary, a water-dispersible ultraviolet scattering agent (component (D)) are added to the emulsion and the resultant mixture is cooled while being stirred and mixed, whereby a sunscreen cosmetic of the present invention can be produced.

[0390]

<1> Coating film having sea-island structure

The sea-island structure refers to a structure in

which two kinds of polymers incompatible with each other undergo phase separation and a dispersed phase containing the other polymer is present on a continuous phase containing one polymer as a point. Moreover, the continuous phase in the sea-island structure is called the sea phase, the dispersed phase is called the island phase, and the particles of the dispersed phase are called island particles.

[0391]

The coating film of the present invention has a sea-island structure in which island particles containing an amphipathic copolymer are dispersed in a sea phase containing an aqueous gel formed by a water-soluble polymer.

Moreover, the amphipathic copolymer to be contained in the island particles has the constitutional unit (i) and the constitutional unit (j) as essential constitutional units.

The constitutional unit (i) is one kind or two or more kinds of constitutional units derived from a hydrophobic monomer, and the constitutional unit (j) is one kind or two or more kinds of constitutional units derived from a hydrophilic monomer.

The coating film of the present invention having such structural features exhibits feel like milk containing an oil agent even though it contains an aqueous component as a main component.

Hereinafter, the coating film of the present invention will be described in more detail.

[0392]

<1-1> Island particles

In the present invention, the amphipathic copolymer to be contained in the island particles of the sea-island structure has the constitutional unit (i) derived from a hydrophobic monomer and the constitutional unit (j) derived from a hydrophilic monomer as essential constitutional

units.

As the amphipathic copolymer in the present invention, it is preferable to use a copolymer containing constitutional units derived from a hydrophobic monomer and a hydrophilic monomer to be described in the following [1] and [2].

[0393]

[1] Hydrophobic monomer

In the present invention, it is preferable to use an amphipathic copolymer (also referred to as an acrylic acid-based amphipathic copolymer) containing one kind or two or more kinds of constitutional units derived from a hydrophobic monomer represented by the general formula (1), (7), or (8) (hereinafter simply referred to as the "constitutional unit (7)" or the like in some cases) as an essential constitutional unit.

Incidentally, in the present invention, the "constitutional unit derived from a monomer" refers to a constitutional unit formed by cleavage of a carbon-carbon unsaturated bond of the corresponding monomer by a polymerization reaction.

Hereinafter, the hydrophobic monomer represented by the general formula (1), (7), or (8) will be described.

[0394]

(1-1) Hydrophobic monomer represented by general formula (7)

In the general formula (7), R14 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R15 represents a branched hydrocarbon group which has from 13 to 30 carbon atoms but does not contain a ring structure or a hydrocarbon group which has from 6 to 12 carbon atoms and two or more branches but does not contain a ring structure.

Here, examples of the alkyl group represented by R14 may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the

present invention, R14 is preferably a hydrogen atom or a methyl group.

[0395]

In addition, examples of the branched hydrocarbon group which is represented by R15, has from 13 to 30 carbon atoms, but does not contain a ring structure may include a 1-methyldodecanyl group, an 11-methyldodecanyl group, a 3-ethylundecanyl group, 3-ethyl-4,5,6-trimethyloctyl group, a 1-methyltridecanyl group, a 1-hexyloctyl group, a 2-butyldecanyl group, a 2-hexyloctyl group, a 4-ethyl-1-isobutyloctyl group, a 1-methylpentadecanyl group, a 2-hexyldecanyl group, a 2-octyldecanyl group, a 2-hexyldodecanyl group, a 16-methylheptadecanyl group, a 9-methylheptadecanyl group, a 7-methyl-2-(3-methylhexyl)decanyl group, a 3,7,11,15-tetramethylhexadecanyl group, a 2-octyldodecanyl group, a 2-decyltetradecanyl group, and a 2-dodecylhexadecanyl group.

[0396]

In addition, examples of the hydrocarbon group which is represented by R15, has from 6 to 12 carbon atoms and two or more branches, but does not contain a ring structure may include a 2,2-dimethylbutyl group, a 2,3-dimethylbutyl group, a 3,3-dimethylbutyl group, a 1,3-dimethylbutyl group, a 1,2,2-trimethylpropyl group, a 1,1-dimethylpentanyl group, a 1-isopropylbutyl group, a 1-isopropyl-2-methylpropyl group, a 1,1-diethylpropyl group, a 1-ethyl-1-isopropylpropyl group, a 2-ethyl-4-methylpentyl group, a 1-propyl-2,2-dimethylpropyl group, a 1,1,2-trimethylpentyl group, a 1-isopropyl-3-methylbutyl group, a 1,2-dimethyl-1-ethylbutyl group, a 1,3-dimethyl-1-ethylbutyl group, a 1-ethyl-1-isopropylpropyl group, a 1,1-dimethylhexyl group, a 1-methyl-1-ethylpentyl group, a 1-methyl-1-propylbutyl group, a 1,4-dimethylhexyl group, a 1-ethyl-3-methylpentyl group, a 1,5-dimethylhexyl group, a 1-ethyl-6-methylheptyl group, a 1,1,3,3-tetramethylbutyl group, a 1,2-dimethyl-1-

isopropylpropyl group, a 3-methyl-1-(2,2-dimethylethyl)butyl group, a 1-isopropylhexyl group, a 3.5.5-trimethylhexyl group, a 2-isopropyl-5-methylhexyl group, a 1,5-dimethyl-1-ethylhexyl group, a 3,7-dimethyloctyl group, a 2,4,5-trimethylheptyl group, a 2,4,6-trimethylheptyl group, and a 3,5-dimethyl-1-(2,2-dimethylethyl)hexyl group.

[0397]

(1-2) Hydrophobic monomer represented by general formula (1) or (8)

In the general formulas (1) and (8), R1 and R16 represent a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R2, R3, R17, R18, and R19 may be the same as or different from one another and represent an acyl group which has from 6 to 22 carbon atoms and a branch but does not contain a ring structure. X represents a group obtained by eliminating an OH group from a trihydric alcohol.

[0398]

Here, examples of the alkyl group represented by R1 and R16 may include a methyl group, an ethyl group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R3 is preferably a hydrogen atom or a methyl group.

[0399]

In addition, examples of the acyl group which is represented by R2, R3, R17, R18, and R19, has from 6 to 22 carbon atoms and a branch, but does not contain a ring structure may include a 2-methylpentanoyl group, a 3-methylpentanoyl group, a 4-methylpentanoyl group, a 2-ethylbutanoyl group, a 2-ethylbutanoyl group, a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2-methylhexanoyl group, a 4-methylhexanoyl group, a 5-methylhexanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2-methylheptanoyl group, a 2-

ethylhexyl group, a 2-propylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl group, a 2-methyloctanoyl group, a 3,3,5-trimethylhexanoyl group, a 2-methylnonanoyl group, a 4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-diethylhexanoyl group, a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group, a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0400]

In addition, in a preferred embodiment of the present invention, in the general formulas (1) and (8), R2, R3, R17, R18, and R19 may be the same as or different from one another and represent an acyl group which has from 10 to 22 carbon atoms and a branch but does not contain a ring structure or an acyl group which has from 6 to 9 carbon atoms and two or more branches but does not contain a ring structure.

[0401]

Examples of such an acyl group which is represented by R2, R3, R17, R18, and R19, has from 10 to 22 carbon atoms and a branch, but does not contain a ring structure in a preferred embodiment may include a 2-methylnonanoyl group, a 4-methylnonanoyl group, an 8-methylnonanoyl group, a 4-ethyloctanoyl group, a 2-ethyloctanoyl group, a 2-butylhexanoyl group, a 2-tert-butylhexanoyl group, a 2,2-diethylhexanoyl group), a 2,2-dimethyloctanoyl group, a 3,7-dimethyloctanoyl group, a neodecanoyl group), a 7-methyldecanoyl group, a 2-methyl-2-ethyloctanoyl group, a 2-methylundecanoyl group, a 10-methylundecanoyl group, a 2,2dimethyldecanoyl group, a 2-ethyldecanoyl group, a 2-butyloctanoyl group, a diethyloctanoyl group, a 2-tert-butyl-2,2,4-trimethylpentanoyl group, a 10-methyldodecanoyl group, a 3-methyldodecanoyl group, a 4-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 2-butyldecanoyl group, a 2-hexyloctanoyl group, a 2-butyl-2-ethyloctanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 2-butyldodecanoyl group, a 2-hexyldecanoyl group, a 16-methylheptadecanoyl group, a 2,2-dimethylhexanoyl group, a 2-butylhexadecanoyl group, a 2-hexyldodecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0402]

In addition, examples of the acyl group which is represented by R2, R3, R17, R18, and R19, has from 6 to 9 carbon atoms and two or more branches, but does not contain a ring structure in a preferred embodiment may include a 2,2-dimethylbutanoyl group, a 3,3-dimethylbutanoyl group, a 2,2-dimethylpentanoyl group, a 4,4-dimethylpentanoyl group, a 2,2-dimethylhexanoyl group, a 2,2,3-trimethylpentanoyl

group, and a 3,5,5-trimethylhexanoyl group.

[0403]

The group which is represented by X in the general formula (1) and derived from a trihydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a trihydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a trihydric alcohol selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

[0404]

In addition, the group which is represented by Y in the general formula (8) and derived from a tetrahydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a tetrahydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a tetrahydric alcohol selected from the group consisting of diglycerin, pentaerythritol, erythritol, D-threitol, and L-threitol.

[0405]

In the present invention, it is particularly preferable to use an amphipathic copolymer containing the constitutional unit (1).

In addition, in a more preferred embodiment of the present invention, the hydrophobic monomer represented by the general formula (1) is a hydrophobic monomer represented by the general formula (15).

[0406]

The number of carbon atoms in the acyl group of R24 and R25 in the general formula (15) is from 12 to 22, more preferably from 14 to 20, and still more preferably from 16 to 20.

In addition, the number of carbon atoms in the main chain of the acyl group of R24 and R25 in the general

formula (15) is preferably from 9 to 21, more preferably from 12 to 20, and still more preferably from 16 to 18.

In addition, the number of branches in the acyl group of R24 and R25 in the general formula (15) is preferably from 1 to 3, more preferably 1 or 2, and still more preferably 1.

Furthermore, in the acyl group of R24 and R25 in the general formula (15), it is more preferable as the position number of the carbon atom in the main chain to which a branched chain is bonded is higher. Specifically, the branched chain is bonded preferably to the 1st to 3rd carbon atom, more preferably to the 1st or 2nd carbon atom, and still more preferably to the 1st carbon atom from the carbon atom at the end of the main chain.

[0407]

Specific examples of R24 and R25 may suitably include a 10-methylundecanoyl group, a 10-methyldodecanoyl group, an 11-methyldodecanoyl group, a 10-ethylundecanoyl group, a 12-methyltridecanoyl group, a 12-methyltetradecanoyl group, a 14-methylpentadecanoyl group, a 16-methylheptadecanoyl group, a 2,4,10,14-tetramethylpentanoyl group, an 18-methylnonadecanoyl group, a 3,7,11,15-tetramethylhexadecanoyl group, and a 19-methyleicosanoyl group.

[0408]

The group which is represented by Z in the general formula (15) and derived from a trihydric alcohol is not particularly limited as long as it is a group obtained by eliminating an OH group from a trihydric alcohol, but examples thereof may suitably include a group obtained by eliminating an OH group from a trihydric alcohol selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

[0409]

[2] Hydrophilic Monomer

As the hydrophilic monomer in the present invention, it is possible to use a polymerizable carboxylic acid and compounds represented by the general formulas (2), (9), (10), and (11).

[0410]

(2-1) Polymerizable carboxylic acid

In the present invention, specific examples of the polymerizable carboxylic acid or any salt thereof may include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid, and sodium salts, potassium salts, ammonium salts, and amine salts thereof. Among these, acrylic acid, methacrylic acid, and salts thereof are particularly preferable because of high polymerizability. In the case of introducing a constitutional unit derived from a salt of a polymerizable carboxylic acid into the amphipathic copolymer of the present invention, the polymerizable carboxylic acid may be converted into a salt in advance and the salt may be subjected to a polymerization reaction or a constitutional unit derived from a polymerizable carboxylic acid may be introduced into a amphipathic copolymer by a polymerization reaction and then neutralized with a base into a salt.

[0411]

(2-2) Hydrophilic monomer represented by general formula (2)

In the general formula (2), R4 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms, R5 represents an alkylene group which has from 2 to 4 carbon atoms and may have a hydroxyl group, and R6 represents a hydrogen atom, an aromatic hydrocarbon group having from 6 to 10 carbon atoms, an aliphatic hydrocarbon group having from 1 to 14 carbon atoms, or an acyl group having from 1 to 12 carbon atoms. n represents an integer from 6 to 40.

[0412]

Examples of the alkyl group represented by R4 in the general formula (2) may include a methyl group, an ethyl

group, a propyl group, an isopropyl group, and a cyclopropyl group. In the present invention, R6 is preferably a hydrogen atom or a methyl group.

