(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau





(10) International Publication Number WO 2023/277194 A1

(43) International Publication Date 05 January 2023 (05.01.2023)

(51) International Patent Classification:

 A61K 8/06 (2006.01)
 A61K 8/58 (2006.01)

 A61K 8/19 (2006.01)
 A61K 8/73 (2006.01)

 A61K 8/25 (2006.01)
 A61Q 17/04 (2006.01)

 A61K 8/37 (2006.01)
 A61K 8/31 (2006.01)

 A61K 8/49 (2006.01)
 A61K 8/362 (2006.01)

(21) International Application Number:

PCT/JP2022/026534

(22) International Filing Date:

21 June 2022 (21.06.2022)

(25) Filing Language: English

(26) **Publication Language:** English

(30) Priority Data:

2021-108691 30 June 2021 (30.06.2021) JP 2108145 27 July 2021 (27.07.2021) FR

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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,

MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))



(54) Title: SUNSCREEN W/O EMULSION

(57) **Abstract:** The present invention relates to a W/O emulsion composition comprising: (a) at least one lipophilic organic UV filter, (b) at least one powder other than microplastic filler, (c) at least one cationic polymer, and (d) at least one oil, wherein the composition comprises microplastic filler in an amount of 5% by weight or less, preferably 3% by weight or less, and more preferably 1% by weight or less, or the composition is free of microplastic filler.

DESCRIPTION

TITLE OF INVENTION

SUNSCREEN W/O EMULSION

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TECHNICAL FIELD

The present invention relates to a W/O emulsion composition, in particular a sun care composition in the form of a W/O emulsion, for a keratinous substance such as skin.

BACKGROUND ART

- Sun care products are widely used in order to protect keratinous substances, in particular skin, from the damage caused by UV radiation. Among sun care products, W/O emulsion sun care compositions are widely distributed since they are in general water resistant and thus can be retained on the surface of the skin even after exposed to water or sweat.
- For example, JP-A-2009-191033 discloses a water-in-oil type sunblock cosmetic including: (A) a partially crosslinked polyester modified organopolysiloxane; (B) an organic titanate-treated fine particulate zinc oxide and/or an organic titanate-treated fine particulate titanium oxide; (C) a silicone oil; (D) one or more oily agents selected from glyceryl trioctanoate, glyceryl tri(caprylcapric acid), and dioctanoic acid neopentyl.
- In recent years, the polluteing of the ocean environment and the destroyuction of the marineecosystem by microplastics have become a big concern. Therefore, cosmetic products including a small amount of microplastic fillers or not including microplastic fillers have been proposed.
- For example, JP-A-2020-97552 discloses a cosmetic preparation for concavo-convex compensation containing the following components (a) to (d): (a) 6 to 10 wt.% of fumed hydrophobic silica; (b) 5 to 20 wt.% of octamethyltrisiloxane and/or decamethyltetrasiloxane; (c) batyl alcohol; and (d) 10 to 30 wt.% of powders other than (a) that contain no microplastic beads, the cosmetic preparation for concavo-convex compensation containing no microplastic beads.
- In sun care cosmetic products, organic UV filters are widely used to impart a UV protecting property to sun care compositions. However, the use of organic UV filters may have a negative impact such as imparting oily, greasy, and sticky sensations during application. Also, oils in W/O emulsion may cause oily, greasy, and sticky sensations on application. Furthermore, there is a problem in that W/O emulsions may not have sufficient stability to maintain their emulsion form over time.
 - Therefore, there is a demand for W/O emulsion compositions comprising organic UV filters, which are well resistant to water resistant, impart an improved texture, such as a fresh sensation, and have good stability without causing phase separation over time. Furthermore, sun care cosmetic compositions which do not contain microplastic fillers are also desired as environmentally-sustainable products.

DISCLOSURE OF INVENTION

An objective of the present invention is to provide a water-resistant W/O emulsion composition

having an improved texture, such as a fresh sensation and having good stability, and not comprising microplastic fillers.

The above objective of the present invention can be achieved by a W/O emulsion composition, comprising:

- (a) at least one lipophilic organic UV filter,
- (b) at least one powder other than microplastic filler,
- (c) at least one cationic polymer, and
- (d) at least one oil,

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- wherein the composition comprises microplastic filler in an amount of 5% by weight or less, preferably 3% by weight or less, and more preferably 1% by weight or less, or the composition is free of microplastic filler.
- The (b) powder may be selected from talc, mica, silica, silicate, magnesium aluminum silicate, kaolin, bentone, calcium carbonate, magnesium hydrogen carbonate, hydroxyapatite, boron nitride, fluorphlogopite, sericite, calcinated talc, calcinated mica, calcinated sericite, synthetic mica, perlite, lauroyl lysine, metal soap, bismuth oxychloride, barium sulfate, magnesium carbonate, and natural polymer powders, such as polysaccharide powders, for example, starch, cellulose powder, and mixtures thereof.

The average particle size of the (b) powder may be 50 μ m or less, preferably 20 μ m or less, and more preferably 15 μ m or less, and may be 0.2 μ m or more, preferably 0.5 μ m or more, and more preferably 1 μ m or more.

25 The (c) cationic polymer may be selected from quaternized hydroxyethyl celluloses modified with at least one quaternary ammonium group comprising at least one fatty chain

The (c) cationic polymer may be selected from quaternized alkylhydroxyethylcelluloses containing C_8 - C_{30} fatty chains.

The composition according to the present invention may be free of microplastic filler.

The (a) lipophilic organic UV filter may comprise a combination of at least one lipophilic organic UV-A filter and at least one lipophilic organic UV-B filter.

The amount of the (a) lipophilic organic UV filter(s) may be 1% by weight or more, preferably 5% by weight or more, more preferably 10% by weight or more, and even more preferably 15% by weight or more, and/or may be 50% by weight or less, preferably 40% by weight or less, more preferably 30% by weight or less, and even more preferably 25% by weight or less, relative to the total weight of the composition.

The amount of the (b) powder(s) may be 1% by weight or more, preferably 3% by weight or more, more preferably 5% by weight or more, even more preferably 8% by weight or more, and in particular 10% by weight or more, and/or may be 30% by weight or less, preferably 25% by weight or less, more preferably 20% by weight or less, even more preferably 18% by weight or less, and in particular 15% by weight or less, relative to the total weight of the composition.

The amount of the (c) cationic polymer(s) may be 0.001% by weight or more, preferably 0.01% by weight or more, and more preferably 0.05% by weight or more, and/or may be 5% by weight or less, preferably 3% by weight or less, more preferably 1% by weight or less, and even more

preferably 0.5% by weight or less, relative to the total weight of the composition.

The amount of the (d) oil(s) may be 3% by weight or more, preferably 5% by weight or more, more preferably 10% by weight or more, even more preferably 15% by weight or more, and in particular 20% by weight or more, and/or may be 50% by weight or less, preferably 40% by weight or less, more preferably 35% by weight or less, and even more preferably 30% by weight or less, relative to the total weight of the composition.

The composition according to the present invention may further comprise at least one inorganic UV filter.

The inorganic UV filter may have an average particle size of less than 200 nm.

The amount of the inorganic UV filter may be 0.5% by weight or more, preferably 1% by weight or more, and more preferably 1.5% by weight or more, and may be 15% by weight or less, preferably 10% by weight or less, more preferably 7% by weight or less, and even more preferably 5% weight or less, relative to the total weight of the composition.

The present invention also relates to a cosmetic process for a keratin substrate, such as skin, comprising applying to the keratin substrate the composition according to the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

After diligent research, the inventors have surprisingly discovered that a W/O emulsion composition comprising a combination of at least one lipophilic organic UV filter, at least one powder other than microplastic filler, and at least one cationic polymer in the water phase can show an improved water resistant property, fresh sensation on application, and good stability, even if it is free of microplastic filler, and thus completed the present invention.

- Thus, the present invention relates to a W/O emulsion composition, comprising:
 - (a) at least one lipophilic organic UV filter,
 - (b) at least one powder other than microplastic filler,
 - (c) at least one cationic polymer, and
 - (d) at least one oil,
- wherein the composition comprises microplastic filler in an amount of 5% by weight or less, preferably 3% by weight or less, and more preferably 1% by weight or less, or the composition is free of microplastic filler.
- Hereinafter, the W/O emulsion composition and cosmetic process according to the present invention will be explained in a more detailed manner.

[Composition]

The composition according to the present invention includes (a) at least one lipophilic organic UV filter, and (b) at least one powder other than microplastic filler, (c) at least one cationic polymer, and (d) at least one oil. The ingredients in the composition will be described in a detailed manner below.

(Lipophilic Organic UV filter)

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The composition according to the present invention comprises (a) at least one lipophilic organic UV filter. Two or more lipophilic organic UV filters may be used in combination. Thus, a single type of lipophilic organic UV filter or a combination of different types of lipophilic organic UV filters may be used.

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The term "UV" here comprises the UV-B region (260-320 nm in wavelength), the UV-A region (320-400 nm in wavelength), and the high energy visible light region (400-450 nm in wavelength). Therefore, a UV filter means any material which has filtering effects in the wavelength of UV rays, in particular the UV-A, UV-B, and high energy visible light regions.

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The UV filter(s) used for the present invention may be active in the UV-A and/or UV-B region, preferably in each of the UV-A and UV-B regions alone or in combination. Therefore, the UV filter(s) used in the present invention include(s) a UV-A filter capable of absorbing UV radiation from 320 to 400 nm, a UV-B filter capable of absorbing UV radiation from 280 to 320 nm, and a UV-A and UV-B filter capable of absorbing UV radiation from 280 to 400 nm.

The term "lipophilic UV filter" here means UV filters which are soluble in oils at a concentration of at least 1% by weight relative to the total weight of the oils at room temperature (25°C) and atmosphere pressure (10⁵ Pa).

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The lipophilic organic UV filter may be solid or liquid. The terms "solid" and "liquid" mean solid and liquid, at room temperature (25°C) and atmosphere pressure (105 Pa).

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The lipophilic organic UV-A filters used in the present invention may include, but are not limited to, aminobenzophenone compounds, dibenzoylmethane compounds, anthranilic acid compounds, and 4,4-diarylbutadiene compounds.

As the aminobenzophenone compounds, mention may be made of n-hexyl 2-(4-diethlamino-2-hydroxybenzoyl)benzoate, the alternative name of which is diethylamino hydroxybenzoyl hexyl benzoate (DHHB), sold under the trade name "Uvinul A+" from BASF.

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As the dibenzoylmethane compounds, mention may be made of 4-isopropyldibenzoylmethane, sold under the name of "Eusolex 8020" from Merck, 1-(4-methoxy-1-benzofuran-5-yl)-3-phenylpropane-1,3-dione, sold under the name of "Pongamol" from Quest, 1-(4-(tert-butyl)phenyl)-3-(2-hydroxyphenyl)propane-1,3-dione, and butyl methoxydibenzoylmethane, sold under the trade name "Parsol 1789" from Hoffmann-La Roche.

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As the anthranilic acid compounds, mention may be made of menthyl anthranilate marketed under the name "NEO HELIPAN MA" by Symrise.

