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## Description

[Title of Invention] COSMETIC FOR PROTECTION AGAINST  
ULTRAVIOLET RADIATION

[Field of the Invention]

[0001]

The present invention relates to a cosmetic for protection against ultraviolet radiation.

[Background of the Invention]

[0002]

Since sunburn by ultraviolet radiation promotes browning of skins, decline in elasticity of skins and generation of wrinkles, in order to prevent these, cosmetics containing ultraviolet absorbers are used.

Among the ultraviolet absorbers, oil-soluble ultraviolet absorbers are excellent in the effect of absorbing ultraviolet radiation. However, when blended in cosmetics as they are, they pose problems in feeling of use and the like including, for example, giving feeling of irritation and feeling of stickiness in some cases.

Hence, several studies are made of cosmetics containing an ultraviolet absorber which is made into a fine emulsion or capsulated (for example, Patent Literatures 1 to 3).

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[0003]

[Patent Literature 1]

JP-A-2012-31125

[Patent Literature 2]

JP-A-2005-504750

[Patent Literature 3]

JP-A-2009-167168

[Summary of the Invention]

[0004]

The present invention relates to a cosmetic for protection against ultraviolet radiation, the cosmetic comprising the following components (A), (B), (C), (D) and (E):

- (A) 0.18 to 2 mass% of an ionic surfactant;
- (B) 1 to 10 mass% of a hydrophobic amphipathic substance;
- (C) 1 to 40 mass% of a liquid oil agent comprising an oil-soluble ultraviolet absorber;
- (D) 0.01 to 6 mass% of a solid oil agent; and
- (E) water,

in which the cosmetic is obtained by a method comprising the following steps:

an emulsification step of mixing a composition comprising the components (A) to (D) with (E) water under heating to form an emulsion; and

a cooling step of cooling the emulsion formed in the emulsification step at a cooling rate of 0.5 to 5°C/sec.

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[Brief Description of the Drawings]

[0005]

[Figure 1] Figure 1 is a schematic view illustrating a vibration-type stirring mixing apparatus suitable for producing the cosmetic of the present invention.

[Figure 2] Figure 2 is an illustrative view of a longitudinal cross-section of the vibration-type stirring mixing apparatus illustrated in Figure 1.

[Figure 3] Figure 3 is a principal portion enlarged view of a stirring gear in the vibration-type stirring mixing apparatus illustrated in Figure 1.

[Detailed Description of the Invention]

[0006]

Conventional cosmetics containing ultraviolet absorbers are inferior in preservation stability and cannot sufficiently satisfy the point of feeling of use as well.

Further when the cosmetics having ultraviolet absorbers are applied on skins, since the ultraviolet absorbers do not adhere uniformly on the skin, a sufficient ultraviolet protection effect cannot be attained. Even when the ultraviolet absorbers are blended in a large amount in order to enhance the ultraviolet protection effect, the cosmetics have

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problems in terms of preservation stability, feeling of use and the like.

The present invention relates to a cosmetic for protection against ultraviolet radiation in which an oil agent comprising an ultraviolet absorber is homogeneously dispersed, and which is excellent in preservation stability, high in the ultraviolet protection effect, and good in feeling of use, and gives no feeling of skin irritation.

[0007]

The present inventors have found that a cosmetic, which is obtained by combining an ionic surfactant, a hydrophobic amphipathic substance, a liquid oil agent comprising an oil-soluble ultraviolet absorber, and a solid oil agent in specific proportions in a specific method, has  $\alpha$ -gel particles including the oil-soluble ultraviolet absorber dispersed therein, and is excellent in preservation stability, high in the ultraviolet protection effect, and good in feeling of use, and gives no feeling of skin irritation.

[0008]

The cosmetic for protection against ultraviolet radiation of the present invention has  $\alpha$ -gel particles including an oil-soluble ultraviolet absorber dispersed therein, and is good also in preservation stability. Further when the cosmetic is applied on skin, the oil-soluble ultraviolet absorber adheres uniformly on the

skin, and the cosmetic brings about a high ultraviolet protection effect, and exhibits no stickiness, is good in feeling of use, low in the transdermal absorbability of the ultraviolet absorber, and gives no feeling of skin irritation.

[0009]

The ionic surfactant of the component (A) to be used in the present invention is one to be used for usual cosmetics, and anionic surfactants, cationic surfactants, amphoteric surfactants, sphingosines and salts thereof can be used.

Examples of the anionic surfactants include fatty acid salts having 12 to 24 carbon atoms such as sodium laurate, potassium palmitate and arginine stearate; alkyl sulfate ester salts such as sodium lauryl sulfate and potassium lauryl sulfate; alkyl ether sulfate ester salts such as a polyoxyethylene laurylsulfuric acid triethanolamine; N-acylsarcosine salts such as a lauroylsarcosine sodium; fatty acid amidosulfonate salts such as an N-myristoyl-N-methyltaurine sodium; alkyl phosphate salts such as sodium monostearyl phosphate; polyoxyethylene alkyl ether phosphate salts such as sodium polyoxyethylene oleyl ether phosphate and sodium polyoxyethylene stearyl ether phosphate; long-chain sulfosuccinate salts such as sodium di-2-ethylhexyl sulfosuccinate; and long-chain N-acylglutamate salts such as sodium dilauroylglutamate, monosodium N-

lauroylglutamate, sodium N-stearoyl-L-glutamate, arginine N-stearoyl-L-glutamate, sodium N-stearoylglutamate and sodium N-myristoyl-L-glutamate.

Among these, from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, and from the viewpoint of improving feeling of use, particularly reducing stickiness, long-chain N-acylglutamate salts are preferable.

[0010]

As the cationic surfactants, quaternary ammonium salts are preferable, and examples thereof include alkyltrimethylammonium chloride salts such as stearyltrimethylammonium chloride and lauryltrimethylammonium chloride; and dialkyldimethylammonium, trialkylmethylammonium chloride and alkylamine salts.

[0011]

Examples of the amphoteric surfactant include alkyl dimethylamine oxide, alkyl carboxy betaine, alkyl sulfobetaine, amidoamino acid salt, and alkyl amidopropyl betaine. Among these, alkyl amidopropyl betaine is preferable.

[0012]

Sphingosines and salts thereof include natural sphingosine, dihydrosphingosine, phytosphingosine, sphingadienine, dehydrosphingosine,

dehydrophytosphingosine and N-alkyl compounds (for example, N-methyl compounds) thereof.

These may be either of extracts from nature and synthetic substances, and commercially available ones can be used. Examples of natural-type sphingosines commercially available include D-Sphingosine (4-Sphingenine) (Shigma-Aldrich Corp.), DS-phytosphingosine (Doosan Corp.), and phytosphingosine (Cosmo Farm KK).

[0013]

Further, salts of these sphingosines include acidic amino acid salts of glutamic acid, aspartic acid and the like; basic amino acid salts of arginine and the like; inorganic acid salts of phosphoric acid, hydrochloric acid and the like; monocarboxylate salts of acetic acid and the like; dicarboxylate salts of succinic acid and the like; and oxycarboxylate salts of citric acid, lactic acid, malic acid and the like, and one or two or more selected from the group consisting of these are preferable.

[0014]

As the ionic surfactant of the component (A), from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, and improving feeling of use, particularly reducing the stickiness, at least one selected from the group consisting of anionic surfactants and sphingosines is preferable, and an anionic surfactant is more preferable.

Among the anionic surfactants, long-chain N-acylglutamate salts are preferable; and among the long-chain N-acylglutamate salts, preferable is at least one selected from the group consisting of sodium dilauroylglutamate, monosodium N-lauroylglutamate, sodium N-stearoyl-L-glutamate, arginine N-stearoyl-L-glutamate, sodium N-stearoylglutamate and sodium N-myristoyl-L-glutamate; more preferable is at least one selected from the group consisting of sodium N-stearoylglutamate and arginine N-stearoyl-L-glutamate; and still more preferable is arginine N-stearoyl-L-glutamate.

[0015]

The component (A) can be used singly or in a combination of two or more, and the content thereof is, from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, and improving feeling of use, particularly reducing stickiness, in the whole composition, 0.18 mass% or higher, preferably 0.2 mass% or higher, more preferably 0.3 mass% or higher, still more preferably 0.4 mass% or higher, and further still more preferably 0.45 mass% or higher, and is 2 mass% or lower, preferably 1.5 mass% or lower, more preferably 1.1 mass% or lower, still more preferably 0.9 mass% or lower, and further still more preferably 0.7 mass% or lower. Further, the content of the component (A) is, in the whole composition, 0.18 to 2 mass%, preferably 0.2 to 1.5

mass%, more preferably 0.3 to 1.1 mass%, still more preferably 0.4 to 0.9 mass%, and further still more preferably 0.45 to 0.7 mass%.

Here, in the present invention, the content of the component (A) is that in terms of acids.

Further, the cosmetic for protection against ultraviolet radiation can comprise a nonionic surfactant in the range not impairing the advantage of the present invention, and from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, and from the viewpoint of improving feeling of use, particularly reducing stickiness, the content of the nonionic surfactant is, in the whole composition, preferably 1 mass% or lower, more preferably 0.5 mass% or lower, still more preferably 0.1 mass% or lower, and further still more preferably substantially 0 mass%.

[0016]

Examples of the hydrophobic amphipathic substance of the component (B) to be used in the present invention include ceramides, alcohols having 10 to 24 carbon atoms, linear saturated fatty acids having 10 to 24 carbon atoms, monofatty acid glycerin esters having 10 to 24 carbon atoms, monoalkyl glyceryl ethers having 10 to 24 carbon atoms, monofatty acid sorbitan esters having 10 to 24 carbon atoms, and monofatty acid sorbit esters having 10 to 24 carbon atoms.

[0017]

As the ceramides, one or two or more selected from the group consisting of natural ceramides and pseudo-ceramides can be used. From the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, specifically, ceramides described in JP-A-2013-53146 are preferable.

[0018]

Specific examples of the natural ceramides include ceramides type 1 to 7 (for example, swine and human ceramides described in figure 2 of J. Lipid Res., 24:759(1983) and figure 4 of J. Lipid Res., 35:2069(1994)) obtained by amidating sphingosine, dihydrosphingosine, phytosphingosine or sphingadienine.

[0019]

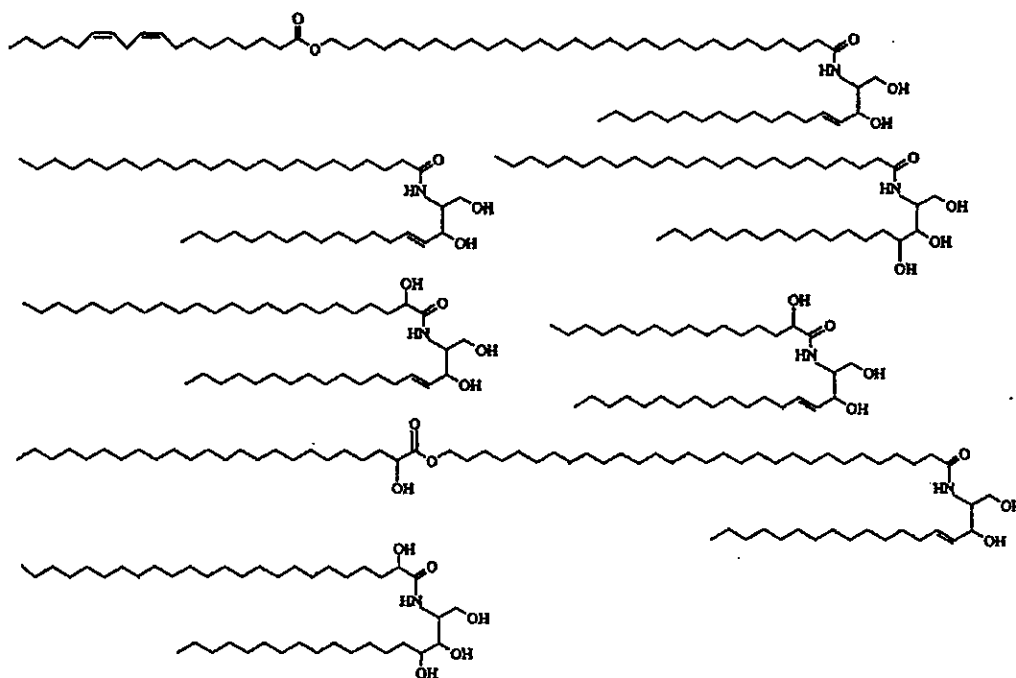
Further, an N-alkyl form thereof (e.g., an N-methyl form) is also included.

As these ceramides, natural-type (D (-) form) optically active substances, non-natural-type (L (+) form) optically active substances, or a mixture of natural-type and non-natural type optically active substances may be used. The relative configuration of the aforementioned compound may be either a natural-type configuration, or another non-natural-type configuration, or otherwise, a mixture of these configurations may be used. These ceramides are especially preferably compounds of CERAMIDE1, CERAMIDE2, CERAMIDE3, CERAMIDE5

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and CERAMIDE6II (hitherto, INCI, 8th Edition), and compounds represented by the following formulae.

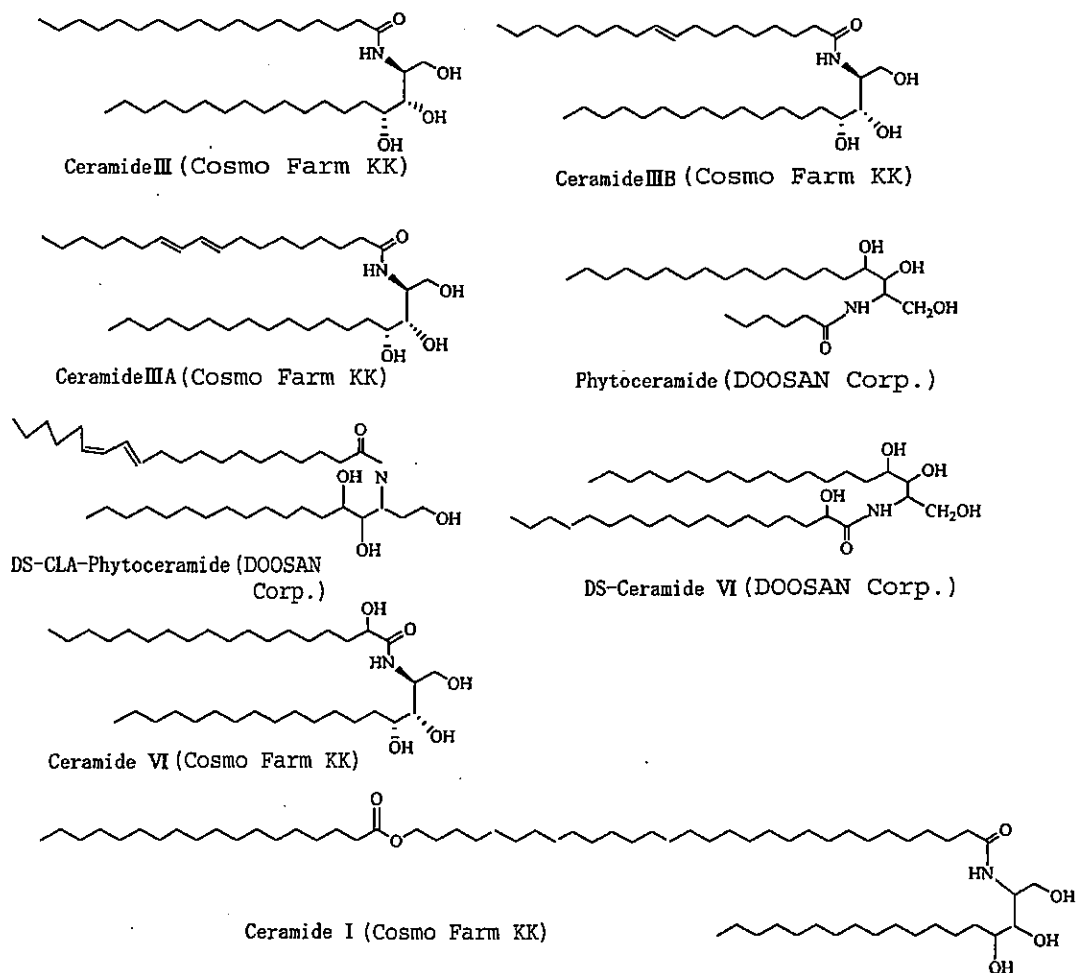
[0020]



[0021]

These may be either of extracts from nature and synthetic substances, and commercially available ones can be used. The commercially available natural ceramides include Ceramide I, Ceramide III, Ceramide IIIA, Ceramide IIIB, Ceramide IIIC and Ceramide VI (hitherto, Cosmo Farm KK), Ceramide TIC-001 (Takasago International Corp.), CERAMIDE II (Quest International, Inc.), DS-Ceramide VI, DS-CLA-Phytoceramide, C6-Phytoceramide and DS-ceramide Y3S (DOOSAN Corp.), and CERAMIDE2 (Sederma).