[0413]

In addition, examples of the alkylene group represented by R5 may include an ethylene group, a propylene group, an isopropylene group, a 2-hydroxypropylene group, a 1-hydroxy-2-methylethylene group, and a 2-hydroxy-1-methylethylene group, and an ethylene group or a propylene group is preferable and an ethylene group is more preferable among these.

[0414]

In addition, among the groups represented by R6, examples of the aromatic group having from 6 to 10 carbon atoms may include a phenyl group, a benzyl group, a methylphenyl group, and an ethylphenyl group; examples of the aliphatic hydrocarbon group having from 1 to 14 carbon atoms may suitably include a methyl group, an ethyl group, a butyl group, a tertiary butyl group, a hexyl group, a cyclohexyl group, an octyl group, a 2-ethylhexyl group, and a lauryl group; and examples of the acyl group having from 1 to 12 carbon atoms may suitably include a formyl group, an acetyl group, a propionyl group, a butyryl group, an isobutyryl group, a valeryl group, and a lauroyl group. Among these, the group represented by R5 is preferably an aliphatic hydrocarbon group having from 1 to 14 carbon atoms and more preferably an alkyl group having from 1 to 12 carbon atoms.

[0415]

Furthermore, n in the general formula (2) is a numerical range of from 6 to 40.

[0416]

Specific examples of the monomer in which R5 is a propylene group among the monomers represented by the general formula (2) may include polypropylene glycol (9)

monoacrylate, polypropylene glycol (13) monoacrylate, polypropylene glycol (9) monomethacrylate, and polypropylene glycol (13) monomethacrylate. Incidentally, the numbers in the parentheses denote N. A large number of these polymers are commercially available. Specific examples of these commercially available products may include "BLEMMER" AP-400, AP-550, AP-800, PP-500, and PP-800 (trade name, all manufactured by NOF CORPORATION).

[0417]

Specific examples of the monomer in which R5 is an ethylene group among the monomers represented by the general formula (2) may include polyethylene glycol (10) monoacrylate, polyethylene glycol (8) monomethacrylate, polyethylene glycol (23) monoacrylate, polyethylene glycol (23) monomethacrylate, methoxypolyethylene glycol (9) acrylate, methoxypolyethylene glycol (9) methacrylate, methoxy polyethylene glycol (23) methacrylate, oleyloxypolyethylene glycol (18) methacrylate, lauroxypolyethylene glycol (18) acrylate, lauroyloxypolyethylene glycol (10) methacrylate, and stearoxypolyethylene glycol (30) monomethacrylate.

[0418]

The hydrophilic monomers described above can be obtained at a high yield by an esterification reaction of the corresponding polyethylene glycol, polyethylene glycol monoether, and polyethylene glycol monoester with a chloride or anhydride of acrylic acid or methacrylic acid. There are also already a large number of commercially available products, and it is also possible to use such commercially available products. Specific examples of such commercially available products may include BLEMMER AE-400, PE-350, AME-400, PME-400, PME-1000, ALE-800, and PSE-1300, (trade name, all manufactured by NOF CORPORATION) and the like.

[0419]

(2-3) Hydrophilic monomer represented by general formula (9)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (9) may be used.

[0420]

Specific examples of the hydrophilic monomer represented by the general formula (9) may include 2-acryloyloxyethyl phosphorylcholine (APC) and 2-methacryloyloxyethyl phosphorylcholine (MPC). These monomers can be synthesized, for example, by the following method described in Polymer Journal, Vol22, No. 5.

<Synthesis method>

After 2-bromoethyl phosphoryl dichloride is reacted with 2-hydroxyethyl methacrylate or 2-hydroxyethyl acrylate to obtain 2-methacryloyloxyethyl-2'-bromoethyl phosphate or 2-acryloyloxyethyl-2'-bromoethyl phosphate, this compound is reacted with triethylamine in methanol.

[0421]

(2-4) Hydrophilic monomer represented by general formula (9)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (10) may be used.

[0422]

In the hydrophilic monomer represented by the general formula (10), specific examples of the reducing sugar of the group which is represented by G-O- and obtained by eliminating a hydrogen atom from the hydroxyl group at the position 1 of a reducing sugar may include one kind or two or more kinds selected from the group consisting of monosaccharides such as glucose, mannose, galactose, arabinose, xylose, and ribose, disaccharides such as maltose, lactose, and cellobiose, trisaccharides such as maltotriose, and oligosaccharides such as maltooligosaccharide, and among these, one kind or two or more kinds selected from the group consisting of glucose,

galactose, arabinose, xylose, ribose, maltose, and lactose cellobiose are preferable and glucose is particularly preferable. In addition, as the monomer represented by the general formula (10), glucosyloxyethyl methacrylate (hereinafter abbreviated as GEMA) or glucosyloxyethyl acrylate (hereinafter abbreviated as GEA) are preferable.

[0423]

(2-5) Hydrophilic monomer represented by general formula (11)

As the hydrophilic monomer in the present invention, a hydrophilic monomer represented by the general formula (11) may be used.

[0424]

In the monomer represented by the general formula (11), the amino acid in the amino acid residue represented by R23 is not particularly limited as long as it is a usually known amino acid, and specific examples thereof may include glycine, alanine, glutamine, lysine, and arginine. Among these, a lysine residue is particularly preferable since the amphipathic copolymer to be obtained exhibits an excellent effect of recovering the skin barrier.

[0425]

In addition, the polyamine in the polyamine residue represented by R23 means an amine having two or more amino groups which may be substituted with an alkyl group in the same molecule, and specific examples thereof may include a diamine, a triamine, a tetraamine, or amines in which hydrogen atoms of these amino groups are substituted with alkyl groups. Among these, a diamine is preferable since the feel of use of the external preparation for skin containing the amphipathic copolymer to be obtained is particularly excellent, and particularly preferred specific examples thereof may include ethylenediamine, 1,4-diamino-n-butane, and 1,6-diamino-n-hexane from the viewpoint of availability of starting materials for synthesis.

[0426]

Furthermore, the amino alcohol in the amino alcohol residue represented by R23 means a compound having an amino group which may be substituted with an alkyl group and an alcoholic hydroxyl group in the same molecule. The amino alcohol is not particularly limited as long as it is usually known, and specific examples thereof may include ethanolamine and triethylaminoethanol.

[0427]

The salt of the monomer represented by the general formula (11) is not particularly limited, but specific examples thereof may include a sodium salt, a potassium salt, an ammonium salt, and an amine salt obtained by neutralizing the acid moiety with a base and a hydrochloride, a sulfate, a nitrate, a phosphate, a citrate, an oxalate, and a carbonate obtained by neutralizing the amino group moiety with an acid. In the case of introducing a constitutional unit derived from a salt of the monomer represented by the general formula (11) into the amphipathic copolymer of the present invention, the monomer represented by the general formula (11) may be converted into a salt in advance and the salt may be subjected to a polymerization reaction or a constitutional unit derived from the monomer represented by the general formula (11) may be introduced into an amphipathic copolymer by a polymerization reaction and then neutralized into a salt.

[0428]

Specific examples of the monomer represented by the general formula (11) and any salt thereof may suitably include the compounds 1 to 11 and salts thereof.

[0429]

The hydrophilic monomer represented by the general formula (11) can be synthesized, for example, by an esterification reaction or an amidation reaction using

(meth)acrylic acid or (meth)acrylic acid chloride as presented in the reaction formulas (1) and (2).

[0430]

As described above, in the present invention, it is possible to use the general formulas (2), (9), (10), and (11) as the hydrophilic polymer.

In a preferred embodiment of the present invention, the amphipathic copolymer contains the constitutional unit (2) derived from the general formula (2).

[0431]

[3] Amphipathic copolymer

In the present invention, it is possible to preferably use an acrylic acid-based amphipathic copolymer having the constitutional unit (1) and the constitutional unit (2). In addition, an acrylic acid-based amphipathic copolymer having the constitutional unit (15) and the constitutional unit (2) is more preferably used.

Among such acrylic acid-based amphipathic copolymers, a (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer is particularly preferably used.

By containing such an acrylic acid-based amphipathic copolymer, it is possible to improve moisture retaining property and flexibility of the coating film.

[0432]

The (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer mainly contains a constitutional unit (i) derived from a hydrophobic monomer in which R24 and R25 are a 16-methylheptadecanoyl group among the hydrophobic monomers represented by the general formula (15) as the constitutional unit (i).

The (methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer also mainly contains a constitutional unit (j) derived from a hydrophilic monomer in which R4 is a methyl group, R5 is an ethylene group, R6 is a methyl group, and n is 23 among the

hydrophilic monomers represented by the general formula (2) as the constitutional unit (j).

[0433]

As the amphipathic copolymer in the present invention, an existing copolymer can be used in addition to the copolymer described above. Specifically, the following existing copolymers can be used as the amphipathic copolymer.

In other words, it is possible to use existing copolymers such as polyquaternium-51 (a copolymer containing 2-methacryloyloxyethyl phosphorylcholine and butyl methacrylate in a molar ratio of about 8 : 2), polyquaternium-61 (a copolymer containing 2-methacryloyloxyethyl phosphorylcholine and stearyl methacrylate in a molar ratio of about 3 : 7), a (glycerylamidoethyl methacrylate/stearyl methacrylate) copolymer (a copolymer which contains glyceryl-N-(2-methacryloyloxyethyl) carbamate and stearyl methacrylate in a molar ratio of about 6 : 4 and has a weight average molecular weight of about 40000), PEG/PPG/polybutylene glycol-8/5/3 glycerin, (hydrolyzed silk/PG propyl methyl silanediol) cross polymer (a silylated copolymer of N-[2-hydroxy-3-[3-(hydroxymethylsilyl)propoxy]propyl] hydrolyzed silk), (eicosanedioic acid/tetradecanedioic acid)polyglyceryl-10 (an oligomeric ester composed of eicosanedioic acid, dibasic acid of tetradecanedioic acid, and polyglycerin having an average polymerization degree of 10), a (glycerin/oxybutylene) copolymer stearyl (a polymer which is obtained by simultaneously reacting glycidol and tetrahydrofuran with stearyl alcohol for addition polymerization and has an HLB of 18.0), polyquaternium-7 (a copolymer of dimethyldiallylammonium chloride and acrylamide), polyquaternium-39 (a terpolymer of acrylic acid, dimethyldiallylammonium chloride, and acrylamide), and a (Na acrylate/acryloyldimethyltaurine) copolymer (a

copolymer of sodium acrylate and sodium acryloyldimethyltaurate).

Among these, particularly preferred examples thereof may include polyquaternium-51, polyquaternium-61, and a (glycerylamidoethyl methacrylate/stearyl methacrylate) copolymer.

[0434]

In the present invention, the proportion of the constitutional unit (i) in the entire constitutional units in the amphipathic copolymer is preferably from 1% to 50% by mass, more preferably from 5% to 40% by mass and from 10% to 30% by mass.

It is possible to improve moisture retaining property and flexibility of the coating film of the present invention by setting the proportion of the constitutional unit (i) in the amphipathic copolymer to be in the above range.

[0435]

In the present invention, the proportion of the constitutional unit (j) in the entire constitutional units in the amphipathic copolymer is preferably from 50% to 99% by mass, more preferably from 60% to 95% by mass and from 70% to 90% by mass.

It is possible to improve moisture retaining property and flexibility of the coating film of the present invention by setting the proportion of the constitutional unit (j) in the amphipathic copolymer to be in the above range.

[0436]

In the present invention, the mass ratio of the constitutional unit (i) constituting the amphipathic copolymer to the constitutional unit (j) constituting the amphipathic copolymer is preferably from 5 : 95 to 50 : 50, more preferably from 10 : 90 to 45 : 55, still more preferably from 20 : 80 to 40 : 60, and still more

preferably from 25 : 75 to 35 : 65.

It is possible to improve moisture retaining property and flexibility of the coating film of the present invention by setting the mass ratio of the constitutional unit (i) to the constitutional unit (j) in the amphipathic copolymer to be in the above range.

[0437]

In the present invention, the molar ratio of the constitutional unit (i) constituting the amphipathic copolymer to the constitutional unit (j) constituting the amphipathic copolymer is preferably from 8 : 92 to 62 : 38, more preferably from 15 : 85 to 57 : 43, still more preferably from 29 : 71 to 52 : 48, and still more preferably from 35 : 65 to 46 : 54.

It is possible to improve moisture retaining property and flexibility of the coating film of the present invention by setting the molar ratio of the constitutional unit (i) to the constitutional unit (j) in the amphipathic copolymer to be in the above range.

[0438]

In the present invention, the average molecular weight of the amphipathic copolymer is preferably from 20,000 to 110,000, more preferably from 20,000 to 80,000, more preferably from 30,000 to 80,000, more preferably from 40,000 to 70,000, still more preferably from 50,000 to 70,000, and still more preferably from 57,000 to 66,000.

It is possible to improve the elasticity and to suppress the sticky feel of the coating film of the present invention by setting the molecular weight of the amphipathic copolymer to be in the above range.

Incidentally, the average molecular weight here refers to the weight average molecular weight in terms of polystyrene measured by GPC.

[0439]

<1-2> Sea phase

The island particles described above are dispersed in the sea phase of the aqueous gel. In the present invention, the aqueous gel is formed by a water-soluble polymer and/or any salt thereof and water hydrating the water-soluble polymer.