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As the 4,4-diarylbutadiene compounds, mention may be made of 1,1 -dicarboxy (2,2'-dimethylpropyl)-4,4-diphenylbutadiene and diphenyl butadiene malonates and malononitriles.

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The lipophilic organic UV-B filters used in the present invention may include, but are not limited to, triazine compounds, para-aminobenzoic acid compounds, salicylic compounds, cinnamate compounds, β , β -diphenylacrylate compounds, benzylidenecamphor compounds, phenylbenzimidazole compounds, imidazoline compounds, benzalmalonate compounds, and merocyanine compounds.

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As the triazine compounds, mention may be made of ethylhexyl triazone, marketed under the

name "UVINUL T-150" by BASF, diethylhexyl butamido triazone, marketed under the name "UVASORB HEB" by SIGMA 2V, 2,4,6-tris(dineopentyl 4'-aminobenzalmalonate)-s-triazine, 2,4,6-tris(diisobutyl 4'-aminobenzalmalonate)-s-triazine, 2,4-bis(dineopentyl 4'-aminobenzalmalonate)-6-(n-butyl 4'-aminobenzoate)-s-triazine, and 2,4-bis(n-butyl 4'-aminobenzoate)-6-(aminopropyltrisiloxane)-s-triazine.

As the para-aminobenzoic acid derivatives, mention may be made of para-aminobenzoates (PABA), for example, ethyl PABA (para-aminobenzoate), ethyl dihydroxypropyl PABA, and ethylhexyl dimethyl PABA, marketed under the name "ESCALOL 5972 from ISP.

As the salicylic compounds, mention may be made of homosalate, marketed under the name "Eusolex HMS" by Rona/EM industries, and ethylhexyl salicylate, marketed under the name "NEO HELIOPAN OS" by Symrise.

- As the cinnamate compounds, mention may be made of ethylhexyl methoxycinnamate, marketed under the name "PARSOL CX" by DSM NUTRITIONAL PRODUCTS, isopropyl ethoxy cinnamate, isoamyl methoxy cinnamate, marketed under the name "NEO HELIOPAN E 1000" by Symrise, diisopropyl methylcinnamate, cinoxate, and glyceryl ethylhexanoate dimethoxycinnamate.
- As the β , β -diphenylacrylate compounds, mention may be made of octocrylene, marketed under the name "UVINUL N539" by BASF, and etocrylene, marketed under the name "UVINUL N35" by BASF.
- As the benzylidenecamphor compounds, mention may be made of 3-benzylidene camphor, marketed under the name "MEXORYL SD" from CHIMEX, methylbenzylidene camphor, marketed under the name "EUSOLEX 6300" by MERCK, polyacrylamidomethyl benzylidene Camphor, marketed under the name "MEXORYL SW" by CHIMEX, and terephthalylidene dicamphor sulfonic acid, marketed under the name "Mexoryl SX" by Chimex.
- As the phenylbenzimidazole compounds, mention may be made of phenylbenzimidazole sulfonic acid, marketed under the name "Eusolex 232" by Merck, and disodium phenyl dibenzimidazole tetrasulfonate, marketed under the name "Neo Heliopan AP" by Haarmann and Reimer.
- As the imidazoline compounds, mention may be made of ethylhexyl dimethoxybenzylidene dioxoimidazoline propionate.
- As the benzalmalonate compounds, mention may be made of polyorganosiloxane containing a benzalmalonate moiety, for example, Polysilicone-15, marketed under the name "Parsol SLX" by DSM NUTRITIONAL PRODUCTS, and di-neopentyl 4'-methoxybenzalmalonate.
 - The lipophilic organic UV filters of the present invention may comprise lipophilic organic UV-A and UV-B filters, which cover UV-A and UV-B regions. The following are non-limiting examples of the lipophilic organic UV-A and UV-B filters:
- Benzophenone compounds, such as benzophenone-1 marketed under the name "UVINUL 400" by BASF, benzophenone-2 marketed under the name "UVINUL 500" by BASF, benzophenone-3 or oxybenzone marketed under the name "UVINUL M40" by BASF, benzophenone-6 marketed under the name "Helisorb 11" by Norquay, benzophenone-8 marketed under the name "Spectra-Sorb UV-24" by American Cyanamid, benzophenone-10, benzophenone-11, and benzophenone-

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- benzotriazole compounds such as drometrizole trisiloxane marketed under the name "Silatrizole" by Rhodia Chimie, bumetrizole marketed under the name "TINOGUARTD AS" by CIBA-GEIGY ,and , phenylbenzotriazole derivatives: 2-(2H-benzotriazole-2-yl)-6-dodecyl-4-methylpheno, branched and linear;

- 5 bis-resorcinyl triazine compounds, such as bis-ethylhexyloxyphenol methoxyphenyl triazine marketed under the name "TINOSORB S" by CIBA-GEIGY; and
 - benzoxazole compounds, such as 2,4-bis[5-(1-dimethylpropyl) benzoxazol-2-yl(4-phenyl)imino]-6-(2-ethylhexyl)imino-1,3,5-triazine marketed under the name "Uvasorb K2A" by Sigma 3V.

Preferably, the lipophilic organic UV filter may be selected from aminobenzophenone compounds, such as diethylamino hydroxybenzoyl hexyl benzoate (DHHB), dibenzoylmethane compounds, such as butyl methoxydibenzoylmethane, triazine compounds, such as ethylhexyl triazone, salicylic compounds, such as homosalate, β , β -diphenylacrylate compounds, such as octocrylene, and benzotriazole compounds, such as drometrizole trisiloxane, and mixtures thereof.

In one preferred embodiment of the present invention, the lipophilic organic UV filter of the present invention comprises a combination of at least one lipophilic organic UV-A filter and at least one lipophilic organic UV-B filter.

Therefore, in another preferred embodiment of the present invention, the lipophilic organic UV filter comprises at least one lipophilic organic UV-A filter selected from aminobenzophenone compounds and dibenzoylmethane compounds, and at least one lipophilic organic UV-B filter selected from triazine compounds, salicylic compounds, β , β -diphenylacrylate compounds, and benzotriazole compounds.

The amount of the lipophilic organic UV filter(s) in the composition according to the present invention may be 1% by weight or more, preferably 5% by weight or more, more preferably 10% by weight or more, and even more preferably 15% by weight or more, relative to the total weight of the composition. The amount of the lipophilic organic UV filter(s) in the composition may be 40% by weight or less, preferably 35% by weight or less, more preferably 30% by weight or less, and even more preferably 25% by weight or less, relative to the total weight of the composition.

In one particular embodiment of the present invention, the amount of the lipophilic organic UV-A filter(s) in the composition is 0.5% by weight or more, preferably 1% by weight or more, and more preferably 2% by weight or more, and is 15% by weight or less, preferably 10% by weight or less, and more preferably 7% by weight or less, relative to the total weight of the composition.

In another particular embodiment of the present invention, the amount of the lipophilic organic UV-B filter(s) in the composition is 1% by weight or more, preferably 5% by weight or more, and more preferably 8% by weight or more, and is 30% by weight or less, preferably 20% by weight or less, and more preferably 15% by weight or less, relative to the total weight of the composition.

In yet another particular embodiment of the present invention, the amount of the lipophilic organic UV-A and UV-B filter(s) in the composition is 0.5% by weight or more, preferably 1% by weight or more, and more preferably 1.5% by weight or more, and is 10% by weight or less, preferably 7% by weight or less, and more preferably 5% by weight or less, relative to the total weight of the composition.

50 (Powder other than microplastic filler)

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The composition according to the present invention comprises (b) at least one powder other than microplastic filler. Two or more powders may be used in combination. Thus, a single type of powder or a combination of different types of powders may be used.

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The term "powder" should be understood as meaning colorless or white, mineral or natural particles of any shape, which are insoluble in the medium of the composition, irrespective of the temperature at which the composition is manufactured.

10 The (b) powder is selected from powders other than microplastic fillers.

The term "microplastic filler" here means a synthetic polymer filler having an average particle size of 5 mm or less. The term "microplastic filler" here is also understood to mean polymeric solid particle insoluble in water which has size less than 5mm (all dimension) and stable throughout the life cycle.

The microplastic filler may include, but not limited to, acrylic polymer powders, silicone powders, wax powders, polyamide powders, urethane polymer powders, tetrafluoroethylene polymer powders, polyacrylonitrile powders, poly-β-alanine powders, polyethylene powders, polytetrafluoroethylene powders, lauroyllysine, tetrafluoroethylene polymer powders.

The (b) powder may be of any shape, platelet-shaped, spherical or oblong, irrespective of the crystallographic form (for example lamellar, cubic, hexagonal, orthorhombic, etc.).

The average particle size of the (b) powder is not limited, but in general is 50 μm or less, preferably 20 μm or less, and more preferably 15 μm or less. The average particle size of the (b) powder is 0.2 μm or more, preferably 0.5 μm or more, and more preferably 1 μm or more. The term "average particle size" used herein represents a number-average size mean diameter which is given by the statistical particle size distribution to half of the population, referred to as D50. For example, the number-average size mean diameter can be measured by a laser diffraction particle size distribution analyzer, such as Mastersizer 2000 by Malvern Corp.

The (b) powder can be an inorganic or organic powder, which may or may not be surface-coated.

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As the inorganic powder, mention may be made of talc, mica, silica, silica silicate, magnesium aluminum silicate, kaolin, bentone, calcium carbonate, magnesium hydrogen carbonate, hydroxyapatite, boron nitride, fluorphlogopite, sericite, calcinated talc, calcinated mica, calcinated sericite, synthetic mica, perlite, lauroyl lysine, metal soap, bismuth oxychloride, barium sulfate, magnesium carbonate, and mixtures thereof, optionally hydrophilic- or hydrophobic-treated.

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As the organic powder, mention may be made of natural polymer powders, such as polysaccharide powders and derivatives thereof, for example, starch, cellulose powder, and mixtures thereof.

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It would be important to mention that the (b) powder of the present invention is different from a so-called "inorganic UV filter", such as titanium oxide. The (b) powder does not have an active, substantive UV filtering effect, while it can contribute to form a homogeneous and fine film on keratinous substances, such as skin, by the composition according to the present invention. Therefore, the (b) powder of the present invention is not an inorganic UV filter, such as titanium oxide. Typically, inorganic UV filler is characterized by its fine particle size, and generally has less than 200 nm of average particle size.

The (b) powder may or may not be surface-coated. The coating may be an inorganic substance and/or an organic substance. In one embodiment of the present invention, the (b) powder is not surface-coated.

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The inorganic coating may be selected from metal oxides, such as silica, aluminum oxides, titanium oxides, zirconium oxides, cerium oxide, chromium oxide, and iron oxides, and metal hydroxides, such as aluminum hydroxide.

The organic coating may be selected from fatty acids or salts thereof (such as sodium, potassium, zinc, iron or aluminum salts), fatty alcohols, lecithin, amino acids, polysaccharides, proteins, alkanolamines, waxes such as beeswax, (meth)acrylic polymers, and (per)fluoro compounds.

In one embodiment of the present invention, the (b) powder does not comprise synthetic coating which may cause the environmental problems in the same manner as microplastic filler.