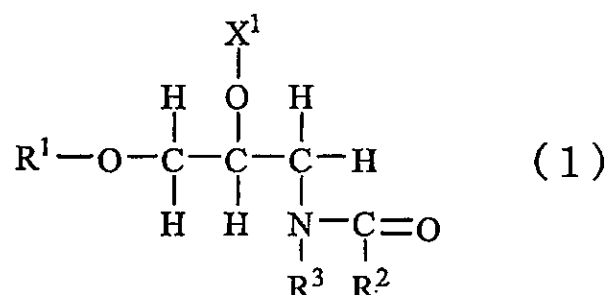
[0022]



[0023]

The pseudo-ceramides are, from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, preferably pseudo-ceramides represented by the following general formula (1).

[0024]



[0025]

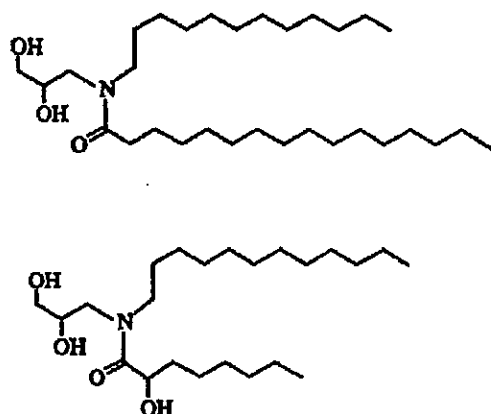
In the formula (1),  $\text{R}^1$  represents an optionally hydroxyl-substituted, linear, branched or cyclic and saturated or unsaturated hydrocarbon group having 10 to 22 carbon atoms, or a hydrogen atom;  $\text{X}^1$  represents a hydrogen atom, an acetyl group, or a glyceryl group;  $\text{R}^2$  represents an optionally hydroxyl- or amino-substituted, linear, branched or cyclic and saturated or unsaturated hydrocarbon group having 5 to 22 carbon atoms, or the aforementioned hydrocarbon group, to the  $\omega$ -terminus of which an optionally hydroxyl-substituted linear or branched and saturated or unsaturated fatty acid having 8 to 22 carbon atoms binds via an ester bond; and  $\text{R}^3$  represents a hydrogen atom, or an alkyl group having a total carbon number of 1 to 30, which is optionally substituted with a hydroxyl group, a hydroxyalkoxy group, an alkoxy group or an acetoxy group.

[0026]

Among these, from the viewpoint of improving the preservation stability of the cosmetic for protection

against ultraviolet radiation, pseudo-ceramides represented by the following formulae are more preferable.

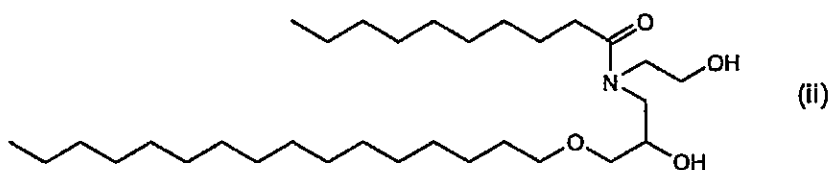
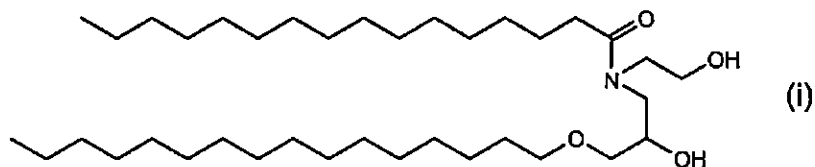
[0027]



[0028]

As the compounds represented by the formula (1), a pseudo-type ceramide in which R<sup>1</sup> represents a hexadecyl group, X<sup>1</sup> represents a hydrogen atom, R<sup>2</sup> represents a pentadecyl group, and R<sup>3</sup> represents a hydroxyethyl group; or a pseudo-type ceramide wherein R<sup>1</sup> represents a hexadecyl group, X<sup>1</sup> represents a hydrogen atom, R<sup>2</sup> represents a nonyl group, and R<sup>3</sup> represents a hydroxyethyl group, are preferable. A pseudo-type ceramide in which, in the formula (1), R<sup>1</sup> represents a hexadecyl group, X<sup>1</sup> represents a hydrogen atom, R<sup>2</sup> represents a pentadecyl group, and R<sup>3</sup> represents a hydroxyethyl group (N-(hexadecyloxyhydroxypropyl)-N-hydroxyethylhexadecanamide) is more preferable. Further, pseudo-ceramides (i) and (ii) represented by the following formulae are also preferable.

[0029]



[0030]

Moreover, examples of the alcohol having 10 to 24 carbon atoms include myristyl alcohol, cetyl alcohol, stearyl alcohol, behenyl alcohol, and oleyl alcohol. Among these alcohols, alcohols having a linear alkyl group are preferable; alcohols having 16 to 18 carbon atoms are more preferable; at least one or two or more selected from the group consisting of cetyl alcohol and stearyl alcohol are even more preferable; and alcohols including cetyl alcohol and stearyl alcohol are further preferable.

[0031]

Examples of the linear saturated fatty acids having 10 to 24 carbon atoms include lauric acid, myristic acid, palmitic acid, stearic acid and behenic acid. Among these, from the viewpoint of the preservation stability of the cosmetic for protection against ultraviolet radiation and improving the ultraviolet protection effect

thereof, linear saturated fatty acids having 14 to 22 carbon atoms are preferable; linear saturated fatty acids having 16 to 22 carbon atoms are more preferable; and a linear saturated fatty acid including at least one selected from the group consisting of palmitic acid and stearic acid is still more preferable.

[0032]

Examples of the monofatty acid glycerin ester having 10 to 24 carbon atoms include glycerin monolauric acid ester, glycerin monomyristic acid ester, glycerin monopalmitic acid ester, glycerin monostearic acid ester, glycerin monobehenic acid ester, glycerin monooleic acid ester, and glycerin monoisostearic acid ester. Among these monofatty acid glycerin esters, at least one or two or more selected from the group consisting of glycerin monobehenic acid ester, glycerin monostearic acid ester, and glycerin monopalmitic acid ester are preferable, and glycerin monobehenic acid ester is more preferable.

[0033]

Examples of the monoalkyl glyceryl ether having 10 to 24 carbon atoms include monodecyl glyceryl ether, monolauryl glyceryl ether, monomyristyl glyceryl ether, monocetyl glyceryl ether, monostearyl glyceryl ether, and monobehenyl glyceryl ether.

[0034]

Examples of the monofatty acid sorbitan ester having 10 to 24 carbon atoms include sorbitan monolaurate,

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sorbitan monomyristate, sorbitan monopalmitate, sorbitan monostearate, and sorbitan monobehenate.

[0035]

The component (B) is, from the viewpoint of the preservation stability of the cosmetic for protection against ultraviolet radiation and improving the ultraviolet protection effect thereof, preferably one or two or more selected from the group consisting of alcohols having 14 to 22 carbon atoms, monofatty acid glycerin esters having 14 to 22 carbon atoms, monoalkyl glyceryl ethers having 14 to 22 carbon atoms and monofatty acid sorbitan esters having 14 to 22 carbon atoms; more preferably one or two or more selected from the group consisting of alcohols having 16 to 22 carbon atoms and monofatty acid glycerin esters having 16 to 22 carbon atoms; and still more preferably one or two or more selected from the group consisting of cetyl alcohol, stearyl alcohol and lipophilic monofatty acid glycerin esters.

[0036]

Moreover, from the same viewpoint as described above, the component (B) preferably comprise an alcohol having 14 to 22 carbon atoms and at least one selected from the group consisting of a monofatty acid glycerin ester having 14 to 22 carbon atoms, a monoalkyl glyceryl ether having 14 to 22 carbon atoms, and a monofatty acid sorbitan ester having 14 to 22 carbon atoms; more

preferably comprise an alcohol having 14 to 22 carbon atoms and a monofatty acid glycerin ester having 14 to 22 carbon atoms; even more preferably comprise an alcohol having 16 to 22 carbon atoms and a monofatty acid glycerin ester having 16 to 22 carbon atoms; and further preferably comprise cetyl alcohol and stearyl alcohol, and a monofatty acid glycerin ester having 16 to 22 carbon atoms.

[0037]

The component (B) can be used singly or in a combination of two or more, and the content thereof is, from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, from the viewpoint of improving the ultraviolet protection effect thereof, and from the viewpoint of making feeling of use good, particularly reducing the stickiness, in the whole composition, 1 mass% or higher, preferably 1.5 mass% or higher, more preferably 2 mass% or higher, and still more preferably 2.5 mass% or higher, and is 10 mass% or lower, preferably 8 mass% or lower, more preferably 5 mass% or lower, and still more preferably 3.8 mass% or lower. Further, the content of the component (B) is, in the whole composition, 1 to 10 mass%, preferably 1.5 to 8 mass%, more preferably 2 to 5 mass%, and still more preferably 2.5 to 3.8 mass%.

[0038]

The component (C) to be used in the present invention is a liquid oil agent comprising an oil-soluble ultraviolet absorber.

As the oil-soluble ultraviolet absorber, oil-soluble ultraviolet absorbers to be used for usual cosmetics can be used. Examples of the oil-soluble ultraviolet absorbers include salicylic acid-based compounds such as homomenthyl salicylate, octyl salicylate and triethanolamine salicylate; p-aminobenzoic acid-based compounds such as p-aminobenzoic acid, ethyldihydroxypropyl p-aminobenzoate, glyceryl p-aminobenzoate, octyldimethyl p-aminobenzoate, amyl p-dimethylaminobenzoate and 2-ethylhexyl p-dimethylaminobenzoate; cinnamic acid-based compounds such as 2-ethylhexyl p-methoxycinnamate (for example, Uvinul MC80, manufactured by BASF AG), glyceryl di-p-methoxycinnamate mono-2-ethylhexanoate, methyl 2,5-diisopropylcinnamate, methylbis(trimethylsiloxy)silylisopentyl trimethoxycinnamate, isopropyl p-methoxycinnamate-diisopropylcinnamate mixtures and p-methoxyhydrocinnamic acid diethanolamine salt; octocrylene (for example, Parsol 340, manufactured by DSM Nutrition Japan Co., Ltd.), 1-(3,4-dimethoxyphenyl)-4,4-dimethyl-1,3-pentanedione, cinoxate and methyl-O-aminobenzoate, 3-(4-methylbenzylidene)camphor; benzophenone-based compounds such as 4-(2- $\beta$ -glucopyranosiloxy)propoxy-2-

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hydroxybenzophenone, dihydroxydimethoxybenzophenone, sodium dihydroxydimethoxybenzophenonedisulfonate, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxybenzophenone-5-sulfuric acid, 2,2'-dihydroxy-4-methoxybenzophenone, 2,4-dihydroxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and 2-hydroxy-4-N-octoxybenzophenone; triazine-based compounds such as 2,4,6-tris[4-(2-ethylhexyloxycarbonyl)anilino]-1,3,5-triazine (for example, Uvinul T150, manufactured by BASF AG) and bis-ethylhexyloxyphenol methoxyphenyl triazine (for example, Tinosorb S, manufactured by BASF AG); benzoylmethane-based compounds such as 2-phenylbenzimidazole-5-sulfuric acid, 4-isopropylidibenzoylmethane and 4-tert-butyl-4'-methoxydibenzoylmethane (for example, Parsol 1789, manufactured by DSM Nutrition Japan Co., Ltd.); and 2-ethylhexyl dimethoxybenzylidenedioxoimidazolidinepropionate (for example, Softshade DH, manufactured by Ajinomoto Co., Inc.), diethylamino hydroxybenzoyl benzoic acid hexyl ester (for example, Uvinul Aplus, manufactured by BASF AG) and methylenebisbenzotriazolyltetramethylbutylphenol (for example, Tinosorb M, manufactured by BASF AG).

Here, among the ultraviolet absorbers, there are some which themselves are solid at normal temperature. However, in the cosmetic for protection against

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ultraviolet radiation of the present invention, since each component is mixed with the component (E) under heating, the oil-soluble ultraviolet absorber of the component (C) is thought to be present in a liquid state in an obtained cosmetic for protection against ultraviolet radiation.

[0039]

Among these, from the viewpoint of improving the ultraviolet protection effect, preferable is one or two or more selected from the group consisting of 2-ethylhexyl p-methoxycinnamate (for example, Uvinul MC80, manufactured by BASF AG), octocrylene ( for example, Parsol 340, manufactured by DSM Nutrition Japan Co., Ltd.), 2,4,6-tris[4-(2-ethylhexyloxycarbonyl)anilino]-1,3,5-triazine (for example, Uvinul T150, manufactured by BASF AG), 4-tert-butyl-4'-methoxydibenzoylmethane (for example, Parsol 1789, manufactured by DSM Nutrition Japan Co., Ltd.), 2-ethylhexyl dimethoxybenzylidenedioxoimidazolidinepropionate (for example, Softshade DH, manufactured by Ajinomoto Co., Inc.), diethylamino hydroxybenzoyl benzoic acid hexyl ester(for example, Uvinul Aplus, manufactured by BASF AG) and bis-ethylhexyloxyphenol methoxyphenyl triazine (for example, Tinosorb S, manufactured by BASF AG). Further from the similar viewpoint, more preferable is one or two or more selected from the group consisting of 2-ethylhexyl p-methoxycinnamate (for example, Uvinul MC80,

manufactured by BASF AG), diethylamino hydroxybenzoyl benzoic acid hexyl ester (for example, Uvinul Aplus, manufactured by BASF AG) and bis-ethylhexyloxyphenol methoxyphenyl triazine (for example, Tinosorb S, manufactured by BASF AG).

Further from the similar viewpoint, as the oil-soluble ultraviolet absorber, more preferable is one or two or more selected from the group consisting of the above cinnamic acid-based oil-soluble ultraviolet absorbers, diethylamino hydroxybenzoyl benzoic acid hexyl ester and the above triazine-based oil-soluble ultraviolet absorbers; still more preferable is the incorporation of the above three kinds of the oil-soluble ultraviolet absorbers; and further still more preferable is the incorporation of 2-ethylhexyl p-methoxycinnamate (for example, Uvinul MC80, manufactured by BASF AG), diethylamino hydroxybenzoyl benzoic acid hexyl ester (for example, Uvinul Aplus, manufactured by BASF AG) and bis-ethylhexyloxyphenol methoxyphenyl triazine (for example, Tinosorb S, manufactured by BASF AG).

[0040]

Liquid oil agents other than the oil-soluble ultraviolet absorber have a fluidity at 25°C. The liquid oil agents are not especially limited as long as being to be used for usual cosmetics, and examples thereof include linear or branched-chain hydrocarbon oils such as liquid paraffin, light isoparaffin, squalane and squalene; ester

oils such as fatty acid esters such as neopentyl glycol dicaprate, isopropyl palmitate and alkyl benzoates, and polyhydric alcohol fatty acid esters such as pentaerythritol tetra-2-ethylhexanoate; silicone oils such as dimethylpolysiloxane, dimethylcyclopolysiloxane, methylphenylpolysiloxane, methylhydrogenpolysiloxane and higher alcohol-modified silicone oils; and fluoro oils such as fluoropolyethers and perfluoroalkyl ether silicones. These may be natural oils including vegetable oils such as jojoba oil and olive oil; and animal oils such as liquid lanoline.