The water-soluble polymer and/or any salt thereof which form the aqueous gel are not particularly limited as long as they can disperse the phase containing the amphipathic copolymer as island particles, but it is possible to preferably use one kind or two or more kinds of water-soluble polymers selected from the group consisting of an acrylic acid-based water-soluble polymer, a water-soluble polypeptide, and a water-soluble polysaccharide and/or salts thereof.

[0440]

Examples of the acrylic acid-based water-soluble polymer may particularly preferably include a non-crosslinked type acrylic acid-based polymer or an acrylic acid-based copolymer which may be crosslinked. In addition, examples of the non-crosslinked type acrylic acid-based polymer may preferably include sodium polyacrylate, and examples of the acrylic acid-based copolymer which may be crosslinked may preferably include sodium polyacrylate and a (acrylates/(C10-30) alkyl acrylate) crosspolymer.

Examples of the water-soluble polypeptide may preferably include sodium polyglutamate.

Examples of the water-soluble polysaccharide may preferably include xanthan gum and Tremella fuciformis polysaccharide. Xanthan gum is particularly preferably used as the water-soluble polysaccharide.

It is possible to improve moisture retaining property and flexibility of the coating film of the present invention by using such a water-soluble polymer and/or any salt thereof.

[0441]

<1-3> Sea-island structure

The coating film of the present invention has a sea-island structure in which an island phase containing an amphipathic copolymer is dispersed in a sea phase containing an aqueous gel.

In the coating film of the present invention having a sea-island structure, the area ratio of the sea phase to the island phase is preferably from 2 : 8 to 10 : 1, more preferably from 3 : 7 to 9 : 1, and still more preferably from 6 : 4 to 7 : 3.

The coating film of the present invention having an area ratio of the sea phase to the island phase in the above range exhibits excellent elasticity, moisture retaining property, and flexibility and less stickiness.

[0442]

In a preferred embodiment of the present invention, the average ratio of major axis to minor axis of the island particles is preferably 0.6 or more, more preferably 0.7 or more, still more preferably 0.8 or more, and still more preferably 0.9 or more.

It is possible to improve moisture retaining property and flexibility of the coating film of the present invention by setting the average ratio of major axis to minor axis of the island particles to be in the above range.

Incidentally, the average ratio of major axis to minor axis can be measured by observing the composition under a microscope. Specifically, it can be determined by observing the composition under a microscope, measuring the ratio of major axis to minor axis of 100 island particles, and arithmetically averaging these values.

[0443]

In addition, in a preferred embodiment of the present invention, the abundance ratio of island particles having a ratio of major axis to minor axis of less than 0.6, more preferably less than 0.7, and more preferably less than 0.8

in the entire island particles to be contained in the coating film is 10% or less.

In addition, in a more preferred embodiment of the present invention, the abundance ratio of island particles having a ratio of major axis to minor axis of less than 0.8 in the entire island particles to be contained in the coating film is 5% or less and more preferably 1% or less.

The coating film of the present invention of such an embodiment exhibits superior moisture retaining property and flexibility.

[0444]

In a preferred embodiment of the present invention, the number particle size distribution of island particles having an average particle diameter of from 0.5 to 10 μm and more preferably island particles having an average particle diameter of from 1 to 5 μm is 80% or more.

In addition, in a still more preferred embodiment of the present invention, the number particle size distribution of island particles having an average particle diameter of from 1 to 5 μm is 85% or more and more preferably 90% or more.

It is possible to further improve moisture retaining property and flexibility of the coating film of the present invention by setting the number particle size distribution of the island particles having such a small particle diameter to be in the above range.

Incidentally, the average particle diameter of the island particles can be measured by observing the composition under a microscope. Specifically, it can be determined by measuring the major axis and the minor axis of the island particles through microscopic observation of the composition and arithmetically averaging these values.

[0445]

The coating film of the present invention can contain arbitrary components to be usually used in an external

preparation for skin. Examples of such components may include oils and waxes, hydrocarbons, higher fatty acids, higher alcohols, synthetic ester oils, silicone-based oil agents, surfactants, polyhydric alcohols, moisturizing components, thickeners, powders, inorganic pigments, organic pigments, organic powders, ultraviolet absorbers, lower alcohols, vitamins, and a polymer having a structure analogous to a living body.

[0446]

Examples of oils and waxes may include macadamia nut oil, avocado oil, corn oil, olive oil, rapeseed oil, sesame oil, castor oil, safflower oil, cottonseed oil, jojoba oil, coconut oil, palm oil, liquid lanolin, hardened coconut oil, hardened oil, vegetable wax, hardened castor oil, beeswax, candelilla wax, carnauba wax, insects wax, lanolin, reduced lanolin, hard lanolin, and jojoba wax, and

examples of hydrocarbons may include liquid paraffin, squalane, pristane, ozokerite, paraffin, ceresin, petroleum jelly, and microcrystalline wax.

[0447]

Examples of higher fatty acids may include oleic acid, isostearic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, and undecylenic acid,

examples of higher alcohols may include cetyl alcohol, stearyl alcohol, isostearyl alcohol, behenyl alcohol, octyldodecanol, myristyl alcohol, and cetostearyl alcohol,

examples of synthetic ester oils may include cetyl isooctanoate, isopropyl myristate, hexyldecyl isostearate, diisopropyl adipate, di-2-ethylhexyl sebacate, cetyl lactate, diisostearyl malate, ethylene glycol di-2-ethylhexanoate, neopentyl glycol dicaprate, glycerin di-2-heptylundecanoate, glycerin tri-2-ethylhexanoate, trimethylolpropane tri-2-ethylhexanoate, trimethylolpropane triisostearate, and pentaneerythritol tetra-2-ethylhexanoate, and

examples of silicone-based oil agents may include silicone oils such as chain polysiloxanes such as dimethylpolysiloxane, methylphenylpolysiloxane, and diphenylpolysiloxane, cyclic polysiloxanes such as octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and dodecamethylcyclohexanesiloxane, and modified polysiloxanes such as amino-modified polysiloxane, polyether-modified polysiloxane, alkyl-modified polysiloxane, and fluorine-modified polysiloxane.

[0448]

The surfactants may be either anionic surfactants or nonionic surfactants.

Examples of anionic surfactants may include fatty acid soap (sodium laurate, sodium palmitate, and the like), potassium lauryl sulfate, and triethanolamine alkyl ether sulfate, and

examples of nonionic surfactants may include sorbitan fatty acid esters (sorbitan monostearate, sorbitan sesquioleate, and the like), glycerin fatty acids (glyceryl monostearate and the like), propylene glycol fatty acid esters (propylene glycol monostearate and the like), hardened castor oil derivatives, glycerin alkyl ether, POE sorbitan fatty acid esters (POE sorbitan monooleate, polyoxyethylene sorbitan monostearate and the like), POE sorbitol fatty acid esters (POE-sorbitol monolaurate and the like), POE glycerin fatty acid esters (POE-glycerin monoisostearate and the like), POE fatty acid esters (polyethylene glycol monooleate, POE distearate, and the like), POE alkyl ethers (POE 2-octyl dodecyl ether and the like), POE alkyl phenyl ethers (POE nonyl phenyl ether and the like), Pluronic type nonionic surfactants, POE·POP alkyl ethers (POE·POP 2-decyltetradecyl ether and the like), Tetronics, POE castor oil · hardened castor oil derivatives (POE castor oil, POE hardened castor oil, and the like), sucrose fatty acid esters, and alkyl glucosides.

[0449]

Examples of polyhydric alcohols may include polyethylene glycol, erythritol, xylitol, propylene glycol, dipropylene glycol, isoprene glycol, 1,2-pentanediol, 2,4-hexylene glycol, 1,2-hexanediol, and 1,2-octanediol,

examples of moisturizing components may include sodium pyrrolidone carboxylate, lactic acid, and sodium lactate, and

examples of thickeners may include guar gum, quince seed, carrageenan, galactan, gum arabic, pectin, mannan, starch, curdlan, methylcellulose, hydroxyethylcellulose, carboxymethylcellulose, methylhydroxypropylcellulose, chondroitin sulfate, dermatan sulfate, glycogen, heparan sulfate, hyaluronic acid, sodium hyaluronate, tragacanth gum, keratan sulfate, chondroitin, mucoitin sulfate, hydroxyethyl guar gum, carboxymethyl guar gum, dextran, keratosulfate, locust bean gum, succinoglucan, caloninic acid, chitin, chitosan, carboxymethyl chitin, agar, polyvinyl alcohol, polyvinyl pyrrolidone, carboxyvinyl polymer, polyethylene glycol, and bentonite.

[0450]

Examples of powders may include mica, talc, kaolin, synthetic mica, calcium carbonate, magnesium carbonate, anhydrous silicic acid (silica), aluminum oxide, and barium sulfate which may have a treated surface,

examples of inorganic pigments may include red iron oxide, yellow iron oxide, black iron oxide, cobalt oxide, ultramarine blue, iron blue, titanium oxide, and zinc oxide which may have a treated surface,

examples of organic coloring matters may include pearlescent agents such as titanium mica, fish phosphorus foil, and bismuth oxychloride which may have a treated surface and Red No. 202, Red No. 228, Red No. 226, Yellow No. 4, Blue No. 404, Yellow No. 5, Red No. 505, Red No. 230, Red No. 223, Orange No. 201, Red No. 213, Yellow No. 204,

Yellow No. 203, Blue No. 1, Green No. 201, Purple No. 201, and Red No. 204 which may be laked, and

examples of organic powders may include polyethylene powder, polymethyl methacrylate, nylon powder, and organopolysiloxane elastomer.

[0451]

Examples of ultraviolet absorbers may include a p-aminobenzoic acid-based ultraviolet absorber, an anthranilic acid-based ultraviolet absorber, a salicylic acid-based ultraviolet absorber, a cinnamic acid-based ultraviolet absorber, a benzophenone-based ultraviolet absorber, a saccharide-based ultraviolet absorber, 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole, and 4-methoxy-4'-t-butyldibenzoylmethane,

examples of lower alcohols may include ethanol, isopropanol, and phenoxyethanol, and

examples of vitamins may preferably include vitamin A or any derivative thereof, vitamin B family such as vitamin B6 hydrochloride, vitamin B6 tripalmitate, vitamin B6 dioctanoate, vitamin B2 or any derivative thereof, vitamin B12, and vitamin B15 or any derivative thereof, vitamin E family such as α-tocopherol, β-tocopherol, γ-tocopherol, and vitamin E acetate, vitamin D family, vitamin H, pantothenic acid, pantethine, and pyrroloquinoline quinone.

Examples of a polymer having a structure analogous to a living body may include poly(methacryloyl lysine) and poly(glycosyl ethyl methacrylate).

[0452]

In the present invention, the content of the oil agents such as oils and waxes, hydrocarbons, higher fatty acids, higher alcohols, synthetic ester oils, and silicone-based oil agents is set to preferably 10% by mass or less, more preferably 5% by mass or less, still more preferably 2.5% by mass or less, still more preferably 2% by mass or less, still more preferably 1% by mass or less, and still

more preferably 0.5% by mass or less.

In addition, in a preferred embodiment of the present invention, an oil agent is not contained.

The coating film of the present invention having a sea-island structure can exert feel of use like milk containing an oil agent even though it contains an aqueous component as a main component.

Hence, the coating film of the present invention having a sea-island structure can be formed into an oil-free form.

[0453]

In addition, in the present invention, the content of the surfactant is set to preferably 10% by mass or less, more preferably 5% by mass or less, still more preferably 2.5% by mass or less, still more preferably 2% by mass or less, still more preferably 1% by mass or less, and still more preferably 0.5% by mass or less.

In addition, in a preferred embodiment of the present invention, a surfactant is not contained.

The coating film of the present invention can form a stable sea-island structure even without containing a surfactant.

Hence, the coating film of the present invention having a sea-island structure can be formed into a surfactant-free form.

[0454]

<2> Composition to form coating film

The present invention also relates to a composition capable of forming the coating film of the present invention having a sea-island structure described above on the skin by being applied to the skin.

The composition of the present invention contains the amphipathic copolymer and water-soluble polymer and/or any salt thereof described above and water.

By being applied to the skin, the water in the

composition evaporates and the amphipathic copolymer and the water-soluble polymer undergo phase separation. As a result of this phase separation, the coating film of the present invention is formed on the skin. Incidentally, after the phase separation, the water and polyol in the composition are incorporated into the aqueous gel formed by the water-soluble polymer.

Hereinafter, the composition of the present invention will be described in more detail. Incidentally, with regard to the composition of the present invention, the matters on the coating film of the present invention described in the section <1> above can be applied.

[0455]

In the composition of the present invention, the content of the amphipathic copolymer is preferably from 0.01% to 10% by mass, more preferably from 0.05% to 7% by mass, still more preferably from 0.1% to 5% by mass, and still more preferably from 0.5% to 3% by mass.

According to the composition of the present invention having a content of the amphipathic copolymer in the above range, it is possible to form a coating film exhibiting excellent elasticity and less stickiness on the skin.

[0456]

In the present invention, the proportion of the water-soluble polymer in the entire composition is preferably from 0.001% to 10% by mass, more preferably from 0.005% to 5% by mass, still more preferably from 0.01% to 1% by mass, and still more preferably from 0.05% to 0.5% by mass.