The amount of the (b) powder(s) in the composition according to the present invention may be 1% by weight or more, preferably 3% by weight or more, more preferably 5% by weight or more, even more preferably 8% by weight or more, and in particular 10% by weight or more, and may be 30% by weight or less, preferably 25% by weight or less, more preferably 20% by weight or less, even more preferably 18% by weight or less, and in particular 15% by weight or less, relative to the total weight of the composition.

(Cationic Polymer)

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The composition according to the present invention comprises (c) at least one cationic polymer. Two or more types of cationic polymer may be used in combination. Thus, a single type of cationic polymer or a combination of different types of cationic polymers may be used.

A cationic polymer has a positive charge density. The charge density of the cationic polymer may be from 0.01 meq/g to 20 meq/g, preferably from 0.05 to 15 meq/g, and more preferably from 0.1 to 10 meq/g.

The cationic polymer is hydrophilic or water soluble. Therefore, the cationic polymer is present in the water phase of the W/O emulsion composition according to the present invention.

It is preferable that the molecular weight of the cationic polymer be 500 or more, preferably 1000 or more, more preferably 2000 or more, and even more preferably 5000 or more.

40 Unless otherwise defined in the description, "molecular weight" means a number average molecular weight.

The cationic polymer may have at least one positively chargeable and/or positively charged moiety selected from the group consisting of a primary, secondary or tertiary amino group, a quaternary ammonium group, a guanidine group, a biguanide group, an imidazole group, an imino group, and a pyridyl group. The term (primary) "amino group" here means the –NH₂ group.

The cationic polymer may be a homopolymer or a copolymer. The term "copolymer" is understood to mean both copolymers obtained from two kinds of monomers and those obtained

from more than two kinds of monomers, such as terpolymers obtained from three kinds of monomers.

The cationic polymer may be selected from natural and synthetic cationic polymers. Non-limiting examples of the cationic polymers are as follows.

(1) Homopolymers and copolymers derived from acrylic or methacrylic esters and amides and comprising at least one unit chosen from units of the following formulas:

10 wherein:

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R₁ and R₂, which may be identical or different, are chosen from hydrogen and alkyl groups comprising from 1 to 6 carbon atoms, for instance, methyl and ethyl groups; R₃, which may be identical or different, is chosen from hydrogen and CH₃; the symbols A, which may be identical or different, are chosen from linear or branched alkyl groups comprising from 1 to 6 carbon atoms, for example, from 2 to 3 carbon atoms and hydroxyalkyl groups comprising from 1 to 4 carbon atoms;

 R_4 , R_5 , and R_6 , which may be identical or different, are chosen from alkyl groups comprising from 1 to 18 carbon atoms and benzyl groups, and in at least one embodiment, alkyl groups comprising from 1 to 6 carbon atoms; and

20 X is an anion derived from an inorganic or organic acid, such as methosulphate anions and halides, for instance chloride and bromide.

The copolymers of family (1) may also comprise at least one unit derived from comonomers which may be chosen from acrylamides, methacrylamides, diacetone acrylamides, acrylamides and methacrylamides substituted on the nitrogen atom with (C_1-C_4) lower alkyl groups, groups derived from acrylic or methacrylic acids and esters thereof, vinyllactams such as vinylpyrrolidone and vinylcaprolactam, and vinyl esters.

Examples of copolymers of family (1) include, but are not limited to:

copolymers of acrylamide and of dimethylaminoethyl methacrylate quaternized with dimethyl sulphate or with a dimethyl halide,

- copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium chloride described, for example, in European Patent Application No. 0 080 976,
- copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium methosulphate, quaternized or nonquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers, described, for example, in French Patent Nos. 2 077 143 and 2 393 573, dimethylaminoethyl methacrylate/vinylcaprolactam/vinylpyrrolidone terpolymers, vinylpyrrolidone/methacrylamidopropyldimethylamine copolymers, quaternized
- vinylpyrrolidone/dimethylaminopropylmethacrylamide copolymers, and crosslinked methacryloyloxy(C₁-C₄)alkyltri(C₁-C₄)alkylammonium salt polymers such as the polymers obtained by homopolymerization of dimethylaminoethyl methacrylate quaternized with methyl chloride, or by copolymerization of acrylamide with dimethylaminoethyl methacrylate quaternized with methyl chloride, the homopolymerization or copolymerization being followed by crosslinking with a compound containing an olefinic unsaturation, for example, methylenebisacrylamide.

Preferably, copolymers of family (1) have a unit derived from vinylpyrrolidone. More preferably, copolymers of family (1) have at least one pendent ring structure derived from vinylpyrrolidone. On the other hand, it is preferable that the copolymers of family (1) comprise no ring structure in the backbone of the polymer.

The copolymers of family (1) having vinylpyrrolidone units can be selected from:

- (i) the copolymers comprising vinylpyrrolidone units and dimethylaminoethyl methacrylate units, for example:
- vinylpyrrolidone/dimethylaminoethyl methacrylate copolymers; for example, vinylpyrrolidone/dimethylaminoethyl methacrylate copolymer (20/80 by weight) sold under the trade name Copolymer 845 by the company I.S.P.,
- vinylpyrrolidone/dimethylaminoethyl methacrylate copolymers quaternized with diethyl sulphate; for example, vinylpyrrolidone/dimethylaminoethyl methacrylate copolymer quaternized with diethyl sulphate, sold under the trade names Gafquat 734, 755, 755S and 755L by the company I.S.P.,
- vinylpyrrolidone/dimethylaminoethyl methacrylate/hydrophilic polyurethane copolymers; for example, vinylpyrrolidone/dimethylaminoethyl methacrylate/hydrophilic polyurethane copolymer, sold under the trade name Pecogel GC-310 by the company U.C.I.B., or under the trade names Aquamere C1031 and C1511 by the company Blagden Chemicals,
- vinylpyrrolidone/dimethylaminoethyl methacrylate/C₈-C₁₆ olefin copolymers, quaternized or non-quaternized; for example, vinylpyrrolidone/dimethylaminoethyl methacrylate/C₈-C₁₆ olefin copolymer sold under the trade names Ganex ACP1050 to 1057, 1062-1069 and 1079-1086 by the company I.S.P.,

and

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- vinylpyrrolidone/dimethylaminoethyl methacrylate/vinylcaprolactam copolymers; for example, vinylpyrrolidone/dimethylaminoethyl methacrylate/vinylcaprolactam copolymer sold under the trade name Gaffix VC713 by the company I.S.P;
- 45 (ii) the copolymers comprising vinylpyrrolidone units and methacrylamidopropyltrimethylammonium (MAPTAC) units, for example:
 - vinylpyrrolidone/methacrylamidopropyltrimethylammonium copolymers; for example, vinylpyrrolidone/MAPTAC copolymer sold under the trade names Gafquat ACP1011 and Gafquat HS100 by the company I.S.P.,
- 50 and

- vinylpyrrolidone/methacrylamidopropyltrimethylammonium/vinylcaprolactam terpolymers; for example, vinylpyrrolidone/MAPTAC/vinylcaprolactam terpolymer sold under the trade names Polymer ACP 1059, 1060 and 1156 by the company I.S.P.; and

(iii) the copolymers comprising vinylpyrrolidone units and methylvinylimidazolium units, for example:

- vinylpyrrolidone/methylvinylimidazolium chloride copolymers; for example, vinylpyrrolidone/methylvinylimidazolium chloride copolymer sold under the trade names Luviquat FC370, FC550, FC905 and HM552 by the company BASF,
- vinylpyrrolidone/methylvinylimidazolium chloride/vinylimidazole copolymers; for example, vinylpyrrolidone/methylvinylimidazolium chloride/vinylimidazole copolymer sold under the trade name Luviquat 8155 by the company BASF,

and

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- vinylpyrrolidone/methylvinylimidazolium methosulphate copolymers; for example, vinylpyrrolidone/methylvinylimidazolium methosulphate copolymer sold under the trade name Luviquat MS370 by the company BASF.

It is preferable that the copolymers of family (1) be chosen from the copolymer comprising vinylpyrrolidone units and dimethylaminoethyl methacrylate units, more preferably chosen from vinylpyrrolidone/dimethylaminoethyl methacrylate copolymers quaternized with diethyl sulphate, and even more preferably Polyquaternium-11.

(2) Cationic cellulose derivatives such as cellulose ether derivatives comprising quaternary ammonium groups described, for example, in French Patent No. 1 492 597, such as the polymers sold under the names "JR" (JR 400, JR 125, JR 30M) or "LR" (LR 400, LR 30M) by the company Union Carbide Corporation. These polymers are also defined in the CTFA dictionary as quaternary ammoniums of hydroxyethylcellulose that have reacted with an epoxide substituted with a trimethylammonium group.

It is preferable that the cationic cellulose derivatives be quaternized hydroxyethyl celluloses modified with at least one quaternary ammonium group comprising at least one fatty chain, such as alkyl, arylalkyl or alkylaryl groups comprising at least 8 carbon atoms, or mixtures thereof. The alkyl radicals borne by the quaternary ammonium group may preferably contain from 8 to 30 carbon atoms, especially from 10 to 30 carbon atoms. The aryl radicals preferably denote phenyl, benzyl, naphthyl or anthryl groups.

More preferably, the cationic cellulose derivatives may comprise at least one quaternary ammonium group including at least one C_8 - C_{30} hydrocarbon group.

Examples of quaternized alkylhydroxyethylcelluloses containing C₈-C₃₀ fatty chains that may be mentioned include the products Quatrisoft LM 200, Quatrisoft LM-X 529-18-A, Quatrisoft LM-X 529-18B (C12 alkyl) and Quatrisoft LM-X 529-8 (C18 alkyl) or Softcat Polymer SL100, Softcat SX-1300X, Softcat SX-1300H, Softcat SL-5, Softcat SL-30, Softcat SL-60, Softcat SK-MH, Softcat SX-400X, Softcat SX-400H, SoftCat SK-L, Softcat SK-M, and Softcat SK-H, sold by the company Amerchol and the products Crodacel QM, Crodacel, QL (C12 alkyl) and Crodacel QS (C18 alkyl) sold by the company Croda.

It is preferable that the cationic polymer be selected from the group consisting of Polyquaternium-24, Polyquaternium-67 and mixtures thereof. Polyquaternium-67 is most preferable.

From another viewpoint, the cationic cellulose derivatives could also be chosen among cationic

cellulose ether(s), comprising from 4 000 to 10 000 anhydroglucose units, said anhydroglucose units being substituted with at least:

(i) one substituent of formula

$5 [R_4R_5R_6R_9N^+](X_2^-)$

in which

R₄ and R₅ represent, independently of one another, a methyl or ethyl group,

 R_6 represents a linear or branched C_8 - C_{24} alkyl group or an aralkyl group in which the linear or branched alkyl part is C_8 - C_{24} ,

R₉ represents a divalent group which allows the attachment to the anhydroglucose group and which is chosen from -(B)_q-CH₂-CHOH-CH₂- and -CH₂CH₂-, a denoting 0 or 1.