Among these, as the liquid oil agents other than the oil-soluble ultraviolet absorber, from the viewpoint of reducing the stickiness, and improving the compatibility with the oil-soluble ultraviolet absorber, preferable is the incorporation of at least one selected from the group consisting of the linear or branched-chain hydrocarbon oils, the ester oils and the silicone oils.

[0041]

The content of the oil-soluble ultraviolet absorber in the whole liquid oil agent of the component (C) is, from the viewpoint of improving the ultraviolet protection effect and reducing the feeling of skin irritation, preferably 60 mass% or higher, more preferably 65 mass% or higher, and still more preferably 70 mass% or higher, and preferably 100 mass% or lower, more preferably 95 mass% or lower, and still more

preferably 85 mass% or lower. Further the content of the oil-soluble ultraviolet absorber in the whole liquid oil agent of the component (C) is preferably 60 to 100 mass%, more preferably 65 to 90 mass%, and still more preferably 70 to 85 mass%.

The content of the cinnamic acid-based oil-soluble ultraviolet absorber in the oil-soluble ultraviolet absorber is, from the viewpoint of improving the protective effect and reducing the feeling of skin irritation, preferably 60 to 100 mass%, and more preferably 70 to 90 mass%. From the similar viewpoint, the total content of the triazine-based oil-soluble ultraviolet absorber and diethylamino hydroxybenzoyl benzoic acid hexyl ester in the oil-soluble ultraviolet absorber is preferably 0 to 40 mass%, and more preferably 10 to 30 mass%.

The content ratio of the cinnamic acid-based oil-soluble ultraviolet absorber to the total amount of the triazine-based oil-soluble ultraviolet absorber + diethylamino hydroxybenzoyl benzoic acid hexyl ester, (the cinnamic acid-based oil-soluble ultraviolet absorber / [the triazine-based oil-soluble ultraviolet absorber + diethylamino hydroxybenzoyl benzoic acid hexyl ester]), in the oil-soluble ultraviolet absorber is, from the viewpoint of improving the ultraviolet protection effect and reducing the feeling of skin irritation, preferably

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9/1 to 5/5, more preferably 8.5/1.5 to 6/4, and still more preferably 8/2 to 6.5/3.5.

The content of the oil-soluble ultraviolet absorber in the cosmetic for protection against ultraviolet radiation is, from the viewpoint of improving the ultraviolet protection effect and reducing the feeling of skin irritation, in the whole composition, preferably 6 mass% or higher, more preferably 8 mass% or higher, and still more preferably 10 mass% or higher, and preferably 20 mass% or lower, more preferably 18 mass% or lower, and still more preferably 15 mass% or lower. Further, the content of the oil-soluble ultraviolet absorber in the cosmetic for protection against ultraviolet radiation is, in the whole composition, preferably 6 to 20 mass%, more preferably 8 to 18 mass%, and still more preferably 10 to 15 mass%.

[0042]

The component (C) can be used singly or in a combination of two or more; and the content thereof is, from the viewpoint of improving the ultraviolet protection effect, reducing the feeling of skin irritation, and further making the feeling of use good, particularly reducing the stickiness, in the whole composition, 1 mass% or higher, preferably 3 mass% or higher, more preferably 10 mass% or higher, and still more preferably 12 mass% or higher, and 40 mass% or lower, preferably 35 mass% or lower, more preferably 25 mass% or

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lower, and still more preferably 17 mass% or lower. Further the content of the component (C) is, in the whole composition, 1 to 40 mass%, preferably 3 to 35 mass%, more preferably 10 to 25 mass%, and still more preferably 12 to 17 mass%.

[0043]

In the present invention, the mass ratio of the component (A) to the component (C),  $[(A)/(C)]$ , is, from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, preferably 0.01 or higher, more preferably 0.015 or higher, still more preferably 0.025 or higher, and further still more preferably 0.034 or higher, and preferably 0.2 or lower, more preferably 0.12 or lower, still more preferably 0.06 or lower, and further still more preferably 0.05 or lower. Further the mass ratio of the component (A) to the component (C),  $[(A)/(C)]$ , is preferably 0.01 to 0.2, more preferably 0.015 to 0.12, still more preferably 0.025 to 0.06, and further still more preferably 0.034 to 0.05.

[0044]

In the present invention, the mass ratio of the component (B) to the component (C),  $[(B)/(C)]$ , is, from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, and from the viewpoint of making the feeling of use good, particularly reducing the stickiness, preferably 0.01 or

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higher, more preferably 0.12 or higher, still more preferably 0.18 or higher, and further still more preferably 0.19 or higher, and preferably 0.5 or lower, more preferably 0.39 or lower, still more preferably 0.27 or lower, and further still more preferably 0.24 or lower. Further the mass ratio of the component (B) to the component (C),  $[(B)/(C)]$ , is preferably 0.01 to 0.5, more preferably 0.12 to 0.39, still more preferably 0.18 to 0.27, and further still more preferably 0.19 to 0.24.

[0045]

The solid oil agent of the component (D) is in a solid state at 25°C.

Such a solid oil agent is not especially limited as long as being to be used for usual cosmetics, and examples thereof include vegetable waxes such as candelilla wax (melting point: 66 to 71°C), rice bran wax (melting point: 77 to 86°C), sunflower wax (melting point: 65 to 80°C), carnauba wax (melting point: 80 to 86°C) and Japan tallow (melting point: 50 to 56°C); animal waxes such as beeswax (melting point: 62 to 65°C) and spermaceti (melting point: 42 to 52 °C); mineral waxes such as montan wax (82 to 95°C) and ozokerite (melting point: 66 to 78°C); petroleum waxes such as microcrystalline wax (melting point: 60 to 90°C), paraffin (40 to 70°C) and ceresin (60 to 80°C); and synthetic waxes such as hydrogenated castor oil (melting point: 85°C), hydrogenated jojoba oil (melting point: 66

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to 70°C), 12-hydroxystearic acid (melting point: 75 to 78°C), stearic acid amide (melting point: 101°C), silicone wax (melting point: 28 to 80°C) and polyethylene wax (melting point: 94 to 152°C).

In the present invention, the melting point of the solid oil agent is measured by Japanese Standards of Quasi-Drug Ingredients, General Test Method 70: Melting Point Measuring Method.

[0046]

The component (D) is, from the viewpoint of carrying out the exact temperature control in a cooling step described later, and improving the preservation stability of the cosmetic, preferably a solid oil agent having a melting point of 60°C or higher and 80°C or lower, and more preferably a wax having a melting point of 60°C or higher and 80°C or lower. Commercially available products can be used, for example, Candelilla Wax MK-2 (manufactured by Yokozeki Oil & Fat Industries Co., Ltd., melting point: 71°C), purified Rice Bran Wax S-100 (manufactured by Yokozeki Oil & Fat Industries Co., Ltd., melting point: 78°C), purified Sunflower Wax (manufactured by Yokozeki Oil & Fat Industries Co., Ltd., melting point: 76°C), BEES WAX SP (manufactured by Strahl & Pitsch Inc., melting point: 62 to 65°C), WHITE OZOKERITE WAX 1025 (manufactured by Strahl & Pitsch Inc., melting point: 68.3 to 71.1°C), Multiwax (manufactured by Sonneborn, melting point: 75°C), HNP-3 (manufactured by

Nippon Seiro Co., Ltd., melting point: 64°C), HNP-9 (manufactured by Nippon Seiro Co., Ltd., melting point: 75°C), HNP-11 (manufactured by Nippon Seiro Co., Ltd., melting point: 68°C), and Ceresin #810 (manufactured by Nikko Rica Corp., melting point: 74°C).

Further, the component (D) is, from the viewpoint of improving the preservation stability of the skin cosmetic and reducing the stickiness, preferably a solid oil agent containing one or more selected from the F group consisting of ceresins and paraffins and having a melting point of 60°C or higher and 80°C or lower.

[0047]

The component (D) can be used singly or in a combination of two or more; and the content thereof is, from the viewpoint of improving the preservation stability of the skin cosmetic, making the feeling of use good, particularly reducing the stickiness, and further from the viewpoint of improving the ultraviolet protection effect, in the whole composition, 0.01 mass% or higher, preferably 0.08 mass% or higher, more preferably 0.1 mass% or higher, and still more preferably 0.5 mass% or higher, and 6 mass% or lower, preferably 4.5 mass% or lower, more preferably 2.5 mass% or lower, and still more preferably 1.5 mass% or lower. Further the content of the component (D) is, in the whole composition, 0.01 to 6 mass%, preferably 0.08 to 4.5 mass%, more

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preferably 0.1 to 2.5 mass%, and still more preferably 0.5 to 1.5 mass%.

[0048]

Further in the present invention, the mass ratio of the component (D) to the component (C),  $[(D)/(C)]$ , is, from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, and improving the feeling of use, particularly reducing the stickiness, preferably 0.01 or higher, more preferably 0.02 or higher, and still more preferably 0.04 or higher, and preferably 0.5 or lower, more preferably 0.3 or lower, and still more preferably 0.1 or lower. Further the mass ratio of the component (D) to the component (C),  $[(D)/(C)]$ , is preferably 0.01 to 0.5, more preferably 0.02 to 0.3, and still more preferably 0.04 to 0.1.

[0049]

The component (E) to be used in the present invention is water, and the amount thereof is the remaining amount to those of the other components; and it is conceivable that depending on the combination of the components (A) to (C) and (E), emulsified particles having a stable  $\alpha$ -gel structure are formed in the cosmetic. The presence of the  $\alpha$ -gel structure makes it possible for the liquid oil agent containing the oil-soluble ultraviolet absorber to be contained in the  $\alpha$ -gel structure. In conventional cosmetics containing

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emulsified particles having an  $\alpha$ -gel structure, there is room for improvement in such recent years' highly required properties that whereas the ultraviolet protection effect is larger, the feeling of use is good and no feeling of skin irritation is given.

The cosmetic of the present invention contains, in addition to the components (A) to (C) and (E), further the component (D), and has an oil agent comprising an ultraviolet absorber homogeneously dispersed therein, resulting in excellent preservation stability, high ultraviolet protection effect, good feeling of use, and no feeling of skin irritation by being produced by a method described later.

The content of the component (E) is, from the viewpoint of improving the preservation stability of the cosmetic for protection against ultraviolet radiation, and improving the freshness, in the whole composition, preferably 35 mass% or higher, and more preferably 45 mass% or higher, and preferably 65 mass% or lower, and more preferably 55 mass% or lower. Further the content of the component (E) is, in the whole composition, preferably 35 to 65 mass%, and more preferably 45 to 55 mass%.

[0050]

The cosmetic for protection against ultraviolet radiation of the present invention can further contain (F) a water-soluble polymer, and the incorporation

thereof can improve the preservation stability of the cosmetic for protection against ultraviolet radiation, and can improve the ultraviolet protection effect.

Such a water-soluble polymer is not especially limited as long as being to be used for usual cosmetics, and any of natural polymers, semi-synthetic polymers and synthetic polymers can be used.

Examples of the natural polymers include xanthan gum, carrageenan and alginic acid. Semi-synthetic polysaccharide-based polymers include modified polysaccharides such as hydroxycellulose, hydroxypropylcellulose, sodium carboxymethylcellulose, methylcellulose, hydroxymethylcellulose and cationized cellulose. The synthetic polymers include acrylic polymers such as acrylate-based polymers such as carbomer (crosslinked polyacrylic acid), polyacrylic acid, sodium polyacrylate, acrylic acid-alkyl methacrylate copolymers, polyacrylamide, (sodium acrylate/sodium acryloyldimethyltaurate) copolymers, (hydroxyethyl acrylate/sodium acryloyldimethyltaurate) copolymers, (acrylamide/ammonium acrylate) copolymers and polyacrylate-13; and polyvinylpyrrolidone, polyvinyl alcohols and cationized polyvinylpyrrolidone. Among these, the acrylic polymers are preferable; more preferable is at least one selected from the group consisting of carbomer, acrylic acid/alkyl methacrylate copolymers, polyacrylamide, (sodium acrylate/sodium

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acryloyldimethyltaurate) copolymers, (hydroxyethyl acrylate/sodium acryloyldimethyltaurate) copolymers, (acrylamide/ammonium acrylate) copolymers and polyacrylate-13; and still more preferable is at least one selected from the group consisting of (sodium acrylate/sodium acryloyldimethyltaurate) copolymers, (hydroxyethyl acrylate/sodium acryloyldimethyltaurate) copolymers, (acrylamide/ammonium acrylate) copolymers and polyacrylate-13.

[0051]

Commercially available products of the carbomer include Carbopol 910, Carbopol 934, Carbopol 940, Carbopol 941, Carbopol 980 and Carbopol 981 (hitherto, manufactured by Lubrizol Advanced Materials, Inc.); commercially available products of the acrylic acid/alkyl methacrylate copolymers include Carbopol 1382, Carbopol ETD2020, Pemulen TR-1 and Pemulen TR-2 (hitherto, manufactured by Lubrizol Advanced Materials, Inc.); commercially available products of the polacrylamides include SEPIGEL 305 (manufactured by Seppic); commercially available products of the (sodium acrylate/sodium acryloyldimethyltaurate) copolymers include SIMULGEL EG (manufactured by Seppic); and commercially available products of the hydroxyethyl acrylate/sodium acryloyldimethyltaurate copolymers include SIMULGEL FL, SIMULGEL NS, SEPIPLUS S and SEPINOV EMT 10 (hitherto, manufactured by Seppic).

[0052]

The component (F) can be used singly or in a combination of two or more, and the content thereof is, from the viewpoint of improving the preservation stability of the emulsified particles, in the whole composition, preferably 0.3 mass% or higher, and more preferably 0.5 mass% or higher, and preferably 1.5 mass% or lower, and more preferably 1.0 mass% or lower. Further the content of the component (F) is, in the whole composition, preferably 0.3 to 1.5 mass%, and more preferably 0.5 to 1.0 mass%.

[0053]

The cosmetic for protection against ultraviolet radiation of the present invention can further contain an ultraviolet scattering agent, and the incorporation thereof can more enhance the ultraviolet protection effect. The ultraviolet scattering agent is not limited as long as being to be used for usual cosmetics, and examples thereof include metal oxides such as titanium oxide, zinc oxide and cerium oxide, and metals such as silicon and aluminum.

The shape of such an ultraviolet scattering agent may be either a sphere or a spindle. In addition, with regard to the mean particle diameter, the maximum minor axis is preferably 0.005 to 0.5  $\mu\text{m}$ , more preferably 0.007 to 0.2  $\mu\text{m}$ , and even more preferably 0.01 to 0.07  $\mu\text{m}$ .

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Here, the mean particle diameter is obtained by measuring maximum minor axis diameters in particle diameters of 300 particles in an image taken under the condition of a magnification of 100,000 by a transmission electron microscope (TEM), and calculating the mean value thereof. In the present invention, the maximum minor axis diameter means a diameter of a minor axis having a maximum diameter among minor axes orthogonal to the major axis.

[0054]

The ultraviolet scattering agent is used, from the viewpoint of improving the ultraviolet protection effect, improving the preservation stability and reducing the stickiness, preferably by having been subjected to a conventionally well-known surface treatment, for example, fluorine compound treatment (preferably a perfluoroalkylphosphate ester treatment, perfluoroalkylsilane treatment, perfluoropolyether treatment, fluorosilicone treatment or fluorosilicone resin treatment), a silicone treatment (preferably a methylhydrogenpolysiloxane treatment, dimethylpolysiloxane treatment or gas-phase tetramethyltetrahydrogencyclotetrasiloxane treatment), a silicone resin treatment (preferably a trimethylsiloxysilicic acid treatment), a pendant treatment (a method of adding an alkyl chain or the like after a gas phase silicone treatment), a silane coupling

agent, a titanium coupling agent, a silane treatment (preferably an alkylsilane or alkylsilazane treatment), an oil agent treatment, an N-acylated lysine treatment, a polyacrylic acid treatment, a metallic soap treatment (preferably stearate or myristate salts), an acryl resin treatment, or a metal oxide treatment, and more preferably by combining a plurality of these treatments.

