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(54) **Title:** STABLE DISPERSION COMPOSITION COMPRISING RETINOID

(57) **Abstract:** The present invention relates to a dispersion composition comprising a continuous phase and a plurality of dispersed phases, comprising: (a) at least one retinoid; (b) at least one compound which is capable of providing a solution thereof with a transmittance of 10% or less, preferably 5% or less, and more preferably 2% or less, for light with a wavelength of from 290 to 420 nm, along a light path length of 10 mm, the concentration of the compound in the solution being 0.9% by weight relative to the total weight of the solution; (c) at least one hydrophilic antioxidant agent other than the ingredient (b); and (d) at least one cationic polymer.

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# DESCRIPTION

## TITLE OF INVENTION

# STABLE DISPERSION COMPOSITION COMPRISING RETINOID

## TECHNICAL FIELD

The present invention relates to a stable dispersion composition comprising at least one retinoid, preferably a stable cosmetic dispersion composition comprising the same.

## BACKGROUND ART

Retinoids have been known to be useful in the field of, for example, cosmetics because they can function as anti-aging active ingredients which may be used for wrinkle treatments and the like. However, they tend to be unstable under some conditions. For example, retinol is soluble in lipophilic solvents, but the solution of retinol may rapidly discolor (yellowing /browning) and the retinol therein may degrade over time.

To date, some prior documents disclose compositions comprising a retinoid. For example, WO 2021/123337 discloses a composition comprising at least retinol; di-t-butyl pentaerythrityl tetrahydroxycinnamate; and an ethylenediaminedisuccinic acid salt.

Also, WO 1996/018380 discloses a use of a) one or more compounds from the group of flavonoids or b) a combination of active substances containing one or more compounds selected from the group of flavonoids in combination with one or more compounds selected from the group of cinnamic acid derivatives, c) optionally with the additional use of one or more compounds from the group of imidazole derivatives and/or d) optionally with the additional use of one or more compounds from the group of antioxidants or metal chelators or comparable substances, for stabilizing sensitive, unstable cosmetic or dermatological active ingredients or constituents, where the sensitive, unstable cosmetic or dermatological active ingredients or ingredients may include Vitamins A, C or E or their derivatives.

Also, WO 1996/007396 discloses a skin care composition comprising an oil-in-water emulsion and a retinoid selected from the group consisting of Vitamin A alcohol, Vitamin A aldehyde, retinyl acetate, retinyl palmitate and mixtures thereof.

Compositions including retinoid(s) also have problems in stability such that they tend to become discolored and give off a bad smell, depending on conditions regarding light or temperature, and the retinoid(s) in the compositions degrade(s) over time under light exposure or at high temperature.

## DISCLOSURE OF INVENTION

An objective of the present invention is to provide a composition in the form of the stable dispersion including at least one retinoid wherein the retinoid is stable under light exposure and high temperature conditions.

The above objective of the present invention can be achieved by a dispersion composition comprising a continuous phase and a plurality of dispersed phases, comprising:

(a) at least one retinoid;
(b) at least one compound which is capable of providing a solution thereof with a transmittance of 10% or less, preferably 5% or less, and more preferably 2% or less, for light with a wavelength of from 290 to 420 nm, along a light path length of 10 mm, the concentration of the compound in the solution being 0.9% by weight relative to the total weight of the solution;
(c) at least one hydrophilic antioxidant agent other than the ingredient (b) and
(d) at least one cationic polymer.

The (a) retinoid is present in the dispersed phases.

The (b) compound, (c) hydrophilic antioxidant agent, and (d) cationic polymer are present in the continuous phase.

The (a) retinoid may be retinol.

The amount of the (a) retinoid(s) in the composition according to the present invention may range from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 1% by weight, relative to the total weight of the composition.

The (b) compound may be selected from polyphenols, preferably quercetin, isoquercetin, rutin, glucosylrutin, and a mixture thereof.

The amount of the (b) compound in the composition according to the present invention may range from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight, relative to the total weight of the composition.

The (c) hydrophilic antioxidant agent may be selected from ascorbic acid, ascorbic acid salts, and combination thereof.

The amount of the (c) hydrophilic antioxidant agent(s) in the composition may range from 1% to 30% by weight, preferably from 5% to 20% by weight, and more preferably from 10% to 15% by weight, relative to the total weight of the composition

The (d) cationic polymer may be selected from cationic polysaccharides, preferably non-cellulose-based cationic polysaccharides, more preferably cationic gums, in particular cationic galactomannan gums.

The amount of the (d) cationic polymer in the composition may range from 0.01% to 10% by weight, preferably from 0.05% to 5% by weight, and more preferably from 0.1% to 2% by weight, relative to the total weight of the composition

The continuous phase may be an aqueous continuous phase.

The dispersed phases comprise capsules.

The amount of the dispersed phases in the composition ranges from 0.1% to 30% by weight, preferably from 1% to 20% by weight, more preferably from 3% to 15% by weight, and even more preferably from 5% to 10% by weight relative to the total weight of the composition.

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

## BEST MODE FOR CARRYING OUT THE INVENTION

After diligent research, the inventors have discovered that it is possible to provide a dispersion composition including at least one retinoid, wherein the composition has a stable dispersion form and can maintain the retinoid therein at a sufficient residual rate even under light exposure or at high temperature.

The composition according to the present invention is a dispersion composition comprising a continuous phase and a plurality of dispersed phases, and which may be characterized by a combination of:

(a) at least one retinoid;
(b) at least one compound which is capable of providing a solution thereof with a transmittance of 10% or less, preferably 5% or less, and more preferably 2% or less, for light with a wavelength of from 290 to 420 nm, along a light path length of 10 mm, the concentration of the compound in the solution being 0.9% by weight relative to the total weight of the solution;
(c) at least one hydrophilic antioxidant agent other than the ingredient (b);
(d) at least one cationic polymer.

Hereinafter, the composition and process according to the present invention will be explained in a more detailed manner.

[Composition]

The composition according to the present invention has a stable dispersion form with a plurality of dispersed phases. The expression "stable dispersion" here means that a plurality of dispersed phases are stable without precipitation or floating over time. Also, the composition according to the present invention can maintain the retinoid therein at a sufficient residual rate even under light exposure and at a high temperature. The dispersion here is different from emulsions in that the dispersed phase of the present invention is not droplets of oils, water, and the like.

The composition according to the present invention may preferably be used as a cosmetic composition, in particular a leave-on type cosmetic composition. The composition according to the present invention may be intended for application onto a keratinous substance, such as skin, for example, facial, neck, or body skin, lip, scalp, and hair. The composition according to the present invention has a cosmetic effect, in particular as anti-aging, whitening, and/or anti-wrinkle efficacy on keratinous substances.

The composition according to the present invention exhibits a stable form as a dispersion. In other words, each of the dispersed phases is well-dispersed in the composition without precipitation or floating. In particular, the composition according to the present invention exhibits a stable form of a dispersion over time even at a high temperature, such as 55 °C. In other words, each of the dispersed phases is well-dispersed in the composition without precipitation or floating over time, even at a high temperature, such as 55 °C.

The composition according to the present invention can maintain the (a) retinoid therein at a sufficient residual rate (such as 75% or more) even under light (e.g., UV rays) exposure and at high temperature (e.g., 55°C). In other words, the degradation of the (a) retinoid in the composition according to the present invention due to light and high temperature can be reduced. Accordingly, the composition according to the present invention can provide stable cosmetic effects over time based on the (a) retinoid in the composition.

The composition according to the present invention may be transparent or translucent.

The transparency may be measured by measuring the turbidity (for example, turbidity can be measured with a 2100Q (marketed by HACH) having a round cell (25 mm in diameter and 60 mm height) and a tungsten filament lamp which can emit visible light (between 400 and 800 nm, preferably from 400 to 500 nm). The measurement can be performed on the undiluted composition. The blank may be determined with distilled water.

The composition according to the present invention may preferably have a turbidity of less than 200 NTU, preferably less than 150 NTU, more preferably less than 100 NTU, and even more preferably less than 50 NTU.

The composition according to the present invention comprises (a) at least one retinoid; (b) at least one compound which is capable of providing a solution thereof with a transmittance of 10% or less for light with a wavelength of from 290 to 420 nm, along a light path length of 10 mm, the concentration of the compound in the solution being 0.9% by weight relative to the total weight of the solution; (c) at least one hydrophilic antioxidant agent other than ingredient (b); and (d) at least one cationic polymer.

Hereinafter, the ingredients in the composition according to the present invention will be explained in a more detailed manner.

(Retinoid)

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

The (a) retinoid may be retinol (vitamin A), retinal (vitamin A aldehyde), retinoic acid (vitamin A acid), or an ester of retinol and of a $C_{2-20}$ acid, such as the propionate, the acetate, the linoleate or the palmitate of retinol (retinyl palmitate).

Among the (a) retinoid, mention may be made of retinol, retinal, retinoic acid, in particular all-trans retinoic acid and 13-cis retinoic acid, retinol derivatives, such as retinyl acetate, propionate or palmitate, and the retinoids described in the following patent applications: FR 2 370 377, EP 0 199 636, EP 0 325 540 and EP 0 402 072:

According to one preferred embodiment of the present invention, the (a) retinoid is retinol or proretinol.

The term "retinol" is intended to mean all the isomers of retinol, i.e., all-trans retinol, 13-cis retinol, 11-cis retinol, 9-cis retinol and 3,4-didehydro retinol.

As a representative of proretinol, mention may be made of retinyl palmitate.

It is preferable that the (a) retinoid be retinol.

The amount of the (a) retinoid(s) in the composition according to the present invention may be 0.01% by weight or more, preferably 0.05% by weight or more, and more preferably 0.1% by weight or more, relative to the total weight of the composition.

On the other hand, the amount of the (a) retinoid(s) in the composition according to the present invention may be 5% by weight or less, preferably 3% by weight or less, and more preferably 1% by weight or less, relative to the total weight of the composition.

The amount of the (a) retinoid(s) in the composition according to the present invention may range from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 1% by weight, relative to the total weight of the composition.

In the context of the present specification, any combinations of the upper limit values and the lower limit values of parameters can be available to represent the preferred range of parameters, such as the amount.

(Light Shielding Compound)

The composition according to the present invention comprises (b) at least one compound which is capable of providing a solution thereof with a transmittance of 10% or less, preferably 5% or less, and more preferably 2% or less, for light with a wavelength of from 290 to 420 nm, along a light path length of 10 mm, wherein the concentration of the (b) compound in the solution is 0.9% by weight relative to the total weight of the solution. Thus, a single type of such (b) compound or a combination of different types of such (b) compounds may be used.

The (b) compound can provide a low light transmittance. Therefore, the (b) compound may be referred to as a light shielding compound.

The (b) compound may be present in the continuous phase of the present invention.

It is more preferable that the (b) compound be capable of providing a solution with a zero (0) transmittance for light with a wavelength of from 290 to 420 nm along a light path length of 10 mm, wherein the concentration of the (b) compound in the solution is 0.9% by weight relative to the total weight of the solution.

It is even more preferable that the (b) compound be capable of providing a solution with a zero (0) transmittance for light with a wavelength of from 290 to 420 nm along a light path length of 10 mm, wherein the concentration of the (b) compound in the solution is more than 0.1% by weight relative to the total weight of the solution.

The solvent for the solution is not limited as long as the (b) compound is solubilized in the solvent, and the solvent does not have any absorbance for light with a wavelength of from 290 to 420 nm. For example, as the solvent, water and hydrophilic solvents such as ethanol may be used.

The transmittance may be measured by a spectrophotometer, e.g., a UV-Visible/NIR spectrophotometer V-750 by JASCO Corp.

The (b) compound can provide a solution with a transmittance of 10% or less, preferably 5% or less, more preferably 2% or less, and even more preferably zero (0)% for any light with a wavelength of from 290 to 420 nm along a light path length of 10 mm. In other words, the solution of the (b) compound can reduce or shield any light whose wavelength is from 290 nm to 420 nm.

The (b) compound can reduce or shield the light with the above specific wavelength which could reach the (a) retinoid in the composition according to the present invention to cause the decomposition of the (a) retinoid. Therefore, the (b) compound can contribute to enhancing the photo-stability of the (a) retinoid, and can reduce the decomposition of the (a) retinoid in the composition according to the present invention.

The (b) compound may be selected from polyphenols.

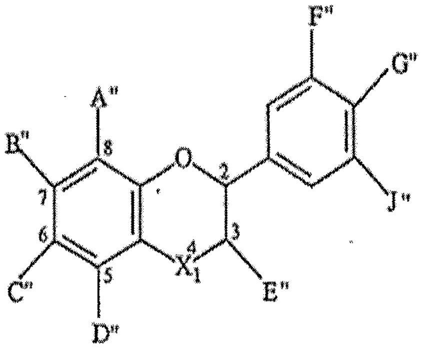
- Polyphenol

The expression "polyphenol" is understood to mean a compound containing a plurality of phenolic hydroxyl groups. The phenolic hydroxyl group means a hydroxyl group bonded to an aromatic ring such as a benzene ring and a naphthalene ring. The phenolic hydroxyl group may be optionally etherified or esterified.

The polyphenol may be chosen from those which have an antioxidizing activity.