B denoting the divalent group -(CH₂CH₂O)_{n'}-,

n' being an integer ranging from 1 to 100,

X₂ represents an anion; and

(ii) one substituent of formula

$[R_1R_2R_3R_8N^+](X_1^-)$

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in which:

 R^1 , R^2 and R^3 represent, independently of one another, a methyl or ethyl group, R^8 represents a divalent group which allows the attachment to the anhydroglucose group and which is chosen from -(A)_p-CH₂-CHOH-CH₂- and -CH₂CH₂-,

p denoting 0 or 1,

A denoting a divalent group -(CH_2CH_2O)_n-, n being an integer ranging from 1 to 100, and X_1 - represents an anion.

Preferably, the substituent (i) of formula $[R_4R_5R_6R_9N^+](X_2^-)$ is present at an average of from 0.0003 to 0.08 mol, per mole of anhydroglucose units.

The cationic cellulose ethers that can be used in the compositions according to the present invention are preferably hydroxyethyl celluloses or hydroxypropyl celluloses. The cationic cellulose ethers that can be used in the compositions according to the present invention preferably comprise more than 4500, advantageously more than 5000, and more preferably more than 6000 anhydroglucose units.

Preferably, the cationic cellulose ethers that can be used in the compositions according to the present invention comprise up to 9000, and more preferably up to 8000 anhydroglucose units.

These cationic cellulose ethers and the process for the preparation thereof are described in application WO 2005/000903.

According to a preferred variant, the cationic cellulose ethers that can be used in the compositions according to the present invention are formed from at least one unit (IV) and at least one of the following units (I), (II) and (III):

5 X₂-

with the proviso that:

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the total number of units (I)+(II)+(III)+(IV) is between 4000 and 10 000; the [(III)+(IV)]/[(I)+(II)+(III)+(IV)] ratio ranges from 0.0003 to 0.8; the [(II)+(IV)]/[(I)+(II)+(II)+(IV)] ratio ranges from 0.02 to 0.9;

the integers n and n', independently of one another, range from 0 to 5;

R₁, R₂, R₃, R₄ and R₅ represent, independently of one another, a methyl or ethyl group;

R₆ represents a linear or branched C₈-C₂₄, preferably C₁₀-C₂₄, more preferably C₁₂-C₂₄ and better still C₁₂-C₁₅, an lkyl group or an aralkyl group in which the linear or branched alkyl part is C₈-C₂₄;

X₁ and X₂ represent anions preferably chosen, independently of one another, from phosphate,

nitrate, sulphate and halide (Cl⁻, Br⁻, F⁻, I⁻) ions.

According to a particular variant, the cationic cellulose ethers that can be used in the compositions according to the present invention are formed from at least one unit (IV) and at least one of the units (I), (II) or (III) above, in which R₆ is a linear dodecyl group.

Among the cationic cellulose ethers that can be used in the compositions of the present invention, mention may be made of the polymers of Softcat SL-5, SL-30, SL-60 and SL-100 type (INCI: Polyquaternium-67) sold by the company Amerchol. The cationic cellulose ethers that are particularly preferred are the polymers of SL-60 and SL-100 type.

(3) Cationic cellulose derivatives such as cellulose copolymers and cellulose derivatives grafted with a water-soluble monomer of quaternary ammonium, and described, for example, in U.S. Pat. No. 4,131,576, such as hydroxyalkylcelluloses, for instance, hydroxymethyl-, hydroxyethyl-, and hydroxypropylcelluloses grafted, for example, with a salt chosen from methacryloylethyltrimethylammonium, methacrylamidopropyltrimethylammonium, and dimethyldiallylammonium salts.

Commercial products corresponding to these polymers include, for example, the products sold under the name "Celquat® L 200" and "Celquat® H 100" by the company National Starch.

(4) Non-cellulose-based cationic polysaccharides described in U.S. Pat. Nos. 3,589,578 and 4,031,307, such as guar gums comprising cationic trialkylammonium groups, cationic hyaluronic acid, and dextran hydroxypropyl trimonium chloride. Guar gums modified with a salt, for example, the chloride, of 2,3-epoxypropyltrimethylammonium (guar hydroxypropyltrimonium chloride) may also be used.

Such products are sold, for instance, under the trade names JAGUAR® C13 S, JAGUAR® C15, JAGUAR® C17, and JAGUAR® C162 by the company MEYHALL.

- 40 (5) Polymers comprising piperazinyl units and divalent alkylene or hydroxyalkylene groups comprising straight or branched chains, optionally interrupted with at least one entity chosen from oxygen, sulphur, nitrogen, aromatic rings, and heterocyclic rings, and also the oxidation and/or quaternization products of these polymers. Such polymers are described, for example, in French Patent Nos. 2 162 025 and 2 280 361.
 - (6) Water-soluble polyamino amides prepared, for example, by polycondensation of an acidic compound with a polyamine; these polyamino amides possibly being crosslinked with an entity chosen from epihalohydrins; diepoxides; dianhydrides; unsaturated dianhydrides; bisunsaturated derivatives; bishalohydrins; bisazetidiniums; bishaloacyidiamines; bisalkyl halides; oligomers resulting from the reaction of a difunctional compound which is reactive with an entity chosen

from bishalohydrins, bisazetidiniums, bishaloacyldiamines, bisalkyl halides, epihalohydrins, diepoxides, and bisunsaturated derivatives; the crosslinking agent being used in an amount ranging from 0.025 to 0.35 mol per amine group of the polyamino amide; these polyamino amides optionally being alkylated or, if they comprise at least one tertiary amine function, they may be quaternized. Such polymers are described, for example, in French Patent Nos. 2 252 840 and 2 368 508.

- (7) Polyamino amide derivatives resulting from the condensation of polyalkylene polyamines with polycarboxylic acids, followed by alkylation with difunctional agents, for example, adipic acid/dialkylaminohydroxyalkyldialkylenetriamine polymers in which the alkyl group comprises from 1 to 4 carbon atoms, such as methyl, ethyl, and propyl groups, and the alkylene group comprises from 1 to 4 carbon atoms, such as an ethylene group. Such polymers are described, for instance, in French Patent No. 1 583 363. In at least one embodiment, these derivatives may be chosen from adipic acid/dimethylaminohydroxypropyldiethylenetriamine polymers.
- (8) Polymers obtained by reaction of a polyalkylene polyamine comprising two primary amine groups and at least one secondary amine group, with a dicarboxylic acid chosen from diglycolic acid and saturated aliphatic dicarboxylic acids comprising from 3 to 8 carbon atoms. The molar ratio of the polyalkylene polyamine to the dicarboxylic acid may range from 0.8:1 to 1.4:1; the polyamino amide resulting therefrom being reacted with epichlorohydrin in a molar ratio of epichlorohydrin relative to the secondary amine group of the polyamino amide ranging from 0.5:1 to 1.8:1. Such polymers are described, for example, in U.S. Pat. Nos. 3,227,615 and 2,961,347.
- (9) Cyclopolymers of alkyldiallylamine and cyclopolymers of dialkyldiallyl-ammonium, such as homopolymers and copolymers comprising, as the main constituent of the chain, at least one unit chosen from units of formulas (Ia) and (Ib):

$$-(CH_{2})t-CR_{12} C(R_{12})k$$

$$C(R_{12})-CH_{2}$$

$$R_{10} R_{11} CH_{2}$$
(Ia)

$$\begin{array}{c|c} -(CH_2)\iota - CR_{12} & C(R_{12}) - CH_2 - \\ & \downarrow & \downarrow \\ & \downarrow & CH_2 \\ & \downarrow & CH_2 \end{array}$$
(Ib)

30 wherein:

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k and t, which may be identical or different, are equal to 0 or 1, the sum k+t being equal to 1; R_{12} is chosen from hydrogen and methyl groups;

 R_{10} and R_{11} , which may be identical or different, are chosen from alkyl groups comprising from 1 to 6 carbon atoms, hydroxyalkyl groups in which the alkyl group comprises, for example, from 1 to 5 carbon atoms, and lower (C_1 - C_4)amidoalkyl groups, or R_{10} and R_{11} may form, together with the nitrogen atom to which they are attached, heterocyclic groups such as piperidinyl and morpholinyl; and

Y' is an anion such as bromide, chloride, acetate, borate, citrate, tartrate, bisulphate, bisulphite,

sulphate, and phosphate. These polymers are described, for example, in French Patent No. 2 080 759 and in its Certificate of Addition 2 190 406.

In one embodiment, R_{10} and R_{11} , which may be identical or different, are chosen from alkyl groups comprising from 1 to 4 carbon atoms.

Examples of such polymers include, but are not limited to, (co)polydiallyldialkyl ammonium chloride such as the dimethyldiallylammonium chloride homopolymer sold under the name "MERQUAT® 100" by the company CALGON (and its homologues of low weight-average molecular mass) and the copolymers of diallyldimethylammonium chloride and of acrylamide sold under the name "MERQUAT® 550".

Quaternary diammonium polymers comprising at least one repeating unit of formula (II):

$$\begin{array}{c|cccc}
R_{13} & R_{15} \\
 & & \\
N_{1} - A_{1} - N_{1} - B_{1} - \\
 & & \\
X_{1} - & & \\
R_{14} & R_{16}
\end{array}$$
(II)

wherein:

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 R_{13} , R_{14} , R_{15} , and R_{16} , which may be identical or different, are chosen from aliphatic, alicyclic, and arylaliphatic groups comprising from 1 to 20 carbon atoms and lower hydroxyalkyl aliphatic groups, or alternatively R_{13} , R_{14} , R_{15} , and R_{16} may form, together or separately, with the nitrogen atoms to which they are attached, heterocycles optionally comprising a second heteroatom other than nitrogen, or alternatively R_{13} , R_{14} , R_{15} , and R_{16} , which may be identical or different, are chosen from linear or branched C_1 - C_6 alkyl groups substituted with at least one group chosen from nitrile groups, ester groups, acyl groups, amide groups, -CO-O- R_{17} -E groups, and -CO-NH- R_{17} -E groups, wherein R_{17} is an alkylene group and E is a quaternary ammonium group;

A₁ and B₁, which may be identical or different, are chosen from polymethylene groups comprising from 2 to 20 carbon atoms, which may be linear or branched, saturated or unsaturated, and which may comprise, linked or intercalated in the main chain, at least one entity chosen from aromatic rings, oxygen, sulphur, sulphoxide groups, sulphone groups, disulphide groups, amino groups, alkylamino groups, hydroxyl groups, quaternary ammonium groups, ureido groups, amide groups, and ester groups, and

X is an anion derived from an inorganic or organic acid;

A₁, R₁₃, and R₁₅ may form, together with the two nitrogen atoms to which they are attached, a piperazine ring;

if A_1 is chosen from linear or branched, saturated or unsaturated alkylene or hydroxyalkylene groups, B_1 may be chosen from:

$$-(CH_2)_n$$
-- CO - E' - OC - $(CH_2)_n$ -

wherein E' is chosen from:

a) glycol residues of formula -O-Z-O-, wherein Z is chosen from linear or branched hydrocarbon-based groups and groups of the following formulas:

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wherein x and y, which may be identical or different, are chosen from integers ranging from 1 to 4, which represent a defined and unique degree of polymerization, and numbers ranging from 1 to 4, which represent an average degree of polymerization;

- b) bis-secondary diamine residue such as piperazine derivatives;
- c) bis-primary diamine residues of formula -NH-Y-NH-, wherein Y is chosen from linear or branched hydrocarbon-based groups and the divalent group -CH₂-CH₂-S-S-CH₂-CH₂-; and
- d) ureylene groups of formula -NH-CO-NH-.