According to the composition of the present invention having a content of the water-soluble polymer in the above range, it is possible to form a coating film exhibiting excellent moisture retaining property and flexibility on the skin.

[0457]

In a preferred embodiment of the present invention, the ratio of the mass of the water-soluble polymer contained to the mass of the amphipathic copolymer contained is preferably from 1 : 100 to 1 : 2, more preferably from 1 : 50 to 1 : 5, still more preferably from 1 : 30 to 1 : 10, and still more preferably from 1 : 25 to 1 : 15.

According to the composition of the present invention in which the ratio of the mass of the water-soluble polymer contained to the mass of the amphipathic copolymer contained is in the above range, it is possible to form a coating film exhibiting high uniformity.

[0458]

In the present invention, it is preferable to contain a polyol which promotes/suppresses separation between the sea phase and the island phase.

In other words, in a preferred embodiment of the present invention, a polyol which promotes phase separation between the aqueous gel and the amphipathic copolymer (hereinafter also referred to as the promoting polyol) and/or a polyol which suppresses phase separation between the aqueous gel and the amphipathic copolymer (hereinafter also referred to as the suppressing polyol). In addition, it is particularly preferable to contain both the promoting polyol and the suppressing polyol.

According to the composition of the present invention containing such polyols, it is possible to form a coating film having a sea-island structure and high uniformity on the skin.

[0459]

Examples of the promoting polyol may preferably include a polyol which increases the cloud point of the aqueous solution by being mixed with an aqueous solution of a nonionic surfactant having a polyether chain at the hydrophilic moiety. Examples of such a promoting polyol

may preferably include 1,3-butylene glycol and polyethylene glycol.

It is possible to form a coating film exhibiting higher uniformity by using such a polyol.

[0460]

In the present invention, the content of the promoting polyol in the entire composition of the present invention is preferably from 0.1% to 30% by mass, more preferably from 1% to 25% by mass, still more preferably from 3% to 20% by mass, and still more preferably from 5% to 15% by mass.

It is possible to further improve the uniformity of the coating film to be formed by setting the content of the promoting polyol in the entire composition of the present invention to be in the above range.

[0461]

Examples of the suppressing polyol may preferably include a polyol which decreases the cloud point of the aqueous solution by being mixed with an aqueous solution of a nonionic surfactant having a polyether chain at the hydrophilic moiety. Examples of such a suppressing polyol may preferably include glycerin, diglycerin, sorbitol, and maltitol.

It is possible to form a coating film exhibiting higher uniformity by using such a polyol.

[0462]

The content of the suppressing polyol in the entire composition of the present invention is preferably from 0.5% to 30% by mass, more preferably from 1% to 25% by mass, still more preferably from 5% to 20% by mass, and still more preferably from 8% to 15% by mass.

It is possible to further improve the uniformity of the coating film to be formed by setting the content of the suppressing polyol to be in the above range.

[0463]

Incidentally, in the present invention, the term "cloud point" refers to a temperature at which phase separation takes place in a transparent or translucent liquid due to a change in temperature and, as a result, the liquid becomes opaque, and it particularly refers to a temperature at which the solute begins to separate from water when an aqueous solution of a nonionic surfactant is heated.

Whether the cloud point of an aqueous solution of a nonionic surfactant having a polyether chain at the hydrophilic moiety is increased or decreased can be specifically confirmed by the following method.

The aqueous solution of a nonionic surfactant having a polyether chain at the hydrophilic moiety is heated and the temperature at which the aqueous solution begins to become cloudy, namely, the cloud point is recorded. Next, a polyol is added to the aqueous solution and the mixture is heated, and the cloud point is recorded in the same manner.

It is evaluated that the polyol added "has increased the cloud point of the aqueous solution" in a case in which the cloud point of the aqueous solution after addition of the polyol is higher than that of the aqueous solution before addition of the polyol.

On the contrary, it is evaluated that the polyol added "has decreased the cloud point of the aqueous solution" in a case in which the cloud point of the aqueous solution after addition of the polyol is lower than that of the aqueous solution before addition of the polyol.

[0464]

Examples of the nonionic surfactant having a polyether chain at the hydrophilic moiety to be used in the measurement of cloud point described above may preferably include a nonionic surfactant having polyethylene glycol at the hydrophilic moiety.

Specific examples of such a nonionic surfactant may include polyoxyethylene oleyl ether (POE (n) OE, n = 3, 10, 15, 20, and 23) (manufactured by Nihon Emulsion Co., Ltd.), POE (20) sorbitan monostearate (manufactured by TOHO CHEMICAL INDUSTRY Co., Ltd.), POE (20) glycerin monostearate (manufactured by RIKEN VITAMIN Co., Ltd.), POE (10) monostearate (manufactured by Nikko Chemicals Co., Ltd.), and polyglyceryl (6) monolaurate (manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.).

[0465]

In the present invention, the mass ratio of the promoting polyol to the suppressing polyol is preferably from 10 : 1 to 1 : 10, more preferably from 6 : 1 to 1 : 5, still more preferably from 4 : 1 to 1 : 3, still more preferably from 3.5 : 1 to 1 : 2.5, and still more preferably from 1.6 : 1 to 1 : 1.

It is possible to provide a composition capable of forming a coating film having a highly stable sea-island structure by setting the mass ratio of the promoting polyol to the suppressing polyol to be in the above range.

[0466]

In the present invention, the ratio of the total mass of the promoting polyol and the suppressing polyol to the mass of the amphipathic copolymer contained is preferably from 5 : 1 to 20 : 1, more preferably from 7 : 1 to 15 : 1, and still more preferably from 8 : 1 to 12 : 1.

It is possible to provide a composition having a highly stable sea-island structure by setting the ratio of the total mass of the promoting polyol and the suppressing polyol to the mass of the amphipathic copolymer to be in the above range.

[0467]

In addition, in the present invention, the ratio of the total mass of the promoting polyol and the suppressing polyol to the total mass of the amphipathic copolymer and

the water-soluble polymer is preferably from 5 : 1 to 20 : 1, more preferably from 7 : 1 to 15 : 1, and still more preferably from 8 : 1 to 12 : 1.

It is possible to provide a composition having a highly stable sea-island structure by setting the ratio of the total mass of the promoting polyol and the suppressing polyol to the mass of the amphipathic copolymer to be in the above range.

[0468]

In a preferred embodiment of the present invention, the content of the promoting polyol in the total amount of three components of the promoting polyol, the suppressing polyol, and the amphipathic copolymer is preferably from 10% to 80% by mass, more preferably from 20% to 70% by mass, still more preferably from 30% to 70% by mass, still more preferably from 40% to 60% by mass, and still more preferably from 40% to 55% by mass.

It is possible to prevent the occurrence of precipitation in the composition and to improve the stability of the composition by setting the content of the promoting polyol to be in the above range. In addition, a composition in such a form can form a coating film exhibiting excellent moisture retaining property and flexibility.

[0469]

In addition, in a preferred embodiment of the present invention, the content of the suppressing polyol in the total amount of the three components of the promoting polyol, the suppressing polyol, and the amphipathic copolymer is preferably from 10% to 80% by mass, more preferably from 20% to 70% by mass, more preferably from 30% to 60% by mass, and still more preferably from 35% to 50% by mass.

It is possible to prevent the occurrence of precipitation in the composition and to improve the

stability of the composition by setting the content of the suppressing polyol to be in the above range. In addition, a composition in such a form can form a coating film exhibiting excellent moisture retaining property and flexibility.

[0470]

In addition, in a preferred embodiment of the present invention, the content of the amphipathic copolymer in the total amount of the three components of the promoting polyol, the suppressing polyol, and the amphipathic copolymer is preferably from 1% to 50% by mass, more preferably from 3% to 20% by mass, still more preferably from 5% to 15% by mass, and still more preferably from 8% to 12% by mass.

It is possible to provide a composition exhibiting viscosity to facilitate application of the composition to the skin by setting the content of the amphipathic copolymer to be in the above range. In addition, a composition in such a form can form a coating film exhibiting excellent moisture retaining property and flexibility.

[0471]

In a preferred embodiment of the present invention, the content of the promoting polyol is from 20% to 70% by mass, the content of the suppressing polyol is from 20% to 70% by mass, and the content of the amphipathic copolymer is from 5% to 20% by mass in the total amount of the three components of the promoting polyol, the suppressing polyol, and the amphipathic copolymer.

It is possible to improve stability of the composition by adopting such an embodiment.

[0472]

In addition, by adjusting the content of the promoting polyol, the content of the suppressing polyol, and the content of the amphipathic copolymer in the total

amount of the three components of the promoting polyol, the suppressing polyol, and the amphipathic copolymer to be in the above ranges, it is possible to adjust the ratio of major axis to minor axis and average particle diameter of the island particles in the coating film to be formed by the composition of the present invention to be in the preferred ranges described in the section <1-3>.

[0473]

The composition of the present invention can be produced by stirring and mixing the starting materials at room temperature.

[0474]

The content of water in the composition of the present invention is preferably from 60% to 99% by mass, more preferably from 70% to 95% by mass, and still more preferably from 80% to 90% by mass.

It is possible to easily form the coating film of the present invention on the skin by applying the composition of the present invention having a content of water in the above range to the skin.

[0475]

<3> Method of forming coating film on skin

The present invention also relates to a method of forming the coating film of the present invention described above on the skin.

The method of the present invention is characterized in that the composition of the present invention is applied to the skin. The phase separation between the aqueous gel formed by the water-soluble polymer and the amphipathic copolymer takes place as the water in the composition evaporates by application. As a result of this phase separation, the coating film of the present invention having a sea-island structure can be formed on the skin.

[0476]

In the present invention, it is preferable to use an

aqueous solution containing a polyol which promotes phase separation between the amphipathic copolymer and the aqueous gel and/or a polyol which suppresses phase separation between the aqueous gel and the amphipathic copolymer.

It is possible to form a coating film exhibiting excellent uniformity on the skin by using such an aqueous solution.

[0477]

In addition, in the composition of the present invention, the content of the oil agents such as oils and waxes, hydrocarbons, higher fatty acids, higher alcohols, synthetic ester oils, and silicone-based oil agents is set to preferably 2% by mass or less, still more preferably 1% by mass or less, and still more preferably 0.5% by mass or less.

In addition, in a preferred embodiment of the present invention, an oil agent is not contained.

[0478]

In addition, in the composition of the present invention, the content of the surfactant is set to preferably 2% by mass or less, still more preferably 1% by mass or less, and still more preferably 0.5% by mass or less.

In addition, in a preferred embodiment of the present invention, a surfactant is not contained.

[0479]

Preferred forms of the composition and coating film in the method of the present invention are as described in the sections <1> and <2>.

Examples

[0480]

<1> Synthesis of hydrophobic monomer

Hereinafter, Production Examples of a hydrophobic

monomer represented by the general formula (1) will be described.

(Production Example 1) Synthesis of glyceryl monoacrylate

In a 3 L four-necked flask, 79.5 g of R)-(+)-2,2-dimethyl-1,3-dioxolane-4-methanol (manufactured by Tokyo Chemical Industry Co., Ltd.), 258.0 g of methyl acrylate, 3.7 g of tetramethoxy titanium were charged. Thereafter, the reaction liquid was stirred and subjected to the transesterification reaction at from 105°C to 110°C for 2.5 hours while introducing nitrogen gas into the liquid. After the reaction was completed, a ketal acrylate 1 (intermediate 1) was obtained by fractionation through distillation under reduced pressure.

[0481]

In a 3 L four-necked flask, 90.2 g of water, 28.4 ml of cation exchange resin RCP 160M (manufactured by Mitsubishi Chemical Corporation) and 94.2 g of the intermediate 1 were charged. Thereafter, the reaction liquid was stirred and subjected to a reaction for removal of ketone of the ketal at 24°C for 27 hours while introducing nitrogen gas into the liquid. After the reaction was completed, the cation exchange resin was filtered off from the reaction mixture, and the reaction mixture thus filtered was washed six times with 100 ml of hexane to remove the unreacted starting materials, and 200 ml of ethyl acetate was then added to the aqueous layer to extract the product. Thereafter, ethyl acetate and water were distilled off from this liquid extracted with ethyl acetate at 40°C or lower under reduced pressure (800 Pa), thereby obtaining glyceryl monoacrylate.

[0482]

(Production Example 2) Synthesis of trimethylolpropane monoacrylate

Step (1): In an eggplant type flask equipped with a calcium tube, a cooling tube, and a Dean-Stark trap, 145.7

g of trimethylolpropane, 300 ml of acetone, 3 g of p-toluenesulfonic acid monohydrate, and 300 ml of petroleum ether were added and heated and refluxed in an oil bath set at 50°C. After 12 hours, it was confirmed that water was not newly generated any more, and the reaction mixture was then cooled to room temperature. Subsequently, 3 g of sodium acetate was added thereto, the mixture was further stirred for 30 minutes, and the petroleum ether and acetone were then distilled off by using an evaporator. The crude product thus obtained was distilled under reduced pressure, thereby obtaining ketalized trimethylolpropane (intermediate 2).