Examples thereof include coating a titanium oxide surface with silane, or a metal oxide such as alumina, and thereafter surface treating with an alkylsilane or a fatty acid. It is preferable that the surface of a titanium oxide be treated with alumina and be then treated with a fatty acid. Moreover, the surface of such an ultraviolet scattering agent is preferably treated with a compound having a carboxyl group, is more preferably treated with a fatty acid having 12 to 22 carbon atoms, and is even more preferably treated with a fatty acid having 14 to 20 carbon atoms.

[0055]

The ultraviolet scattering agent can be used singly or in a combination of two or more, and the content thereof is, from the viewpoint of improving the ultraviolet protection effect, in the whole composition, preferably 0.1 mass% or higher, more preferably 0.5 mass% or higher, and still more preferably 1 mass% or higher, and preferably 10 mass% or lower, more preferably 8 mass% or lower, and still more preferably 5 mass% or lower.

Further the content of the ultraviolet scattering agent is, in the whole composition, preferably 0.1 to 10 mass%, more preferably 0.5 to 8 mass%, and still more preferably 1 to 5 mass%.

[0056]

The cosmetic for protection against ultraviolet radiation of the present invention can suitably further contain, as components to be used for usual cosmetics, other than the components (A) to (F), for example, thickeners, germicides, humectants, wetting agents, colorants, antiseptics, feeling improvers, powders, perfumes, anti-inflammatory agents, whitening agents, antiperspirants and antioxidants.

[0057]

The cosmetic for protection against ultraviolet radiation of the present invention is produced by a method comprising an emulsification step of mixing a composition comprising the components (A) to (D) with (E) water under heating to form an emulsion, and a cooling step of cooling the emulsion formed in the emulsification step at a cooling rate of 0.5 to 5°C/sec.

Here, in the case where the cosmetic for protection against ultraviolet radiation of the present invention contains the component (F), the production method of the cosmetic for protection against ultraviolet radiation preferably comprises a step of mixing a mixed liquid previously prepared by mixing a part of the component (E)

with the component (F), with the emulsion obtained by the cooling step.

[0058]

In the emulsification step, the emulsion can be obtained by mixing blending components under heating preferably at 60 to 120°C, more preferably at 80 to 100°C by using a homomixer, an ultrasonic emulsifying machine, a high-pressure emulsifying machine or the like, which are usually used when cosmetics are produced.

Further in the cooling step, there can be used a method of continuously quickly cooling the obtained emulsion by using a vibration-type stirring mixing apparatus, a scraped surface heat exchanger (Onlator, Sakura Seisakusho, Ltd.), a static mixer (Noritake Co., Ltd.), a usual plate-type heat exchanger, a double-pipe heat exchanger, or the like, or a method of stirring and cooling in a usual blending tank; and the cooling rate is, from the viewpoint of forming the  $\alpha$ -gel structure and from the viewpoint of solidifying the solid oil agent, 0.5°C/sec or higher, and preferably 0.8°C/sec or higher, and 5°C/sec or lower, and preferably 1.5°C/sec or lower. Further the cooling rate of the emulsion is 0.5 to 5°C/sec, and preferably 0.8 to 1.5°C/sec.

It is preferable that the emulsion be cooled down to a temperature equal to or lower than the solidification temperature of the oily component by such a cooling step.

[0059]

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In the emulsification step and the cooling step, preferably, the emulsification step uses a high-pressure emulsifying machine or an ultrasonic emulsifying machine; the cooling step uses a vibration-type stirring mixing apparatus equipped with a stirring gear composed of a driving shaft and stirring blades attached to the driving shaft in a tubular casing wherein the driving shaft is configured to vibrate in the shaft direction; the stirring blades each have one or more holes and/or one or more notches; and the emulsion obtained in the emulsification step is made to pass through the vibration-type stirring mixing apparatus to continuously cool the emulsion in the cooling step, whereby a cosmetic (fine-particle dispersion) containing fine emulsified particles dispersed therein can be obtained.

[0060]

More specifically, in Figure 1, there is illustrated a schematic view of a production apparatus to be suitably used in the present invention. A production apparatus 100 illustrated in Figure 1 is equipped with an emulsifying unit 20 to mix a composition containing the components (A) to (D) with (E) water under heating to form an emulsion, and a cooling unit 30 to cool the formed emulsion. Further the emulsifying unit 20 is equipped with a first emulsifying section 21 and a second emulsifying section 22. The first emulsifying section 21 is used to be charged with all of or part of components

constituting the fine particle dispersion, and to mix the charged components with water under heating to thereby obtain a pre-emulsion. The second emulsifying section 22 is located on the downstream side of the first emulsifying section 21, and is used to impart a high energy to the pre-emulsion obtained in the first emulsifying section 21 to thereby obtain a fine emulsion. The cooling unit 30 is located on the downstream side of the emulsifying unit 20, and is used to cool the heated and mixed emulsion to a temperature equal to or lower than the solidification temperature of the oily component being a solid at 25°C to thereby obtain a fine particle dispersion being a target.

[0061]

The first emulsifying section 21 of the emulsifying unit 20 is, as illustrated in Figure 1, equipped with a mixing tank 211. The mixing tank 211 is heated by a jacket 212 covering the side part of the mixing tank 211, and configured to be regulated at a predetermined temperature. In the mixing tank 211, a stirring blade 213 is installed. The stirring blade 213 is connected to a motor 215 installed outside the mixing tank 211 through a shaft 214, and configured to be rotatable. To the bottom part of the mixing tank 211, a pipe 216 to take out the pre-emulsion mixed in the tank 211 is connected. The pipe 216 is connected to the second emulsifying section 22 through a valve. Here, for the purpose of

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quantitatively feeding the pre-emulsion obtained in the first emulsifying section 21, as required, a metering pump (not illustrated in figure) may be interposed midway the pipe 216.

[0062]

As the first emulsifying section 21 having the above configuration, T.K. COMBIMIX (trade name), manufactured by PRIMIX Corporation., T.K. AGIHOMOMIXER (trade name), manufactured by PRIMIX Corporation., or the like can be used. These stirring apparatuses are used mostly singly, but, when occasion demands, may suitably be used in a combination of two or more thereof.

[0063]

The second emulsifying section 22 of the emulsifying unit 20 is, as illustrated in Figure 1, equipped with a high-energy processing part 221. The high-energy processing part 221 is configured to be capable of impart a high energy to the pre-emulsion obtained in the first emulsifying section 21 by using a high-pressure emulsifying machine or an ultrasonic emulsifying machine.

To the downstream part of the high-energy processing part 221, there is connected a pipe 222 to take out an emulsion to which the high energy has been imparted in the high-energy processing part 221. The emulsion obtained in the second emulsifying section 22 is designed to be fed to the cooling unit 30 through the pipe 222. Here, for the purpose of quantitatively feeding the

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emulsion obtained in the second emulsifying section 22, as required, a metering pump (not illustrated in figure) may be interposed midway the pipe 222.

[0064]

In the case where a high-pressure emulsifying machine is used as the second emulsifying section 22 having the above configuration, there can be used, for example, Star Burst Mini (item number: HJP-25001) (manufactured by SUGINO MACHINE LIMITED), Ultimixer (manufactured by SUGINO MACHINE LIMITED), Gaulin (manufactured by APV Rannie AS), Microfluidizer (manufactured by Microfluidics International Corp.), and a high-pressure jet emulsifier (manufactured by Nippon BEE Chemical Co., Ltd.), which are high-pressure emulsifying machines.

[0065]

Further in the case where an ultrasonic emulsifying machine is used as the second emulsifying section 22, there can be used, for example, Ikasonic (item number: U200S) (manufactured by IKA-Werk GmbH & Co.KG), an ultrasonic homogenizer (manufactured by NISSEI Corp.), and an ultrasonic homogenizer (manufactured by Ultrasonic Engineering Co., Ltd.), which are equipped with an ultrasonic generation horn. The above-mentioned high-pressure emulsifying machines and ultrasonic emulsifying machines are mostly used singly, but when occasion

demands, may suitably be used in a combination of two or more thereof.

[0066]

The cooling unit 30 is equipped with a vibration-type stirring mixing apparatus 40. The vibration-type stirring mixing apparatus 40 has a nearly cylindrical structure, and has an inflow port 31 connected to the pipe 222 on its one end side and a discharge port 32 on its other end side. The discharge port 32 is connected to a discharging pipe 33. The emulsion fed from the emulsifying unit 20 is fed into the vibration-type stirring mixing apparatus 40 through the inflow port 31, passes through the apparatus 40, and is discharged from the end of the discharging pipe 33 through the discharge port 32. By allowing the fed emulsion to pass through the vibration-type stirring mixing apparatus 40, the emulsion is further mixed and continuously cooled down to a temperature equal to or lower than the solidification temperature of the oily component being a solid at 25°C. In order to carry out the continuous cooling, the vibration-type stirring mixing apparatus is preferably equipped with cooling jackets in which cooling water is circulated on the outer side of a casing 41 described later; and to the vibration-type stirring mixing apparatus 40, there are attached four jackets 34, 35, 36 and 37 in this order from the inflow port 31 side toward the discharge port 32. The each jacket is configured

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such that cooling water is circulated. The temperature of the cooling water can suitably be established; and by these jackets, the fed emulsion can be continuously or stepwise cooled from the inflow port 31 side toward the discharge port 32 side.

[0067]

In Figure 2, there is illustrated an illustrative view of a longitudinal cross-section of the vibration-type stirring mixing apparatus 40. The apparatus 40 is equipped with a stirring gear 44 composed of a driving shaft 42 and stirring blades 43 attached to the driving shaft 42 in a tubular casing 41. The driving shaft 42 is connected to a vibrator 45a, and is configured to vertically vibrate along the shaft direction by the vibrator 45a.

[0068]

The casing 41 is of a tubular shape whose cross-section is circular, and is installed with an inflow port 31 near its lower part. Near the upper part of the casing 41, a discharge port 32 is installed. The emulsion flowing in from the inflow port 31 is mixed and continuously cooled while passing through in the casing 41, and discharged from the discharge port 32.

[0069]

In the casing 41, the above-mentioned stirring gear 44 is disposed. The driving shaft 42 of the stirring gear 44 extends in the longitudinal direction of the

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casing 41. The upper end of the driving shaft 42 is connected to the vibrator 45a through a joint 45b. The vibrator 45a is equipped with a motor (not illustrated in figure) and a well-known cam mechanism (not illustrated in figure) connected to an output shaft of the motor. The cam mechanism is composed of a rotary part (not illustrated in figure) and a rocking part (not illustrated in figure). The rotary part is attached eccentrically to the output shaft of the motor. The rocking part is configured to rock by the eccentric rotation of the rotary part. Then, rocking of the rocking part is transmitted to the driving shaft 42 as vertical vibration.

[0070]

On the inner wall of the casing 41, a plurality of annular partition parts 46 are installed. Any of the partition parts 46 has the same shape, and projects from the inner wall of the casing 41 to the horizontal direction. In the circular holes formed in the centers of the partition parts 46, the driving shaft 42 is inserted. The diameter of the circular holes is made to be larger than a diameter of the driving shaft 42. The adjoining two partition parts zone a plurality of mixing chambers 47 in the interior of the casing 41. The mixing chambers 47 are arranged in series along the longitudinal direction of the casing 41.

[0071]

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In Figure 3(a) and (b), there is illustrated a principal portion enlarged view of the stirring gear 44. The stirring gear 44 is equipped with the driving shaft 42 and the stirring blades 43 attached helically on its circumferential surface. In the Figure, the stirring blades 43 are each attached helically in three rounds. The stirring gear 44 as one set therein in this state is disposed in the each mixing chamber 47 in the casing. Therefore, the number of the sets in the stirring gear 44 is equal to the number of the mixing chambers 47. In the stirring gear 44 in the sets, the directions of the helices of the stirring blades 43 are identical.

[0072]

The stirring blades 43 of the sets in the stirring gear 44 are each provided with one or more holes 48 and/or one or more notches 49. The holes 48 and the notches 49 are provided such that when the stirring gear 44 is viewed from the shaft axis direction of the driving shaft 42 (see Figure 3(a)), the formation positions thereof on vertically adjacent portions of the stirring blade are not coincident. The reason therefor is to prevent generation of short-cut flow in the shaft direction to thereby enhance the stirring mixing effect.

[0073]

As the vibration-type stirring mixing apparatus 40 having the above configuration, for example, one described in JP-A-04-235729 can be used. Further as the

vibration-type stirring mixing apparatus 40 having the above configuration, commercially available ones can also be used. Examples of such commercially available ones include a Vibro Mixer (trade name), manufactured by Reica Co., Ltd., equipped with a cooling jacket.

[0074]

A production method of the fine particle dispersion using the production apparatus 100 having the above configuration will be described. First, all of or part of components constituting the intended fine particle dispersion is charged in the mixing tank 211 of the first emulsifying section 21 of the emulsifying unit 20 (the components charged in the mixing tank 211 include water being a disperse medium). In the case where part of components constituting the fine particle dispersion is charged, the other part of the components may be fed, for example, from the high-energy processing part 221 of the second emulsifying section 22, or from the vibration-type stirring mixing apparatus 40. Here, in the case where the first emulsifying section 21 is provided as two or more sections thereof, all of the components constituting the intended fine particle dispersion may be charged in an upstream-side first emulsifying section 21, or part by part of the components constituting the intended fine particle dispersion may be charged in every first emulsifying section 21. Charging by part by part thereof

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enables mixing conditions and the like of the each component to be suitably regulated each individually.

[0075]

Components to be charged in the mixing tank 211 contain at least one oily component being a solid at 25°C. When charging of the intended components in the mixing tank 211 has been completed, the oily components being a solid at 25°C are made to be in a melted state by heating the mixing tank 211 by the jacket 212. Then, the each component is mixed and dispersed by the stirring blade 213 in the mixing tank 211 to thereby obtain a pre-emulsion. The heating temperature can suitably be established according to the melting points of the solid fats. It is generally preferable that the heating temperature be established at a temperature on the higher side by about 10°C than the melting point of a solid fat having the highest melting point.

[0076]

When the each component charged in the mixing tank 211 is stirred and sufficiently mixed, a valve attached to the bottom part of the mixing tank 211 is opened and the pre-emulsion in the mixing tank 211 is taken out. The pre-emulsion is fed to the high-energy processing part 221 of the second emulsifying section 22 through the pipe 216.

[0077]

In the high-energy processing part 221, a high energy is imparted to the pre-emulsion obtained in the first emulsifying section 21 by using a high-pressure emulsifying machine or an ultrasonic emulsifying machine to thereby obtain an emulsion. The invested energy imparted by using the high-pressure emulsifying machine or the ultrasonic emulsifying machine is, from the viewpoint of making the particle diameter small, preferably  $5 \times 10^4$  J/kg or higher, and more preferably  $2 \times 10^5$  J/kg or higher. The upper limit value of the invested energy is not especially limited, and a higher invested energy is better. Here, the "invested energy" in each emulsifying machine is a value calculated by the following expressions (1) to (3).

[0078]

(High-pressure emulsifying machine)

$$\text{Invested energy} = \frac{Q \Delta P}{\rho V} t \text{ [J/kg]} \quad \dots (1)$$

$$V = 81.6 d \cdot \pi d^2 / 4$$

In the expression, Q: flow volume,  $\Delta P$ : operating pressure,  $\rho$ : density, V: microjet space volume, t: time and d: inner diameter

[0079]

(Ultrasonic emulsifying machine)

$$\text{Invested energy} = \frac{WA}{\rho V} t \text{ [J/kg]} \quad \dots (2)$$

In the expression,  $\rho$ : density,  $W$ : output,  $A$ : horn area,  $V$ : mixing field volume and  $t$ : time

[0080]

(Homomixer)

$$\text{Invested energy} = \frac{\rho N_p n^3 d^5}{V} t \text{ [J/kg]} \quad \dots (3)$$

In the expression,  $\rho$ : density,  $N_p$ : power number,  $n$ : rotation frequency,  $d$ : blade diameter,  $V$ : mixing field volume and  $t$ : time

[0081]

Then, the number of times of passing through the high-energy processing part 221 is preferably once or more. When passing through the high-energy processing part 221 is carried out plural times, the invested energy means the sum total of invested energies imparted in each passing through the high-energy processing part 221.