In at least one embodiment, X is an anion such as chloride or bromide.

Polymers of this type are described, for example, in French Patent Nos. 2 320 330; 2 270 846; 2 316 271; 2 336 434; and 2 413 907 and U.S. Pat. Nos. 2,273,780; 2,375,853; 2,388,614; 2,454,547; 3,206,462; 2,261,002; 2,271,378; 3,874,870; 4,001,432; 3,929,990; 3,966,904; 4,005,193; 4,025,617; 4,025,627; 4,025,653; 4,026,945; and 4,027,020.

Non-limiting examples of such polymers include those comprising at least one repeating unit of formula (III):

$$\begin{array}{c|c}
R_{13} & R_{15} \\
\hline
 & & \\
N^{+} & (CH_{2})_{n} - N^{+} - (CH_{2})_{p} - \\
\downarrow & X^{-} & X^{-} \\
R_{16} & (III)
\end{array}$$

wherein R₁₃, R₁₄, R₁₅, and R₁₆, which may be identical or different, are chosen from alkyl and hydroxyalkyl groups comprising from 1 to 4 carbon atoms, n and p, which may be identical or different, are integers ranging from 2 to 20, and X⁻ is an anion derived from an inorganic or organic acid.

(11) Polyquaternary ammonium polymers comprising units of formula (IV):

$$\begin{array}{c|c} R_{18} & R_{20} \\ \hline -N+-(CH_2)_r-NH-CO-(CH_2)_q-CO-NH-(CH_2)_s-N+-A- \\ X- & X-\\ R_{19} & X-R_{21} \end{array} \qquad (IV)$$

wherein:

 R_{18} , R_{19} , R_{20} , and R_{21} , which may be identical or different, are chosen from hydrogen, methyl groups, ethyl groups, propyl groups, β -hydroxyethyl groups, β -hydroxypropyl groups, -

CH₂CH₂(OCH₂CH₂)_pOH groups, wherein p is chosen from integers ranging from 0 to 6, with the proviso that R₁₈, R₁₉, R₂₀, and R₂₁ are not simultaneously hydrogen, r and s, which may be identical or different, are chosen from integers ranging from 1 to 6,

r and s, which may be identical or different, are chosen from integers ranging from 1 to 6, q is chosen from integers ranging from 0 to 34,

X is an anion such as a halide, and

40 A is chosen from radicals of dihalides and -CH₂-CH₂-O-CH₂-CH₂-.

Such compounds are described, for instance, in European Patent Application No. 0 122 324.

(12) Quaternary polymers of vinylpyrrolidone and of vinylimidazole.

Other examples of suitable cationic polymers include, but are not limited to, cationic proteins and cationic protein hydrolysates, polyalkyleneimines, such as polyethyleneimines, polymers comprising units chosen from vinylpyridine and vinylpyridinium units, condensates of polyamines and of epichlorohydrin, quaternary polyureylenes, and chitin derivatives.

According to one embodiment of the present invention, the at least one cationic polymer is chosen from cellulose ether derivatives comprising quaternary ammonium groups, such as the products sold under the name "JR 400" by the company UNION CARBIDE CORPORATION, cationic cyclopolymers, for instance, the homo-polymers and copolymers of dimethyldiallylammonium chloride sold under the names MERQUAT® 100, MERQUAT® 550, and MERQUAT® S by the company CALGON, guar gums modified with a 2,3-epoxypropyltrimethylammonium salt, and quaternary polymers of vinylpyrrolidone and of vinylimidazole.

(13) Polyamines

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As the cationic polymer, it is also possible to use (co)polyamines, which may be homopolymers or copolymers, with a plurality of amino groups. The amino group may be a primary, secondary, tertiary or quaternary amino group. The amino group may be present in a polymer backbone or a pendent group, if present, of the (co)polyamines.

As examples of the (co)polyamines, mention may be made of chitosan, (co)polyallylamines, (co)polyvinylamines, (co)polyvinylimidazoles, (co)polydimethylaminoethylenemethacrylates, (co)polyvinylpyridines such as (co)poly-1-methyl-2-vinylpyridines, (co)polyimines such as (co)polyethyleneimines, (co)polypyridines such as (co)poly(quaternary pyridines), (co)polybiguanides such as (co)polyaminopropyl biguanides, (co)polylysines, (co)polyornithines, (co)polyarginines, (co)polyhistidines, aminodextrans, aminocelluloses, amino(co)polyvinylacetals, and salts thereof.

As the (co)polyamines, it is preferable to use (co)polylysines. Polylysine is well known. Polylysine can be a natural homopolymer of L-lysine that can be produced by bacterial fermentation. For example, polylysine can be ε-Poly-L-lysine, typically used as a natural preservative in food products. Polylysine is a polyelectrolyte which is soluble in polar solvents such as water. Polylysine is commercially available in various forms, such as poly D-lysine and poly L-lysine. Polylysine can be in salt and/or solution form.

(14) Cationic Polyaminoacids

As the cationic polymer, it may be possible use cationic polyaminoacids, which may be cationic homopolymers or copolymers, with a plurality of amino groups and carboxyl groups. The amino group may be a primary, secondary, tertiary or quaternary amino group. The amino group may be present in a polymer backbone or a pendent group, if present, of the cationic polyaminoacids. The carboxyl group may be present in a pendent group, if present, of the cationic polyaminoacids.

As examples of the cationic polyaminoacids, mention may be made of cationized collagen, cationized gelatin, steardimonium hydroxypropyl hydrolyzed wheat protein, cocodimonium

hydroxypropyl hydrolyzed wheat protein, hydroxypropyltrimonium hydrolyzed conchiolin protein, steardimonium hydroxypropyl hydrolyzed soy protein, hydroxypropyltrimonium hydrolyzed soy protein, cocodimonium hydroxypropyl hydrolyzed soy protein, and the like.

- It may be preferable that the cationic polymer be selected from the group consisting of cyclopolymers of alkyldiallylamine and cyclopolymers of dialkyldiallylammonium such as (co)polydiallyldialkyl ammonium chloride, (co)polyamines such as (co)polylysines, cationic (co)polyaminoacids such as cationized collagen, and salts thereof.
- It is preferable that the cationic polymer be a polyquaternium polymer or a polymeric quaternary ammonium salt.

Polymeric quaternary ammonium salts are cationic polymers comprising at least one quaternized nitrogen atom. Mention may in particular be made, as polymeric quaternary ammonium salts, of

- the Polyquaternium products (CTFA name), which contribute mainly to the quality of the foam and the feeling of the skin after use, in particular the feeling of the skin after use. These polymers can preferably be chosen from the following polymers:
 - Polyquaternium-5, such as the product Merquat 5 sold by Nalco;

Polyquaternium-6, such as the product Salcare SC 30 sold by BASF and the product Merquat 100 sold by Nalco;

Polyquaternium-7, such as the products Merquat S, Merquat 2200, Merquat 7SPR, and Merquat 550 sold by Nalco and the product Salcare SC 10 sold by BASF;

Polyquaternium-10, such as the product Polymer JR400 sold by Amerchol;

Polyquaternium-11, such as the products Gafquat 755, Gafquat 755N and Gafquat 734 sold by ISP:

Polyquaternium-15, such as the product Rohagit KF 720 F sold by Röhm;

Polyquaternium-16, such as the products Luviquat FC905, Luviquat FC370, Luviquat HM552 and Luviquat FC550 sold by BASF;

Polyquaternium-28, such as the product Styleze CC10 sold by ISP;

- Polyquaternium-44, such as the product Luviquat Care sold by BASF; Polyquaternium-46, such as the product Luviquat Hold sold by BASF; Polyquaternium-47, such as the product Merquat 2001 sold by Nalco; and Polyquaternium-67, such as the product Softcat sold by Amerchol.
- 35 The amount of the cationic polymer(s) in the composition according to the present invention may be 0.001% by weight or more, preferably 0.01% by weight or more, and more preferably 0.05% by weight or more, and may be 5% by weight or less, preferably 3% by weight or less, more preferably 1% by weight or less, and even more preferably 0.5% by weight or less, relative to the total weight of the composition.

(Oil)

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The composition according to the present invention comprises (d) at least one oil. Two or more oils may be used in combination. Thus, a single type of oil or a combination of different types of oils may be used.

Here, "oil" means a fatty compound or substance which is in the form of a liquid or a paste (non-solid) at room temperature (25°C) under atmospheric pressure (760 mmHg). As the oils, those generally used in cosmetics can be used alone or in combination thereof. These oils may be volatile or non-volatile.

The oil forms an oil phase of the W/O emulsion composition according to the present invention.

The oil may be a non-polar oil such as a hydrocarbon oil, a silicone oil, or the like; a polar oil such as a plant or animal oil and an ester oil or an ether oil; or a mixture thereof.

The oil may be selected from the group consisting of oils of plant or animal origin, synthetic oils, silicone oils, hydrocarbon oils, fatty alcohols and fatty acids.

As examples of plant oils, mention may be made of, for example, linseed oil, camellia oil, macadamia nut oil, corn oil, olive oil, avocado oil, sasanqua oil, castor oil, safflower oil, jojoba oil, sunflower oil, almond oil, rapeseed oil, sesame oil, soybean oil, peanut oil, and mixtures thereof. As examples of animal oils, mention may be made of, for example, squalene and squalane. As examples of synthetic oils, mention may be made of alkane oils such as isododecane and isohexadecane, ester oils, ether oils, and artificial triglycerides.

The ester oils are preferably liquid esters of saturated or unsaturated, linear or branched C_1 - C_{26} aliphatic monoacids or polyacids and of saturated or unsaturated, linear or branched C_1 - C_{26} aliphatic monoalcohols or polyalcohols, the total number of carbon atoms of the esters being greater than or equal to 10.

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Preferably, for the esters of monoalcohols, at least one from among the alcohol and the acid from which the esters of the present invention are derived is branched. Among the monoesters of monoacids and of monoalcohols, mention may be made of ethyl palmitate, ethyl hexyl palmitate, isopropyl palmitate, dicaprylyl carbonate, alkyl myristates such as isopropyl myristate or ethyl myristate, isocetyl stearate, 2-ethylhexyl isononanoate, isononyl isononanoate, isodecyl neopentanoate, and isostearyl neopentanoate.

Mention may especially be made of: diethyl sebacate; isopropyl lauroyl sarcosinate; diisopropyl sebacate; bis(2-ethylhexyl) sebacate; diisopropyl adipate; di-n-propyl adipate; dioctyl adipate; bis(2-ethylhexyl) adipate; diisostearyl adipate; bis(2-ethylhexyl) maleate; triisopropyl citrate; triisocetyl citrate; triisostearyl citrate; glyceryl trilactate; glyceryl trioctanoate; trioctyldodecyl citrate; trioleyl citrate; neopentyl glycol diheptanoate; and diethylene glycol diisononanoate.