[0483]

Step (2): Into a 3 L four-necked flask, 104.8 g of the intermediate 2 obtained in the step (1), 258.0 g of methyl acrylate, and 3.7 g of tetramethoxy titanium were charged. Thereafter, the reaction liquid was stirred and subjected to the transesterification reaction at from 105°C to 110°C for 2.5 hours while introducing nitrogen gas into the liquid. After the reaction was completed, an acrylic acid ester of ketalized trimethylolpropane (intermediate 3) was obtained by fractionation through distillation under reduced pressure.

[0484]

Step (3): Into a 3 L four-necked flask, 90.2 g of water, 28.4 ml of cation exchange resin RCP 160M (manufactured by Mitsubishi Chemical Corporation), and 115.3 g of the intermediate 3 obtained in the step (2) were charged. Thereafter, the reaction liquid was stirred and subjected to a reaction for removal of ketone of the ketal at 24°C for 27 hours while introducing nitrogen gas into the liquid. After the reaction was completed, the cation exchange resin was filtered off from the reaction mixture, and the reaction mixture thus filtered was washed six times with 100 ml of hexane to remove the unreacted starting

materials, and 200 ml of ethyl acetate was then added to the aqueous layer to extract the product. Thereafter, ethyl acetate and water were distilled off from this liquid extracted with ethyl acetate at 40°C or lower under reduced pressure (800 Pa), thereby obtaining trimethylolpropane monoacrylate.

[0485]

(Production Example 3) Synthesis of trimethylolpropane monomethacrylate

Trimethylolpropane monomethacrylate was synthesized by conducting the same operation as in Production Example 2 except that trimethylolpropane, methyl acrylate (acrylate), the charged amount of the intermediate obtained in the step (1), and the charged amount of the intermediate obtained in the step (2) were changed as presented in Table 1 in Production Example 2. The trihydric alcohol and the charged amount thereof, the intermediate obtained in the step (1) and the charged amount thereof, and the intermediate obtained in the step (2) and the charged amount thereof are presented in Table 1.

[0486]

[Table 1]

	Trihydric alcohol	Acrylate	Intermediate obtained in step (1)		Compound obtained in step (2)		Trihydric alcohol mono(meth)acrylate obtained
				Charged amount in step (2)		Charged amount in step (3)	
Production Example 3	Trimethylolethane 130.4 g	Methyl methacrylate 300.0 g	Intermediate 4	96.5 g	Intermediate 5	115.3 g	Trimethylolethane monomethacrylate

[0487]

(Production Example 4) Production Example Part 1 of hydrophobic monomer represented by general formula (1)

In a reaction vessel equipped with a stirrer and a cooling tube, 28.4 g of 16-methylheptadecanoic acid (manufactured by Sigma-Aldrich Co. LLC.), 35.7 g of thionyl chloride (manufactured by Tokyo Chemical Industry Co., Ltd.), and 200 ml of benzene were taken and stirred and

mixed. The mixture was refluxed for 4 hours while being continuously stirred and then subjected to purification through distillation under reduced pressure, thereby obtaining 16-methylheptadecanoic acid chloride.

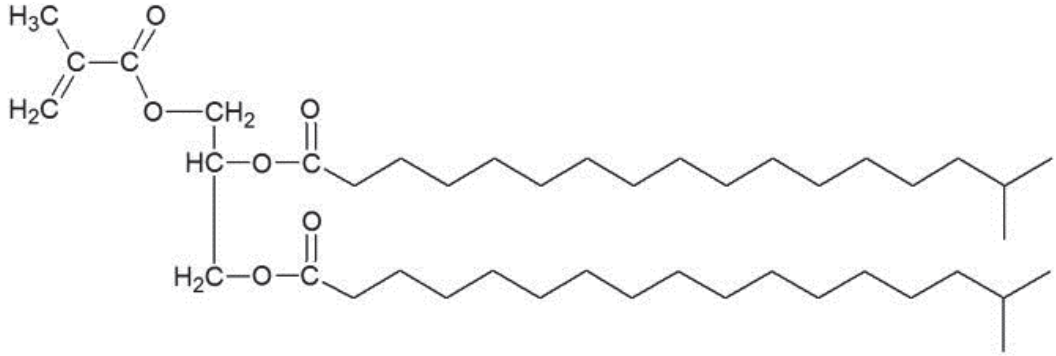
[0488]

In a reaction vessel equipped with a stirring device, 16.0 g of glycerol monomethacrylate ("BLEMMER GLM" manufactured by NOF CORPORATION) and 30.0 g of triethylamine were dissolved in 300 ml of tetrahydrofuran. While ice cooling and stirring the solution thus obtained, a solution prepared by dissolving 60.6 g of 16-methylheptadecanoic acid chloride obtained above in 100 ml of tetrahydrofuran was added to the solution dropwise over 2 hours. After the dropwise addition was completed, the white precipitate thus generated was filtered, and tetrahydrofuran and triethylamine were removed from the filtrate by using a rotary evaporator, thereby obtaining a product. It has been confirmed by NMR measurement that the compound thus obtained is a hydrophobic monomer (hydrophobic monomer 1) which is represented by the following formula (29) and from which an essential constitutional unit of the copolymer of the present invention is derived.

[0489]

Hydrophobic monomer 1

[Chemical Formula 29]



Formula (29)

[0490]

(Production Example 5) Production Example Part 2 of hydrophobic monomer represented by general formula (1)

In a reaction vessel equipped with a stirrer and a cooling tube, 25.6 g of 2-hexyldecanoic acid (manufactured by Sigma-Aldrich Co. LLC.), 35.7 g of thionyl chloride (manufactured by Tokyo Chemical Industry Co., Ltd.), and 200 ml of benzene were taken and stirred and mixed. The mixture was refluxed for 4 hours while being continuously stirred and then subjected to purification through distillation under reduced pressure, thereby obtaining 2-hexyldecanoic acid chloride.

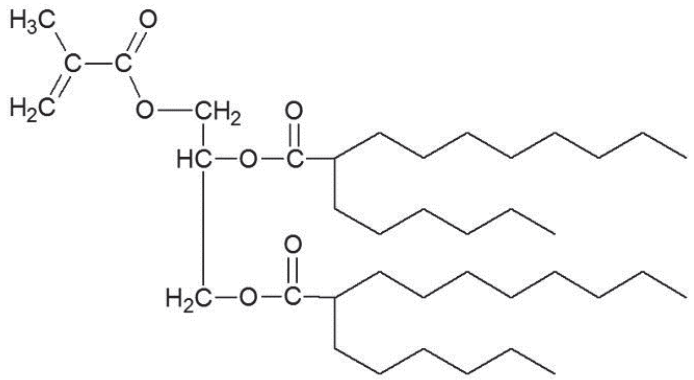
[0491]

In a reaction vessel equipped with a stirring device, 16.0 g of glycerol monomethacrylate ("BLEMMER GLM" manufactured by NOF CORPORATION) and 30.0 g of triethylamine were dissolved in 300 ml of tetrahydrofuran. While ice cooling and stirring the solution thus obtained, a solution prepared by dissolving 55.0 g of 2-hexyldecanoic acid chloride obtained above in 100 ml of tetrahydrofuran was added to the solution dropwise over 2 hours. After the dropwise addition was completed, the white precipitate thus generated was filtered, and tetrahydrofuran and triethylamine were removed from the filtrate by using a rotary evaporator, thereby obtaining a product. It has been confirmed by NMR measurement that the compound thus obtained is a hydrophobic monomer (hydrophobic monomer 2) which is represented by the following formula (30) and from which an essential constitutional unit of the copolymer of the present invention is derived.

[0492]

Hydrophobic monomer 2

[Chemical Formula 30]



Formula (30)

[0493]

(Production Example 6) Production Example Part 3 of hydrophobic monomer represented by general formula (1)

In a reaction vessel equipped with a stirrer and a cooling tube, 28.4 g of 9-methylheptadecanoic acid (manufactured by Sigma-Aldrich Co. LLC.), 35.7 g of thionyl chloride (manufactured by Tokyo Chemical Industry Co., Ltd.), and 200 ml of benzene were taken and stirred and mixed. The mixture was refluxed for 4 hours while being continuously stirred and then subjected to purification through distillation under reduced pressure, thereby obtaining 9-methylheptadecanoic acid chloride.

[0494]

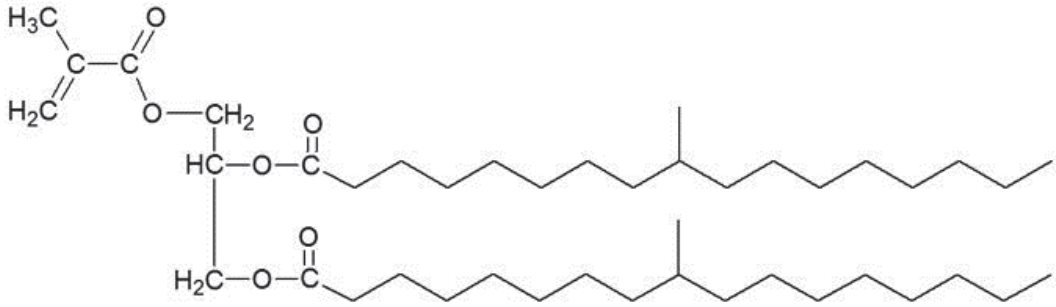
In a reaction vessel equipped with a stirring device, 16.0 g of glycerol monomethacrylate ("BLEMMER GLM" manufactured by NOF CORPORATION) and 30.0 g of triethylamine were dissolved in 300 ml of tetrahydrofuran. While ice cooling and stirring the solution thus obtained, a solution prepared by dissolving 60.6 g of 9-methylheptadecanoic acid chloride obtained above in 100 ml of tetrahydrofuran was added to the solution dropwise over 2 hours. After the dropwise addition was completed, the white precipitate thus generated was filtered, and tetrahydrofuran and triethylamine were removed from the filtrate by using a rotary evaporator, thereby obtaining a

product. It has been confirmed by NMR measurement that the compound thus obtained is a hydrophobic monomer (hydrophobic monomer 3) which is represented by the following formula (31) and from which an essential constitutional unit of the copolymer of the present invention is derived.

[0495]

Hydrophobic monomer 3

[Chemical Formula 31]



Formula (31)

[0496]

<2> Synthesis of copolymer of present invention

(1) Synthesis of copolymers of Example 1 and Comparative Example 1

In a flask equipped with a nitrogen introducing tube, a condenser, and a stirring device, 24.0 g of hydrophobic monomer 1 (Production Example 4), 90.0 g of methoxypolyethylene glycol (23) methacrylate (trade name "BLEMMER PME-1000" manufactured by NOF CORPORATION), 300 ml of isopropyl alcohol, and 300 ml of a phosphate-buffered saline (pH 6.8) (manufactured by Nacalai Tesque, Inc.) were taken and stirred and mixed. Nitrogen gas purging was conducted for 1 hour while continuously stirring the mixture. A solution prepared by dissolving 2.0 g of ammonium persulfate in 20 ml of water was added to this, and the mixture was subjected to a reaction at 65°C for 10 hours (the reaction was conducted for 16 hours under the same conditions to synthesize the copolymer of Comparative

Example 1) while further continuously stirring the mixture. After the reaction was completed, the pH of the resultant was adjusted to 7.0 with an aqueous solution of sodium hydroxide, and isopropyl alcohol was removed therefrom by using a rotary evaporator, thereby obtaining an aqueous solution of the copolymer of Example 1 (treatments were conducted under the same conditions to obtain an aqueous solution of the copolymer of Comparative Example 1).

The weight average molecular weight (in terms of polystyrene) of the copolymer of Example 1 determined by GPC was 61,000. In addition, the mass ratio of the constitutional unit (a) to the constitutional unit (b) measured by NMR was about 3 : 7.

On the other hand, the weight average molecular weight of the copolymer of Comparative Example 1 was 122,500, and the mass ratio of the constitutional unit (a) to the constitutional unit (b) was about 3 : 7.

[0497]

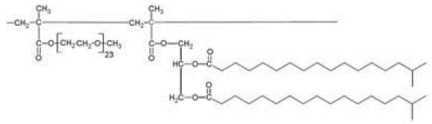
(2) Synthesis of copolymers of Examples 2 to 8

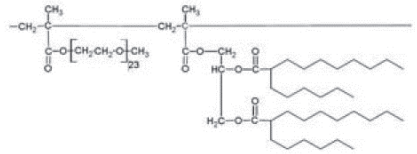
Copolymers having structures, weight average molecular weights, and molar ratios of the constitutional unit (a) to the constitutional unit (b) presented in Table 2 were synthesized by the same method as in (1) above. The weight average molecular weights of the copolymers were adjusted by changing the reaction time. In addition, the molar ratio of the constitutional unit (a) to the constitutional unit (b) can be adjusted by adjusting the molar ratio of the charged amounts of the hydrophobic monomer and hydrophilic monomer to be added to the reaction liquid.

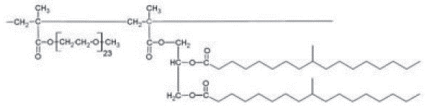
Incidentally, Examples 2 to 6 are copolymers synthesized by using the hydrophobic monomer 1. In addition, Example 7 and Example 8 are copolymers synthesized by using the hydrophobic monomer 2 and the hydrophobic monomer 3, respectively.