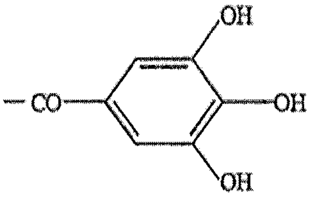
The polyphenol may be chosen, for example, from flavonoids.

Preferred flavonoids may correspond to general formula (I):

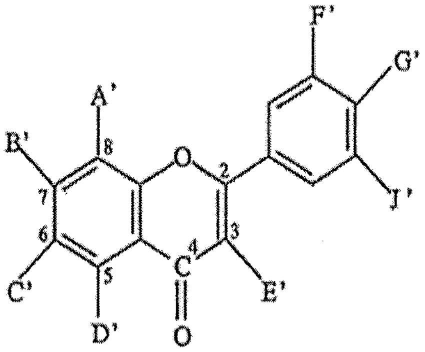


(I)

in which
A", B", C" and D", independently of one another, represent H, OH, -R' or -OR', where R' represents the residue of a sugar of formula R'OH;
E" represents H, -OH or -OX', where X' represents:



F'', G'' and J'' represent, independently of one another, H, –OH or $-OCH_3$; and $X_1$ represents $-CH_2-$, -CO- or -CHOH-,or general formula (II):



(II)

in which A', C' and D', independently of one another, represent H, -OH, $-OCH_3$, -R' or -OR', where R' represents the residue of a sugar of formula R'OH; E' represents H, -OH or -OR', where R' represents the residue of a sugar of formula R'OH; and B', F', G' and J', independently of one another, represent H, -OH, $-OCH_3$, $-OCH_2-CH_2-OH$, or -OR', where R' represents the residue of a sugar of formula R'OH.

Rutinose, glucose, apiose, rhamnose, robinose, neohesperidose, or a combination thereof may be mentioned among the sugars R'OH.

The compounds of formulae (I) and (II) are known. They can be obtained especially according to the processes described in "The Flavonoids", Harborne J. B., Mabry T. J., Helga Mabry, 1975, pages 1 to 45.

The flavonolds may be selected from flavones, flavonols, isoflavones, flavanols, flavanones, anthocyanidins, and mixtures thereof.

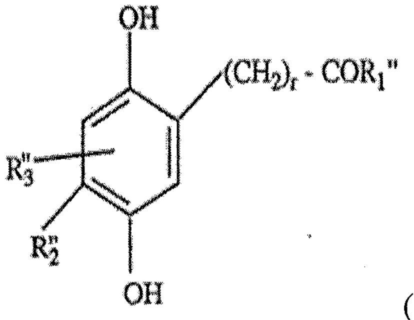
Among the flavonoids which can be used for the present invention, mention may be made of apigenin, apiin, apigetrin, vitexin, chrysin, toringin, luteolin, orientin, galangin, quercetin, isoquercetin, rutin, glucosylrutin, quercitrin, isoquercitrin, kaempferol, astragalin, kaempferitrin, robinin, myricetin, daidzein, daidzin, genistein, genistein, glycitein, glycitin, catechin, epicatechin, epigallocatechin, epicatechin gallate, epigallocatechin gallate, theaflavin, naringenin, narirutin, naringin, hesperetin, hesperidin, glucosylhesperidin, anthocyanidin, anthocyanin, cyanidin, cyanin, delphinidin, delphinin, pelargonidin, and pelargonin.

Certain polyphenols which can be used are present in plants from which they can be extracted in a known way. It is possible to use extracts from tea leaves (Camellia sinensis or Camellia japonica). Mention will in particular be made of the green tea extracts sold under the name SUNPHENON® by the Company Taiyo, which especially contain flavonoids.

As the polyphenol, it is possible to use a mixture of glucosylrutin and rutin sold under the name ALPHA GLUCOSYL RUTIN by the company QINGDAO TAITONG PHARMACEUTICAL.

Among the polyphenols which can be used, mention will also be made of the polyphenols such as carnosic acid and carnosol which can be extracted, for example, from rosemary, either by extraction followed by distillation (Chang et al., JOSC, Vol. 61, No. 6, June 1984) or by extraction with a polar solvent such as ethanol preceded by extraction using a nonpolar solvent such as hexane to remove the odorant substances, as described in EP-A-307,626.

Polyphenol may also be chosen from (2,5-dihydroxyphenyl)alkylenecarboxylic acids of formula (III) and their derivatives (especially esters and amides):



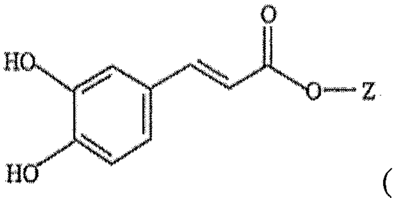
(III)

in which
$R_1''$ represents -O-Alk, OH or -N(r')(r"), wherein Alk denotes a linear or branched $C_1$-$C_{20}$ alkyl, optionally substituted by one or more hydroxyl or alkoxy groups, or a $C_2$-$C_{20}$ alkenyl,
r' and r" independently represent H, $C_1$-$C_{20}$ alkyl, $C_2$-$C_6$ hydroxyalkyl or $C_3$-$C_6$ polyhydroxyalkyl, or alternatively r' and r" form, together with a nitrogen atom to which they are attached, a heterocycle,
r is a number, including zero, such that the $-(CH_2)_r-COR_1$ chain contains at most 21 carbon atoms, and
$R_2''$ and $R_3''$ independently represent H or a $C_1$-$C_4$ alkyl, it additionally being possible for $R_2''$ to represent a $C_1$-$C_4$ alkoxy.

The compounds of formula (III) are known or can be prepared according to known methods, for example analogous to those described in patents FR-2,400,358 and FR-2,400,359.

Polyphenol may also be chosen from esters or amides of caffeic acid.

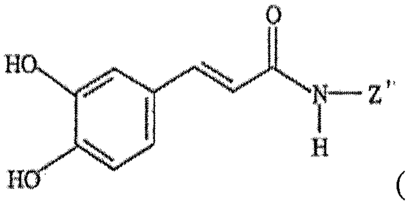
Among the esters of caffeic acid, mention may especially be made of the compounds of formula (IV):



(IV)

in which
Z represents a $C_1$-$C_8$ alkyl, for example methyl, or the residue of a phytol.

Among the amides of caffeic acid, mention may especially be made of the compounds of formula (V):


(V)

in which
Z' represents a $C_1$-$C_8$, in particular $C_6$-$C_8$, alkyl.

The compounds of formula (IV) or (V) are known or can be prepared according to known methods.

The (b) compound may be selected from the group consisting of:
quercetin, isoquercetin, rutin, glucosylrutin, and a mixture thereof.

The amount of the (b) compound(s) in the composition according to the present invention may be 0.01% by weight or more, preferably 0.05% by weight or more, and more preferably 0.1% by weight or more, relative to the total weight of the composition.

On the other hand, the amount of the (b) compound(s) in the composition according to the present invention may be 5% by weight or less, preferably 3% by weight or less, and more preferably 2% by weight or less, relative to the total weight of the composition.

The amount of the (b) compound(s) in the composition according to the present invention may range from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight, relative to the total weight of the composition.

(Hydrophilic Antioxidant Agent)

The composition according to the present invention comprises (c) at least one hydrophilic antioxidant agent other than the ingredient (b). A single type of hydrophilic antioxidant agent may be used, but two or more different types of hydrophilic antioxidant agents may be used in combination.

The (c) at least one hydrophilic antioxidant agent is different from the (b) compound, which is capable of providing a solution thereof with a transmittance of 10% or less, preferably 5% or less, and more preferably 2% or less, for light with a wavelength of from 290 to 420 nm, along a light path length of 10 mm, the concentration of the compound in the solution being 0.9% by weight relative to the total weight of the solution.

The (c) hydrophilic antioxidant agent may be present in the continuous phase of the present invention.

The term "antioxidant agent" here refers to a chemical compound, an enzyme or other organic molecule which prevents free radicals from causing oxidation of molecules such as are found in keratinous substances. The antioxidant agent, by reacting with the oxidant, can protect such molecules from being damaged.

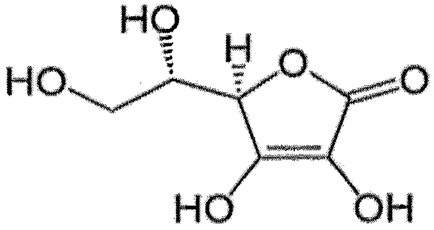
The (c) antioxidant agent is hydrophilic. The term "hydrophilic" here means a substance which is water-soluble. The term “water-soluble” here means a substance which can dissolve in an amount of 0.1 g or more, 1 g or more, or 10 g or more in 100 mL water at room temperature (25 °C) and atmospheric pressure ($10^5$ Pa).

The hydrophilic antioxidant agents may be selected from natural and synthetic antioxidant agents, and preferably natural antioxidant agents.

Examples of the (c) hydrophilic antioxidant agent includes, without limitation, ascorbic acid and derivatives thereof, hydroxyacetophenone, dihydrochalone, zinc PCA, baicalin, ferulic acid, pine bark extract, and polydatin. Preferably, the (c) hydrophilic antioxidant agent is selected from natural antioxidant agents, such as ascorbic acid, dihydrochalone, baicalin, ferulic acid, pine bark extract, and polydatin.

Ascorbic acid, which is also known as Vitamin C, is known as a cosmetically active ingredient. Ascorbic acids are used as anti-aging, whitening, and/or anti-wrinkle ingredients on keratinous substances, in particular skin, since they have functions of stimulating collagen synthesis and reducing melanin. Ascorbic acid in general means L-ascorbic acid.

The ascorbic acid is preferably L-ascorbic acid, or vitamin C. Its structure is represented by the following formula.



The derivative of ascorbic acid may be a salt of ascorbic acid. The salt of ascorbic acid is preferably a pharmaceutically acceptable salt. The salts of ascorbic acid include, but are not limited to, salts with an organic base (for example, salts with a tertiary amine such as trimethylamine salts, triethylamine salts, monoethanolamine salts, triethanolamine salts and pyridine salts, basic ammonium salts such as arginine, and the like), salts with an inorganic base (for example, alkali metal salts such as ammonium salts, sodium salts and potassium salts, alkaline earth metal salts such as calcium salts and magnesium salts, aluminum salts, and the like) and the like.

On account of its chemical structure (α-keto lactone), which makes it very sensitive to certain environmental parameters such as light, heat and aqueous media, it may be advantageous to use an ascorbic acid derivative in the form of a saccharide ester of ascorbic acid or a metal salt of phosphorylated ascorbic acid.

The saccharide esters of ascorbic acid that may be used in the present invention are especially glycosyl, mannosyl, fructosyl, fucosyl, galactosyl, N-acetylglucosamine, N-acetylmuramic derivatives of ascorbic acid and mixtures thereof, and more especially ascorbyl-2 glucoside or 2-O-α-D glucopyranosyl of L-ascorbic acid or 6-O-D galactopyranosyl of L-ascorbic acid. The latter compounds and processes for preparing them are described in particular in documents EP-A-487 404, EP-A-425 066 and J-05 213 736.

For its part, the metal salt of phosphorylated ascorbic acid may be chosen from alkali metal ascorbyl phosphates, alkaline-earth metal ascorbyl phosphates and transition metal ascorbyl phosphates..

It may be preferable that the derivatives of ascorbic acid be selected from salts of ascorbic acid or phosphorylated ascorbic acid, such as, especially, sodium ascorbate, sodium or magnesium ascorbyl phosphate, acetic ester of ascorbic acid, or sugar esters of ascorbic acid, including saccharide esters and especially such as glycosyl ascorbic acid.

In one preferred embodiment, the (c) antioxidant agent is selected from ascorbic acid, salts thereof, and combination thereof.

The amount of the (c) hydrophilic antioxidant agent(s) in the composition according to the present invention may be 1% by weight or more, preferably 5% by weight or more, and more preferably 10% by weight or more, relative to the total weight of the composition.

On the other hand, the amount of the (c) hydrophilic antioxidant agent(s) in the composition according to the present invention may be 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.

The amount of the (c) hydrophilic antioxidant agent(s) in the composition according to the present invention may range from 1% to 30% by weight, preferably from 5% to 20% by weight, and more preferably from 10% to 15% by weight, relative to the total weight of the composition.

(Cationic Polymer)

The composition according to the present invention comprises (d) at least one cationic polymer. A single type of cationic polymer may be used, but two or more different types of cationic polymers may be used in combination.

The (d) cationic polymer may be present in the continuous phase of the present invention.

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 to15 meq/g, and more preferably from 0.1 to 10 meq/g.

The molecular weight of the cationic polymer may be 1000 or more, preferably 50000 or more, more preferably 100000 or more, and even more preferably 1000000 or more.