[0082]

When the intended energy has been invested, the valve attached to the high-energy processing part 221 is opened, and the emulsion in the high-energy processing part 221 is taken out. The emulsion is fed to the

vibration-type stirring mixing apparatus 40 through the pipe 222. The proceeding time from the emulsification step (emulsifying unit 20) to the cooling step (cooling unit 30) is, from the viewpoint of preventing the emulsion obtained in the emulsifying unit 20 from flocculating, preferably 60 sec or shorter, and more preferably 10 sec or shorter. The lower limit value of the proceeding time is not especially limited, and a shorter proceeding time is better. The proceeding time from the emulsifying unit 20 to the cooling unit 30 refers to a time taken for the emulsion obtained in the second emulsifying section 22 of the emulsifying unit 20 to go out from the second emulsifying section 22 and then reach the vibration-type stirring mixing apparatus 40 of the cooling unit 30 through the pipe 222. The proceeding time can be regulated, for example, by the length of the pipe 222.

[0083]

To the vibration-type stirring mixing apparatus 40, as described above, the four cooling jackets 34, 35, 36 and 37 are attached. The cooling jackets are arranged on the outer side of the casing 41 so as to cover the cylindrical casing 41 illustrated in Figure 2; in the each jacket, cooling water at a predetermined temperature is circulated; and by making the emulsion obtained in the emulsifying unit 20 to pass through in the casing 41, heat exchange to cool the fluid is carried out.

[0084]

The upper limit value of the total flow volume of the cooling water circulated in the cooling jackets is not especially limited, from the viewpoint of efficiently cooling the emulsion obtained in the emulsifying unit 20 without flocculation of the emulsion, and a higher upper limit value thereof is better. Specifically, the total flow volume of the cooling water is, with respect to the flow volume of the emulsion, preferably 10 or more times, and more preferably 30 or more times. Here, the flow volume of the emulsion means a flow volume of the emulsion obtained in the emulsifying unit 20 when the emulsion passes through in the casing 41. Further the total flow volume of the cooling water, in the case where four jackets 34, 35, 36 and 37 are provided as in the vibration-type stirring mixing apparatus 40, means a total flow volume of flow volumes of the cooling water circulated in the each jacket.

[0085]

The temperature of the cooling water can suitably be established, and the emulsion can be cooled continuously or stepwise from the inflow port 31 side toward the discharge port 32 side by these jackets. In this case, the temperatures of the cooling water circulated in each of the four jackets 34, 35, 36 and 37 may be gradually made lower as proceeding from the inlet port side of the

vibration-type stirring mixing apparatus 31 toward the outlet port side thereof, or may be made identical.

[0086]

Further the cooling water of the four jackets 34, 35, 36 and 37 may be circulated, for example, with respect to the emulsion flowing from the inflow port 31 side (upstream side) to the discharge port 32 side (downstream side) of the vibration-type stirring mixing apparatus 40, from the upstream side to the downstream side in the forward direction of the flow of the emulsion, or from the downstream side to the upstream side in the reverse direction of the flow of the emulsion.

[0087]

In the vibration-type stirring mixing apparatus 40, by allowing the stirring gear 44 to vertically vibrate along its shaft direction, the emulsion passing through in the casing 41 is further mixed without flocculating by the flow thereof along the stirring gear 44 and the turbulence of the flow passing through the holes 48 and the notches 49 provided on the stirring blades 43. Thereby, fine particles of the solid fat can be highly dispersed.

[0088]

Then, when the emulsion is gradually cooled through heat exchange with the cooling water, its fluidity gradually decreases. Since the emulsion is cooled while being mixed by the flow thereof along the stirring gear

44 and the turbulence of the flow passing through the holes 48 and the notches 49 provided on the stirring blades 43, cooling unevenness hardly occurs. Further since almost no dead space is present in the vibration-type stirring mixing apparatus 40, stirring unevenness hardly occurs. The vibration-type stirring mixing apparatus 40 can carry out good stirring and mixing even in the case where the fluidity of the emulsion is high or low. These advantages the vibration-type stirring mixing apparatus 40 has bring about a preferable effect of being capable of making the emulsified particles containing the solid oil agent (wax component and the like) contained in the emulsion to be homogeneously fine. Moreover, the vibration-type stirring mixing apparatus 40, since being low in the quantity of heat generation, is excellent in the cooling efficiency, and since being capable of quickly cooling the emulsified particles as the emulsified particles remain homogeneously fine, is capable of well dispersing the emulsified particles containing the solid fat. That the quantity of heat generation is low is advantageous also in that the temperature is easily controlled.

[0089]

Since the emulsion is thus cooled without flocculating continuously down to a temperature equal to or lower than the solidification temperature of the solid oil agent, the productivity of the fine particle

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dispersion is high, and the fine particle dispersion excellent in the quality can be provided. The intended dispersion is discharged from the discharging pipe 33 through the discharge port 32 of the vibration-type stirring mixing apparatus 40. The temperature of the intended dispersion in this state becomes about 30°C.

[0090]

In cooling by using the vibration-type stirring mixing apparatus 40, the mean cooling rate is set preferably at 0.1 to 8°C/sec, more preferably at 0.5 to 5°C/sec, and still more preferably at 0.8 to 5°C/sec. The mean cooling rate is a value obtained by dividing a difference in the temperature of the fluid between when the fluid enters the vibration-type stirring mixing apparatus 40 and when the fluid goes out therefrom by a residence time of the fluid. Further the vibration frequency of the vibration-type stirring mixing apparatus 40 is preferably in the range of 2.5 to 30 Hz, and more preferably in the range of 5 to 25 Hz. The vibration amplitude of the vibration-type stirring mixing apparatus 40 is preferably 4 to 15 mm. Further the total vibration amount imparted during the cooling by the vibration-type stirring mixing apparatus 40 is preferably 50 to 100,000 strokes, and especially preferably 200 to 20,000 strokes.

[0091]

The fine particle dispersion thus obtained by the production apparatus 100 becomes the one having a

fluidity at 25°C, and includes paste-like ones and cream-like ones. Such a fine particle dispersion is applied as the cosmetic for protection against ultraviolet radiation of the present invention. The fine particle dispersion obtained by the production apparatus 100, since the solid oil agent is made homogeneously fine in the high-energy processing part 221, and is cooled as remaining homogeneously fine in the cooling unit 30, becomes the one good in the feeling of use, particularly reduced in the stickiness, and enhanced in cosmetic effects including the ultraviolet protection effect.

[0092]

Here, the production method has been described based on the preferred embodiment, but is not limited thereto. For example, in the above embodiment, one apparatus of the vibration-type stirring mixing apparatus 40 is used, but instead, a plurality of the vibration-type stirring mixing apparatuses 40 connected in series can be used.

[0093]

The cosmetic for protection against ultraviolet radiation of the present invention thus obtained, since being produced by the above-mentioned steps, becomes the one containing fine emulsified particles. The volume median diameter of the emulsified particles is, from the viewpoint of improving the ultraviolet protection effect and reducing the feeling of skin irritation, preferably

0.1 to 10  $\mu\text{m}$ , more preferably 0.15 to 0.35  $\mu\text{m}$ , and still more preferably 0.20 to 0.25  $\mu\text{m}$ .

Further from the similar view point, the coefficient of variation of the emulsified particles is preferably 18 to 40, more preferably 19 to 30, and still more preferably 20 to 25. Here, the coefficient of variation is a numerical value obtained by dividing a standard deviation in the volume median diameter by the volume median diameter, and a lower numerical value thereof indicates a sharper particle size distribution.

The cosmetic for protection against ultraviolet radiation of the present invention has a small particle diameter and a sharp particle size distribution as described above, and the particle size distribution is conceivably one factor of making the cosmetic to be excellent in the preservation stability, high in the ultraviolet protection effect and good in the feeling of use, and to give no feeling of skin irritation.

In the present invention, the volume median diameter is measured by a laser diffraction scattering method using a laser diffraction/scattering-type particle size analyzer (manufactured by HORIBA Ltd., model number: LA-920).

[0094]

The cosmetic for protection against ultraviolet radiation of the present invention can be made, for example, into toning lotion, milky lotion, cream, gel and

beauty essence, and is preferably made into cream and gel. Further the cosmetic can be made also into sheet-form cosmetics in which the cosmetic is impregnated in or coated on a sheet-form base material of woven fabric or nonwoven fabric.

The cosmetic for protection against ultraviolet radiation of the present invention can be used by being applied on skins, preferably skins excluding scalps, more preferably skins of faces, body, limbs and the like.

With respect to the above-mentioned embodiment, the present invention further discloses the following inventions.

[0095]

<1> A cosmetic for protection against ultraviolet radiation, the cosmetic comprising the following components (A), (B), (C), (D) and (E):

- (A) 0.18 to 2 mass% of an ionic surfactant;
- (B) 1 to 10 mass% of a hydrophobic amphipathic substance;
- (C) 1 to 40 mass% of a liquid oil agent comprising an oil-soluble ultraviolet absorber;
- (D) 0.01 to 6 mass% of a solid oil agent; and
- (E) water,

wherein the cosmetic is obtained by a method comprising the following steps:

an emulsification step of mixing a composition comprising the components (A) to (D) with (E) water under heating to form an emulsion; and

a cooling step of cooling the emulsion formed in the emulsification step at a cooling rate of 0.5 to 5°C/sec.

[0096]

<2> The cosmetic for protection against ultraviolet radiation according to the above <1>, wherein the ionic surfactant of the component (A) is preferably an anionic surfactant, a cationic surfactant, an amphoteric surfactant, a sphingosine or a salt thereof, more preferably at least one selected from the group consisting of anionic surfactants and sphingosines, still more preferably an anionic surfactant, and further still more preferably a long-chain N-acylglutamate salt wherein the long-chain N-acylglutamate salt is more preferably at least one selected from the group consisting of sodium dilauroylglutamate, monosodium N-lauroylglutamate, sodium N-stearoyl-L-glutamate, arginine N-stearoyl-L-glutamate, sodium N-stearoylglutamate and sodium N-myristoyl-L-glutamate, and still more preferably at least one selected from the group consisting of sodium N-stearoylglutamate and arginine N-stearoyl-L-glutamate and further still more preferably arginine N-stearoyl-L-glutamate.

<3> The cosmetic for protection against ultraviolet radiation according to the above <1> or <2>, wherein the content of the component (A) is, in the whole composition, preferably 0.2 mass% or higher, more preferably 0.3 mass% or higher, still more preferably 0.4 mass% or higher, and

further still more preferably 0.45 mass% or higher, and preferably 1.5 mass% or lower, more preferably 1.1 mass% or lower, still more preferably 0.9 mass% or lower, and further still more preferably 0.7 mass% or lower.

<4> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <3>, wherein the content of the nonionic surfactant is, in the whole composition, preferably 1 mass% or lower, more preferably 0.5 mass% or lower, still more preferably 0.1 mass% or lower, and further still more preferably substantially 0 mass%.

[0097]

<5> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <4>, wherein the hydrophobic amphipathic substance of the component (B) is preferably at least one selected from the group consisting of ceramides, alcohols having 10 to 24 carbon atoms, linear saturated fatty acids having 10 to 24 carbon atoms, monofatty acid glycerin esters having 10 to 24 carbon atoms, monoalkyl glyceryl ethers having 10 to 24 carbon atoms, monofatty acid sorbitan esters having 10 to 24 carbon atoms and monofatty acid sorbit esters having 10 to 24 carbon atoms, more preferably at least one selected from the group consisting of alcohols having 14 to 22 carbon atoms, monofatty acid glycerin esters having 14 to 22 carbon atoms, monoalkyl glyceryl ethers having 14 to 22 carbon atoms and monofatty acid

sorbitan esters having 14 to 22 carbon atoms, still more preferably an alcohol having 16 to 22 carbon atoms, monofatty acid glycerin ester having 16 to 22 carbon atoms, and further still more preferably at least one selected from the group consisting of cetyl alcohol, stearyl alcohol and lipophilic monofatty acid glycerin esters.

<6> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <5>, wherein the hydrophobic amphipathic substance of the component (B) preferably comprises alcohols having 14 to 22 carbon atoms and at least one selected from the group consisting of monofatty acid glycerin esters having 14 to 22 carbon atoms, monoalkyl glyceryl ethers having 14 to 22 carbon atoms and monofatty acid sorbitan esters having 14 to 22 carbon atoms, more preferably comprises an alcohol having 14 to 22 carbon atoms and a monofatty acid glycerin ester having 14 to 22 carbon atoms, still more preferably comprises an alcohol having 16 to 22 carbon atoms and a monofatty acid glycerin ester having 16 to 22 carbon atoms, and further still more preferably comprises cetyl alcohol, stearyl alcohol and a monofatty acid glycerin ester having 16 to 22 carbon atoms.

<7> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <6>, wherein the content of the component (B) is, in the whole composition, preferably 1.5 mass% or higher, more

preferably 2 mass% or higher, and still more preferably 2.5 mass% or higher, and preferably 8 mass% or lower, more preferably 5 mass% or lower, and still more preferably 3.8 mass% or lower.

[0098]

<8> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <7>, wherein the oil-soluble ultraviolet absorber of the component (C) preferably comprises at least one selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, octocrylene, 2,4,6-tris[4-(2-ethylhexyloxycarbonyl)anilino]-1,3,5-triazine, 4-tert-butyl-4'-methoxydibenzoylmethane, 2-ethylhexyl dimethoxybenzylidenedioxoimidazolidinepropionate, diethylamino hydroxybenzoyl benzoic acid hexyl ester and bis-ethylhexyloxyphenol methoxyphenyl triazine, more preferably comprises at least one selected from the group consisting of 2-ethylhexyl p-methoxycinnamate, diethylamino hydroxybenzoyl benzoic acid hexyl ester and bis-ethylhexyloxyphenol methoxyphenyl triazine, and still more preferably comprises 2-ethylhexyl p-methoxycinnamate, diethylamino hydroxybenzoyl benzoic acid hexyl ester and bis-ethylhexyloxyphenol methoxyphenyl triazine.

<9> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <8>, wherein the oil-soluble ultraviolet absorber is more preferably at least one selected from the group

consisting of cinnamic acid-based oil-soluble ultraviolet absorbers, diethylamino hydroxybenzoyl benzoic acid hexyl ester and triazine-based oil-soluble ultraviolet absorbers, still more preferably comprises the above three kinds of the oil-soluble ultraviolet absorbers, and further still more preferably comprises 2-ethylhexyl p-methoxycinnamate, diethylamino hydroxybenzoyl benzoic acid hexyl ester and bis-ethylhexyloxyphenol methoxyphenyl triazine.

<10> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <9>, wherein the liquid oil agent other than the oil-soluble ultraviolet absorber preferably comprises at least one selected from the group consisting of linear or branched-chain hydrocarbon oils, ester oils and silicone oils.

[0099]

<11> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <10>, wherein the content of the oil-soluble ultraviolet absorber in the whole liquid oil agent of the component (C) is preferably 60 mass% or higher, more preferably 65 mass% or higher, and still more preferably 70 mass% or higher, and preferably 100 mass% or lower, more preferably 90 mass% or lower, and still more preferably 85 mass% or lower.

<12> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <10>,

wherein the content of the oil-soluble ultraviolet absorber in the cosmetic for protection against ultraviolet radiation is, in the whole composition, preferably 6 mass% or higher, more preferably 8 mass% or higher, and still more preferably 10 mass% or higher, and preferably 20 mass% or lower, more preferably 18 mass% or lower, and still more preferably 15 mass% or lower.

<13> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <12>, wherein the content of the cinnamic acid-based oil-soluble ultraviolet absorber in the oil-soluble ultraviolet absorber is preferably 60 to 100 mass%, and more preferably 70 to 90 mass%.