[0498]

[Table 2]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1
Mass ratio of constitutional unit (a) to constitutional unit (b)	70/30	60/40	70/30	70/30	70/30	70/30	70/30
Weight average molecular weight	61000	40200	27600	41000	57000	66000	122500
Outline of structure							

	Example 7
Mass ratio of constitutional unit (a) to constitutional unit (b)	70/30
Weight average molecular weight	34800
Outline of structure	

	Example 8
Mass ratio of constitutional unit (a) to constitutional unit (b)	70/30
Weight average molecular weight	38100
Outline of structure	

[0499]

<Test Example 1>

Aqueous solutions of the copolymers of Examples 1 to 6 and Comparative Example 1 at 2% by mass were prepared. Each of the aqueous copolymer solutions was applied to the skin of three professional organoleptic evaluators and the elastic feel was evaluated by the evaluators according to the following criteria. The results are presented in Table 3.

· Elastic feel

◉ · · · It exhibits significantly strong elastic feel

○ · · · It exhibits strong elastic feel

△ · · · It exhibits elastic feel

× · · · It hardly exhibits elastic feel

[0500]

[Table 3]

	Mass ratio of constitutional unit (a) to constitutional unit (b)	Weight average molecular weight	Elastic feel
Example 1	70/30	61000	◉
Example 2	60/40	40200	○
Example 3	70/30	27600	○
Example 4	70/30	41000	○
Example 5	70/30	57000	◉
Example 6	70/30	66000	◉
Comparative Example 1	70/30	122500	△

[0501]

As presented in Table 3, the aqueous copolymer solutions of Examples 1 to 6 exhibit stronger elastic feel as compared to the aqueous copolymer solution of Comparative Example 1 when the copolymers of Examples 1 to 6 and Comparative Example 1 in which the structure of the constitutional unit (a) is the same are compared to each other. In particular, the copolymers of the present invention of Examples 1, 5, and 6 exhibit significantly

strong elastic feel.

The results described above indicate that a copolymer which has a weight average molecular weight of from 20,000 to 110,000 and particularly preferably from 57,000 to 66,000 and contains the constitutional unit (a) and the constitutional unit (b) exhibits excellent elastic feel.

[0502]

<Test Example 2>

The elastic feel of the copolymers of Examples 7 and 8 was also evaluated by the same method as in Test Example 1. As a result, it has been found that the copolymers of Examples 7 and 8 are also equipped with elastic feel.

This result indicates that a copolymer exhibiting elastic feel can be obtained even when the structure of the constitutional unit (a) is variously changed.

[0503]

<Test Example 3>

A gel cosmetic was prepared by adding 0.5% by mass of xanthan gum to a 2% by mass aqueous solution of the copolymer of Example 1 or the copolymer of Comparative Example 1. This gel cosmetic was applied to the skin of three professional organoleptic evaluators in the same manner as in Test Example 1 and evaluated on the absence of stickiness, elastic feel, and moist feel. The evaluation was conducted by the evaluators according to the following evaluation criteria by taking the feel of use when milky lotion (reference cosmetic) containing trimethylolpropane triisostearate was applied to the skin as the reference. The average value of the evaluation values by the three evaluators are presented in Table 4 and Fig. 1.

· Evaluation criteria

4 points · · · It exhibits feel superior to feel of reference cosmetic

3 points · · · It exhibits feel to the same extent as feel of reference cosmetic

2 points · · · It exhibits feel close to but slightly inferior to feel of reference cosmetic

1 point · · · It exhibits feel inferior to feel of reference cosmetic

0 points · · · It exhibits feel significantly inferior to feel of reference cosmetic

[0504]

[Table 4]

	Example 1	Comparative Example 1
Absence of stickiness	2.23	1.75
Elastic feel	3.31	2.25
Moist feel	2.69	2.5

[0505]

As presented in Table 4 and Fig. 1, the gel cosmetic of Example 1 exhibits remarkably stronger elastic feel and superior absence of stickiness and moist feel as compared to the gel cosmetic of Comparative Example 1.

This result indicates that a copolymer which has a weight average molecular weight of from 20,000 to 110,000 and contains the constitutional unit (a) and the constitutional unit (b) exhibits excellent absence of stickiness and moist feel as well as elastic feel.

[0506]

Emulsified compositions were produced by stirring and mixing the components presented in the following Tables 5 to 7.

Incidentally, in the present Example, as a water-soluble copolymer which is an emulsifying agent of the present invention, a (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer which was obtained by copolymerizing glyceryl diisostearate methacrylate of a hydrophobic monomer and methoxy PEG-23 methacrylate of a hydrophilic monomer at a mass ratio of about 3 : 7 and had an average molecular weight of 61,000

was used.

In addition, a composition was produced by using PEG/PPG-60/11 glycerin (ADEKA NOL M-3228) which is an ether of polyoxypropylene (polymerization degree: 60) and polyoxyethylene (average polymerization degree: 11) with glycerin as a water-soluble copolymer (Comparative Examples 2, 4, and 6).

Furthermore, an emulsified composition was produced by using polyoxyethylene hardened castor oil as a surfactant (Comparative Examples 3, 5, and 7).

[0507]

[Table 5]

	Examples	Comparative Example 2	Comparative Example 3
(Glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer	X		
ADEKA NOL M-3228		1	
Polyoxyethylene hardened castor oil			1
Squalane	Y	10	10
Citric acid	0.01	0.01	0.01
Sodium citrate	0.1	0.1	0.1
Methyl paraben	0.2	0.2	0.2
Water	Balance	Balance	Balance
Sum	100	100	100

※The values of X and Y in Examples 9 to 31 are presented in the following table.

	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15
X	1	1	1	1	5	5	10
Y	10	30	40	60	10	30	10
	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21	Example 22
X	10	10	10	10	10	15	15
Y	30	40	50	60	70	20	30
	Example 23	Example 24	Example 25	Example 26	Example 27	Example 28	Example 29
X	20	20	20	20	20	25	25
Y	10	20	30	40	50	10	30
	Example 30	Example 31					
X	30	30					
Y	10	30					

※The unit is % by mass

A three-component system phase diagram in which the blending ratio among the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer, squalane, and water in Examples 9 to 31 is plotted is illustrated in Fig. 2.

[0508]

[Table 6]

	Examples	Comparative Example 4	Comparative Example 5
(Glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer	X		
ADEKA NOL M-3228		1	
Polyoxyethylene hardened castor oil			1
Caprylic/capric triglyceride	Y	10	10
Citric acid	0.01	0.01	0.01
Sodium citrate	0.1	0.1	0.1
Methyl paraben	0.2	0.2	0.2
Water	Balance	Balance	Balance
Sum	100	100	100

※The values of X and Y in Examples 32 to 62 are presented in the following table.

	Example 32	Example 33	Example 34	Example 35	Example 36	Example 37	Example 38
X	1	1	1	1	1	1	5
Y	10	30	40	50	60	70	10
	Example 39	Example 40	Example 41	Example 42	Example 43	Example 44	Example 45
X	5	5	5	5	5	10	10
Y	30	40	50	60	70	10	30
	Example 46	Example 47	Example 48	Example 49	Example 50	Example 51	Example 52
X	10	10	10	15	15	15	15
Y	40	60	70	10	30	40	50
	Example 53	Example 54	Example 55	Example 56	Example 57	Example 58	Example 59
X	15	20	20	20	25	25	25
Y	60	10	30	40	10	30	40
	Example 60	Example 61	Example 62				
X	30	30	30				
Y	10	30	40				

※The unit is % by mass

A three-component system phase diagram in which the blending ratio among the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer, caprylic/capric triglyceride, and water in Examples 32 to 62 is plotted is illustrated in Fig. 3.

[0509]

[Table 7]

	Examples	Comparative Example 6	Comparative Example 7
(Glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer	X		
ADEKA NOL M-3228		1	
Polyoxyethylene hardened castor oil			1
Dimethicone	Y	10	10
Citric acid	0.01	0.01	0.01
Sodium citrate	0.1	0.1	0.1
Methyl paraben	0.2	0.2	0.2
Water	Balance	Balance	Balance
Sum	100	100	100

※The values of X and Y in Examples 63 to 89 are presented in the following table.

	Example 63	Example 64	Example 65	Example 66	Example 67	Example 68	Example 69
X	1	1	1	1	1	5	5
Y	10	30	50	60	70	10	30
	Example 70	Example 71	Example 72	Example 73	Example 74	Example 75	Example 76
X	5	5	10	10	10	10	10
Y	50	70	10	30	50	60	70
	Example 77	Example 78	Example 79	Example 80	Example 81	Example 82	Example 83
X	15	15	15	15	20	20	20
Y	10	30	50	60	10	30	50
	Example 84	Example 85	Example 86	Example 87	Example 88	Example 89	
X	20	25	25	25	30	30	
Y	60	10	30	50	10	30	

※The unit is % by mass

A three-component system phase diagram in which the blending ratio among the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer, dimethicone, and water in Examples 63 to 89 is plotted is illustrated in Fig. 4.

[0510]

The emulsified compositions of Examples 9 to 89 were in a stable emulsified form even after being stored at room temperature for three months. In other words, it was possible to produce a stable emulsified composition with a (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer even in the case of using any oil agent of squalane which was non-polar hydrocarbon oil, caprylic/capric triglyceride which was polar hydrocarbon oil, or silicone oil.

On the other hand, the compositions of Comparative Examples 2, 4 and 6 containing PEG/PPG-60/11 glycerin of a water-soluble copolymer were not emulsified even when being stirred and mixed but were completely separated into an oil phase and an aqueous phase immediately after being produced. This result indicates that a stable emulsified composition can be produced by using various oil agents according to the water-soluble copolymer which is an emulsifying agent of the present invention.

[0511]

In addition, as presented in Tables 5 to 7, it was possible to produce an emulsified composition even when the content of the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer was any prescription of from 1% to 30% by mass.

In addition, as presented in Tables 5 to 7, it was possible to produce an emulsified composition even when the content of the oil phase was any case of from 10% to 70% by mass.

[0512]

Examples 9 to 89 and Comparative Examples 3, 5 and 7 were applied to the skin in an appropriate amount. As a result, the emulsified compositions of Examples 9 to 89 did not exhibit irritating feel and were less sticky as compared to the emulsified compositions of Comparative Examples 3, 5 and 7.

This result indicates that the emulsified composition emulsified with the water-soluble copolymer which is an emulsifying agent of the present invention is superior to a general emulsified composition emulsified with a surfactant in feel of use.

[0513]

Particularly, the emulsified compositions of Examples in which the content of the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer was 15% by mass and still more preferably 1% by mass exhibited superior feel of use.

[0514]

<Production Example 7>

The facial cleansers of Examples 90 to 92 and Comparative Examples 8 and 9 were produced according to the following prescription. In other words, facial cleansers were obtained by heating the components of (A) and (B) to 80°C, respectively, adding the components of (B) to the components of (A) while stirring, stirring the mixture, and cooling the resultant mixture.

Incidentally, as the water-soluble copolymer, a (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer which was obtained by copolymerizing glyceryl diisostearate methacrylate of a hydrophobic monomer and methoxy PEG-23 methacrylate of a hydrophilic monomer at a molar ratio of about 3 : 7 and had an average molecular weight of 61,000 was used.

[0515]

[Table 8]

		Example 90	Example 91	Example 92	Comparative Example 8	Comparative Example 9
A	Lauric acid	9	9	9	9	9
	Myristic acid	14	14	14	14	14
	Palmitic acid	12	12	12	12	12
	Stearic acid	5	5	5	5	5
B	(Glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer	0.5	1	5		
	Carboxymethylcellulose					1
	Glycerin	17	17	17	17	17
	Potassium hydroxide	8.5	8.5	8.5	8.5	8.5
	Water	Balance	Balance	Balance	Balance	Balance
	Sum	100	100	100	100	100
Evaluation	Foaming	○	◉	◉	○	×
	Foam quality	○	○	○	○	○
	Absence of tight feel	○	○	○	×	○
	Absence of slimy feel	◉	◉	○	◉	×

[0516]

<Test Example 4>

The facial cleansers of Examples 90 to 92 and Comparative Examples 8 and 9 were used for face washing and evaluated on the foaming and foam quality at the time of use and the absence of tight feel and slimy feel of the skin after face washing according to the following evaluation criteria by experienced evaluators. The results are presented in Table 8.

· Foaming

◉ · · · It significantly favorably foams

○ · · · It favorably foams

△ · · · It slightly foams

× · · · It does not foam

· Foam quality

◉ · · · It exhibits significantly creamy foam quality

○ · · · It exhibits creamy foam quality

△ · · · It exhibits slightly creamy foam quality

× · · · It does not exhibit creamy foam quality

· Absence of tight feel

◉ · · · It does not cause tight feel

○ · · · It hardly causes tight feel

△ · · · It causes tight feel

× · · · It causes strong tight feel

· Absence of slimy feel

◉ · · · It does not cause slimy feel

○ · · · It hardly causes slimy feel

△ · · · It causes slimy feel

× · · · It causes strong slimy feel

[0517]

As presented in Table 8, the facial cleanser of Comparative Example 8 caused strong tight feel to the skin after face washing but the facial cleansers of Examples 90 to 92 hardly caused tight feel after face washing.