As examples of ether oils, mention may be made of, for example, ether oils with a short hydrocarbon chain or chains, such as dicaprylyl ether.

As examples of artificial triglycerides, mention may be made of, for example, capryl caprylyl glycerides, glyceryl trimyristate, glyceryl tripalmitate, glyceryl trilinolenate, glyceryl trilaurate, glyceryl tricaprate, glyceryl tricaprylate, glyceryl tri(caprate/caprylate), and glyceryl tri(caprate/caprylate/linolenate).

As examples of silicone oils, mention may be made of, for example, linear organopolysiloxanes such as dimethylpolysiloxane, methylphenylpolysiloxane, methylhydrogenpolysiloxane, and the like; cyclic organopolysiloxanes such as cyclohexasiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, and the like; and mixtures thereof. Preferably, the silicone oil is chosen from liquid polydialkylsiloxanes, especially liquid polydimethylsiloxanes (PDMS, dimethicone) and liquid polyorganosiloxanes comprising at least one aryl group. These silicone oils may also be organomodified. The organomodified silicones that can be used in accordance with the present invention are silicone oils as defined above and

comprise in their structure one or more organofunctional groups attached via a hydrocarbon-based group.

Hydrocarbon oils may be chosen from:

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- linear or branched, optionally cyclic, C₆-C₁₆ lower alkanes. Examples that may be mentioned include hexane, undecane, dodecane, tridecane, and isoparaffins, for instance isohexadecane, isododecane, and isodecane;
- linear or branched hydrocarbons containing more than 16 carbon atoms, such as liquid paraffins, liquid petroleum jelly, polydecenes and hydrogenated polyisobutenes such as Parleam®, and squalene;
- mixtures of alkanes, for example, C9-12 Alkane, C10-13 Alkane, C13-14 Alkane, C13-15 Alkane, C14-17 Alkane, C14-19 Alkane, C15-19 Alkane, C15-23 Alkane, C18-21 Alkane, C8-9 Alkane/Cycloalkane, C9-10 Alkane/Cycloalkane, C9-11 Alkane/Cycloalkane, C9-16 Alkane/Cycloalkane, C10-12 Alkane/Cycloalkane, C11-14 Alkane/Cycloalkane, C11-15 Alkane/Cycloalkane, and C12-13 Alkane/Cycloalkane.

The term "fatty" in the fatty alcohol means the inclusion of a relatively large number of carbon atoms. Thus, alcohols which have 4 or more, preferably 6 or more, and more preferably 12 or more carbon atoms are encompassed within the scope of fatty alcohols. The fatty alcohol may be saturated or unsaturated. The fatty alcohol may be linear or branched.

The fatty alcohol may have the structure R-OH wherein R is chosen from saturated and unsaturated, linear and branched radicals containing from 4 to 40 carbon atoms, preferably from 6 to 30 carbon atoms, and more preferably from 12 to 20 carbon atoms. In at least one embodiment, R may be chosen from C₁₂-C₂₀ alkyl and C₁₂-C₂₀ alkenyl groups. R may or may not be substituted with at least one hydroxyl group. As examples of the fatty alcohol, mention may be made of lauryl alcohol, cetyl alcohol, stearyl alcohol, isostearyl alcohol, behenyl alcohol, undecylenyl alcohol, myristyl alcohol, octyldodecanol, hexyldecanol, oleyl alcohol, linoleyl alcohol, palmitoleyl alcohol, arachidonyl alcohol, erucyl alcohol, and mixtures thereof. It is preferable that the fatty alcohol be a saturated fatty alcohol. Thus, the fatty alcohol may be selected from straight or branched, saturated or unsaturated C₆-C₃₀ alcohols, preferably straight or branched, saturated C₆-C₃₀ alcohols, and more preferably straight or branched, saturated C₁₂-C₂₀ alcohols. As examples of saturated fatty alcohols, mention may be made of lauryl alcohol, cetyl alcohol, stearyl alcohol, isostearyl alcohol, behenyl alcohol, undecylenyl alcohol, myristyl alcohol, octyldodecanol, hexyldecanol, and In one embodiment, cetyl alcohol, stearyl alcohol, octyldodecanol, mixtures thereof. hexyldecanol, or a mixture thereof (e.g., cetearyl alcohol) as well as behenyl alcohol, can be used as a saturated fatty alcohol.

The fatty acids that may be used in the composition of the present disclosure may be saturated or unsaturated and comprise from 6 to 30 carbon atoms such as from 9 to 30 carbon atoms. As non-limiting examples, they may be chosen from myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, linoleic acid, linolenic acid, and isostearic acid.

The amount of the oil(s) in the composition according to the present invention may be 3% by weight or more, preferably 5% by weight or more, more preferably 10% by weight or more, even more preferably 15% by weight or more, and in particular 20% by weight or more, and may be 50% by weight or less, preferably 40% by weight or less, more preferably 35% by weight or less, and even more preferably 30% by weight or less, relative to the total weight of the composition.

50 (Other ingredients)

• Cosmetically Acceptable Hydrophilic Organic Solvent

The composition according to the present invention may comprise at least one cosmetically acceptable hydrophilic organic solvent. The cosmetically acceptable hydrophilic organic solvent(s) may include, for example, substantially linear or branched lower mono-alcohols having from 1 to 8 carbon atoms, such as ethanol, propanol, butanol, isopropanol, and isobutanol; aromatic alcohols, such as benzyl alcohol and phenylethyl alcohol; polyols or polyol ethers, such as propylene glycol, dipropylene glycol, isoprene glycol, butylene glycol, pentylene glycol, glycerine, propanediol, sorbitol, ethylene glycol monomethyl, monoethyl and monobutyl ethers, propylene glycol ethers, such as propylene glycol monomethylether, diethylene glycol alkyl ethers, such as diethylene glycol monoethylether or monobutylether; polyethylene glycols, such as PEG-4, PEG-6, and PEG-8, and their derivatives, and a combination thereof.

The amount of the cosmetically acceptable hydrophilic organic solvent(s) in the composition according to the present invention may range from 1 to 30% by weight, preferably from 2 to 25% by weight, and more preferably from 3 to 20% by weight, relative to the total weight of the composition.

20 • Surfactant

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The composition according to the present invention may comprise at least one surfactant chosen from amphoteric, anionic, cationic, or nonionic surfactants, used alone or as a mixture. Preferably, the composition comprises at least one nonionic surfactant.

Examples of nonionic surfactants usable in the compositions of the invention may include polyethoxylated fatty alcohols or polyglycerolated fatty alcohols, such as the adducts of ethylene oxide with lauryl alcohol, especially those containing from 9 to 50 oxyethylene units (Laureth-9 to Laureth-50 as the INCI names), in particular Laureth-9; esters of polyols and of a fatty acid possessing a saturated or unsaturated chain comprising, for example, from 8 to 24 carbon atoms, and their oxyalkylenated derivatives, that is to say comprising oxyethylene and/or oxypropylene units, such as esters of glycerol and of a C₈-C₂₄ fatty acid, and their oxyalkylenated derivatives, in particular polyoxyethylenated glyceryl stearate (mono-, di- and/or tristearate), for example PEG-20 glyceryl triisostearate; esters of sugar and of a C₈-C₂₄ fatty acid and their oxyalkylenated derivatives, such as polyethoxylated sorbitol esters of C₈-C₂₄ fatty acids, in particular Polysorbate 80, such as the product marketed under the name "TWEEN 80" by Croda; ethers of a sugar and of C₈-C₂₄ fatty alcohols, such as caprylyl/capryl glucoside; polyoxyethylene alkyl ethers; polyoxyethylene oxypropylene alkyl ethers; fatty acid alkanol amides; alkyl amine oxides; alkyl polyglycosides and silicone surfactants, such as polydimethylsiloxane containing oxyethylene groups and/or oxypropylene groups, for example, PEG-10 dimethicone, bis-PEG/PPG-14/14 dimethicone, bis-PEG/PPG-20/20 dimethicone, and PEG/PPG-20/6 dimethicone, and alkyl dimethicone copolyols, notably those having an alkyl radical with 10 to 22 carbon atoms and having 2 to 50 oxyethylene groups and 2 to 50 oxypropylene groups, such as cetyl dimethicone copolyol (INCI name: Cetyl PEG/PPG-10/1 Dimethicone), and lauryl dimethicone copolyol (INCI name: Lauryl PEG/PPG-18/18 Methicone); and polyglyceryl fatty acid ester such as polyglyceryl-4 caprate, polyglyceryl-6 dicaprate, polyglyceryl-6 dicaprate, polyglyceryl-6 dioleate, polyglyceryl-6 caprylate, polyglyceryl-2 oleate, and polyglyceryl-6 polyricinoleate; and mixtures thereof.

In addition, mention can be made of alkylpolyglycosides as nonionic surfactants, represented by the following general formula (1):

$R-O-(G)_{x}(1)$

in which R represents a branched and/or unsaturated alkyl radical comprising from 14 to 24 carbon atoms, G represents a reduced sugar comprising 5 or 6 carbon atoms and x denotes a value ranging from 1 to 10 and preferably from 1 to 4, and G in particular denotes glucose, fructose or galactose. Mention may be made, as alkyl polyglycosides of this type, of alkyl polyglucosides (G = glucose in 5 the formula (I)) and in particular the compounds of formula (I) in which R more particularly represents an oleyl radical (unsaturated C₁₈ radical) or isostearyl (saturated C₁₈ radical). G denotes glucose and x is a value ranging from 1 to 2, in particular isostearyl glucoside, oleyl glucoside and This alkyl polyglucoside can be used as a mixture with a coemulsifier, more 10 especially with a fatty alcohol and in particular a fatty alcohol having the same fatty chain as that of the alkyl polyglucoside, that is to say comprising from 14 to 24 carbon atoms and having a branched and/or unsaturated chain, for example isostearyl alcohol when the alkyl polyglucoside is isostearyl glucoside and oleyl alcohol when the alkyl polyglucoside is oleyl glucoside. Use may be made, for example, of the mixture of isostearyl glucoside and isostearyl alcohol, sold under the name Montanov WO 18 by Seppic, and also the mixture of octyldodecanol and octyldodecyl xyloside 15 sold under the name Fludanov 20X by Seppic.

The amount of the surfactant(s) in the composition may be from 0.1 to 15% by weight, preferably from 0.5 to 10% by weight, and more preferably from 1 to 5% by weight, relative to the total weight of the composition.

• Thickener

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The composition according to the present invention may comprise at least one thickener. Two or more thickeners can be combined. The thickener may be hydrophilic or lipophilic, and preferably lipophilic.

The lipophilic thickener may be in the form of polymer or particles.

The lipophilic polymer thickener may be chosen from carboxyvinyl polymers such as the Carbopol products (carbomers) and the Pemulen products (acrylate/C10-C30-alkyl acrylate copolymer) or polymers having the INCI name "Poly C10-30 Alkyl Acrylate", such as the Intelimer® products from Air Products, such as the product Intelimer® IPA 13-1, which is a polystearyl acrylate, or the product 30 Intelimer® IPA 13-6 which is a behenyl polymer.