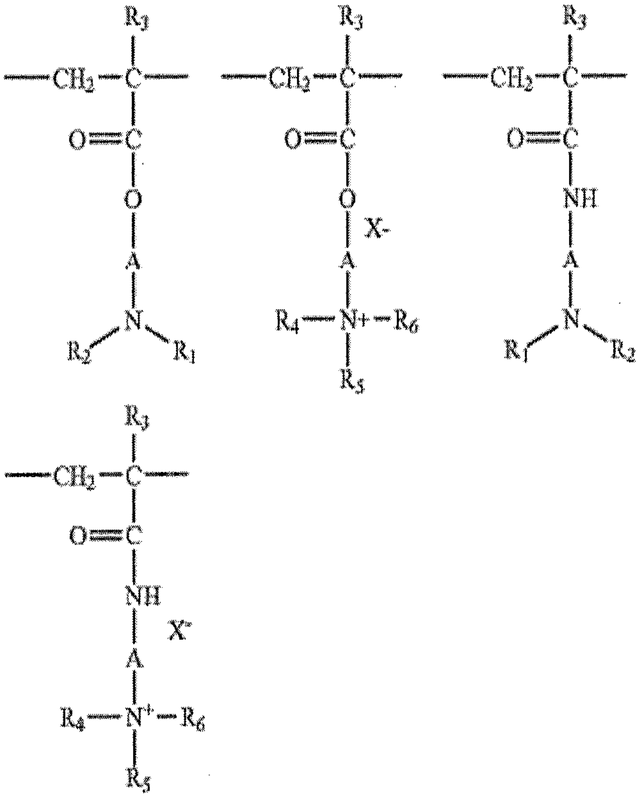
Unless otherwise defined in the descriptions, “molecular weight” means a number-average molecular weight.

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 a group of $-NH_2$.

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:



wherein:
$R_1$ and $R_2$, 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;
$R_3$, which may be identical or different, is chosen from hydrogen and $CH_3$;
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
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($C_1$-$C_4$)alkyltri($C_1$-$C_4$)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.

(2) 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.

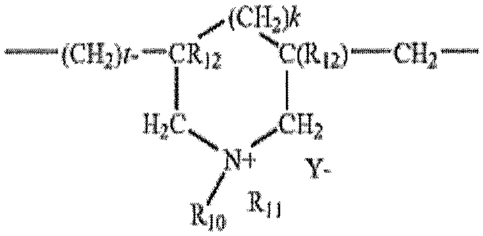
(3) Water-soluble polyamino amides prepared, for example, by polycondensation of an acidic compound with a polyamine; these polyamino amides possibly being crosslinked with an entity chosen from epihalohydrins; diepoxides; dianhydrides; unsaturated dianhydrides; bisunsaturated derivatives; bishalohydrins; 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.

(4) 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.

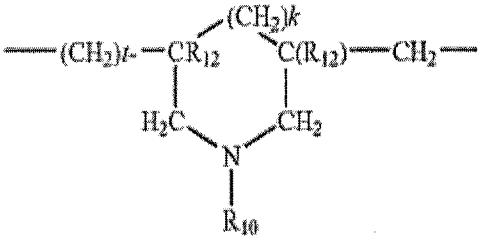
(5) Polymers obtained by reaction of a polyalkylene polyamine comprising two primary amine groups and at least one secondary amine group, with a dicarboxylic acid chosen from diglycolic acid and saturated aliphatic dicarboxylic acids comprising from 3 to 8 carbon atoms. The molar ratio of the polyalkylene 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.

(6) 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):



(Ia)



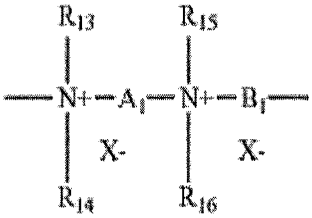
(Ib)

wherein:
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 dimethyidiallylammonium 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):



$$-\overset{R_{13}}{\underset{R_{14}}{N^{+}}}-A_1-\overset{R_{15}}{\underset{R_{16}}{N^{+}}}-B_1- \qquad X^- \qquad X^-$$

(II)

wherein:

$R_{13}$, $R_{14}$, $R_{15}$, 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;

$A_1$ and $B_1$, 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;

$A_1$, $R_{13}$, and $R_{15}$ 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:

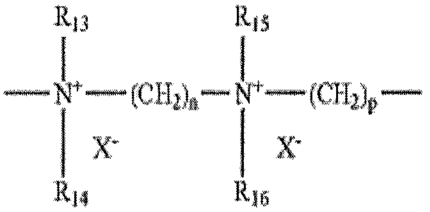
$-(CH_2-CH_2-O)_x-CH_2-CH_2-$
$-[CH_2-CH(CH_3)-O]_y-CH_2-CH(CH_3)-$

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 $-CH_2-CH_2-S-S-CH_2-CH_2-$; 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):



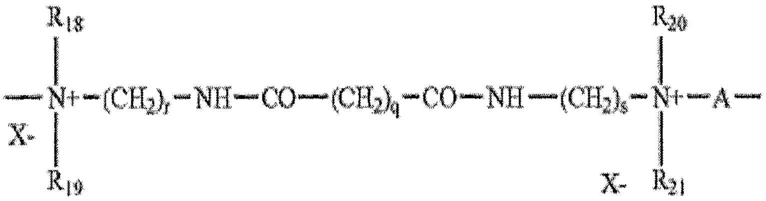
$$-N^{+}(R_{13})(R_{14})\,X^{-}-(CH_2)_n-N^{+}(R_{15})(R_{16})\,X^{-}-(CH_2)_p-$$

(III)

wherein

$R_{13}$, $R_{14}$, $R_{15}$, and $R_{16}$, 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.

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



$$-N^{+}(R_{18})(R_{19})\,X^{-}-(CH_2)_r-NH-CO-(CH_2)_q-CO-NH-(CH_2)_s-N^{+}(R_{20})(R_{21})\,X^{-}-A-$$

(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, $-CH_2CH_2(OCH_2CH_2)_pOH$ groups, wherein p is chosen from integers ranging from 0 to 6, with the proviso that $R_{18}$, $R_{19}$, $R_{20}$, and $R_{21}$ are not simultaneously hydrogen,

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

A is chosen from radicals of dihalides and $-CH_2-CH_2-O-CH_2-CH_2-$.

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

(8) 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.

(9) Polyamines

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 example of the (co)polyamines, mention may be made of chitosan, (co)polyallylamines, (co)polyvinylamines, (co)polyanilines, (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, propylene glycol and glycerol. 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.

(10) 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, steardimoium hydroxyprolyl 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.

(11) Cationic polysaccharides.

The (d) cationic polymer of the present invention may be preferably selected from cationic polysaccharide.

The charge density of the cationic polysaccharide may be from 0.01 meq/g to 20 meq/g, preferably from 0.05 to15 meq/g, and more preferably from 0.1 to 10 meq/g.

The molecular weight of the cationic polysaccharide may be 1000 or more, preferably 50,000 or more, more preferably 100,000 or more, and even more preferably 1,000,000 or more.

Unless otherwise defined in the description, “molecular weight” means a number average molecular weight.

The cationic polysaccharide 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 group $-NH_2$. It is preferable that the (a) cationic polysaccharide have at least one quaternary ammonium group.

The cationic polysaccharide 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 polysaccharide may be selected from natural and synthetic cationic polysaccharides.

It is preferable that the cationic polysaccharide be selected from cationic cellulose polymers.

According to the present invention, a "cationic cellulose polymer" denotes any non-siliconized (comprising no silicon atoms) cellulose polymer containing cationic groups and/or groups ionizable into cationic groups, and preferably not containing anionic groups and/or groups ionizable into anionic groups.

The term "*cellulose*" polymer denotes according to the invention any polysaccharide compound having in the structure thereof at least 20 glucose residue chains joined by β-1,4 bonds. The cellulose polymer can be associative, i.e., having the structure thereof at least one $C_8$-$C_{30}$ fatty chain.

The cationic cellulose polymers suitable for use preferably have a weight-average molecular weight (Mw) between about 5000 and $5.10^6$, preferably between about $10^3$ and $3.10^6$.

Non-limiting examples of the cationic cellulose polymers are as follows.

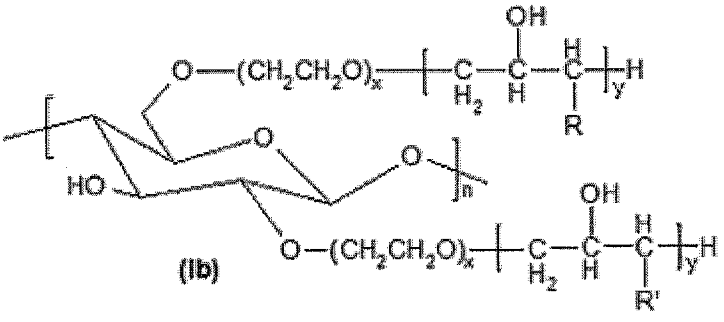
(10-1) Cationic cellulose derivatives such as cellulose ether derivatives comprising quaternary ammonium groups described, for example, in French Patent No. 1 492 597, such as the polymers sold under the names "JR" (JR 400, JR 125, JR 30M) or "LR" (LR 400, LR 30M) by the company Union Carbide Corporation. 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.

(10-2) 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.

(10-3) Cationic cellulose polymers having at least one quaternary ammonium group comprising at least one fatty chain.

The fatty chain of the quaternized celluloses modified by groups including at least one linear fatty chain may be linear alkyl, linear or branched arylalkyl, linear alkylaryl, preferably linear alkyl, these groups including at least 8 carbon atoms, particularly 8 to 30 carbon atoms, more preferably 10 to 24, or 10 to 14, carbon atoms; or mixtures thereof.

Preferably, mention can be made of quaternized hydroxyethylcelluloses modified by groups including at least one linear fatty chain, such as linear alkyl, linear arylalkyl, linear alkylaryl, preferably linear alkyl, groups, these groups including at least 8 carbon atoms, particularly 8 to 30 carbon atoms, more preferably 10 to 24, or 10 to 14, carbon atoms; or mixtures thereof. Preferably, mention can be made of hydroxyethylcelluloses of formula (Ib):



(Ib)

wherein:

- R represents an ammonium group RaRbRcN$^+$-, Q- wherein Ra, Rb, Rc, identical or different represent a hydrogen atom or linear, C1-C30, alkyl, preferably an alkyl and Q- represents an anionic counterion such as a halide such as chloride or bromide;
- R’ represents an ammonium group R’aR’bR’cN$^+$–, Q’- wherein R’a, R’b, R’c, identical or different represent a hydrogen atom or linear, C1-C30, alkyl, preferably an alkyl and Q’- represents an anionic counterion such as a halide such as chloride or bromide; preferably an alkyl;

it being understood that at least one of the radicals Ra, Rb, Rc, R’a, R’b, R’c represents a linear, C8-C30, alkyl;

- n, x and y, identical or different, represent an integer between 1 and 10000.

Preferably, in formula (Ib), at least one of the radicals Ra, Rb, Rc, R’a, R’b, R’c represents a linear C8-C30 alkyl; preferably C10-C24, or C10-C14; mention can particularly be made of the dodecyl radical (C12). Preferably, the other radicals represent a linear C1-C4 alkyl, particularly methyl.

Preferably, in formula (Ib), only one of the radicals Ra, Rb, Rc, R'a, R'b, R'c represents a linear C8-C30 alkyl; preferably C10-C24, or C10-C14; mention can particularly be made of the dodecyl radical (C12). Preferably, all the other radicals represent a linear C1-C4 alkyl, particularly methyl.

More preferably, R can be a group chosen from $-N^+(CH_3)_3$, $Q'^-$ and $-N^+(C_{12}H_{25})(CH_3)_2$, $Q'^-$, preferably a group $-N^+(CH_3)_3$, $Q'^-$.

More preferably, R' can be a group $-N^+(C_{12}H_{25})(CH_3)_2$, $Q'^-$.

The nitrogen percentage can be vary from 0.1 to 10% by weight with respect to the total polymer weight, preferably from 0.2 to 5% by weight and more preferably from 0.5 to 3% by weight.

Mention can particularly be made of polymers having the INCI names:
- Polyquaternium-24, such as the product QUATRISOFT LM 200®, marketed by AMERCHOL/DOW CHEMICAL;
- PG-Hydroxyethylcellulose Cocodimonium Chloride, such as the product CRODACEL QM®;
- PG-Hydroxyethylcellulose Lauryldimonium Chloride (C12 alkyl), such as the product CRODACEL QL® and
- PG-Hydroxyethylcellulose Stearyldimonium Chloride (C18 alkyl) such as the product CRODACEL QS®, marketed by CRODA.

Mention can also be made of hydroxyethylcelluloses of formula (Ib) wherein R represents trimethylammonium halide and R' represents dimethyldodecylammonium halide, preferably R represents trimethylammonium chloride Cl-,(CH3)3N+– and R' represents dimethyldodecylammonium chloride Cl-,(CH3)2(C12H25)N+–. This type of polymer is known under the INCI name Polyquaternium-67; as commercial products, mention can be made of SOFTCAT POLYMER SL® polymers such as SL-100, SL-60, SL-30, SL-5 and SX-1300X from AMERCHOL/DOW CHEMICAL.

More particularly, the cationic cellulose polymer is chosen from hydroxyethyl celluloses having reacted with a trimethyl ammonium epoxide and a lauryl dimethyl ammonium epoxide (INCI name POLYQUATERNIUM-67). It is preferably marketed under the name Softcat Polymer SL-100 or Softcat Polymer SX-1300X by Amerchol.

(10-4) Non-cellulose-based cationic polysaccharides may be chosen from cationic gums, in particular cationic galactomannan gums (cationic guar), cationic starches, cationic hyaluronic acid, chitosans, and dextran hydroxypropyl trimonium chloride.