<14> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <13>, wherein in the oil-soluble ultraviolet absorber, the total content of the triazine-based oil-soluble ultraviolet absorber and diethylamino hydroxybenzoyl benzoic acid hexyl ester is preferably 0 to 40 mass%, and more preferably 10 to 30 mass%.

<15> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <14>, wherein in the oil-soluble ultraviolet absorber, the content ratio of the cinnamic acid-based oil-soluble ultraviolet absorber to the total amount of the triazine-based oil-soluble ultraviolet absorber and diethylamino hydroxybenzoyl benzoic acid hexyl ester, the cinnamic

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acid-based oil-soluble ultraviolet absorber / [the triazine-based oil-soluble ultraviolet absorber + diethylamino hydroxybenzoyl benzoic acid hexyl ester], is preferably 9/1 to 5/5, more preferably 8.5/1.5 to 6/4, and still more preferably 8/2 to 6.5/3.5.

<16> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <15>, wherein the content of the component (C) is, in the whole composition, preferably 3 mass% or higher, more preferably 10 mass% or higher, and still more preferably 12 mass% or higher, and preferably 35 mass% or lower, more preferably 25 mass% or lower, and still more preferably 17 mass% or lower.

[0100]

<17> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <16>, wherein the mass ratio of the component (A) to the component (C),  $[(A)/(C)]$ , is preferably 0.01 or higher, more preferably 0.015 or higher, still more preferably 0.025 or higher, and further still more preferably 0.034 or higher, and preferably 0.2 or lower, more preferably 0.12 or lower, still more preferably 0.06 or lower, and further still more preferably 0.05 or lower.

<18> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <17>, wherein the mass ratio of the component (B) to the component (C),  $[(B)/(C)]$ , is preferably 0.01 or higher,

more preferably 0.12 or higher, still more preferably 0.18 or higher, and further still more preferably 0.19 or higher, and preferably 0.5 or lower, more preferably 0.39 or lower, still more preferably 0.27 or lower, and further still more preferably 0.24 or lower.

[0101]

<19> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <18>, wherein the solid oil agent of the component (D) is preferably a solid oil agent having a melting point of 60°C or higher and 80°C or lower, and more preferably a solid oil agent containing at least one selected from the group consisting of ceresins and paraffins and having a melting point of 60°C or higher and 80°C or lower.

<20> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <19>, wherein the content of the component (D) is, in the whole composition, preferably 0.08 mass% or higher, more preferably 0.1 mass% or higher, and still more preferably 0.5 mass% or higher, and preferably 4.5 mass% or lower, more preferably 2.5 mass% or lower, and still more preferably 1.5 mass% or lower.

<21> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <20>, wherein the mass ratio of the component (D) to the component (C),  $[(D)/(C)]$ , is preferably 0.01 or higher, more preferably 0.02 or higher, and still more preferably

0.04 or higher, and preferably 0.5 or lower, more preferably 0.3 or lower, and still more preferably 0.1 or lower.

[0102]

<22> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <21>, wherein the content of the component (E) is, in the whole composition, preferably 35 mass% or higher and more preferably 45 mass% or higher, and preferably 65 mass% or lower, and more preferably 55 mass% or lower.

<23> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <22>, further comprising (F) a water-soluble polymer.

<24> The cosmetic for protection against ultraviolet radiation according to the above <23>, wherein the component (F) is preferably an acrylic polymer, more preferably at least one selected from the group consisting of carbomer, acrylic acid/alkyl methacrylate copolymers, polyacrylamide, (sodium acrylate/sodium acryloyldimethyltaurate) copolymers, (hydroxyethyl acrylate/sodium acryloyldimethyltaurate) copolymers, (acrylamide/ammonium acrylate) copolymers and polyacrylate-13, and still more preferably at least one selected from the group consisting of (sodium acrylate/sodium acryloyldimethyltaurate) copolymers, (hydroxyethyl acrylate/sodium

acryloyldimethyltaurate) copolymers, (acrylamide/ammonium acrylate) copolymers and polyacrylate-13.

<25> The cosmetic for protection against ultraviolet radiation according to the above <23> or <24>, wherein the content of the component (F) is, in the whole composition, preferably 0.3 mass% or higher, and more preferably 0.5 mass% or higher, and preferably 1.5 mass% or lower, and more preferably 1.0 mass% or lower.

[0103]

<26> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <25>, wherein the emulsification step comprises mixing blending components under heating preferably at 60 to 120°C, more preferably at 80 to 100°C preferably by using a homomixer, an ultrasonic emulsifying machine or a high-pressure emulsifying machine.

<27> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <26>, wherein the cooling step comprises cooling an obtained emulsion preferably by a method of continuously quickly cooling the obtained emulsion by using a vibration-type stirring mixing apparatus, a scraped surface heat exchanger, a static mixer, a plate-type heat exchanger or a double-pipe heat exchanger, or a method of stirring and cooling in a usual blending tank.

<28> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <27>,

wherein the cooling rate is preferably 0.8°C/sec or higher, and preferably 1.5°C/sec or lower.

<29> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <28>, wherein the volume median diameter of the emulsified particles is preferably 0.1 to 10  $\mu\text{m}$ , more preferably 0.15 to 0.35  $\mu\text{m}$ , and still more preferably 0.20 to 0.25  $\mu\text{m}$ .

<30> The cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <29>, wherein the coefficient of deviation of the emulsified particles is preferably 18 to 40, more preferably 19 to 30, and still more preferably 20 to 25.

<31> Use of the cosmetic for protection against ultraviolet radiation according to any one of the above <1> to <30>, comprising applying the cosmetic on skins, on any of preferably skins excluding scalps, more preferably skins of faces, body, limbs and the like.

[0104]

<32> A method for producing a cosmetic for protection against ultraviolet radiation, comprising:  
an emulsification step of mixing a composition comprising the following components (A), (B), (C) and (D):

- (A) 0.1 to 2 mass% of an ionic surfactant;
- (B) 1 to 10 mass% of a hydrophobic amphipathic substance;
- (C) 1 to 40 mass% of a liquid oil agent comprising an oil-soluble ultraviolet absorber; and

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(D) 0.01 to 6 mass% of a solid oil agent,  
with (E) water under heating to form an emulsion; and  
a cooling step of cooling the emulsion formed in the  
emulsification step at a cooling rate of 0.5 to 5°C/sec.

[Examples]

[0105]

Examples 1 to 29 and Comparative Examples 1 to 5

Cosmetics for protection against ultraviolet radiation having compositions indicated in Table 1 to Table 3 were produced; volume median diameters and coefficients of variation were measured; confirmation of  $\alpha$ -gels was performed; and the SPF value, preservation stability, feeling of use and feeling of skin irritation were evaluated. The results are shown in Table 1 to Table 3 collectively.

[0106]

(Production method)

(1) Example 1:

The components (A) to (D) and a part of the component (E), propanediol, glycerol, arginine and phenoxyethanol were dispersed under heating at 85°C by a homomixer, and thereafter emulsified by using a high-pressure emulsifying machine (manufactured by SUGINO MACHINE LIMITED, Star Burst Mini HJP-25001) to thereby obtain an emulsion. The number of times of passing through the high-pressure emulsifying machine was once.

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The emulsion was fed to a vibration-type stirring mixing apparatus (manufactured by Reica Co., Ltd., Vibro Mixer) in a proceeding time of 10 sec with the temperature thereof being held at 85°C, and then continuously cooled down to a temperature equal to or lower than 40°C while the emulsion was being stirred by vertically vibrating a stirring gear in the apparatus (step (1)). The cooled emulsion and a mixed liquid obtained by mixing a part of the component (E), the component (F), and the other components indicated in Tables were mixed at room temperature (25°C) (step (2)) to thereby obtain a cosmetic for protection against ultraviolet radiation.

In the vibration-type stirring mixing apparatus, the flow volume of the emulsion was 1 g/sec; the total flow volume of cooling water circulated in cooling jackets was 10 g/sec; thus, the emulsion was cooled by the cooling water of the total flow volume 10 times the flow volume of the emulsion. The mean cooling rate at this time was 1°C/sec. Further the vibration frequency of the vibration-type stirring mixing apparatus was 20 Hz.

[0107]

(2) Examples 2 to 28 and Comparative Examples 1 to 4

Cosmetics for protection against ultraviolet radiation of Examples 2 to 28 and Comparative Examples 1 to 4 were obtained as in Example 1.

[0108]

(3) Example 29:

An emulsion was obtained as in (1). The obtained emulsion was cooled down to 40°C under stirring by using an anchor blade (rotation frequency: 75 rpm) in a vessel to thereby obtain a cosmetic for protection against ultraviolet radiation. The mean cooling rate at this time was 1°C/sec.

[0109]

(4) Comparative Example 5:

The emulsification step as in Example 1 was carried out, and thereafter, the cooling was carried out at a cooling rate of 0.01°C/sec in a temperature-controllable thermostatic chamber without stirring.

[0110]

(Evaluation methods)

(1) Volume median diameter, and Coefficient of variation:

The median diameter in terms of volume and the coefficient of variation at 25°C were measured by a laser diffraction scattering method using a laser diffraction/scattering-type particle size analyzer (manufactured by HORIBA Ltd., model number: LA-920). The coefficient of variation is a value obtained by dividing a standard deviation by a median diameter in terms of volume.

[0111]

(2) Confirmation of the  $\alpha$ -gel:

Whether an  $\alpha$ -gel was formed was confirmed for the each cosmetic by XRD. Specifically, a cosmetic

developing sharp diffraction peaks, at least one, at a Bragg angle of nearly  $21^{\circ}$  to  $22^{\circ}$  in a diffraction pattern in a wide-angle X-ray diffractometry was regarded as having an  $\alpha$ -gel structure, and was indicated as " $\alpha$ " in Tables.

[0112]

(3) SPF value:

The each cosmetic was applied on a PMMA plate over 1 min uniformly so as to make an application amount of 2 mg/cm<sup>2</sup>, and dried in a cool dark place for 15 min. After the drying, the transmittances (%) of absorption spectra (wavelength: 350 nm) of 9 positions in total of the center, each vertex, and the middle point of each side connecting the vertices, of the square PMMA plate, were measured by an SPF analyzer (SPF 290S plus, manufactured by Optometricus USA, Inc.), and a mean value of the 9 positions was determined. The results are indicated as SPF values (-) determined from the transmittances (%) (N = 3).

[0113]

(4) Preservation stability:

40 mL of the each cosmetic was put in a 50-mL glass bottle, which was then hermetically closed, and was preserved at  $-5^{\circ}\text{C}$  for 1 month; and the appearance and the fluidity of the cosmetic after the preservation was visually observed. The fluidity was evaluated by

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visually checking the flowing state when the bottle was inclined by 45°. The criteria were as follows.

4: No change in the appearance and/or the fluidity was observed.

3: Slight changes in the appearance and the fluidity were observed.

2: a rather large change in at least either one of the appearance and the fluidity was observed.

1: A large change in the appearance (separation of the oil phase) or a large change in the fluidity (gelatinous change) was observed.

[0114]

(5) Feeling of use:

Five expert panelists each applied 0.02 mL of the each cosmetic in a circle of 3 cm in diameter on their forearm inner side, and spread it over 1 min (at 25°C, at 57RH%). Thereafter, the case where no stickiness was felt at all was taken to be 5 for the feeling of use (sticky feeling); and the case where the stickiness was felt very much was taken to be 1 therefor, in which the feeling of use was evaluated at intervals of 0.1, and the mean evaluation score of the five panelists was determined.

[0115]

(6) Feeling of skin irritation:

Five expert panelists each applied 0.02 mL of the each cosmetic in a circle of 3 cm in diameter on their

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forearm inner side, and spread it over 1 min (at 25°C, at 57RH%). Thereafter, the case where no feeling of irritation was felt at all was taken to be 5; and the case where the feeling of irritation was felt very much was taken to be 1, in which the feeling of irritation was evaluated at intervals of 0.1, and the mean evaluation score of the five panelists was determined.

[0116]

[Table 1]

| Component (mass%) |                                                                                                    | Example |      |      |      |      |      |      |      |      |     |      |
|-------------------|----------------------------------------------------------------------------------------------------|---------|------|------|------|------|------|------|------|------|-----|------|
|                   |                                                                                                    | 1       | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    | 10  | 11   |
| (A)               | Stearoylglutamic acid                                                                              | 0.29    | 0.44 | 1.16 | 1.74 |      |      |      | 0.6  | 0.6  | 0.6 | 0.6  |
|                   | Sodium stearoylmethylaurate                                                                        |         |      |      |      | 0.6  |      |      |      |      |     |      |
|                   | Phytosphingosine                                                                                   |         |      |      |      |      | 0.3  |      |      |      |     |      |
|                   | Distearyl dimethylammonium chloride                                                                |         |      |      |      |      |      | 0.6  |      |      |     |      |
| (B)               | Cetyl alcohol                                                                                      |         |      |      |      |      |      |      |      |      |     |      |
|                   | Stearyl alcohol                                                                                    |         |      |      |      |      |      |      |      |      |     |      |
|                   | Cetearyl alcohol                                                                                   | 1.8     | 1.8  | 1.8  | 1.8  | 1.8  | 1.8  | 1.8  | 0.6  | 0.9  | 1.2 | 1.5  |
|                   | Glyceryl stearate                                                                                  |         |      |      |      |      |      |      |      |      |     |      |
| Step (1)          | Glyceryl behenate                                                                                  | 1.25    | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 1.25 | 0.90 | 1.35 | 1.8 | 2.25 |
|                   | Sorbitan monostearate                                                                              |         |      |      |      |      |      |      |      |      |     |      |
|                   | Sorbitan distearate                                                                                | 0.3     | 0.3  | 0.3  | 0.3  | 0.3  | 0.3  | 0.3  | 0.5  | 0.75 | 1   | 1.25 |
|                   | Ethylhexyl methoxycinnamate (Uvinul MC80, manufactured by BASF AG)                                 | 9       | 9    | 9    | 9    | 9    | 9    | 9    | 9    | 9    | 9   | 9    |
| (C)               | Hexyl diethylamino hydroxybenzoyl benzoic acid hexyl ester (Uvinul Aplus, manufactured by BASF AG) | 2       | 2    | 2    | 2    | 2    | 2    | 2    | 2    | 2    | 2   | 2    |

Step  
(1)

[illegible]

|     |                                                                                    |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |
|-----|------------------------------------------------------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
|     | Arginine                                                                           | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 |
|     | Phenoxyethanol (Hisolve EPH, manufactured by TOHO Chemical Industry Co., Ltd.)     | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  |
| (E) | Water                                                                              | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   | 20                   |
| (F) | Sodium acrylate/sodium acryloyl/dimethyltaurate copolymer (manufactured by Seppic) | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 | 0.75                 |
| (E) | Water                                                                              | 54.3                 | 54.2                 | 53.4                 | 52.9                 | 54.0                 | 54.3                 | 54                   | 55.3                 | 54.3                 | 54.3                 | 54                   | 55.3                 | 54.3                 | 53.3                 | 53.3                 | 52.3                 | 52.3                 | 52.3                 |
|     | Total                                                                              | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  | 100                  |
|     | (A) Ionic surfactant                                                               | 0.29                 | 0.44                 | 1.16                 | 1.74                 | 0.6                  | 0.3                  | 0.6                  | 0.6                  | 0.3                  | 0.6                  | 0.6                  | 0.6                  | 0.6                  | 0.6                  | 0.6                  | 0.6                  | 0.6                  | 0.6                  |
|     | (B) Hydrophobic amphiphathic substance                                             | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 | 3.35                 |
|     | (C) Liquid oil agent                                                               | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   | 15                   |
|     | (D) Solid oil agent                                                                | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    |
|     | A/C                                                                                | 0.02                 | 0.03                 | 0.08                 | 0.12                 | 0.04                 | 0.02                 | 0.04                 | 0.04                 | 0.02                 | 0.04                 | 0.04                 | 0.04                 | 0.04                 | 0.04                 | 0.04                 | 0.04                 | 0.04                 | 0.04                 |
|     | B/C                                                                                | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.22                 | 0.27                 | 0.27                 | 0.33                 | 0.33                 | 0.33                 |
|     | D/C                                                                                | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 |
|     | Cooling step: cooling rate (°C/sec)                                                | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    |
|     | Cooling step: mixing                                                               | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring |
|     | Median diameter in terms of volume                                                 | 0.36                 | 0.25                 | 0.22                 | 0.21                 | 0.22                 | 0.21                 | 0.23                 | 0.23                 | 0.21                 | 0.23                 | 0.23                 | 0.23                 | 0.24                 | 0.24                 | 0.24                 | 0.24                 | 0.24                 | 0.24                 |
|     | Particle diameter, Coefficient of variation                                        | 38.3                 | 24.5                 | 23.1                 | 21.6                 | 22.3                 | 24.5                 | 26.1                 | 21.3                 | 22.5                 | 24                   | 23.6                 | 23.6                 | 24                   | 23.6                 | 23.6                 | 23.6                 | 23.6                 | 23.6                 |
|     | Confirmation of α-gel                                                              | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    |
|     | SPF                                                                                | 40.1                 | 47.2                 | 30.2                 | 30.1                 | 41.2                 | 40.3                 | 39.8                 | 24.3                 | 41.3                 | 38.7                 | 36.2                 | 36.2                 | 38.7                 | 38.7                 | 38.7                 | 36.2                 | 36.2                 | 36.2                 |

|                            |     |     |     |     |     |     |     |     |     |     |     |
|----------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Preservation stability     | 2   | 3   | 3   | 2   | 3   | 3   | 3   | 2   | 4   | 3   | 2   |
| Feeling of use             | 4   | 4.5 | 3.7 | 3.4 | 3.9 | 3.7 | 3.7 | 3.8 | 4.6 | 4.2 | 3.2 |
| Feeling of skin irritation | 3.1 | 4.1 | 3.8 | 3.4 | 4   | 4   | 4   | 3.9 | 4.5 | 4.5 | 4.4 |