The lipophilic thickener according to the present invention may be chosen from:

- organomodified clays, which are clays treated with compounds chosen especially from quaternary amines and tertiary amines. Organomodified clays that may be mentioned include organomodified bentonites, such as the product sold under the name Bentone 34 by the company Rheox, and organomodified hectorites such as the products sold under the names Bentone 27 and Bentone 38 by the company Rheox. Mention may be made especially of modified clays such as modified magnesium silicate (Bentone gel[®] VS38 from Rheox), modified hectorites such as hectorite modified with a C10 to C22 fatty acid ammonium chloride, for instance hectorite modified with distearyldimethylammonium chloride (disteardimonium hectorite) such as the product sold under the name Bentone 38 VCG by the company Elementis or the product sold under the name Bentone Gel[®] V5 5V by the company Elementis, or the product sold under the name Bentone gel[®] ISD V by the company Elementis;

- and mixtures thereof.

The amount of the thickener(s) in the composition may be from 0.1 to 10% by weight, preferably from 0.2 to 5% by weight, and more preferably from 0.3 to 3% by weight, relative to the total weight of the composition.

• Inorganic UV filter

The composition according to the present invention may comprise at least one inorganic UV filter. Two or more inorganic UV filters can be combined.

The inorganic UV filter used for the present invention may be active in the UV-A and/or UV-B region. The inorganic UV filter may be hydrophilic and/or lipophilic. The inorganic UV filter is preferably insoluble in solvents such as water and ethanol, commonly used in cosmetics.

The inorganic UV filter used for the present invention is different from the (b) powder of the present invention.

It is preferable that the inorganic UV filter be in the form of a fine particle such that the mean (primary) particle diameter thereof ranges from 1 nm to 150 nm, preferably 5 nm to 100 nm, and more preferably 10 nm to 50 nm. The mean (primary) particle size or mean (primary) particle diameter here is an arithmetic mean diameter.

The inorganic UV filter can be selected from the group consisting of metal oxides which may or may not be coated, and mixtures thereof.

Preferably, the inorganic UV filters may be selected from pigments (mean size of the primary particles: generally from 5 nm to 50 nm, preferably from 10 nm to 50 nm) formed of metal oxides, such as, for example, pigments formed of titanium oxide (amorphous or crystalline in the rutile and/or anatase form), iron oxide, zinc oxide, zirconium oxide or cerium oxide, which are all UV photoprotective agents that are well known per se. Preferably, the inorganic UV filters may be selected from titanium oxide, zinc oxide, and more preferably titanium oxide.

The inorganic UV filter may or may not be coated. The inorganic UV filter may have at least one coating. The coating may comprise at least one compound selected from the group consisting of alumina, silica, aluminum hydroxide, silicones, silanes, fatty acids or salts thereof (such as sodium, potassium, zinc, iron, or aluminum salts), fatty alcohols, lecithin, amino acids, polysaccharides, proteins, alkanolamines, waxes such as beeswax, (meth)acrylic polymers, organic UV filters, and (per)fluoro compounds.

In a known manner, the silicones in the coating(s) may be organosilicon polymers or oligomers comprising a linear or cyclic and branched or cross-linked structure, of variable molecular weight, obtained by polymerization and/or polycondensation of suitable functional silanes and essentially composed of repeated main units in which the silicon atoms are connected to one another via oxygen atoms (siloxane bond), optionally substituted hydrocarbon radicals being connected directly to said silicon atoms via a carbon atom.

The silicones used for the coating(s) can preferably be selected from the group consisting of alkylsilanes, polydialkylsiloxanes, and polyalkylhydrosiloxanes. More preferably still, the silicones are selected from the group consisting of octyltrimethylsilanes, polydimethylsiloxanes, and polymethylhydrosiloxanes.

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Of course, the inorganic UV filters made of metal oxides may, before their treatment with silicones, have been treated with other surfacing agents, in particular, with cerium oxide, alumina, silica, aluminum compounds, silicon compounds, or their mixtures.

The amount of the inorganic UV filter(s) in the composition may be from 0.5% by weight or more, preferably 1% by weight or more, and more preferably 1.5% by weight or more, and 15% by weight or less, preferably 10% by weight or less, more preferably 7% by weight or less, and even more preferably 5% weight or less, relative to the total weight of the composition.

10 • Water

The composition according to the present invention can comprise water.

The amount of water in the composition may be from 2% by weight or more, preferably 5% by weight or more, more preferably 10% by weight or more, and even more preferably 15% by weight or more, and 60% by weight or less, preferably 50% by weight or less, more preferably 40% by weight or less, and even more preferably 30% by weight or less, relative to the total weight of the composition.

20 • Adjuvants

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The compositions according to the present invention may also contain various adjuvants conventionally used in compositions for sun care products, which may be selected from a physiologically acceptable medium, anionic, non-ionic, amphoteric or zwitterionic polymers or mixtures thereof, antioxidants, neutralizing agents, alkaline agents, such as sodium hydroxide, sequestering agents, such as trisodium ethylenediamine disuccinate, disodium EDTA, and phytin acid, buffers, such as tromethamine, fragrances, emollients, dispersing agents, dyes and/or pigments, film-forming agents and/or thickeners, ceramides, preservatives, such as phenoxy ethanol and caprylyl glycol, co-preservatives and opacifying agents.

The adjuvants may be present in the composition of the present invention in an amount preferably ranging from 0.01% to 30% by weight, more preferably from 0.1% to 20% by weight, and even more preferably from 0.5% to 10% by weight, relative to the total weight of the composition.

- 35 The composition according to the present invention comprises microplastic filler in an amount of 5% by weight or less, preferably 3% by weight or less, more preferably 1% by weight or less, even more preferably 0.05% by weight or less, and in particular 0.01% by weight, relative to the total weight of the composition.
- 40 Most preferably, the composition according to the present invention is free of microplastic filler.

The composition according to the present invention may be intended for use as a cosmetic topical composition. Thus, the composition according to the present invention may be intended for application onto a keratinous substance. Keratinous substance here means a material containing keratin as a main constituent element, and examples thereof include the skin, scalp, nails, lips, hair, and the like. In particular, the composition according to the present invention may be a skin sun care cosmetic composition for protecting skin from UV rays.

The viscosity of the composition according to the present invention is not particularly limited. Preferably, the viscosity of the composition according to the present invention ranges from 1 to

1,000,000 mm²/s, more preferably from 2 mm²/s to 500,000 mm²/s, and even more preferably from 5 mm²/s to 100,000 mm²/s at 25°C. The viscosity of the composition according to the present invention can be measured using a Poiseuille rheometer, at a temperature of 25°C, according to standard ASTM-D445-97.

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The composition according to the present invention can be prepared by mixing ingredients (a) to (d), as essential ingredients, as well as optional ingredient(s), as explained above.

[Cosmetic Process]

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The present invention also relates to: a cosmetic process for a keratin substrate, such as skin, comprising applying to the keratin substrate the composition according to the present invention.

The composition according to the present invention may preferably be used as a cosmetic composition. The cosmetic composition may be a sun care composition for protecting keratinous substances, such as skin, from UV rays.

The cosmetic process here means a non-therapeutic cosmetic method for caring for and/or making up the surface of a keratin substrate such as skin.

Therefore, the present invention relates to a cosmetic process for protecting keratinous substances from UV radiation, comprising, at least one step of applying the composition according to the present invention to the keratinous substance, such as skin.

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EXAMPLES

The present invention will be described in more detail by way of examples which however should not be construed as limiting the scope of the present invention.

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[Compositions]

Each of the W/O emulsion compositions according to Examples 1 and 2 (Ex. 1 and Ex. 2) and Comparative Examples 1 to 8 (Comp. Ex. 1 to Comp. Ex. 8) was prepared by mixing the ingredients listed in the following Tables 1 and 2. Specifically, the W/O emulsion compositions were prepared by first mixing the ingredients of the "oil phase" and the ingredients of the "water phase", then adding "powder" ingredients and ethanol to the mixture, and then mixing it until it became homogenous. The numerical values in parentheses in the powder ingredients indicate average particle size of the powder ingredients. Titanium dioxide and zinc oxide in the oil phase were used as inorganic UV filters. The numerical values for the amounts of the ingredients are all based on "% by weight" as active raw materials.

[Evaluation]

45 (Water Resistance)

The following evaluations were conducted in order to determine the water resistant property of each of the compositions.

50 - Change in Skin Color

After applying 1g of each of the compositions on the back side of the hand, the composition was dried for 1 to 2 minutes. Subsequently, after putting the hand into a beaker containing 2L of tap water for 1 minute, a change in skin color was observed with the naked eye. The change in skin color was evaluated for each composition under the following criteria.

- 1: No skin color change was observed.
- 2: Slight skin color change was observed.
- 3: Moderate skin color change was observed.
- 10 4: Skin color change was clearly observed.
 - Water Clearness

After applying 1 g of each of the compositions on the back side of the hand, the composition was dried for 1 to 2 minutes. Subsequently, after putting the hand into a beaker containing 2L of tap water for 1 minute, a change in the surface of the water was observed with the naked eye. The change in skin color was evaluated for each composition under the following criteria.

- 1: No change in the water surface was observed.
- 2: Slight change in the water surface was observed.
- 3: Moderate change in the water surface was observed.
- 4: Change in the water surface was clearly observed.

(Fresh Sensation)

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30 mg of each of the compositions was applied on and around a 30 mm \times 30 mm area of a panel member's forearm (n=5) with the fingers. The fresh sensation was evaluated for each composition under the following criteria.

- 30 1: Watery fresh
 - 4: Greasy

(Stability)

- The obtained emulsion compositions in a 100 mL were kept at 25°C for 24 hours after they were manufactured. The appearance of each sample was then observed with the naked eye. The stability property was evaluated for each composition under the following criteria.
 - 1: No phase separation was observed
- 40 3: Slight phase separation was observed
 - 4: Phase separation was clearly observed.

The results are shown in Table 3 below.