The term "*cationic galactomannan gum*" denotes any galactomannan gum containing cationic groups and/or groups ionizable into cationic groups.

Galactomannans are polysaccharides essentially composed of galactose and mannose units, wherein the mannose units are bound by a 1-4-glycoside bond and galactose branching takes place by means of a 1-6 bridge to the mannose units. Each ring of the galactose or mannose units (or sugar units) carries three free hydroxyl groups available for the chemical reaction. Galactomannans are generally found in the endosperm of the grains of legumes such as guar or carob.

The preferred cationic groups are chosen from those including primary, secondary, tertiary and/or quaternary amine groups.

The cationic galactomannan gums used generally have a weight-average molecular weight between about 500 and $5x10^6$, and preferably between about $10^3$ and $3x10^6$.

The galactomannan groups suitable for use according to the present invention are for example gums including trialkyl ($C_1$-$C_4$) ammonium cationic groups. Preferably, 2% to 30% in number of the hydroxyl functions of these gums carry trialkylammonium cationic groups.

Among these trialkylammonium groups, mention can very particularly be made of trimethylammonium and triethylammonium groups.

Even more preferably, these groups represent from 5% to 20% by weight of the total weight of the modified galactomannan gum.

The gums may be, for example, selected from the group consisting of guar gum, cassia gum, karaya gum, konjac gum, gum tragacanth, tara gum, and acacia gum.

These galactomannan gums in particular from guar modified by cationic groups are products already known per se and are for example described in the patents US 3 589 578 and US 4 031 307.

According to the invention, the cationic galactomannan gum is preferably a guar gum including hydroxypropyl trialkylammonium groups, more preferably a guar gum including hydroxypropyl trimethylammonium groups, i.e., a guar gum modified for example with 2,3-epoxypropyl trimethylammonium chloride.

These galactomannan gums in particular from guar modified by cationic groups are products already known per se and are for example described in the patents US 3 589 578 and US 4 031 307. Such products are moreover sold particularly under the trade names Jaguar EXCEL, Jaguar C13 S, Jaguar C 15, Jaguar C 17 and Jaguar C162 (Guar Hydroxypropyltrimonium Chloride) by Rhodia, under the name Amilan® Guar (Guar Hydroxypropyltrimonium Chloride) by Degussa, and under the name N-Hance® 3000 (Guar Hydroxypropyltrimonium Chloride) by Aqualon. Hydroxypropyl Guar hydroxypropyltrimonium chloride, which is hydroxypropyl derivative of guar hydroxypropyltrimonium chloride, is commercially available under the Jaguar™ trade name series from Rhodia Inc. Cassia Hydroxypropyltrimonium Chloride is commercially available under the Sensomer™ CT-250 and Sensomer™ CT-400 trademarks from Lubrizol Advanced Materials, Inc or the ClearHance™ from Ashland Inc.

As examples of the cationic starches, mention may be made of starches modified with a 2,3-epoxypropyltrimethylammonium salt (e.g. chloride), such as the product known as starch hydroxypropyltrimonium chloride according to the INCl nomenclature and sold under the name SENSOMER Cl-50 from Ondeo or Pencare™ DP 1015 from Ingredion.

In the preferred embodiment of the present invention, the (d) cationic polymer is selected from cationic polysaccharides, preferably non-cellulose-based cationic polysaccharides, more preferably cationic gums, in particular cationic galactomannan gums.

The amount of the (d) cationic polymer(s) in the composition according to the present invention may be 0.01% by weight or more, preferably 0.05% by weight or more, and more preferably 0.1% by weight or more, relative to the total weight of the composition.

The amount of the (d) cationic polymer(s) in the composition according to the present invention may be 10% by weight or less, preferably 5% by weight or less, and more preferably 2% by weight or less, relative to the total weight of the composition.

The amount of the (d) cationic polymer(s) in the composition according to the present invention may be from 0.01% to 10% by weight, preferably from 0.05% to 5% by weight, and more preferably from 0.1% to 2% by weight, relative to the total weight of the composition.

## Dispersed Phase

The composition according to the present invention comprise a plurality of dispersed phases. Each of dispersed phases is well-dispersed in the composition without precipitation or float. In addition, the dispersion composition according to the present invention is not emulsions, since the dispersed phase of the present invention is not droplets of oils, water, and the like.

The shape of the dispersed phase is not particularly limited. The dispersed phase may of any shape, platelet-shaped, spherical or oblong, irrespective of the crystallographic form (for example lamellar, cubic, hexagonal, orthorhombic, etc.).

The size of the dispersed phase is not particularly limited. For example, the number-average primary size of the dispersed phase ranges from 5 nm to 10 mm, preferably from 10 nm to 5 mm.

For the purposes of the present invention, the term "primary particle size" means the maximum dimension that it is possible to measure between two diametrically opposite points on an individual particle. The term “number-average size" means diameter which is given by the statistical particle size distribution to half of the population, referred to as D50. The size of the dispersed phase may be measured by observing SEM (Scanning Electron Microscope), TEM (Transmission Electron Microscope), optical microscope, or a laser diffraction particle size distribution analyzer.

The dispersed phase of the present invention may comprise or consist of capsules or inorganic fillers. The term “filler” should be understood as meaning 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.

In one preferred embodiment, the dispersed phase is water-insoluble or maintain its shape in water, because the continuous phase may be an aqueous continuous phase in one prefer embodiment. For the purpose of the present invention, the term “water-insoluble” here indicates materials which are soluble in water at a concentration of less than 0.1% by weight, in particular less than 0.01% by weight, relative to the total weight of the water at room temperature (25°C) and atmospheric pressure ($10^5$ Pa).

## Capsule

The term "capsule" here intends to mean a particle or a bead comprising a core, which is also called "inner core", surrounded by a coating based on one or more layer(s) or film(s), which is also called as "shell" or "outer layer". The shell may comprise one layer or two or more layers.

The form of the capsule is not limited. For example, the capsule may be in the form of a sphere.

It is preferable that the capsule comprises one core and at least one shell surrounding the core.

The number of the layer or film in the shell is not limited, but it may be preferable that the shell comprises one layer or film.

In one embodiment of the present invention, the shell may comprise at least one polysaccharide other than the (d) cationic polymer. In other words, the layer or file in the shell may be formed with least one polysaccharide other than the (d) cationic polymer.

The capsule can be prepared by surrounding a core which can be performed by any conventional process. For example, it is possible to coextrude a core-forming composition and a shell-forming composition. In this, case, the excluded core-forming composition can form a core, while the shell-forming composition can form a shell. The coextruded core/shell structure can transform into a core/shell particle which corresponds to the capsule.

The size of the capsule is not particularly limited. For example, the number-average primary size of the capsule ranges from 100 μm to 10 mm, preferably from 250 μm to 7 mm, more preferentially from 500 μm to 5 mm, even more preferably from 750 μm to 3 mm, and in particular from 1 mm to 2 mm.

## Inorganic Fillers

The inorganic fillers may be preferably selected from inorganic UV filter powder and inorganic coloring fillers.

- Inorganic UV filter powder

The inorganic UV filter powder used for the present invention may be active in the UV-A and/or UV-B region, preferably in the UV-B region or in the UV-A and UV-B region. The powdery cosmetic composition according to the present invention can comprise a further additional UV filter other than the inorganic UV filter powder. It is preferable that the active UV filtering region of the inorganic UV filter powder and that of the additional UV filter are complementary to each other, in order to provide comprehensive UV protection. For example, it is preferable that the inorganic UV filter powder is active at least in the UV-B region and the additional UV filter is active at least in the UV-A region. The inorganic UV filter powder may be hydrophilic and/or lipophilic.

The inorganic UV filter powder may be in the form of a fine particle having an average primary particle size of lower than 200 nm, preferably lower than 180 nm, and more preferably from 5 nm to 180 nm, and even more preferably from 5 nm to 150 nm, and still more preferably from 10 nm to 100 nm. The average primary particle size here means 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, such a number-average size mean diameter of the inorganic UV filter powder can be measured by SEM (Scanning Electron Microscope) and/or TEM (Transmission Electron Microscope).

The inorganic UV filter powder may be selected from metal oxides, such as titanium oxide (amorphous or crystalline in the rutile and/or anatase form), zinc oxide, zirconium oxide or cerium oxide, which are all well-known UV photoprotective agents. Preferably, the inorganic UV filter powder is selected from the group consisting of titanium dioxide, zinc oxide, and cerium oxide.

The inorganic UV filter powder may or may not be coated. The coating is not particularly limited, and any conventional coating may be used. For example, 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.

- Inorganic coloring fillers

The term “inorganic coloring filler” here should understood as encompassing inorganic pigments, nacres, and reflective particles, and mixtures thereof.

The term “pigments” should be understood to mean white or colored particles of any shape, which are insoluble in a physiological medium, and which are intended to color the composition.

Among the pigments that may be mentioned are titanium dioxide, such as pigmentary titanium dioxide rutile type, optionally surface-treated, zirconium oxide or cerium oxide, and also zinc oxide, iron (black, yellow or red) oxide or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue, and metal powders, for instance aluminium powder and copper powder.

The term “nacres” should be understood as meaning colored particles of any form, which may or may not be iridescent, especially produced by certain molluscs in their shell, or alternatively synthesized, and which have a color effect via optical interference.

Examples of nacres that may be mentioned include nacreous pigments such as titanium mica coated with an iron oxide, mica coated with bismuth oxychloride, titanium mica coated with chromium oxide, and nacreous pigments based on bismuth oxychloride. They may also be mica particles at the surface of which are superposed at least two successive layers of metal oxides and/or of organic dyestuffs. The nacres may more particularly have a yellow, pink, red, bronze, orange, brown, gold and/or coppery color or glint.

The term “reflective particles” denotes particles whose size, structure, especially the thickness of the layer(s) of which they are made and their physical and chemical nature, and surface state, allow them to reflect incident light. This reflection may, where appropriate, have an intensity sufficient to create at the surface of the composition or of the mixture, when it is applied to the support to be made up, points of overbrightness that are visible to the naked eye, i.e. more luminous points that contrast with their environment by appearing to sparkle.

The reflective particles may be selected so as not to significantly alter the coloration effect generated by the coloring agents with which they are combined, and more particularly so as to optimize this effect in terms of color yield.

The reflective particles, whatever their form, may or may not have a multilayer structure and, in the case of a multilayer structure, may have, for example, at least one layer of uniform thickness, in particular of a reflective material.

When the reflective particles do not have a multilayer structure, they may be composed, for example, of metal oxides, especially titanium or iron oxides obtained synthetically.

When the reflective particles have a multilayer structure, they may comprise, for example, a natural or synthetic substrate, especially a synthetic substrate at least partially coated with at least one layer of a reflective material, especially of at least one metal or metallic material. The substrate may be made of one or more organic and/or inorganic materials.

More particularly, it may be chosen from glasses, ceramics, graphite, metal oxides, aluminas, silicas, silicates, especially aluminosilicates and borosilicates, and synthetic mica, and mixtures thereof, this list not being limiting.

The reflective material may comprise a layer of metal or of a metallic material.

Again as an example of reflective particles comprising a mineral substrate coated with a layer of metal, mention may also be made of particles comprising a silver-coated borosilicate substrate.

Use may also be made of particles comprising a metallic substrate such as silver, aluminium, iron, chromium, nickel, molybdenum, gold, copper, zinc, tin, manganese, steel, bronze or titanium, said substrate being coated with at least one layer of at least one metal oxide such as titanium oxide, aluminium oxide, iron oxide, cerium oxide, chromium oxide or silicon oxides, and mixtures thereof.

In some specific embodiment of the present invention, the dispersed phases comprise or consist of at least one capsule.

In further specific embodiments, the (a) retinoid is present in the capsule. For example, the core of the capsule may comprise the (a) retinoid. The encapsulation of the (a) retinoid can prevent or reduce the contact of the (a) retinoid with (c) at least one hydrophilic antioxidant agent, such as ascorbic acid, and may be able to reduce the change in color (in particular, brightness) of the composition according to the present invention. Thus, the capsule may be able to reduce color evolution of the composition according to the present invention.

In some embodiments, the essential ingredients (b) to (d) are present in the continuous phase of the composition.

The amount of the dispersed phases in the composition according to the present invention may be 0.1% by weight or more, preferably 1% by weight or more, more preferably 3% by weight or more, and even more preferably 5% by weight or more, relative to the total weight of the composition.

On the other hand, the amount of the dispersed phases in the composition according to the present invention may be 30% by weight or less, preferably 20% by weight or less, more preferably 15% by weight or less, and even more preferably 10% by weight or less, relative to the total weight of the composition.

The amount of the dispersed phases in the composition according to the present invention may range from 0.1% to 30% by weight, preferably from 1% to 20% by weight, more preferably from 3% to 15% by weight, and even more preferably from 5% to 10% by weight relative to the total weight of the composition.

Continuous Phase

The continuous phase can be a dispersing medium for the plurality of dispersed phases of the present invention. Thus, the continuous phase can be in the form of a liquid at 25°C and under atmospheric pressure (760 mmHg).