[0117]

[Table 2]

| Step<br>(1) | Component (mass%)                                                                            | Example |      |      |      |      |      |      |      |      |      |      |
|-------------|----------------------------------------------------------------------------------------------|---------|------|------|------|------|------|------|------|------|------|------|
|             |                                                                                              | 12      | 13   | 14   | 15   | 16   | 17   | 18   | 19   | 20   | 21   | 22   |
| (A)         | Stearoylglutamic acid                                                                        | 0.60    | 0.60 | 0.60 | 0.60 | 0.60 | 0.58 | 0.58 | 0.58 | 0.58 | 0.58 | 0.66 |
|             | Sodium stearylmyristate                                                                      |         |      |      |      |      |      |      |      |      |      |      |
|             | Phytosphingosine                                                                             |         |      |      |      |      |      |      |      |      |      |      |
|             | Distearyltrimethylammonium chloride                                                          |         |      |      |      |      |      |      |      |      |      |      |
| (B)         | Cetyl alcohol                                                                                |         | 0.55 | 1.61 | 1.50 | 1.50 |      |      |      |      |      |      |
|             | Stearyl alcohol                                                                              | 0.55    |      |      |      |      |      |      |      |      |      |      |
|             | Cetearyl alcohol                                                                             |         |      |      |      |      | 0.90 | 1.53 | 1.53 | 0.96 | 0.96 | 0.96 |
|             | Glyceryl stearate                                                                            |         | 0.49 |      |      |      |      |      |      |      |      |      |
|             | Glyceryl behenate                                                                            | 0.49    |      | 1.12 |      |      | 1.35 | 2.30 | 2.30 | 1.44 | 1.44 | 1.44 |
|             | Sorbitan monostearate                                                                        |         |      |      | 1.50 |      |      |      |      |      |      |      |
|             | Sorbitan distearate                                                                          | 1.96    | 1.96 | 0.27 |      | 1.50 | 0.75 | 1.28 | 1.28 | 0.80 | 0.80 | 0.80 |
| (C)         | Ethylhexyl methoxycinnamate (Uvinul MC80, manufactured by BASF AG)                           | 9       | 9    | 9    | 9    | 9    | 5    | 9    | 9    | 9    | 9    | 9    |
|             | Diethylamino hydroxybenzoyl benzoic acid hexyl ester (Uvinul Aplus, manufactured by BASF AG) | 2       | 2    | 2    | 2    | 2    | 1    | 2    | 2    | 2    | 2    | 2    |
|             | bis-Ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S, manufactured by BASF AG)         | 1       | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    |
|             | Alkyl (C12-15) benzoate (FINSOLV TN, manufactured by Innospec Active Chemicals LLC)          | 3       | 3    | 3    | 3    | 3    | 1    | 18   |      | 3    | 3    | 3    |

[illegible]

|                                             |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |                      |
|---------------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| (C) Liquid oil agent                        | 15                   | 15                   | 15                   | 15                   | 15                   | 8                    | 30                   | 18                   | 15                   | 15                   | 15                   |
| (D) Solid oil agent                         | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    |
| A/C                                         | 0.04                 | 0.04                 | 0.04                 | 0.04                 | 0.04                 | 0.07                 | 0.02                 | 0.03                 | 0.04                 | 0.04                 | 0.04                 |
| B/C                                         | 0.20                 | 0.20                 | 0.20                 | 0.20                 | 0.20                 | 0.38                 | 0.17                 | 0.28                 | 0.21                 | 0.21                 | 0.21                 |
| D/C                                         | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.13                 | 0.03                 | 0.06                 | 0.07                 | 0.07                 | 0.07                 |
| Cooling step: cooling rate<br>(°C/sec)      | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    | 1                    |
| Cooling step: mixing                        | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring |
| Median diameter in terms of volume          | 0.24                 | 0.23                 | 0.23                 | 0.22                 | 0.24                 | 0.24                 | 0.39                 | 0.33                 | 0.23                 | 0.24                 | 0.21                 |
| Particle diameter, Coefficient of variation | 25.2                 | 22.8                 | 26.3                 | 27.2                 | 26.9                 | 23.8                 | 38.7                 | 34.2                 | 23.6                 | 22.7                 | 26.5                 |
| Confirmation of α-gel                       | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    | α                    |
| SPF                                         | 40.2                 | 39.9                 | 41.1                 | 38.7                 | 39.1                 | 16.3                 | 33.3                 | 38.2                 | 43.6                 | 44.7                 | 27.7                 |
| Preservation stability                      | 3                    | 3                    | 4                    | 3                    | 3                    | 2                    | 2                    | 3                    | 3                    | 3                    | 2                    |
| Feeling of use                              | 4.5                  | 4.4                  | 4.5                  | 4.3                  | 4.3                  | 4.6                  | 2.8                  | 3.5                  | 4.3                  | 4.2                  | 3.5                  |
| Feeling of skin irritation                  | 4.5                  | 4.5                  | 4.5                  | 4.2                  | 4.3                  | 4.5                  | 3.6                  | 4                    | 4.5                  | 4.5                  | 3.6                  |

[0118]

[Table 3]

| Component (mass%) |                                                                                              | Example |      |      |      |      |      |      |      | Comparative Example |      |      |      |  |
|-------------------|----------------------------------------------------------------------------------------------|---------|------|------|------|------|------|------|------|---------------------|------|------|------|--|
|                   |                                                                                              | 23      | 24   | 25   | 26   | 27   | 28   | 29   | 1    | 2                   | 3    | 4    | 5    |  |
| (A)               | Stearoylglutamic acid                                                                        | 0.66    | 0.58 | 0.62 | 0.66 | 0.66 | 0.58 | 0.58 | 0    | 0.15                | 0.60 | 0.54 | 0.58 |  |
|                   | Sodium stearoylmethylaurate                                                                  |         |      |      |      |      |      |      |      |                     |      |      |      |  |
|                   | Phytosphingosine                                                                             |         |      |      |      |      |      |      |      |                     |      |      |      |  |
|                   | Distearyl dimethylammonium chloride                                                          |         |      |      |      |      |      |      |      |                     |      |      |      |  |
| (B)               | Cetyl alcohol                                                                                |         |      |      |      |      |      |      |      |                     |      |      |      |  |
|                   | Stearyl alcohol                                                                              |         |      |      |      |      |      |      |      |                     |      |      |      |  |
|                   | Cetearyl alcohol                                                                             | 0.96    | 0.96 | 1.02 | 1.02 | 1.02 | 0.90 | 0.90 | 1.80 | 1.80                | 0    | 0.9  | 0.9  |  |
|                   | Glyceryl stearate                                                                            |         |      |      |      |      |      |      |      |                     |      |      |      |  |
| Step (1)          | Glyceryl behenate                                                                            | 1.44    | 1.44 | 1.53 | 1.53 | 1.53 | 1.35 | 1.35 | 1.25 | 1.25                | 0    | 1.35 | 1.35 |  |
|                   | Sorbitan monostearate                                                                        |         |      |      |      |      |      |      |      |                     |      |      |      |  |
|                   | Sorbitan distearate                                                                          | 0.8     | 0.8  | 0.85 | 0.85 | 0.85 | 0.75 | 0.75 | 0.30 | 0.30                | 0    | 0.75 | 0.75 |  |
|                   | Ethylhexyl methoxycinnamate (Uvinul MC80, manufactured by BASF AG)                           | 9       | 9    | 9    | 9    | 9    | 9    | 9    | 9    | 9                   | 9    | 9    | 9    |  |
| (C)               | Diethylamino hydroxybenzoyl benzoic acid hexyl ester (Uvinul Aplus, manufactured by BASF AG) | 2       | 2    | 2    | 2    | 2    | 2    | 2    | 2    | 2                   | 2    | 2    | 2    |  |
|                   | bis-Ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S, manufactured by BASF AG)         | 1       | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1                   | 1    | 1    | 1    |  |
|                   | Alkyl (C12-15) benzoate (FINSOLV TN, manufactured by Innospec Active Chemicals LLC)          | 3       | 3    | 3    | 3    | 3    | 3    | 3    | 3    | 3                   | 3    | 3    | 3    |  |

Step  
(1)

[illegible]

|                                             |                       |                       |                       |                       |                       |                       |                       |                       |                       |                       |                       |                       |                       |                       |                       |                       |          |
|---------------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|----------|
| (C) Liquid oil agent                        | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15                    | 15       |
| (D) Solid oil agent                         | 1                     | 1                     | 2                     | 3                     | 5                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1        |
| A/C                                         | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04                  | 0.04     |
| B/C                                         | 0.21                  | 0.21                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.21     |
| D/C                                         | 0.07                  | 0.07                  | 0.13                  | 0.20                  | 0.33                  | 0.07                  | 0.07                  | 0.07                  | 0.07                  | 0.07                  | 0.07                  | 0.07                  | 0.07                  | 0.07                  | 0.07                  | 0.07                  | 0.07     |
| Cooling step: cooling rate (°C/sec)         | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1                     | 0.01     |
| Cooling step: mixing                        | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | anchor blade stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | vibra-tional stirring | -        |
| Median diameter in terms of volume          | 0.23                  | 0.23                  | 0.22                  | 0.23                  | 0.22                  | 0.23                  | 0.22                  | 0.23                  | 0.22                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.23                  | 0.22                  | 0.22     |
| Particle diameter, Coefficient of variation | 24.7                  | 23.1                  | 26.4                  | 24.1                  | 21.9                  | 22.8                  | 21.7                  | 82.4                  | 60.5                  | 64.4                  | 24.5                  | 21.5                  | 21.5                  | 21.5                  | 21.5                  | 21.5                  | 21.5     |
| Confirmation of $\alpha$ -gel               | $\alpha$              | $\alpha$              | $\alpha$              | $\alpha$              | $\alpha$              | $\alpha$              | $\alpha$              | -                     | -                     | -                     | $\alpha$              | $\alpha$              | $\alpha$              | $\alpha$              | $\alpha$              | $\alpha$              | $\alpha$ |
| SPF                                         | 45.3                  | 45.1                  | 48.4                  | 52.7                  | 50.3                  | 18.5                  | 31.1                  | 8.3                   | 12.3                  | 9.6                   | 20.3                  | 19.8                  | 19.8                  | 19.8                  | 19.8                  | 19.8                  | 19.8     |
| Preservation stability                      | 2                     | 4                     | 3                     | 2                     | 2                     | 3                     | 3                     | 1                     | 2                     | 1                     | 4                     | 1                     | 1                     | 1                     | 1                     | 1                     | 1        |
| Feeling of use                              | 3.1                   | 4.5                   | 3.8                   | 2.9                   | 2.3                   | 4.4                   | 4.1                   | 2.5                   | 2.9                   | 3.6                   | 4.8                   | 3.5                   | 3.5                   | 3.5                   | 3.5                   | 3.5                   | 3.5      |
| Feeling of skin irritation                  | 4.2                   | 4.5                   | 4.6                   | 4.5                   | 4.7                   | 4.5                   | 4.2                   | 2.3                   | 3                     | 2.2                   | 3.6                   | 2.3                   | 2.3                   | 2.2                   | 2.2                   | 2.3                   | 2.3      |

[0119]

## Example 30

A cosmetic for protection against ultraviolet radiation having a composition indicated in Table 4 was produced as in Examples 1 to 28.

In the obtained cosmetic for protection against ultraviolet radiation, emulsified particles of 0.22  $\mu\text{m}$  in volume median diameter were dispersed, and an  $\alpha$ -gel was confirmed.

Further, the cosmetic had the oil agent containing the ultraviolet absorber homogeneously dispersed therein, and was excellent in the preservation stability, and high in the ultraviolet protection effect, and exhibited no stickiness, a good feeling of use, and no feeling of skin irritation.

[0120]

[Table 4]

(UV cream)

| (Component) |     |                                                                                              | (mass%) |
|-------------|-----|----------------------------------------------------------------------------------------------|---------|
| Step<br>(1) | (A) | Stearoylglutamic acid                                                                        | 0.6     |
|             | (C) | Ethylhexyl methoxycinnamate (Uvinul MC80, manufactured by BASF AG)                           | 8       |
|             |     | Diethylamino hydroxybenzoyl benzoic acid hexyl ester (Uvinul Aplus, manufactured by BASF AG) | 2       |
|             |     | bis-Ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S, manufactured by BASF AG)         | 1       |
|             |     | Alkyl (C12-15) benzoate (FINSOLV TN, manufactured by Innospec Active Chemicals LLC)          | 3       |

|          |     |                                                                                      |      |
|----------|-----|--------------------------------------------------------------------------------------|------|
|          |     | Neopentyl glycol dicaprate (Estemol N-0, manufactured by Nisshin Oillio Group, Ltd.) | 1    |
|          | (B) | Cetyl alcohol                                                                        | 0.96 |
|          |     | Pseudo-ceramide (ii) (Sphingolipid E, manufactured by Kao Corp.)                     | 0.8  |
|          |     | Glyceryl behenate                                                                    | 1.44 |
|          | (D) | Ceresin (Ceresin #810K, manufactured by Nikko Rica Corp., melting point: 74°C)       | 0.47 |
|          |     | Paraffin wax (HNP-9, manufactured by Nippon Seiro Co., Ltd., melting point: 75°C)    | 0.53 |
|          |     | Dextrin palmitate (Rheoparl KL2, manufactured by Chiba Flour Milling Co., Ltd.)      | 0.1  |
|          |     | Propanediol (Zemea select PD, manufactured by Du Pont)                               | 2    |
|          |     | Glycerol                                                                             | 4.3  |
|          |     | Arginine                                                                             | 0.34 |
|          |     | Methylparaben                                                                        | 0.2  |
|          | (E) | Water                                                                                | 20   |
| Step (2) | (F) | Sodium acrylate/sodium acryloyldimethyltaurate copolymer (manufactured by Seppic)    | 1.13 |
|          | (E) | Water                                                                                | 52.1 |
| Total    |     |                                                                                      | 100  |

[0121]

## Example 31

A cosmetic for protection against ultraviolet radiation having a composition indicated in Table 5 was produced as in Examples 1 to 28.

In the obtained cosmetic for protection against ultraviolet radiation, emulsified particles of 0.24  $\mu\text{m}$  in volume median diameter were dispersed, and an  $\alpha$ -gel was confirmed.