This result indicates that tight feel of the skin due

to fatty acid soap is decreased by the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer.

[0518]

In addition, favorable foaming which has an advantage of fatty acid soap was not observed in the facial cleanser of Comparative Example 9 containing carboxymethylcellulose which was a water-soluble polymer instead of the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer. On the other hand, the facial cleansers of Examples 90 to 92 exhibited favorable foaming.

This result indicates that it is possible to decrease tight feel of the skin after use without inhibiting favorable foaming of fatty acid soap according to the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer.

In addition, as presented in Table 8, the facial cleansers of Examples 91 and 92 were superior to the facial cleanser of Comparative Example 8 in foaming.

This result indicates that it is possible to improve foaming of fatty acid soap by setting the content of the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer to 0.8% by mass or more.

[0519]

In addition, as presented in Table 8, the facial cleanser of Comparative Example 9 caused strong slimy feel to the skin after face washing. On the other hand, the facial cleansers of Examples 90 to 92 hardly caused slimy feel after face washing.

This result indicates that it is possible to decrease tight feel of the skin after use of the skin cleanser without causing slimy feel according to the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer.

In addition, as presented in Table 8, the facial

cleansers of Examples 90 and 91 are superior to the facial cleanser of Example 92 in the absence of slimy feel.

This result indicates that it is possible to decrease tight feel of the skin after use of the skin cleanser without causing slimy feel by setting the content of the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer to 3% by mass or less.

[0520]

<Production Example 8>

Gel facial cleansers of Examples 93 to 96 and Comparative Examples 10 to 12 were obtained by stirring and mixing the components presented in Table 9.

[0521]

[Table 9]

		Example 93	Example 94	Example 95	Example 96	Comparative Example 10	Comparative Example 11	Comparative Example 12
	(Glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer	0.5	1	5	1			
	Carboxymethylcellulose							1
	Polyoxyethylene caprylic/capric glyceride	5	5	5		5		5
	Polyoxyethylene glyceryl isostearate				5		5	
	Glycerin	20	20	20	20	20	20	20
	Carbomer	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	Potassium hydroxide	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	Water	Balance	Balance	Balance	Balance	Balance	Balance	Balance
	Sum	100	100	100	100	100	100	100
Evaluation	Detergency	○	○	◉	○	×	×	×
	Ease of spreading	○	◉	○	◉	○	○	○
	Absence of tight feel	○	◉	◉	◉	×	×	○

[0522]

<Test Example 5>

The gel facial cleansers were used for face washing in the same manner as in Test Example 4 and evaluated on the detergency, ease of spreading on the skin at the time of use, and the absence of tight feel of the skin after face washing according to the following evaluation criteria by experienced evaluators (evaluation criteria for the absence of tight feel are the same as those in Test Example 4). The results are presented in Table 9.

· Detergency

◉ · · · It exhibits significantly strong detergency

○ · · · It exhibits strong detergency

△ · · · It exhibits weak detergency

× · · · It exhibits significantly weak detergency

· Ease of spreading on the skin

◉ · · · It is significantly easily spread

○ · · · It is easily spread

△ · · · It is hardly spread

× · · · It is significantly hardly spread

[0523]

As presented in Table 9, the gel facial cleansers of Comparative Examples 10 and 11 caused strong tight feel to the skin after face washing but the facial cleansers of Examples 93 to 96 hardly caused tight feel after face washing.

This result indicates that tight feel of the skin due to a nonionic surfactant is decreased by the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer.

In addition, as presented in Table 9, the gel facial cleansers of Examples 94 and 95 are superior to the gel facial cleanser of Example 93 in the effect of decreasing tight feel of the skin after use.

This result indicates that it is possible to more

effectively decrease tight feel of the skin after use by setting the content of the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer to 0.7% by mass or more.

[0524]

In addition, as presented in Table 9, the gel facial cleansers of Examples 93 to 96 are superior to the gel facial cleansers of Comparative Examples 10 to 12 in detergency.

This result indicates that it is possible to improve the detergency of a skin cleanser containing a nonionic surfactant according to the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer.

Furthermore, the gel facial cleanser of Example 95 is superior to the gel facial cleansers of Examples 93 and 94 in detergency.

This result indicates that it is possible to improve the detergency of a skin cleanser containing a nonionic surfactant by setting the content of the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer to 2% by mass or more.

[0525]

In addition, as presented in Table 9, the gel facial cleanser of Example 94 is superior to the gel facial cleansers of Examples 93 and 95 in ease of spreading on the skin.

This result indicates that it is possible to improve ease of spreading on the skin at the time of use of the gel facial cleanser by setting the content of the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer to from 0.6% to 3% by mass.

[0526]

In addition, the contents of nonionic surfactants are the same but the kinds thereof are different from each other in the gel facial cleanser of Example 91 and the gel

facial cleanser of Example 93. However, as presented in Table 9, these two kinds of gel facial cleansers exhibited equivalent effects in detergency, ease of spreading on the skin, and absence of tight feel.

This result indicates that the advantageous effect exhibited by containing the (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer in a skin cleanser is not dependent on the kind of surfactant to be contained in the skin cleanser.

[0527]

The results of Test Examples 4 and 5 indicate that it is possible to decrease tight feel of the skin after use of the skin cleanser according to the present invention.

In addition, it is indicated that it is possible to decrease tight feel of the skin after use without impairing or while improving the advantageous effects inherent in a skin cleanser such as favorable foaming, creamy foam quality, detergency, and ease of spreading on the skin according to the present invention.

[0528]

<Production Example 9>

Oil-in-water type sunscreen cosmetics of Examples 98 to 103 and Comparative Examples 13 to 15 were produced according to the prescription presented in Table 10 by the following method.

A mixture of oil phase components was prepared by mixing, heating, and dissolving (A) and hydrophobized micro titanium oxide were dispersed in the mixture by using a disper.

Next, (A) was added to the heated (B) and emulsified by using a homogenizer. After emulsification, (C) and (D) were added to the emulsion, and the resultant emulsion was cooled while being stirred and mixed, thereby producing a sunscreen cosmetic.

Incidentally, in the present Example, as a water-

soluble copolymer of the component (A), a (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer which was obtained by copolymerizing glyceryl diisostearate methacrylate of a hydrophobic monomer and methoxy PEG-23 methacrylate of a hydrophilic monomer at a molar ratio of about 3 : 7 and had an average molecular weight of 61,000 was used.

[0529]

[Table 10]

			Example 97	Example 98	Example 99	Example 100	Example 101	Example 102	Comparative Example 13	Comparative Example 14	Comparative Example 15
A	Cyclopentasiloxane		20	20	20	20	20	20	20	20	20
	Diphenylsiloxy phenyl trimethicone		5	5	5	5	5	5	5	5	5
	Behenyl alcohol		1	1	1	1	1	1	1	1	1
	Polyglyceryl-10 pentastearate	Component (B)	1	0.3	7	1		1	1		1
	Polyglyceryl-10 tristearate						1				
	Hydrophobized micro titanium oxide	Component (D)	5	5	5	5	5	7	5	5	5
	2-Ethylhexyl p-methoxycinnamate		7	7	7	7	7	7	7	7	7
B	Water		51.75	52.65	44.5	51.75	51.75	51.75	53.75	52.75	52
	1,3-Butanediol		5	5	5	5	5	5	5	5	5
	Sodium stearyl lactate	Component (C)	0.25	0.05	1.5		0.25	0.25	0.25	0.25	
	Sodium cocoglyceride sulfate					0.25					
C	Sodium polyacrylate-coated micro titanium dioxide	Component (D)	2	2	2	2	2		2	2	2
D	(Glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer	Component (A)	2	2	2	2	2	2		2	2
	Sum		100	100	100	100	100	100	100	100	100
Evaluation	Emulsion stability		◉	○	○	○	○	◉	○	×	×
	Absence of stickiness		◉	◉	○	◉	◉	◉	×	○	◉
	Moisturizing feel		◉	◉	◉	◉	◉	○	○	◉	○

[0530]

<Test Example 6>

The oil-in-water type sunscreen cosmetics of Examples 97 to 102 and Comparative Examples 13 to 15 thus prepared were evaluated on the emulsion stability and the absence of sticky feel and the moisturizing feel when being used according to the following criteria. The results are presented in Table 10.

· Emulsion stability (state when stored at room temperature for 1 month)

◉ · · · Separation of oil phase is not observed at all

○ · · · Separation of oil phase is hardly observed

△ · · · Oil film is floating on surface of preparation

× · · · Separation of oil phase is clearly observed

· Absence of stickiness

◉ · · · It does not exhibit sticky feel at all

○ · · · It hardly exhibits sticky feel

△ · · · It exhibits sticky feel

× · · · It significantly exhibits sticky feel

· Moisturizing feel

◉ · · · It exhibits significantly strong moist feel

○ · · · It exhibits strong moist feel

△ · · · It exhibits weak moist feel

× · · · It exhibits significantly weak moisty feel

[0531]

As presented in Table 10, the oil-in-water type sunscreen cosmetics of Examples 97 to 102 containing all of the components (A) to (D) exhibited favorable emulsion stability, absence of sticky feel, and moisturizing feel.

On the other hand, the sunscreen cosmetic of Comparative Example 13 which did not contain the component (A) exhibited significantly strong sticky feel. In addition, the sunscreen cosmetic of Comparative Example 14 which did not contain the component (B) and the sunscreen cosmetic of Comparative Example 15 which did not contain

the component (C) were inferior in emulsion stability.

These results indicate that an oil-in-water type sunscreen cosmetic containing the components (A) to (D) exhibits excellent emulsion stability, absence of stickiness, and moisturizing feel.

[0532]

In addition, as presented in Table 10, the sunscreen cosmetic of Example 97 containing sodium stearyl lactate as the component (C) is superior to the sunscreen cosmetic of Example 100 containing sodium cocoglyceride sulfate as the component (C) in emulsion stability.

This result indicates that an oil-in-water type sunscreen cosmetic containing sodium acyl lactate as the component (C) exhibits excellent emulsion stability.

[0533]

In addition, as presented in Table 10, the sunscreen cosmetic of Example 97 containing polyglyceryl-10 pentastearate as the component (B) is superior to the sunscreen cosmetic of Example 101 containing polyglyceryl-10 tristearate as the component (B) in emulsion stability.

This result indicates that an oil-in-water type sunscreen cosmetic containing polyglyceryl-10 pentastearate as the component (B) exhibits excellent emulsion stability.

[0534]

In addition, as presented in Table 10, the sunscreen cosmetic of Example 97 containing sodium polyacrylate-coated micro titanium dioxide as an ultraviolet scattering agent of the component (D) is superior to the sunscreen cosmetic of Example 102 which does not contain the coated micro titanium dioxide in moisturizing feel.

This result indicates that an oil-in-water type sunscreen cosmetic containing an ultraviolet scattering agent having a surface treated with sodium polyacrylate, namely, a water dispersible ultraviolet scattering agent as the component (D) exhibits excellent moisturizing feel.

[0535]

In addition, the sunscreen cosmetic of Example 102 is superior to the sunscreen cosmetics of Example 98 and Example 99 in which the content of the component (B) is 0.3% by mass and 7% by mass, respectively in emulsion stability and absence of sticky feel.

This result indicates that it is preferable to set the content of the component (B) to 0.5% by mass or more from the viewpoint of improving emulsion stability and to 5% by mass or less from the viewpoint of suppressing stickiness.

[0536]

In addition, the sunscreen cosmetic of Example 97 is superior to the sunscreen cosmetics of Example 98 and Example 99 in which the content of the component (C) is 0.05% by mass and 1.5% by mass, respectively in emulsion stability and absence of sticky feel.

This result indicates that it is preferable to set the content of the component (C) to 0.07% by mass or more from the viewpoint of improving emulsion stability and to 1% by mass or less from the viewpoint of suppressing stickiness.

[0537]

<Production Example 10>

As presented in Table 11, compositions of the present invention of Examples 103 to 123 were prepared by fixing the contents of xanthan gum and the amphipathic copolymer and variously changing the contents of 1,3-butylene glycol (promoting polyol) and glycerin (suppressing polyol). The contents of 1,3-butylene glycol and glycerin in each Example were adjusted as presented in the three-component system phase diagram illustrated in Fig. 5 in the relation with the total amount of xanthan gum and the amphipathic copolymer.

Incidentally, as the amphipathic copolymer, a

(glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer which was obtained by copolymerizing glyceryl diisostearate methacrylate of a hydrophobic monomer and methoxy PEG-23 methacrylate of a hydrophilic monomer at a molar ratio of about 3 : 7 and had an average molecular weight of 61,000 was used.

In addition, in the following Test Examples, a composition was prepared by using a (glyceryl diisostearate methacrylate/methoxy PEG-23 methacrylate) copolymer into which a fluorescent probe "NBD-COCl" was chemically introduced in order to facilitate the observation of the sea-island structure under a microscope.