Table 1

		Table I		r	,	
Phase	Ingredients	Ex.1	Ex.2	Comp.	Comp.	Comp.
		2.0.2		Ex.1	Ex.2	Ex.3
	Bis-ethylhexyloxyphenol Methoxyphenyl Triazine	2	3	3	3	3
	Diethylamino Hydroxybenzóyl Hexyl Benzoate	4	4	4	4	4
	Drometrizole Trisiloxane	0.5	0.5	0.5	0.5	0.5
	Ethylhexyl Triazone	1.5	3.5	3.5	3.5	3.5
	Homosalate	7	7	7	7	7
	Ethylhexyl Salicylate	3	3.5	3.5	3.5	3.5
	Poly C10-30 Alkyl Acrylate	0.2	0.2	0.2	0.2	0.2
	Caprylyl Glycol	0.5	0.5	0.5	0.5	0.5
Oil Phase	Diisopropyl Sebacate	5	5	5	5	5
	C15-19 Alkane	2.78	-	-	-	-
	Isostearic Acid	1	1	1	1	1
	PEG-10 Dimethicone	0.5	0.5	0.5	0.5	0.5
	Cetyl PEG/PPG-10/1 Dimethicone	1	1	1	1	1
	Polyglyceryl-6 Polyricinoleate	1	1	1	1	1
	Titanium Dioxide (15 nm)	4	2	2	2	2
	Disteardimonium Hectorite	0.3	0.4	0.4	0.4	0.4
•	Dimethicone	QS 100	QS 100	QS 100	QS 100	QS 100
	Isododecane	11	5	5	5	5
	Water	20	20	20	20	20
	Propylene Glycol	3	3	3	3	3
	Pentylene Glycol	3	3	3	3	3
	Polyquaternium-67	0.085	0.085	0.085	-	-
Water Phase	Acrylates/C10-30 Alkyl Acrylate Crosspolymer	-	_	-	-	0.085
	Phytic Acid	0.035	0.035	0.035	-	0.035
	Sodium Hydroxide	-	0.002	0.002	0.002	0.002
	Trisodium Ethylenediamine Disuccinate	0.1	0.1	0.1	0.1	0.1
Powder	Cellulose (10 µm)	6.1	6.6	_	6.6	6.6
	Silica (4 µm)	5.9	5.9	-	5.9	5.9
	Mica (8 µm)	2.5	-	-	-	-
	Vinyl Dimethicone/Methicone Silsesquioxane Crosspolymer	-	-	6.6	-	-
	Nyrone-12	-	-	5.9	-	-
•	Ethanol	8	8	8	8	8

Table 2

Phase	Ingredients	Comp.	Comp.	Comp.
111111111111111111111111111111111111111		Ex.4	Ex.5	Ex.6
	Ethylhexyl Methoxycinnamate	-	-	7.5
	Octocrylene	-	-	3.1
	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	3	3	0.7
	Diethylamino Hydroxybenzoyl Hexyl Benzoate	4	4	3
	Drometrizole Trisiloxane	0.5	0.5	-
	Ethylhexyl Triazone	3.5	3.5	-
	Homosalate	7	7	-
	Ethylhexyl Salicylate	3.5	3.5	-
	Dextrin Palmitate	-	-	0.3
	Poly C10-30 Alkyl Acrylate	0.2	0.2	0.2
Oil Phase	Caprylyl Glycol	0.5	0.5	-
On Flase	Isopropyl Myristate	-	-	4
	Diisopropyl Sebacate	5	5	-
	Isostearic Acid	1	1	-
	PEG-10 Dimethicone	0.5	0.5	-
	Cetyl PEG/PPG-10/1 Dimethicone	1	,1	1
	Polyglyceryl-6 Polyricinoleate	1	1	-
	Titanium Dioxide (15 nm)	2	2	1.5
	Zinc Oxide Powder (20 nm)	-	-	9
	Disteardimonium Hectorite	0.4	0.4	0.3
	Dimethicone	QS 100	QS 100	QS 100
	Isododecane	5	5	10
	Water	20	20	13
	Glycerin	-	-	2
	Propylene Glycol	3	3	-
	Pentylene Glycol	3	3	-
Water	Polyquaternium-67	0.085	0.085	-
Phase	Phytic Acid	0.035	0.035	-
	Disodium EDTA	•	-	0.05
	Sodium Hydroxide	0.002	0.002	-
	Trisodium Ethylenediamine Disuccinate	0.1	0.1	-
Powder	Cellulose (10 μm)	6.6	6.6	-
	Talc (5 µm)	-	-	1
	Silica (4 µm)	5.9	5.9	-
	Styrene/Acrylates Copolymer	_	-	1
	Methyl Methacrylate Crosspolymer	-	-	5
	Vinyl Dimethicone/Methicone Silsesquioxane	10		2
	Crosspolymer	10	-	4
	Nyrone-12	-	10	-
	Polymethylsilsesquioxane		-	1
	Ethanol	8	8	10

Table 3

Evaluation	Ex.1	Ex.2	Comp. Ex.1	Comp. Ex.2	Comp. Ex.3	Comp. Ex.4	Comp. Ex.5	Comp. Ex.6
Change in Skin Color	1	1	1	1	2	2	2	4
Water Resistance	1	1	2	2	3	3	3	4
Fresh Sensation	1	1	1	1	1	1	1 .	1
Stability	1	1	1	4	3	1	1	1

As can be seen from the evaluation results in Table 3, the W/O emulsion composition according to Examples 1 and 2, which include a combination of at least one lipophilic organic UV filter, at least one powder other than microplastic filler, and at least one cationic polymer exerted an improved water resistance property, fresh sensation on application, and a good stability.

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On the other hand, the composition according to Comparative Example 1, which does not include any powder other than microplastic filler but includes microplastic fillers, did not show a good water resistance property because of the inferior water clearness result. The composition according to Comparative Examples 2 and 3, which do not include any cationic polymer, did not show a good water resistance property and showed an inferior stability of W/O emulsion. The composition according to Comparative Examples 4 to 6, which include microplastic fillers in a large amount, showed a poor water resistant property because of the inferior water clearness result.

Therefore, it can be concluded that the W/O emulsion composition according to the present invention is very preferable as a sun care cosmetic composition.

CLAIMS

- 1. A W/O emulsion composition comprising:
 - (a) at least one lipophilic organic UV filter,
 - (b) at least one powder other than microplastic filler,
 - (c) at least one cationic polymer, and
 - (d) at least one oil,

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wherein the composition comprises microplastic filler in an amount of 5% by weight or less, preferably 3% by weight or less, and more preferably 1% by weight or less, or the composition is free of microplastic filler.

- The composition according to Claim 1 wherein the (b) powder is selected from talc, mica, silica, magnesium aluminum silicate, silica silicate, kaolin, bentone, calcium carbonate, magnesium hydrogen carbonate, hydroxyapatite, boron nitride, fluorphlogopite, sericite, calcinated talc, calcinated mica, calcinated sericite, synthetic mica, perlite, lauroyl lysine, metal soap, bismuth oxychloride, barium sulfate, magnesium carbonate, and natural polymer powders, such as polysaccharide powders, for example, starch, cellulose powder, and mixtures thereof.
- The composition according to Claim 1 or 2, wherein the average particle size of the (b) powder is 50 μ m or less, preferably 20 μ m or less, and more preferably 15 μ m or less, and is 0.2 μ m or more, preferably 0.5 μ m or more, and more preferably 1 μ m or more.
- 4. The composition according to any one of Claims 1 to 3, wherein the (c) cationic polymer is selected from quaternized hydroxyethyl celluloses modified with at least one quaternary ammonium group comprising at least one fatty chain.
 - 5. The composition according to any one of Claims 1 to 4, wherein the (c) cationic polymer is selected from quaternized alkylhydroxyethylcelluloses containing C₈-C₃₀ fatty chains.
- 6. The composition according to any one of Claims 1 to 5, which is free of microplastic filler.
- 7. The composition according to any one of Claims 1 to 6, wherein the (a) lipophilic organic UV filter comprises a combination of at least one lipophilic organic UV-A filter and at least one lipophilic organic UV-B filter.
- 8. The composition according to any one of Claims 1 to 7, wherein the amount of the (a) lipophilic organic UV filter(s) is 1% by weight or more, preferably 5% by weight or more, more preferably 10% by weight or more, and even more preferably 15% by weight or more, and is 50% by weight or less, preferably 40% by weight or less, more preferably 30% by weight or less, and even more preferably 25% by weight or less, relative to the total weight of the composition.
- The composition according to any one of Claims 1 to 8, wherein the amount of the (b) powder(s) is 1% by weight or more, preferably 3% by weight or more, more preferably 5% by weight or more, even more preferably 8% by weight or more, and in particular 10% by weight or more, and is 30% by weight or less, preferably 25% by weight or less, more preferably 20% by weight or less, even more preferably 18% by weight or less, and in particular 15% by weight or less, relative to the total weight of the composition.

10. The composition according to any one of Claims 1 to 9, wherein the amount of the (c) cationic polymer(s) is 0.001% by weight or more, preferably 0.01% by weight or more, and more preferably 0.05% by weight or more, and is 5% by weight or less, preferably 3% by weight or less, more preferably 1% by weight or less, and even more preferably 0.5% by weight or less, relative to the total weight of the composition.

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- The composition according to any one of Claims 1 to 10, wherein the amount of the (d) oil(s) is 3% by weight or more, preferably 5% by weight or more, more preferably 10% by weight or more, even more preferably 15% by weight or more, and in particular 20% by weight or more, and is 50% by weight or less, preferably 40% by weight or less, more preferably 35% by weight or less, and even more preferably 30% by weight or less, relative to the total weight of the composition.
- 15 12. The composition according to any one of Claims 1 to 11, further comprising at least one inorganic UV filter.
 - 13. The composition according to Claim 12, wherein the inorganic UV filter has an average particle size of less than 200 nm.
 - 14. The composition according to Claim 12 or 13, wherein the amount of the inorganic UV filter is 0.5% by weight or more, preferably 1% by weight or more, and more preferably 1.5% by weight or more, and is 15% by weight or less, preferably 10% by weight or less, more preferably 7% by weight or less, and even more preferably 5% weight or less, relative to the total weight of the composition.
 - 15. A cosmetic process for a keratin substrate, such as skin, comprising applying to the keratin substrate the composition according to any one of Claims 1 to 14.

INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2022/026534 A. CLASSIFICATION OF SUBJECT MATTER A61K8/19 A61K8/06 A61K8/25 A61K8/37 A61K8/49 INV. A61K8/58 A61K8/73 A61Q17/04 A61K8/31 A61K8/362 ADD. According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) A61K A610 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category* Citation of document, with indication, where appropriate, of the relevant passages Х DATABASE GNPD [Online] 1-15 MINTEL; 16 April 2018 (2018-04-16), anonymous: "Perfect UV Protector SPF 50+/PA++++", XP055908480, Database accession no. 5591817 the whole document 1-15 х DATABASE GNPD [Online] MINTEL; 17 October 2019 (2019-10-17), anonymous: "Advanced Anti-Aging Sunscreen SPF 50+ PA+++", XP055908722, Database accession no. 6956183 the whole document -/--See patent family annex. Further documents are listed in the continuation of Box C. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other step when the document is taken alone document of particular relevance;; the claimed invention cannot be special reason (as specified) considered to involve an inventive step when the document is combined with one or more other such documents, such combination "O" document referring to an oral disclosure, use, exhibition or other means being obvious to a person skilled in the art document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 18 October 2022 26/10/2022 Name and mailing address of the ISA/ Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2022/026534

		PCT/JP2022/026534		
C(Continua	tion). DOCUMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
x	DATABASE GNPD [Online]	1–15		
	MINTEL; 11 October 2011 (2011-10-11),			
	anonymous: "Sun Block Lotion SPF 40",			
	XP055908737,			
	Database accession no. 1647711			
	the whole document			
A	DATABASE WPI	1-10		
	Week 202005			
	Thomson Scientific, London, GB;			
	AN 2020-56559R XP002806132,			
	& JP 2020 097552 A (NIPPON MENARD KESHOHIN			
	KK) 25 June 2020 (2020-06-25)			
	abstract			

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2022/026534

itent document I in search report		Publication date	Patent family member(s)	Publication date
2020097552	A	25-06-2020	NONE	