Further, the cosmetic had the oil agent containing the ultraviolet absorber homogeneously dispersed therein, and was excellent in the preservation stability, and high in the ultraviolet protection effect, and exhibited no stickiness, a good feeling of use, and no feeling of skin irritation.

[0122]

[Table 5]

(UV gel)

| (Component) |     |                                                                                              | (mass%) |
|-------------|-----|----------------------------------------------------------------------------------------------|---------|
| Step<br>(1) | (A) | Stearoylglutamic acid                                                                        | 1       |
|             | (B) | Cetyl alcohol                                                                                | 1.2     |
|             |     | Glyceryl behenate                                                                            | 0.8     |
|             |     | Sorbitan distearate                                                                          | 1       |
|             | (C) | Ethylhexyl methoxycinnamate (Uvinul MC80, manufactured by BASF AG)                           | 8       |
|             |     | Diethylamino hydroxybenzoyl benzoic acid hexyl ester (Uvinul Aplus, manufactured by BASF AG) | 2       |
|             |     | bis-Ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S, manufactured by BASF AG)         | 1       |
|             |     | Alkyl (C12-15) benzoate (FINSOLV TN, manufactured by Innospec Active Chemicals LLC)          | 3       |
|             |     | Neopentyl glycol dicaprate (Estemol N-0, manufactured by Nisshin Oillio Group, Ltd.)         | 1       |
|             | (D) | Ceresin (Ceresin #810K, manufactured by Nikko Rica Corp., melting point: 74°C)               | 0.47    |
|             |     | Paraffin wax (HNP-9, manufactured by Nippon Seiro Co., Ltd., melting point: 75°C)            | 0.53    |
|             |     | Dextrin palmitate (Rheoparl KL2, manufactured by Chiba Flour Milling Co., Ltd.)              | 0.1     |
|             |     | Propanediol (Zemea select PD,                                                                | 2       |

|             |     |                                                                                         |      |
|-------------|-----|-----------------------------------------------------------------------------------------|------|
|             |     | manufactured by Du Pont)                                                                |      |
|             |     | Glycerol                                                                                | 2.58 |
|             |     | Arginine                                                                                | 0.34 |
|             |     | Methylparaben                                                                           | 0.2  |
|             | (E) | Water                                                                                   | 20   |
| Step<br>(2) | (F) | Sodium acrylate/sodium<br>acryloyldimethyltaurate copolymer<br>(manufactured by Seppic) | 1.13 |
|             | (E) | Water                                                                                   | 47.1 |
|             |     | Dimethicone                                                                             | 3    |
|             |     | Lauryl methacrylate/sodium<br>methacrylate crosspolymer                                 | 4    |
|             |     | perfume                                                                                 | q.s. |
| Total       |     |                                                                                         | 100  |

[0123]

Examples 32 to 34 and Comparative Example 6

Cosmetics for protection against ultraviolet radiation having compositions indicated in Table 6 were produced as in Examples 1 to 28; volume median diameters and coefficients of variation were measured; confirmation of  $\alpha$ -gels was performed; and the SPF value, preservation stability, feeling of use and feeling of skin irritation were evaluated. The results are shown in Table 6 collectively.

Here, the cooling rates when the cosmetics of Examples 32 to 34 and Comparative Example 6 were produced were as indicated in Table 6.

[0124]

[Table 6]

| Component (mass%) |                                                                                              | Example |      |      | Comparative Example |
|-------------------|----------------------------------------------------------------------------------------------|---------|------|------|---------------------|
|                   |                                                                                              | 32      | 33   | 34   |                     |
| Step (1)          | (A) Stearoylglutamic acid                                                                    | 0.6     | 0.6  | 0.6  | 0.6                 |
|                   | (B) Cetearyl alcohol                                                                         | 0.9     | 0.9  | 0.9  | 0.9                 |
|                   | Glyceryl behenate                                                                            | 1.35    | 1.35 | 1.35 | 1.35                |
|                   | Sorbitan distearate                                                                          | 0.75    | 0.75 | 0.75 | 0.75                |
|                   | (C) Ethylhexyl methoxycinnamate (Uvinul MC80, manufactured by BASF AG)                       | 9       | 9    | 9    | 9                   |
|                   | Diethylamino hydroxybenzoyl benzoic acid hexyl ester (Uvinul Aplus, manufactured by BASF AG) | 2       | 2    | 2    | 2                   |
|                   | bis-Ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S, manufactured by BASF AG)         | 1       | 1    | 1    | 1                   |
|                   | Alkyl (C12-15) benzoate (FINSOLV TN, manufactured by Innospec Active Chemicals LLC)          | 3       | 3    | 3    | 3                   |
|                   | (D) Ceresin (Ceresin #810K, manufactured by Nikko Rica Corp., melting point: 74°C)           | 0.47    | 0.47 | 0.47 | 0.47                |
|                   | Paraffin wax (HNP-9, manufactured by Nippon Seiro Co., Ltd., melting point: 75°C)            | 0.53    | 0.53 | 0.53 | 0.53                |
|                   | Propanediol (Zemea select PD, manufactured by Du Pont)                                       | 2       | 2    | 2    | 2                   |
|                   | Glycerol                                                                                     | 2.58    | 2.58 | 2.58 | 2.58                |

|             |                                                                                   |                      |                      |                      |                      |                      |
|-------------|-----------------------------------------------------------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
|             | Arginine                                                                          | 0.33                 | 0.33                 | 0.33                 | 0.33                 | 0.33                 |
|             | Phenoxyethanol (Hisolve EPH, manufactured by TOHO Chemical Industry Co., Ltd.)    | 0.4                  | 0.4                  | 0.4                  | 0.4                  | 0.4                  |
| (E)         | Water                                                                             | 20                   | 20                   | 20                   | 20                   | 20                   |
| Step<br>(2) | Sodium acrylate/sodium acryloyldimethyltaurate copolymer (manufactured by Seppic) | 0.75                 | 0.38                 | 0                    | 0.75                 |                      |
|             | Acrylic acid/alkyl methacrylate copolymer (Pemulen TR-1)                          |                      |                      | 0.3                  |                      |                      |
|             | Caustic soda                                                                      |                      |                      | 0.07                 |                      |                      |
|             | Water                                                                             | 57.9                 | 58.3                 | 58.3                 | 57.9                 |                      |
|             | Total                                                                             | 100                  | 100                  | 100                  | 100                  | 100                  |
|             | (A) Ionic surfactant                                                              | 0.6                  | 0.6                  | 0.6                  | 0.6                  | 0.6                  |
|             | (B) Hydrophobic amphipathic substance                                             | 3                    | 3                    | 3                    | 3                    | 3                    |
|             | (C) Liquid oil agent                                                              | 15                   | 15                   | 15                   | 15                   | 15                   |
|             | (D) Solid oil agent                                                               | 1                    | 1                    | 1                    | 1                    | 1                    |
|             | A/C                                                                               | 0.04                 | 0.04                 | 0.04                 | 0.04                 | 0.04                 |
|             | B/C                                                                               | 0.20                 | 0.20                 | 0.20                 | 0.20                 | 0.20                 |
|             | D/C                                                                               | 0.07                 | 0.07                 | 0.07                 | 0.07                 | 0.07                 |
|             | Cooling step: cooling rate (°C/sec)                                               | 0.5                  | 1                    | 1                    | 0.1                  | 0.1                  |
|             | Cooling step: mixing                                                              | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring | vibrational stirring |
|             | Median diameter in terms of volume                                                | 0.23                 | 0.24                 | 0.24                 | 0.24                 | 0.38                 |
|             | Particle diameter, Coefficient of variation                                       | 21.3                 | 22.5                 | 22.5                 | 39.1                 |                      |
|             | Confirmation of $\alpha$ -gel                                                     | $\alpha$             | $\alpha$             | $\alpha$             | $\alpha$             | $\alpha$             |
|             | SPF                                                                               | 40.1                 | 25.3                 | 21.6                 | 32.5                 |                      |

| Preservation stability     | 3   | 4   | 4   | 1   |
|----------------------------|-----|-----|-----|-----|
| Feeling of use             | 4.3 | 4.7 | 4.5 | 4   |
| Feeling of skin irritation | 4.1 | 4.5 | 4.5 | 3.8 |

[0125]

Example 35 and Comparative Example 7

Cosmetics for protection against ultraviolet radiation having compositions indicated in Table 7 were produced as in Examples 1 to 28, and the transdermal absorbability of the ultraviolet absorber was evaluated.

[0126]

[Table 7]

| Component (mass%) |     |                                                                                              | Example | Comparative |
|-------------------|-----|----------------------------------------------------------------------------------------------|---------|-------------|
|                   |     |                                                                                              | 35      | Example 7   |
| Step (1)          | (A) | Stearoylglutamic acid                                                                        | 0.6     | 0.0         |
|                   | (B) | Cetearyl alcohol                                                                             | 0.9     | 0.0         |
|                   |     | Glyceryl behenate                                                                            | 1.35    | 0.00        |
|                   |     | Sorbitan distearate                                                                          | 0.75    | 0.00        |
|                   | (C) | Ethylhexyl methoxycinnamate (Uvinul MC80, manufactured by BASF AG)                           | 9       | 9           |
|                   |     | Diethylamino hydroxybenzoyl benzoic acid hexyl ester (Uvinul Aplus, manufactured by BASF AG) | 2       | 2           |
|                   |     | bis-Ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S, manufactured by BASF AG)         | 2       | 2           |
|                   |     | Alkyl (C12-15) benzoate (FINSOLV TN, manufactured by Innospec Active Chemicals LLC)          | 3       | 3           |
|                   | (D) | Ceresin (Ceresin #810K, manufactured by Nikko Rica Corp., melting point: 74°C)               | 0.47    | 0.00        |
|                   |     | Paraffin wax (HNP-9, manufactured by Nippon Seiro Co., Ltd., melting point: 75°C)            | 0.53    | 0.00        |
|                   |     | Propanediol (Zemea select PD, manufactured by Du Pont)                                       | 2       | 2           |
|                   |     | Glycerol                                                                                     | 2.58    | 2.58        |
|                   |     | Arginine                                                                                     | 0.33    | 0.33        |
|                   |     | Phenoxyethanol (Hisolve EPH,                                                                 | 0.4     | 0.4         |

|             |       |                                                                                                |      |      |
|-------------|-------|------------------------------------------------------------------------------------------------|------|------|
|             |       | manufactured by TOHO Chemical Industry Co., Ltd.)                                              |      |      |
|             | (E)   | Water                                                                                          | 20   | 20   |
| Step<br>(2) | (F)   | Sodium acrylate/sodium acryloyldimethyltaurate copolymer (SIMULGEL EG, manufactured by Seppic) | 0.75 | 0.75 |
|             |       | Acrylic acid/alkyl methacrylate copolymer (Pemulen TR-1)                                       |      |      |
|             |       | Caustic soda                                                                                   |      |      |
|             | (E)   | Water                                                                                          | 53.3 | 57.9 |
|             | Total |                                                                                                | 100  | 100  |

[0127]

Evaluation of the transdermal absorbability of the ultraviolet absorber

#### Test procedure

The test procedure was as follows. A human excised skin cryopreserved at  $-80^{\circ}\text{C}$  was thawed at room temperature for about 30 min; and surplus fat deposited on the skin was removed, and thereafter, the skin was cut into a square of about 2 cm and used for the measurement. A sample cosmetic was applied to the skin thus obtained and provided for a penetration test.

The penetration test was carried out by using a Franz diffusion cell (preparation application area:  $1\text{ cm}^2$ , receptor phase: 16 mL). 10  $\mu\text{L}$  of the prepared sample was charged in the donor phase, and held at  $37^{\circ}\text{C}$  for 24 hours. After the 24 hours, the sample on the surface of the skin was clearly removed with purified water, and thereafter, the skin was divided into an epidermis and a dermis, which were then each subjected to an ultrasonic treatment

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with 5 mL of methanol for 20 min, then filtered with a membrane filter (PTFE, 0.45  $\mu\text{m}$ , Advantec Co., Ltd.), and thereafter measured for the concentration of the ultraviolet absorber by an ultraviolet-visible spectrometer UV3600 (Shimadzu Corp.).

[0128]

Test results

The transdermal absorbability of the samples in Table 7 was evaluated. The results are shown in the following Table 8.

[0129]

[Table 8]

|                           | Concentration in<br>Epidermis ( $\mu\text{g}/\text{cm}^3$ ) | Concentration in<br>Dermis ( $\mu\text{g}/\text{cm}^3$ ) |
|---------------------------|-------------------------------------------------------------|----------------------------------------------------------|
| Example 35                | 1.33                                                        | 0.31                                                     |
| Comparative<br>Example 77 | 13.7                                                        | 1.33                                                     |

[0130]

It is clear that the sample of Example 35 including the ultraviolet absorber was far more decreased in the transdermal absorbability of the ultraviolet absorber than the sample of Comparative Example 7 including no ultraviolet absorber.

[Reference Signs List]

[0131]

100      APPARATUS  
20        EMULSIFYING UNIT

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- 21 FIRST EMULSIFYING SECTION
  - 211 MIXING TANK
- 22 SECOND EMULSIFYING SECTION
  - 221 HIGH-ENERGY PROCESSING PART
- 30 COOLING UNIT
  - 34, 35, 36, 37 JACKET
- 40 VIBRATION-TYPE STIRRING MIXING APPARATUS
- 41 CASING
- 42 DRIVING SHAFT
- 43 STIRRING BLADE
- 44 STIRRING GEAR
- 45a VIBRATOR
- 45b JOINT
- 46 PARTITION PART
- 47 MIXING CHAMBER
- 48 HOLE
- 49 NOTCH

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## Claims

## [Claim 1]

A cosmetic for protection against ultraviolet radiation, the cosmetic comprising the following components (A), (B), (C), (D) and (E):

- (A) 0.18 to 2 mass% of an ionic surfactant;
- (B) 1 to 10 mass% of a hydrophobic amphipathic substance;
- (C) 1 to 40 mass% of a liquid oil agent comprising an oil-soluble ultraviolet absorber;
- (D) 0.01 to 6 mass% of a solid oil agent; and
- (E) water,

wherein the cosmetic is obtained by a method comprising the following steps:

an emulsification step of mixing a composition comprising the components (A) to (D) with (E) water under heating to form an emulsion; and

a cooling step of cooling the emulsion formed in the emulsification step at a cooling rate of 0.5 to 5°C/sec.

## [Claim 2]

The cosmetic for protection against ultraviolet radiation according to claim 1, further comprising (F) a water-soluble polymer.

## [Claim 3]

The cosmetic for protection against ultraviolet radiation according to claim 1 or 2, wherein a mass ratio

of the component (A) to the component (C),  $(A)/(C)$ , is 0.01 to 0.2.

[Claim 4]

The cosmetic for protection against ultraviolet radiation according to any one of claims 1 to 3, wherein a mass ratio of the component (B) to the component (C),  $(B)/(C)$ , is 0.01 to 0.5.

[Claim 5]

The cosmetic for protection against ultraviolet radiation according to any one of claims 1 to 4, wherein a mass ratio of the component (D) to the component (C),  $(D)/(C)$ , is 0.01 to 0.5.

[Claim 6]

The cosmetic for protection against ultraviolet radiation according to any one of claims 1 to 5, further comprising (F) a water-soluble polymer.

[Claim 7]

The cosmetic for protection against ultraviolet radiation according to any one of claims 1 to 6, wherein a volume median diameter of emulsified particles is 0.1 to 10  $\mu\text{m}$ .

[Claim 8]

A method for producing a cosmetic for protection against ultraviolet radiation, comprising:  
an emulsification step of mixing a composition comprising the following components (A), (B), (C) and (D):  
(A) 0.1 to 2 mass% of an ionic surfactant;

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(B) 1 to 10 mass% of a hydrophobic amphipathic substance;  
(C) 1 to 40 mass% of a liquid oil agent comprising an  
oil-soluble ultraviolet absorber; and  
(D) 0.01 to 6 mass% of a solid oil agent,  
with (E) water under heating to form an emulsion; and  
a cooling step of cooling the emulsion formed in the  
emulsification step at a cooling rate of 0.5 to 5°C/sec.