The form of the continuous phase is not particularly limited. In general, the continuous phase is liquid at room temperature (25°C) and atmospheric pressure ($10^5$ Pa). The continuous phase may take various forms, such as a solution, an aqueous solution, a lotion, a milky lotion, a cream, a gel, a liquid gel, a paste, a serum, a suspension, a dispersion, a fluid, a milk, an emulsion (O/W or W/O form), or the like.

It is preferable that the continuous phase of the present invention can be an aqueous continuous phase. In another preferred embodiment, the continuous phase can be an aqueous solution.

In some specific embodiments of the present invention, the continuous phase of the present invention comprises a low amount of oils or is free of oils. For example, the continuous phase may comprise oils in an amount from 0% to 5% by weight, preferably from 0% to 3% by weight, more preferably from 0% to 1% by weight, in particular from 0% to 0.1% by weight, relative to the total weight of the continuous phase. In another embodiment, the continuous phase is free of any oils.

The viscosity of the continuous phase in the composition according to the present invention is not particularly limited, but in general, may range for example, from 4000 to 8000 Pa.s at 25°C. For the purpose of the present invention, the viscosity can be measured at 25°C with viscosimeters or rheometers preferably with cone-plate or parallel-plate geometry.

(Optional Ingredients)

The dispersed phases and the continuous phase in the composition may comprise optional ingredients in addition to the essential ingredients (a) to (d) as explained above.

- Oil

The composition according to the present invention may comprise 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 oils, those generally used in cosmetics can be used alone or in combination thereof. These oils may be volatile or non-volatile.

The oil may be present in the dispersed phases. In one embodiment, the dispersed phases includes at least one oil.ls.

The oil may be selected from polar or non-polar oils.

The term "polar oil" here means any lipophilic compound having, at 25°C, a solubility parameter $\delta_d$ characteristic of dispersive interactions of greater than 16 and a solubility parameter $\delta_p$ characteristic of polar interactions strictly greater than 0. The solubility parameters $\delta_d$ and $\delta_p$ are defined according to the Hansen classification.

The definition and calculation of the solubility parameters in the Hansen three-dimensional solubility space are described in the paper by C. M. Hansen: "The three dimensional solubility parameters", J. Paint Technol. 39, 105 (1967).

According to this Hansen space:
$\delta_D$ characterizes the London dispersion forces derived from the formation of dipoles induced during molecular impacts;
$\delta_p$ characterizes the Debye interaction forces between permanent dipoles and also the Keesom interaction forces between induced dipoles and permanent dipoles;
$\delta_h$ characterizes the specific interaction forces (such as hydrogen bonding, acid/base, donor/acceptor, etc.); and
$\delta_a$ is determined by the equation: $\delta a=(\delta_p^2+\delta_h^1)^{1/2}$. The parameters $\delta_p$, $\delta_h$, $\delta_d$ and $\delta_a$ are expressed in $(J/cm^3)^{1/2}$.

It may be preferable that the polar oil be selected from the group consisting of plant or animal oils, such as triglycerides, ester oils, ether oils and mixtures thereof, more preferably from the group consisting of ester oils, ether oils and mixtures thereof, and even more preferably from ester oils.

The polar oil may be chosen especially from the following oils:

- hydrocarbon-based polar oils such as phytostearyl esters, such as phytostearyl oleate, phytostearyl isostearate and lauroyl/octyldodecyl/phytostearyl glutamate (Ajinomoto, Eldew PS203), triglycerides consisting of fatty acid esters of glycerol, in particular the fatty acids of which may have chain lengths ranging from $C_4$ to $C_{36}$, and especially from $C_{18}$ to $C_{36}$, these oils possibly being linear or branched, and saturated or unsaturated; these oils may especially be heptanoic or octanoic triglycerides, wheatgerm oil, sunflower oil, grapeseed oil, sesame seed oil (820.6 g/mol), corn oil, apricot oil, castor oil, shea oil, avocado oil, olive oil, soybean oil, sweet almond oil, palm oil, rapeseed oil, cottonseed oil, hazelnut oil, macadamia oil, jojoba oil, alfalfa oil, poppy oil, pumpkin oil, marrow oil, blackcurrant oil, evening primrose oil, millet oil, barley oil, quinoa oil, rye oil, safflower oil, candlenut oil, passionflower oil or musk rose oil; shea butter; or alternatively caprylic/capric acid triglycerides, for instance those sold by the company Stearineries Dubois or those sold under the names Miglyol 810®, 812® and 818® by the company Dynamit Nobel;

- synthetic ethers containing from 10 to 40 carbon atoms, such as dicaprylyl ether;
- hydrocarbon-based esters of formula RCOOR' in which RCOO represents a carboxylic acid residue comprising from 2 to 40 carbon atoms, and R' represents a hydrocarbon-based chain containing from 1 to 40 carbon atoms, such as cetostearyl octanoate, isopropyl alcohol esters, such as isopropyl myristate or isopropyl palmitate, ethyl palmitate, isopropyl stearate or isostearate, isostearyl isostearate, octyl stearate, diisopropyl adipate, heptanoates, and especially isostearyl heptanoate, alcohol or polyalcohol octanoates, decanoates or ricinoleates, for instance propylene glycol dioctanoate, cetyl octanoate, tridecyl octanoate, 2-ethylhexyl 4-diheptanoate and palmitate, alkyl benzoate, polyethylene glycol diheptanoate, propylene glycol 2-diethyl hexanoate, and mixtures thereof, $C_{12}$ to $C_{15}$ alcohol benzoates, hexyl laurate, neopentanoic acid esters, for instance isodecyl neopentanoate, isotridecyl neopentanoate, isostearyl neopentanoate and 2-octyldodecyl neopentanoate, isononanoic acid esters, for instance isononyl isononanoate, isotridecyl isononanoate and octyl isononanoate, oleyl erucate, isopropyl lauroyl sarcosinate, diisopropyl sebacate, isocetyl stearate, isodecyl neopentanoate, isostearyl behenate, and myristyl myristate;
- polyesters obtained by condensation of an unsaturated fatty acid dimer and/or trimer and of diol, such as those described in patent application FR 0 853 634, in particular such as dilinoleic acid and 1,4-butanediol. Mention may especially be made in this respect of the polymer sold by Biosynthis under the name Viscoplast 14436H (INCI name: dilinoleic acid/butanediol copolymer), or else copolymers of polyols and of dimer diacids, and esters thereof, such as Hailuscent ISDA;
- polyol esters and pentaerythritol esters, for instance dipentaerythrityl tetrahydroxystearate/tetraisostearate;
- fatty alcohols containing from 12 to 26 carbon atoms, for instance octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol and oleyl alcohol;
- higher $C_{12}$-$C_{22}$ fatty acids, such as oleic acid, linoleic acid and linolenic acid, and mixtures thereof;
- fatty acids containing from 12 to 26 carbon atoms, for instance oleic acid;
- dialkyl carbonates, the two alkyl chains possibly being identical or different, such as dicaprylyl carbonate sold under the name Cetiol CC® by Cognis; and
- non-volatile oils of high molecular mass, for example between 400 and 10 000 g/mol, in particular between 650 and 10 000 g/mol, for instance:

  i) vinylpyrrolidone copolymers such as the vinylpyrrolidone/1-hexadecene copolymer, Antaron V-216 sold or manufactured by the company ISP (MW=7300 g/mol),

  ii) esters such as:

    a) linear fatty acid esters with a total carbon number ranging from 35 to 70, for instance pentaerythrityl tetrapelargonate (MW=697.05 g/mol),

    b) hydroxylated esters such as polyglycerol-2 triisostearate (MW=965.58 g/mol),

    c) aromatic esters such as tridecyl trimellitate (MW=757.19 g/mol), $C_{12}$-$C_{15}$ alcohol benzoate, the 2-phenylethyl ester of benzoic acid, and butyloctyl salicylate,

    d) esters of $C_{24}$-$C_{28}$ branched fatty acids or fatty alcohols such as those described in patent application EP-A-0 955 039, and especially triisoarachidyl citrate (MW=1033.76 g/mol), pentaerythrityl tetraisononanoate (MW=697.05 g/mol), glyceryl triisostearate (MW=891.51 g/mol), glyceryl tris(2-decyl)tetradecanoate (MW=1143.98 g/mol),

pentaerythrityl tetraisostearate (MW=1202.02 g/mol), polyglyceryl-2 tetraisostearate (MW=1232.04 g/mol) or else pentaerythrityl tetrakis(2-decyl)tetradecanoate (MW=1538.66 g/mol),
e) esters and polyesters of dimer diol and of monocarboxylic or dicarboxylic acid, such as esters of dimer diol and of fatty acid and esters of dimer diol and of dimer dicarboxylic acid, such as Lusplan DD-DA5® and Lusplan DD-DA7® sold by the company Nippon Fine Chemical and described in patent application US 2004-175 338, the content of which is incorporated into the present application by reference,

- and mixtures thereof.

The term "polar hydrocarbon-based oil" here means a polar oil formed essentially from, or even constituted by, carbon and hydrogen atoms, and optionally oxygen and nitrogen atoms, and not containing any silicon or fluorine atoms. It may contain alcohol, ester, ether, carboxylic acid, amine and/or amide groups.

It is preferable that the oil has a logP value of 7.0 or less, more preferably 6.5 or less, and even more preferably 6.0 or less. It may be preferable that theoil has a logP value of 1.0 or more, more preferably 1.5 or more, and even more preferably 2.0 or more. Thus, it may be preferable that the oil has a logP value of from 1.0 to 7.0, more preferably from 1.5 to 6.5, and even more preferably from 2.0 to 6.0.

A logP value is a value for the base-ten logarithm of the apparent octan-1-ol/water partition coefficient. The logP values are known and are determined by a standard test which determines the concentration of the oil in octan-1-ol and water. The logP may be calculated according to the method described in the article by Meylan and Howard: *Atom/Fragment contribution method for estimating octanol-water partition coefficients*, J. Pharm. Sci., 84: 83-92, 1995. This value may also be calculated using numerous commercially available software packages, which determine the logP as a function of the structure of a molecule. By way of example, mention may be made of the Epiwin software from the United States Environmental Agency.

The values may especially be calculated using the ACD (Advanced Chemistry Development) Solaris software V4.67; they may also be obtained from Exploring QSAR: hydrophobic, electronic and steric constants (ACS professional reference book, 1995). There is also an Internet site which provides estimated values (address: http://esc.syrres.com/interkow/kowdemo.htm).

The oil may have at least two moieties selected from the group consisting of an amide bond, an ester bond, and mixtures thereof. The amide bond here means -CONR- (R denotes a hydrogen atom or a linear or branched $C_1$-$C_{18}$ alkyl group, preferably a methyl group) and the ester bond here means -COO-. In other words, the oil may have two or more amide bonds, two or more ester bonds or a mixture of at least one amide bond and at least one ester bond.

The oil may have at least two moieties selected from the group consisting of an ether bond, an ester bond, and mixtures thereof. The ether bond here means -O- and the ester bond here means -COO-. In other words, the oil may have two or more ether bonds, two or more ester bonds or a mixture of at least one ether bond and at least one ester bond.

It may be preferable that the oil be selected from the group consisting of isopropyl lauroyl sarcosinate, octyldodecanol and a mixture thereof.

On the other hand, as an example of the non-polar oil, mention may be made of squalane.

The oil may be selected form triglycerides. Triglyceride is an ester derived from glycerol and three fatty acids, and may be referred to as triacylglycerol.

It is preferable that the triglyceride for the oil have at least one unsaturated fatty acid residue. In other words, it is preferable that the triglyceride for the oil be an ester derived from glycerol and at least one unsaturated fatty acid. Thus, the triglyceride for the oil may be (i) an ester derived from glycerol and one unsaturated fatty acid and two saturated fatty acids, (ii) an ester derived from glycerol and two unsaturated fatty acids and one saturated fatty acid, or (iii) an ester derived from three unsaturated fatty acids. If two or more unsaturated fatty acids are used, they may be the same or different. If two saturated fatty acids are used, they may be the same or different.

According to the present invention, "unsaturated fatty acid" means a fatty acid comprising at least one carbon-carbon double or triple bond. They are more particularly fatty acids with long chains, i.e., being able to have 8-32 carbon atoms, preferably 12-26 carbon atoms, and more preferably 14-22 carbon atoms.

The fatty acids can be monounsaturated such as petroselenic acid (C12), palmitoleic acid (C16) and oleic acid (C18), or can be polyunsaturated, i.e., presenting at least two carbon-carbon double bonds, such as linoleic acid (C18) and linolenic acid (C18).

It is more preferable that the triglyceride for the oil have at least one polyunsaturated fatty acid residue. In other words, it is more preferable that the triglyceride for the oil be an ester derived from glycerol and at least one polyunsaturated fatty acid.

The polyunsaturated fatty acid may be selected from ω-3, ω-6, and ω-9 fatty acids, characterized by the closest unsaturation position to the terminal methyl group.

The polyunsaturated fatty acid comprising between 18 and 22 carbon atoms, notably those selected from ω-3 and ω-6 fatty acids, may be more preferable.