[0538]

[Table 11]

% by mass

Xanthan gum	Water-soluble polymer	0.1
1,3-Butylene glycol	Promoting polyol	X
Glycerin	Suppressing polyol	Y
Methyl paraben		0.2
(Methoxy PEG-23 methacrylate/glyceryl diisostearate methacrylate) copolymer	Amphipathic copolymer	2
Citric acid		0.01
Sodium citrate		0.1
Water		Balance
Sum		100

[0539]

<Test Example 7> Observation of sea-island structure of coating film

About 0.5 g of the compositions of Examples 103 to 123 was applied to a range of about 1.5 cm × 1.5 cm on a microscope slide and allowed to stand at 40°C for 3 days to evaporate moisture in the composition, thereby forming a coating film on the microscope slide. The structures of the coating films of Examples 103 to 123 thus formed were observed under a confocal laser scanning microscope.

As a result, a sea-island structure was formed in all the compositions. The photomicrographs of the compositions

of Examples 105, 106, 108, 111, 113, 114, 115, 119, 120, 122, and 123 are illustrated in Fig. 6.

[0540]

As illustrated in Fig. 6, in the compositions of Examples 115, 119, and 120, aggregation of island particles was observed and island particles having an average particle diameter exceeding 10 μm and island particles having a ratio of major axis to minor axis of less than 0.5 were observed in a great amount.

On the other hand, in all the compositions of Examples 106 to 114, aggregation of island particles was not observed and the number particle size distribution of fine island particles having an average particle diameter of from 1 to 5 μm was 80% or more.

This result indicates that aggregation of island particles is hardly caused in a composition in which the total amount of the water-soluble polymer and the amphipathic copolymer in the total amount of the components illustrated in the three-component system phase diagram of Fig. 5 is 15% by mass or less.

[0541]

In addition, the area ratio of the sea phase to the island phase in the coating films of Examples 103 to 114 in which aggregation of the island particles was not observed and the number particle size distribution of fine island particles having an average particle diameter of from 1 to 5 μm was 80% or more was from 6 : 4 to 7 : 3.

[0542]

<Test Example 8> Organoleptic evaluation

The coating film formed on the skin by applying the composition of Example 103 to the skin of 48 evaluators was evaluated on the moist feel, elastic feel, softness, bouncy feel, luxuriant feel, and stickiness by the evaluators by taking 7 points as the top grade as illustrated in Fig. 7. In addition, commercially available skin lotion and milky

lotion were used for comparison. The results are illustrated in Fig. 7.

Incidentally, general skin lotion containing water as a main component and a polyol, a known water-soluble polymer, a preservative, and extracts was used as the lotion. In addition, an oil-in-water type emulsified cosmetic containing mineral oil, macadamia nut oil, and the like as oil phase components was used as the milky lotion.

[0543]

As illustrated in Fig. 7, the coating film formed by applying the composition of Example 103 to the skin was evaluated to be equivalent to or higher than the milky lotion containing an oil agent on the items of moist feel, elastic feel, softness, bouncy feel, and luxuriant feel.

In addition, as illustrated in Fig. 7, the coating film formed by the composition of Example 103 exhibited sticky feel to be remarkably lower than that of the milky lotion and equivalent to that of the skin lotion.

[0544]

This result indicates that the composition of the present invention can form a coating film exhibiting feel like milk containing an oil agent on the skin even though it contains an aqueous component as a main component. In particular, it is indicated that the composition of the present invention can achieve both moisture retaining property and flexibility which have been hardly achieved by a cosmetic containing a water-soluble component as a main component.

In addition, this result indicates that the composition of the present invention has few disadvantages such as stickiness to be found in a cosmetic containing an oil agent since it is mainly composed of an aqueous component.

[0545]

<Production Example 11>

The compositions of the present invention of Examples 124 and 125 were prepared according to the prescription of Table 12.

[0546]

[Table 12]

		Example 124	Example 125
Xanthan gum	Water-soluble polymer	0.05	0.05
1,3-Butylene glycol	Promoting polyol	12	12
Glycerin	Suppressing polyol	8	8
Methyl paraben		0.2	0.2
Polyquaternium-61	Amphipathic copolymer	1	
(Glycerylamidoethyl methacrylate/stearyl methacrylate) copolymer			1
Citric acid		0.01	0.01
Sodium citrate		0.1	0.1
Water		Balance	Balance

(% by mass)

[0547]

The coating films formed by the compositions of Examples 124 and 125 were observed under a microscope by the same method as in Test Example 8. As a result, aggregation of the island particles was not observed and the number particle size distribution of the fine island particles having an average particle diameter of from 1 to 5 μm was 80% or more in the same manner as the coating films of Examples 103 to 114.

This result indicates that it is possible to form a coating film having a favorable sea-island structure even in the case of using polyquaternium-61 and a (glycerylamidoethyl methacrylate/stearyl methacrylate) copolymer as amphipathic copolymers. In other words, it is indicated that a composition capable of forming a coating film having a sea-island structure can be prepared by combining a water-soluble polymer and water even in the case of variously changing the kind of amphipathic copolymer having a constitutional unit derived from a hydrophobic monomer and a constitutional unit derived from a hydrophilic monomer.

Industrial Applicability

[0548]

The copolymer of the present invention to achieve the first object can be applied to a cosmetic.

[0549]

The present invention to achieve the second object can be applied to an emulsified cosmetic.

[0550]

The present invention to achieve the third and fourth objects can be applied to a facial cleanser.

[0551]

The present invention to achieve the fifth object can be applied to a sunscreen cosmetic.

[0552]

The present invention to achieve the sixth object can be applied to an oil-free cosmetic.

Reference Signs List

[0553]

1 Example 103
2 Example 104
3 Example 105
4 Example 106
5 Example 107
6 Example 108
7 Example 109
8 Example 110
9 Example 111
10 Example 112
11 Example 113
12 Example 114
13 Example 115
14 Example 116
15 Example 117

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16    Example 118
17    Example 119
18    Example 120
19    Example 121
20    Example 122
21    Example 123
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CLAIMS

1. A copolymer comprising:

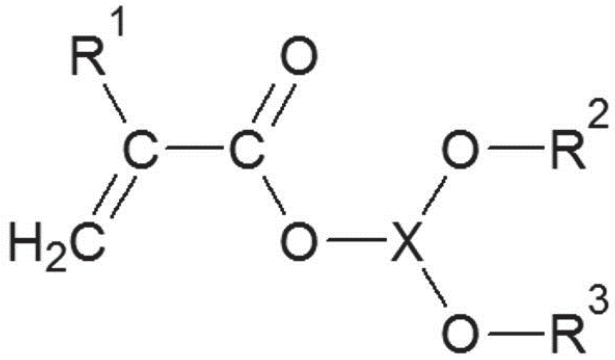
one kind or two or more kinds of constitutional units (a) derived from a hydrophobic monomer represented by the following general formula (1); and

one kind or two or more kinds of constitutional units (b) derived from a hydrophilic monomer represented by the following general formula (2) as essential constitutional units,

wherein a weight average molecular weight of the copolymer is from 20,000 to 110,000:

General Formula (1)

[Chemical Formula 1]

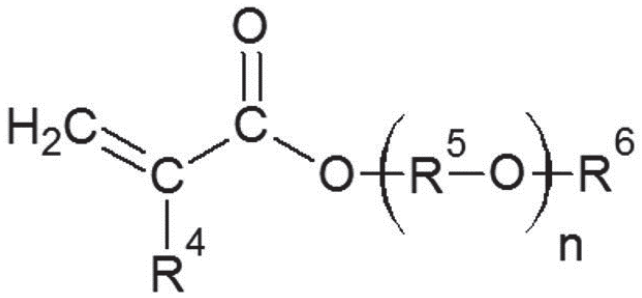


(1)

(in the general formula (1), R1 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R2 and R3 may be the same as or different from each other and represent an acyl group which has from 6 to 22 carbon atoms and a branch but does not contain a ring structure. X represents a group obtained by eliminating an OH group from a trihydric alcohol.), and

General Formula (2)

[Chemical Formula 2]



(2)

(in the general formula (2), R4 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms, R5 represents an alkylene group which has from 2 to 4 carbon atoms and may have a hydroxyl group, and R6 represents a hydrogen atom, an aromatic hydrocarbon group having from 6 to 10 carbon atoms, an aliphatic hydrocarbon group having from 1 to 14 carbon atoms, or an acyl group having from 1 to 12 carbon atoms. n represents an integer from 6 to 40.).

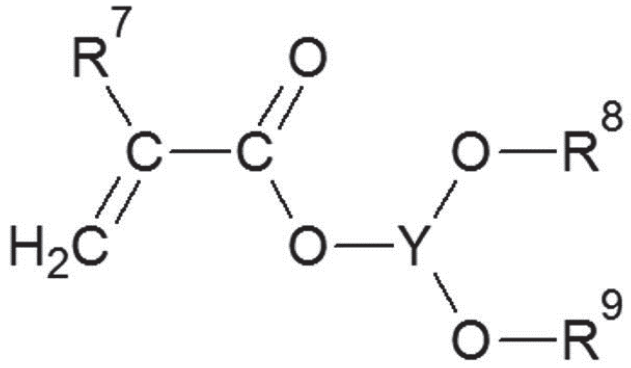
2. The copolymer according to claim 1, wherein a mass ratio of the constitutional unit (a) to the constitutional unit (b) is from 25 : 75 to 35 : 65.

3. The copolymer according to claim 1 or 2, wherein a molar ratio of the constitutional unit (a) to the constitutional unit (b) is from 35 : 65 to 46 : 54.

4. The copolymer according to any one of claims 1 to 3, wherein the hydrophobic monomer is a hydrophobic monomer represented by the following general formula (3):

General Formula (3)

[Chemical Formula 3]



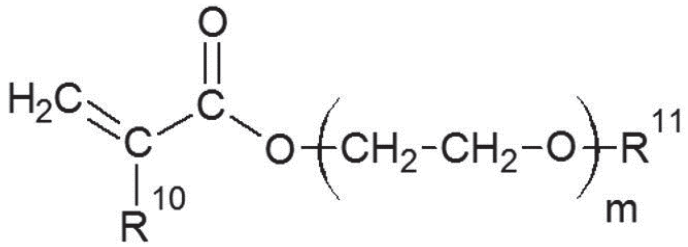
(3)

(in the general formula (3), R7 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R8 and R9 may be the same as or different from each other and represent an acyl group which has from 10 to 22 carbon atoms and a branch but does not contain a ring structure or an acyl group which has from 6 to 9 carbon atoms and two or more branches but does not contain a ring structure. Y represents a group obtained by eliminating an OH group from a trihydric alcohol.).

5. The polymer according to any one of claims 1 to 4, wherein the hydrophilic monomer is a hydrophilic monomer represented by the following general formula (4):

General Formula (4)

[Chemical Formula 4]



(4)

(in the general formula (4), R10 represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms and R11 represents a hydrogen atom, an aromatic hydrocarbon group having from 6 to 10 carbon atoms, an aliphatic hydrocarbon

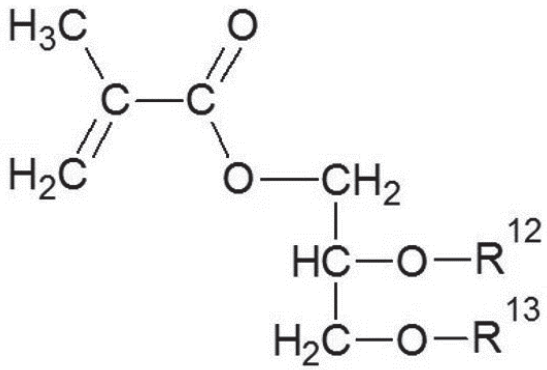
group having from 1 to 14 carbon atoms, or an acyl group having from 1 to 12 carbon atoms. m represents an integer from 6 to 40.).

6. The copolymer according to any one of claims 1 to 5, wherein the trihydric alcohol is selected from the group consisting of glycerin, trimethylolpropane, and trimethylolethane.

7. The copolymer according to any one of claims 1 to 6, wherein the hydrophobic monomer is a compound represented by the following general formula (5):

General Formula (5)

[Chemical Formula 5]



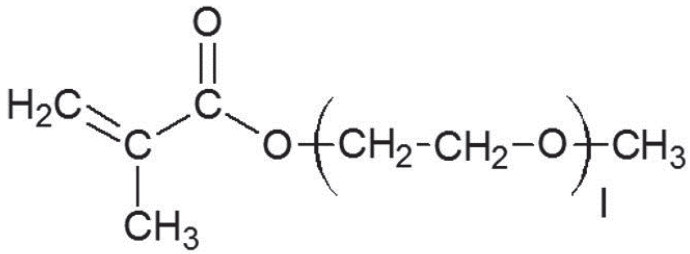
(5)

(R12 and R13 in the general formula (5) may be the same as or different from each other and represent an acyl group which has 18 carbon atoms and a branch but does not contain a ring structure.).

8. The polymer according to any one of claims 1 to 7, wherein the hydrophilic monomer is a hydrophilic monomer represented by the following general formula (6):

General Formula (6)

[Chemical Formula 6]



(6)

(l in the general formula (6) represents an integer from 6 to 40.).

9. An external preparation for skin comprising the copolymer according to any one of claims 1 to 8.