Among the polyunsaturated fatty acids of the ω-3 series, mention may be made of α-linolenic acid (18:3, ω-3), stearidonic acid (18:4, ω-3), 5,8,11,14,17-eicosapentaenoic acid or EPA (20:5, ω-3), and 4,7,10,13,16,19-docosahexaenoic acid or DHA (22:6, ω-3), docosapentaenoic acid (22,5, ω-3), and n-butyl-5,11,14-eicosatrienonic acid.

Among the polyunsaturated fatty acids of the ω-6 series, mention may be made of linolenic acid with 18 carbon atoms and two unsaturations (18:2, ω-6), γ-linolenic acid with 18 carbon atoms and three unsaturations (18:3, ω-6), dihomogamalinolenic acid with 20 carbon atoms and 3 unsaturations (20:3, ω-6), arachidonic acid or 5,8,11,14 eicosatetraenoic acid (20:4, ω-6), and docosatetraenoic acid (22:4, ω-6).

As the ω-9 fatty acid, mention may be made of mead acid (20:3, ω-9).

The polyunsaturated fatty acid may be selected form α-linolenic acid, γ-linolenic acid, stearidonic acid, eicosapentaenoic acid, docosahexaenoic acid, mixtures thereof.

The amount of the polyunsaturated fatty acid among the fatty acids forming the fatty acid residues in the triglyceride for the oil may be 10% by weight or more, preferably 30% by weight or more, and more preferably 50% by weight or more, relative to the total weight of the fatty acids.

The weight ratio of the amount of polyunsaturated fatty acid(s)/the amount of monounsaturated fatty acid(s) among the fatty acids forming the fatty acid residues in the triglyceride for the oil may be more than 1.0, preferably more than 1.5, and more preferably more than 2.0.

The oil may be selected from plant oils.

For example, the oil may be selected from the group consisting of soybean oil, rapeseed oil, cotton seed oil, rice oil, corn oil, grape seed oil, sesame oil, linseed oil, and a mixture thereof.

It is preferable that the oil be selected from the group consisting of soybean oil, corn oil, cotton seed oil, grape seed oil, and a mixture thereof.

The amount of the oil(s) in the composition according to the present invention may range from 0.1% to 20% by weight, preferably from 0.5% to 15% by weight, more preferably from 1% to 10% by weight, relative to the total weight of the composition.

- Polysaccharide

The composition according to the present invention may comprise at least one polysaccharide other than the (d) cationic polymer. A single type of polysaccharide may be used, but two or more different types of polysaccharide may be used in combination.

The polysaccharide other than (d) cationic polymer may be present in the dispersed phases and/or in the continuous phase. Preferably, the polysaccharide are present in both of the dispersed phases and the continuous phase.

It is preferable that the polysaccharide be selected from polysaccharides derived from plants. In other words, it is preferable that the polysaccharide be of plant origin.

On the other hand, it is also preferable that the polysaccharide not be selected from cellulose and derivatives thereof.

According to the present invention, the term "polysaccharides derived from plants" especially means polysaccharides obtained from the plant kingdom (plants or algae), as opposed to polysaccharides obtained via biotechnology, as is the case, for example, for xanthan gum, which is produced especially by fermentation of a bacterium, Xanthomonas campestris.

As examples of polysaccharides of plant origin that may be used according to the present invention, mention may be made especially of:

a) algal extracts, such as alginates, carrageenans and agars, and mixtures thereof. Examples of carrageenans that may be mentioned include Satiagum UTC30® and

UTC10® from the company Degussa; an alginate that may be mentioned is the sodium alginate sold under the name Kelcosol® by the company ISP;

b) gums, such as guar gum and nonionic derivatives thereof (hydroxypropyl guar), gum arabic, konjac gum or mannan gum, gum tragacanth, ghatti gum, karaya gum or locust bean gum; examples that may be mentioned include the guar gum sold under the name Jaguar HP105® by the company Rhodia; the mannan and konjac gum® (1% gluconomannan) sold by the company GfN;

c) modified or unmodified starches, such as those obtained, for example, from cereals, for instance wheat, corn or rice, from legumes, for instance blonde pea, from tubers, for instance potato or cassava, and tapioca starches; dextrins, such as corn dextrins; examples that may especially be mentioned include the rice starch Remy DR I® sold by the company Remy; the corn starch B® from the company Roquette; the potato starch modified with 2-chloroethylaminodipropionic acid neutralized with sodium hydroxide, sold under the name Structure Solanace® by the company National Starch; the native tapioca starch powder sold under the name Tapioca pure® by the company National Starch;

d) dextrins, such as the dextrin extracted from corn under the name Index® from the company National Starch; and

mixtures thereof.

Preferably, the polysaccharide be chosen from algal extracts.

The algal extracts may be chosen from alginates, carrageenans and agars, and mixtures thereof. Preferably, alginates or agars, or mixtures thereof, may be used.

The amount of the polysaccharide(s) in the composition according to the present invention may range from 0.001% to 5% by weight, preferably from 0.005% to 3% by weight, more preferably from 0.01% to 1% by weight, relative to the total weight of the composition.

- Lipophilic Antioxidant Agent

The composition according to the present invention may comprise at least one lipophilic antioxidant agent. A single type of lipophilic antioxidant agent may be used, but two or more different types of lipophilic antioxidant agent may be used in combination.

The lipophilic antioxidant agent is different from the (a) retinoid.

The lipophilic antioxidant agent may preferably be present in the dispersed phases.

The lipophilic antioxidant agent means that the partition coefficient of the antioxidant agent between n-butanol and water is >1, more preferably >10 and even more preferably >100.

As the lipophilic antioxidant agents, mention may be made of, phenolic antioxidants which have a hindered phenol structure or a semi-hindered phenol structure within the molecule. As specific examples of such compounds, mention may be made of 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid) which has the INCI name of pentaerythrityl tetra-di-t-butyl hydroxyhydrocinnamate, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, mono- or di- or tri-(α-methylbenzyl)phenol, 2,2’-methylenebis(4-ethyl-6-tert-butylphenol), 2,2’-methylenebis(4-methyl-6-tert-butylphenol), 4,4’-butylidenebis(3-methyl-6-tert-butylphenol), 4,4’-thiobis(3-methyl-6-tert-butylphenol), 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, tris[N-(3,5-di-tert-butyl-4-hydroxybenzyl)]isocyanurate, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, butylidene-1,1bis[3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionate], octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionato]methane, triethylene glycol bis[3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionate], 3,9-bis{2-[3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy]-1,1-dimethylethyl}-2,4,8,10-tetraoxaspiro [5.5]undecane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 2,2-thiodiethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], N,N'-hexamethylenebis(3,5-di-tert-butyl-4-hydroxyhydrocinnamide), 1,6-hexanediol bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 1,3,5-tris[(4-tert-butyl-3-hydroxy-2,6-xylyl)methyl]-1,3,5-triazine-2,4,6-trione, 2,4-bis(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine, 2-tert-butyl-6-(3'-tert-butyl-5'-methyl-2'-hydroxybenzyl)-4-methylphenyl acrylate, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, 4,6-bis[(octylthio)methyl]-o-cresol, 2,4-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxybenzoate and 1,6-hexanediolbis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate].

As the lipophilic antioxidant agents, mention may also be made of: BHA (butylated hydroxyl anisole) and BHT (butylated hydroxyl toluene), vitamin E (or tocopherols and tocotrienol) and derivatives thereof, such as the phosphate derivative, for instance TPNA® sold by the company Showa Denko, coenzyme Q10 (or ubiquinone), idebenone, certain carotenoids such as lutein, astaxanthin, beta-carotene, and phenolic acids and derivatives (e. g., chlorogenic acid).

The lipophilic antioxidant agents that may also be mentioned include dithiolanes, for instance asparagusic acid, or derivatives thereof, for instance siliceous dithiolane derivatives, especially such as those described in patent application FR 2 908 769.

The lipophilic antioxidant agents that may also be mentioned include:
glutathione and derivatives thereof (GSH and/or GSHOEt), such as glutathione alkyl esters (such as those described in patent applications FR 2 704 754 and FR 2 908 769);
cysteine and derivatives thereof, such as N-acetylcysteine or L-2-oxothiazolidine-4-carboxylic acid. Reference may also be made to the cysteine derivatives described in patent applications FR 2 877 004 and FR 2 854 160;
certain enzymes for defending against oxidative stress, such as catalase, superoxide dismutase (SOD), lactoperoxidase, glutathione peroxidase and quinone reductases;
benzylcyclanones; substituted naphthalenones; pidolates (as described especially in patent application EP 0 511 118); caffeic acid and derivatives thereof, gamma-oryzanol; melatonin, sulforaphane and extracts containing it (excluding cress);
the diisopropyl ester of N,N'-bis(benzyl)ethylenediamine-N,N'-diacetic acid, as described especially in patent applications WO 94/11338, FR 2 698 095, FR 2 737 205 or EP 0 755 925;
deferoxamine (or desferal) as described in patent application FR 2 825 920.

The lipophilic antioxidant agents that may also be used are chalcones, more particularly phloretin or neohesperidin, the diisopropyl ester of N,N'-bis(benzyl)ethylenediamine-N,N'-diacetic acid or an extract of pinaster bark such as PYCNOGENOL®.

As examples of the lipophilic antioxidant agents, mention may also be made of pentaerythrityl tetra-di-t-butyl hydroxyhydrocinnamate, nordihydroguaiaretic acid, tocopherol, resveratrol, propyl gallate, butylated hydroxyl toluene, butylated hydroxyl anisole, ascorbyl palmitate, tocopherol, and mixtures thereof.

It is preferable that the lipophilic antioxidant agent be biodegradable. In this sense, BHT which is not biodegradable, is not preferable as the lipophilic antioxidant agent. Thus, it is preferable not to use BHT as the lipophilic antioxidant agent. Furthermore, it is preferable that the composition according to the present invention is free from BHT.

The term "free from" here means that the composition according to the present invention may contain a limited amount of BHT. However, it is preferable that the amount of BHT be limited such that it is less than 1% by weight, more preferably less than 0.1% by weight, and even more preferably less than 0.01% by weight, relative to the total weight of the composition. It is most preferable that the composition according to the present invention comprise no BHT.

It is more preferable that the lipophilic antioxidant agent be selected from tocopherol, pentaerythrityl tetra-di-t-butyl hydroxyhydrocinnamate, and a mixture thereof.

The amount of the lipophilic antioxidant agent(s) in the composition according to the present invention may range from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 1% by weight, relative to the total weight of the composition.

- Chelating Agent

The composition according to the present invention may comprise at least one chelating agent. A single type of chelating agent may be used, but two or more different types of chelating agents may be used in combination.

The chelating agent may be present in the continuous phase of the present invention.

As the chelating agent, mention may be made of

(i) aminocarboxylic acids such as the compounds having the following INCI name: diethylenetriaminepentaacetic acid (DTPA), ethylenediaminedisuccinic acid (EDDS) and trisodium ethylenediamine disuccinate such as Octaquest E30 from Octel, ethylenediaminetetraacetic acid (EDTA), ethylenediamine-N,N'-diglutaric acid (EDDG), glycinamide-N,N'-disuccinic acid (GADS), 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS), ethylenediamine-N,N'-bis(ortho-hydroxyphenylacetic acid) (EDDHA), N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED), nitrilotriacetic acid (NTA), methylglycine diacetic acid (MGDA), N-2-hydroxyethyl-N,N-diacetic acid and glyceryl imino diacetic acid (as described in documents EP-A-317 542 and EP-A-399 133), iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid (as described in EP-A-516 102), beta-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid and aspartic acid-N-monoacetic acid (described in EP-A-509 382), chelating agents based on iminodisuccinic acid (IDSA) (as described in EP-A-509 382), ethanoldiglycine acid, phosphonobutane tricarboxylic acid, such as the compound sold by Bayer under the reference Bayhibit AM, tetrasodium glutamate diacetate (GLDA) such as Dissolvine GL38 or 45S from Akzo Nobel,

(ii) chelating agents based on mono- or polyphosphonic acid, such as the compounds having the following INCI name: diethylenetriaminepenta(methylenephosphonic acid) (DTPMP), ethane-1-hydroxy-1,1,2-triphosphonic acid (E1HTP), [0263]ethane-2-hydroxy-1,1,2-triphosphonic acid (E2HTP), ethane-1-hydroxy-1,1-diphosphonic acid (EHDP), ethane-1,1,2-triphosphonic acid (ETP), ethylenediaminetetramethylenephosphonic acid (EDTMP), and hydroxyethane-1,1-diphosphonic acid (HEDP), and

(iii) chelating agents based on polyphosphoric acid, such as the compounds having the following INCI name: sodium tripolyphosphate (STP), tetrasodium diphosphate, hexametaphosphoric acid, sodium metaphosphate, phytic acid, salts and derivatives thereof,

and
mixtures thereof.

It is more preferable that the chelating agent be trisodium ethylenediamine disuccinate.

The amount of the chelating agent(s) in the composition according to the present invention may range from 0.001% to 3% by weight, preferably from 0.005% to 2% by weight, more preferably from 0.01% to 1% by weight, relative to the total weight of the composition.

- Water

The composition according to the present invention may comprise water.

The water in the composition according to the present invention can form a continuous phase. The water also may be present in the dispersed phases.

The amount of the water in the composition according to the present invention may be 50% by weight or more, preferably 55% by weight or more, and more preferably 60% by weight or more, relative to the total weight of the composition.

On the other hand, the amount of the water in the composition according to the present invention may be 90% by weight or less, preferably 85% by weight or less, and more preferably 80% by weight or less, relative to the total weight of the composition.

The amount of water in the composition according to the present invention may range from 50% to 90% by weight, preferably from 55% to 85% by weight, more preferably from 60% to 80% by weight, relative to the total weight of the composition.

- Polyol

The composition according to the present invention may further comprise at least one polyol which is different from polyphenol. A single type of polyol may be used, but two or more different types of polyol may be used in combination.

The polyol may be present in the continuous phase.

The term “polyol” here means an alcohol having two or more hydroxy groups, and does not encompass a saccharide or a derivative thereof. The derivative of a saccharide includes a sugar alcohol which is obtained by reducing one or more carbonyl groups of a saccharide, as well as a saccharide or a sugar alcohol in which the hydrogen atom or atoms in one or more hydroxy groups thereof has or have been replaced with at least one substituent such as an alkyl group, a hydroxyalkyl group, an alkoxy group, an acyl group or a carbonyl group.

The polyol may be a $C_2$-$C_{12}$ polyol, preferably a $C_2$-$C_9$ polyol, comprising at least 2 hydroxy groups, and preferably 2 to 5 hydroxy groups.

The polyol may be a natural or synthetic polyol. The polyol may have a linear, branched or cyclic molecular structure.

The polyol may be selected from glycerins and derivatives thereof, and glycols and derivatives thereof. The polyol may be selected from the group consisting of glycerin, diglycerin, polyglycerin, ethyleneglycol, diethyleneglycol, propyleneglycol, dipropyleneglycol, butyleneglycol, pentyleneglycol, hexyleneglycol, caprylylglycol, 1,3-propanediol, 1,5-pentanediol, polyethyleneglycol (5 to 50 ethyleneoxide groups), and mixtures thereof.

The amount of the polyol(s) in the composition according to the present invention may be 0.1% by weight or more, preferably 0.5% by weight or more, and more preferably 1% by weight or more, relative to the total weight of the composition.

On the other hand, the amount of the polyol(s) in the composition according to the present invention may be 30% by weight or less, preferably 20% by weight or less, and more preferably 10% by weight or less, relative to the total weight of the composition.

Thus, the polyol(s) may be present in the composition according to the present invention in an amount ranging from 0.1% to 30% by weight, and preferably from 0.5% to 20% by weight, such as from 1% to 10% by weight, relative to the total weight of the composition.

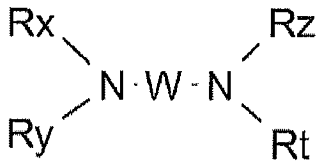
- pH Adjusting Agent

The pH of the composition according to the present invention may be adjusted to the desired value using at least one pH adjusting agent, such as an acidifying or a basifying agent, for example, which are commonly used in cosmetic products.

The pH of the composition according to the present invention may be 9.0 or less, preferably 8.5 or less, more preferably 8.0 or less, even more preferably 7.5 or less, and in particular 7.0 or less, and may be 2.5 or more, preferably 3.0 or more, and more preferably 3.5 or more at 25°C.

The pH adjusting agent may be present in the continuous phase of the present invention. Among the acidifying agents, mention may be made, by way of example, of mineral or organic acids such as hydrochloric acid, ortho-phosphoric acid, sulfuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid, and lactic acid, and sulfonic acids.

Among the basifying agents, mention may be made, by way of example, of hydroxides of an alkali metal or an alkaline-earth metal, for instance sodium hydroxide or potassium hydroxide; quaternary ammonium hydroxides and guanidinium hydroxide; alkali metal silicates, such as sodium metasilicates; carbonates and bicarbonates, particularly of a primary amine, secondary amine or tertiary amine, of an alkali metal or alkaline-earth metal, or of ammonium; and the compounds of the following formula:



in which
W is a $C_1$-$C_6$ alkylene residue optionally substituted with a hydroxyl group or a $C_1$-$C_6$ alkyl group;
Rx, Ry, Rz and Rt, which may be identical or different, represent a hydrogen atom or a $C_1$-$C_6$ alkyl, $C_1$-$C_6$ hydroxyalkyl or $C_1$-$C_6$ aminoalkyl group. Mention may especially be made of 1,3-diaminopropane, 1,3-diamino-2-propanol, spermine and spermidine.

The pH adjusting agent(s) may be used in an amount ranging from 0.001% to 15% by weight, preferably from 0.01% to 10% by weight, more preferably from 0.1% to 5% by weight, and in particular from 1% to 5% by weigh, relative to the total weight of the composition.

- Nonionic surfactant

The composition according to the present invention may comprise at least one nonionic surfactant. If two or more nonionic surfactants are used, they may be the same or different.

The nonionic surfactant may be present in the continuous phase of the present invention.

The nonionic surfactant may have an HLB (Hydrophilic Lipophilic Balance) value of from 3.0 to 7.0, preferably from 3.5 to 6.0, and more preferably from 4.0 to 5.0. Alternatively, the nonionic surfactant may have an HLB value of from 11 to 17, preferably from 12 to 16, and more preferably from 13 to 15. If two or more nonionic surfactants are used, the HLB value is determined by the weighted average of the HLB values of all the nonionic surfactants.

The nonionic surfactant may be chosen from:
(1) surfactants chosen from polyglyceryl fatty acid esters, polyoxyalkylenated alkyl glycerides, and polyoxyalkylenated fatty ethers;
(2) mixed esters of fatty acid or of fatty alcohol, of carboxylic acid and of glycerol;
(3) fatty acid esters of sugars and fatty alcohol ethers of sugars;
(4) surfactants chosen from fatty esters of sorbitan and oxyalkylenated fatty esters of sorbitan, and oxyalkylenated fatty esters;
(5) block copolymers of ethylene oxide (A) and of propylene oxide (B),
(6) polyoxyethylenated (1-40 EO) and polyoxypropylenated (1-30 PO) alkyl ($C_{16}$-$C_{30}$) ethers,
(7) silicone surfactants, and
(8) mixtures thereof.

The surfactant (1) may be a fluid at a temperature of less than or equal to 45°C.

The surfactant (1) may be in particular:
- polyglyceryl fatty acid esters of at least one, preferably one, fatty acid comprising at least one saturated or unsaturated, linear or branched $C_8$-$C_{22}$ hydrocarbon group such as $C_8$-$C_{22}$ alkyl or alkenyl group, preferably $C_8$-$C_{18}$ alkyl or alkenyl group, and more preferably $C_8$-$C_{12}$ alkyl or alkenyl group, and of 2-12 glycerols, preferably 2-10 glycerols and more preferably 2-8 glycerols;

- polyoxyethylenated (PEGylated) alkyl glycerides such as polyethylene glycol derivatives of a mixture of mono-, di- and tri-glycerides of caprylic and capric acids (preferably 2 to 30 ethylene oxide units, more preferably 2 to 20 ethylene oxide units, and even more preferably 2 to 10 ethylene oxide units), e.g., PEG-6 Caprylic/Capric Glycerides, PEG-7 Caprylic/Capric Glycerides, and PEG-7 glyceryl cocoate;
- polyoxyethylenated fatty ethers of at least one, preferably one, fatty alcohol comprising at least one saturated or unsaturated, linear or branched $C_8$-$C_{22}$ hydrocarbon group such as $C_8$-$C_{22}$ alkyl or alkenyl group, preferably $C_8$-$C_{18}$ alkyl or alkenyl group, and more preferably $C_8$-$C_{12}$ alkyl or alkenyl group, and of 2 to 60 ethylene oxides, preferably from 2 to 30 ethylene oxides, and more preferably from 2 to 10 ethylene oxides; and
- mixtures thereof.

It is preferable that the polyglyceryl fatty acid ester have a polyglycerol moiety derived from 2 to 30 glycerols, more preferably from 2 to 20 glycerols, and further more preferably 4 to 12 glycerols.

The polyglyceryl fatty acid ester may be chosen from the mono, di and tri esters of saturated or unsaturated acid, preferably saturated acid, including 8 to 22 carbon atoms, preferably 8 to 18 carbon atoms, and more preferably 8 to 12 carbon atoms, such as caprylic acid, capric acid, lauric acid, oleic acid, stearic acid, isostearic acid, and myristic acid. As an example of the polyglyceryl fatty acid ester, mention can be made of polyglyceryl-10 isostearate.

The polyoxyalkylenated fatty ethers, preferably polyoxyethylenated fatty ethers, may comprise from 2 to 60 ethylene oxide units, preferably from 2 to 30 ethylene oxide units, and more preferably from 2 to 10 ethylene oxide units. The fatty chain of the ethers may be chosen in particular from lauryl, behenyl, arachidyl, stearyl and cetyl units, and mixtures thereof, such as cetearyl. Examples of ethoxylated fatty ethers which may be mentioned are lauryl alcohol ethers comprising 2, 3, 4, and 5 ethylene oxide units (CTFA names: Laureth-2, Laureth-3, Laureth-4, and Laureth-5), such as the products sold under the names Nikkol BL-2 by the company Nikko Chemicals, Emalex 703 by the company Nihon Emulsion Co., Ltd, Nikkol BL-4 by the company Nikko Chemicals, and EMALEX 705 by the company Nihon Emulsion Co., Ltd. Mention may also be made of, for example, stearyl alcohol ethers comprising 2, 3, 4, 5, and 20 ethylene oxide units (CTFA names: Steareth-2, Steareth-3, Steareth-4, Steareth-5, and Steareth-20), such as the products sold under the names Emalex 602 by the company Nihon Emulsion Co., Ltd., Emalex 603 by the company Nihon Emulsion Co., Ltd, Nikkol BS-4 by the company Nikko Chemicals, and Emalex 605 by the company Nihon Emulsion Co., Ltd.

It is also preferred that polyoxyalkylenated fatty ethers be polyethylene glycol ethers of $C_8$-$C_{24}$ fatty alcohol or alcohols and polyoxyalkylenated derivatives thereof and polypropylene glycol ethers of $C_4$-$C_{24}$ fatty alcohol or alcohols such as PPG-14 butyl ether and PPG-15 stearyl ether.

The (2) mixed esters of fatty acids, or of fatty alcohol, of carboxylic acid and of glycerol, which can be used as the above nonionic surfactant, may be chosen in particular from the group comprising mixed esters of fatty acid or of fatty alcohol with an alkyl or alkenyl chain containing from 8 to 22 carbon atoms, preferably from 8 to 18 carbon atoms, and more preferably from 8 to 12 carbon atoms, and of α-hydroxy acid and/or of succinic acid, with glycerol. The α-hydroxy acid may be, for example, citric acid, lactic acid, glycolic acid or malic acid, and mixtures thereof.

The alkyl chain of the fatty acids or alcohols from which are derived the mixed esters which can be used in the nanoemulsion of the present invention may be linear or branched, and saturated or unsaturated. They may especially be stearate, isostearate, linoleate, oleate, behenate, arachidonate, palmitate, myristate, laurate, caprate, isostearyl, stearyl, linoleyl, oleyl, behenyl, myristyl, lauryl or capryl chains, and mixtures thereof.

As examples of mixed esters which can be used in the nanoemulsion of the present invention, mention may be made of the mixed ester of glycerol and of the mixture of citric acid, lactic acid, linoleic acid and oleic acid (CTFA name: Glyceryl citrate/lactate/linoleate/oleate) sold by the company Hüls under the name Imwitor 375; the mixed ester of succinic acid and of isostearyl alcohol with glycerol (CTFA name: Isostearyl diglyceryl succinate) sold by the company Hüls under the name Imwitor 780 K; the mixed ester of citric acid and of stearic acid with glycerol (CTFA name: Glyceryl stearate citrate) sold by the company Hüls under the name Imwitor 370; the mixed ester of lactic acid and of stearic acid with glycerol (CTFA name: Glyceryl stearate lactate) sold by the company Danisco under the name Lactodan B30 or Rylo LA30.

The (3) fatty acid esters of sugars, which can be used as the above nonionic surfactant, may be chosen in particular from the group comprising esters or mixtures of esters of $C_8$-$C_{22}$ fatty acid and of sucrose, of maltose, of glucose or of fructose, and esters or mixtures of esters of $C_{14}$-$C_{22}$ fatty acid and of methylglucose.

The $C_8$-$C_{22}$ or $C_{14}$-$C_{22}$ fatty acids forming the fatty unit of the esters which can be used in the present invention comprise a saturated or unsaturated linear alkyl or alkenyl chain containing, respectively, from 8 to 22 or from 14 to 22 carbon atoms. The fatty unit of the esters may be chosen in particular from stearates, behenates, arachidonates, palmitates, myristates, laurates and caprates, and mixtures thereof. Stearates are preferably used.

The (3) fatty alcohol ethers of sugars, which can be used as the above nonionic surfactant, may be solid at a temperature of less than or equal to 45°C and may be chosen in particular from the group comprising ethers or mixtures of ethers of $C_8$-$C_{22}$ fatty alcohol and of glucose, of maltose, of sucrose or of fructose, and ethers or mixtures of ethers of a $C_{14}$-$C_{22}$ fatty alcohol and of methylglucose. These are in particular alkylpolyglucosides.

The $C_8$-$C_{22}$ or $C_{14}$-$C_{22}$ fatty alcohols forming the fatty unit of the ethers which may be used in the nanoemulsion of the present invention comprise a saturated or unsaturated, linear alkyl or alkenyl chain containing, respectively, from 8 to 22 or from 14 to 22 carbon atoms. The fatty unit of the ethers may be chosen in particular from decyl, cetyl, behenyl, arachidyl, stearyl, palmityl, myristyl, lauryl, capryl and hexadecanoyl units, and mixtures thereof, such as cetearyl. As an example of the fatty alcohol ethers of sugars, mention can be made of caprylyl/capryl glucoside.

The (4) fatty esters of sorbitan and oxyalkylenated fatty esters of sorbitan which may be used as the above nonionic surfactant may be chosen from the group comprising $C_{16}$-$C_{22}$ fatty acid esters of sorbitan and oxyethylenated $C_{16}$-$C_{22}$ fatty acid esters of sorbitan. They may be formed from at least one fatty acid comprising at least one saturated linear alkyl chain containing, respectively, from 16 to 22 carbon atoms, and from sorbitol or from ethoxylated sorbitol. The oxyethylenated esters may generally comprise from 1 to 100 ethylene glycol units and preferably from 2 to 40 ethylene oxide (EO) units.

These esters may be chosen in particular from stearates, behenates, arachidates, palmitates, and mixtures thereof. Stearates and palmitates are preferably used.

The (4) oxyalkylenated fatty esters, preferably ethoxylated fatty esters, which may be used as the above nonionic surfactant, may be esters formed from 1 to 100 ethylene oxide units, preferably from 2 to 60 ethylene oxide units, and more preferably from 2 to 30 ethylene oxide units, and from at least one fatty acid chain containing from 8 to 22 carbon atoms, preferably from 8 to 18 carbon atoms, and more preferably from 8 to 12 carbon atoms. The fatty chain in the esters may be chosen in particular from stearate, behenate, arachidate and palmitate units, and mixtures thereof. Examples of ethoxylated fatty esters which may be mentioned are the ester of stearic acid comprising 40 ethylene oxide units, such as the product sold under the name Myrj 52 (CTFA name: PEG-40 stearate) by the company ICI, as well as the ester of behenic acid comprising 8 ethylene oxide units (CTFA name: PEG-8 behenate), such as the product sold under the name Compritol HD5 ATO by the company Gattefosse.

The (5) block copolymers of ethylene oxide (A) and of propylene oxide (B), which may be used as the above nonionic surfactant, may be chosen in particular from block copolymers of formula (I):

$HO(C_2H_4O)_x(C_3H_6O)_y(C_2H_4O)_zH$ (I)

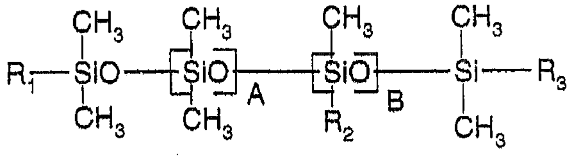
in which x, y and z are integers such that x+z ranges from 2 to 100 and y ranges from 14 to 60, and mixtures thereof, and more particularly from the block copolymers of formula (I) having an HLB value ranging from 8.0 to 14.0.

The (6) polyoxyethylenated (1-40 EO) and polyoxypropylenated (1-30 PO) alkyl ($C_{16}$-$C_{30}$) ethers, which may be used as the above nonionic surfactant, may be selected from the group consisting of:
PPG-6 Decyltetradeceth-30; Polyoxyethylene (30) Polyoxypropylene (6) Tetradecyl Ether such as those sold as Nikkol PEN-4630 from Nikko Chemicals Co.,
PPG-6 Decyltetradeceth-12; Polyoxyethylene (12) Polyoxypropylene (6) Tetradecyl Ether such as those sold as Nikkol PEN-4612 from Nikko Chemicals Co.,
PPG-13 Decyltetradeceth-24; Polyoxyethylene (24) Polyoxypropylene (13) Decyltetradecyl Ether such as those sold as UNILUBE 50MT-2200B from NOF Corporation,
PPG-6 Decyltetradeceth-20; Polyoxyethylene (20) Polyoxypropylene (6) Decyltetradecyl Ether such as those sold as Nikkol PEN-4620 from Nikko Chemicals Co.,
PPG-4 Ceteth-1; Polyoxyethylene (1) Polyoxypropylene (4) Cetyl Ether such as those sold as Nikkol PBC-31 from Nikko Chemicals Co.,
PPG-8 Ceteth-1; Polyoxyethylene (1) Polyoxypropylene (8) Cetyl Ether such as those sold as Nikkol PBC-41 from Nikko Chemicals Co.,
PPG-4 Ceteth-10; Polyoxyethylene (10) Polyoxypropylene (4) Cetyl Ether such as those sold as Nikkol PBC-33 from Nikko Chemicals Co.,
PPG-4 Ceteth-20; Polyoxyethylene (20) Polyoxypropylene (4) Cetyl Ether such as those sold as Nikkol PBC-34 from Nikko Chemicals Co.,
PPG-5 Ceteth-20; Polyoxyethylene (20) Polyoxypropylene (5) Cetyl Ether such as those sold as Procetyl AWS from Croda Inc.,
PPG-8 Ceteth-20; Polyoxyethylene (20) Polyoxypropylene (8) Cetyl Ether such as those sold as Nikkol PBC-44 from Nikko Chemicals Co., and
PPG-23 Steareth-34; Polyoxyethylene Polyoxypropylene Stearyl Ether (34 EO) (23 PO) such

as those sold as Unisafe 34S-23 from Pola Chemical Industries. They can provide a composition with stability over a long time, even though the temperature of the composition is increased and decreased in a relatively short period of time.

As (7) silicone surfactants, which may be used as the above nonionic surfactant, mention may be made of those disclosed in documents US-A-5364633 and US-A-5411744.

The (7) silicone surfactant as the above nonionic surfactant may preferably be a compound of formula (I):

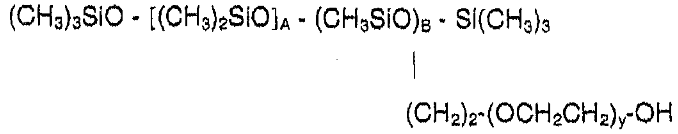


$$R_1-\overset{CH_3}{\underset{CH_3}{Si}}O-\left[\overset{CH_3}{\underset{CH_3}{Si}}O\right]_A-\left[\overset{CH_3}{\underset{R_2}{Si}}O\right]_B-\overset{CH_3}{\underset{CH_3}{Si}}-R_3 \qquad (I)$$

in which:
$R_1$, $R_2$ and $R_3$, independently of each other, represent a $C_1$-$C_6$ alkyl radical or a radical -$(CH_2)_x$-$(OCH_2CH_2)_y$-$(OCH_2CH_2CH_2)_z$-$OR_4$, at least one radical $R_1$, $R_2$ or $R_3$ not being an alkyl radical; $R_4$ being a hydrogen, an alkyl radical or an acyl radical;
A is an integer ranging from 0 to 200;
B is an integer ranging from 0 to 50; with the proviso that A and B are not simultaneously equal to zero;
x is an integer ranging from 1 to 6;
y is an integer ranging from 1 to 30;
z is an integer ranging from 0 to 5.

According to one preferred embodiment of the present invention, in the compound of formula (I), the alkyl radical is a methyl radical, x is an integer ranging from 2 to 6, and y is an integer ranging from 4 to 30.

As examples of silicone surfactants of formula (I), mention may be made of the compounds of formula (II):



$$(CH_3)_3SiO-[(CH_3)_2SiO]_A-(CH_3\underset{\substack{|\\(CH_2)_2-(OCH_2CH_2)_y-OH}}{SiO})_B-Si(CH_3)_3 \qquad (II)$$

in which A is an integer ranging from 20 to 105, B is an integer ranging from 2 to 10, and y is an integer ranging from 10 to 20.

As examples of silicone surfactants of formula (I), mention may also be made of the compounds of formula (III):

$H$-$(OCH_2CH_2)_y$-$(CH_2)_3$-$[(CH_3)_2SiO]_{A'}$-$(CH_2)_3$-$(OCH_2CH_2)_y$-$OH$ (III)

in which A' and y are integers ranging from 10 to 20.

The nonionic surfactant(s) may be present in the composition according to the present invention in an amount of 0.01% to 5% by weight, preferably 0.05% to 3% by weight, and more preferably 0.1% to 1% by weight, relative to the total weight of the composition.

- Additives

The composition according to the present invention, in particular the continuous phase of the present invention, may also include various adjuvants conventionally used in cosmetic and dermatological compositions, such as anionic, non-ionic, cationic, and amphoteric or zwitterionic polymers, anionic, cationic, amphoteric, and nonionic surfactants, hydrophilic antioxidants, hydrophilic active ingredients, coloring agents, thickeners, sequestering agents, fragrances, dispersing agents, conditioning agents, film-forming agents, preservatives, co-preservatives, photo-stabilizers, such as tris(tetramethylhydroxypiperidinol) citrate, and mixtures thereof, except for the ingredients as explained above.

As the hydrophilic active ingredient, mention may be made of Vitamin B3 and derivatives, ascorbic acid and derivatives thereof, resorcinol derivatives, C-glycoside derivatives, salicylic acid and derivatives thereof, α-hydroxy acids, niacinamide and mixtures thereof.

The hydrophilic active ingredient may be present in the continuous phase of the present invention.

The amount of the additives included in the composition according to the present invention is not limited, but may be from 0.01 to 30% by weight relative to the total weight of the composition according to the present invention.

The composition according to the present invention can be prepared by mixing the essential ingredient(s) as explained above, and optional ingredient(s), if necessary, as explained above.

The method and means to mix the above essential and optional ingredients are not limited. Any conventional method and means can be used to mix the above essential and optional ingredients to prepare the composition according to the present invention. The dispersion composition according to the present invention can be prepared by mixing the dispersed phases and the continuous phase.

[Process and Use]

It is preferable that the composition according to the present invention be a cosmetic or dermatological composition, preferably a cosmetic composition, and more preferably a cosmetic composition for a keratin substance such as skin.

The composition according to the present invention can be used for a non-therapeutic process, such as a cosmetic process, for treating a keratin substance such as skin, hair, mucous membranes, nails, eyelashes, eyebrows and/or scalp, by being applied to the keratin substance.

Thus, the present invention also relates to a cosmetic process for treating a keratin substance such as skin, comprising the step of applying the composition according to the present invention to the keratin substance.

The composition according to the present invention may be used as an anti-aging, anti-wrinkling, or turnover promoting product for a keratinous substance such as skin. In particular, the composition according to the present invention may be used as an anti-wrinkling skin cosmetic product.

The above explanations regarding the ingredients (a) to (d), as well as the optional ingredients, for the composition according to the present invention can apply to those for the above uses and processes according to the present invention.

## 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.

[Example 1 and Comparative Examples 1-3]

The following compositions according to Example 1 and Comparative Examples 1-3 were prepared in accordance with the following protocol. The numerical values for the amounts of the components shown in Table 1 are all based on "% by weight" as active raw materials.

The preparations of the dispersion compositions were performed as follows:
(1) mixing isopropyl lauroyl sarcosinate, octyldodecanol, glycine soya (soybean) oil, butylparaben, and tocopherol, and heat at 75-80 °C to form a uniform mixture, then cool to room temperature and introduce retinol to obtain a uniform core-forming composition;
(2) mixing water, agar, and alginate, and heat at 75-80 °C, to form a uniform shell-forming composition;
(3) coextruding the uniform core-forming composition and the uniform shell-forming composition to form capsules as a plurality of dispersed phases;
(4) mixing the ingredients listed as continuous phase in Table 1 to prepare a continuous phase; and
(5) mixing the dispersed phases with the continuous phase to prepare the dispersion.

[Evaluations]

(Thermo- and Photo- Stability)

Each of the compositions according to Example 1 and Comparative Examples 1-3 was filled into a transparent vessel and was held under temperature conditions of 55°C for 2 weeks, or under irradiation with UV rays using Suntest CPS (TOYO SEIKI, 765W/m$^2$) for 24 hours at room temperature. After the storage, each of the compositions was homogenized by a homogenizer, 15,000 prm for 10 minute to break the capsules therein to prepare samples for HPLC analysis. The residual rate (%) of retinol and ascorbic acid after storage was measured by HLPC and calculated as a function of the reference % (those stored at 4°C for 2 weeks) measured by HPLC. The retinol and ascorbic acid residual rate (%) thus calculated for each composition was evaluated in accordance with the following criteria.

- Thermo-Stability (storage at 55°C for 2 weeks)

OK: 90 ≤
NG: < 90

- Photo-Stability (storage under sunlight for 24 hours)

OK: 75 ≤
NG: < 75

(Dispersion and Color Stability)

Each of the compositions according to Example 1 and Comparative Examples 1-3 was filled into a glass bottle, and each of the glass bottles was held under temperature conditions of 55°C for 2 weeks.

Each glass bottle was then investigated in terms of dispersion and color stability by visual observation. Regarding the dispersion stability, the sample was investigated if the dispersion (capsules) was evenly dispersed in the composition or not. Regarding color stability, the sample was investigated if there is a color evolution or not. These properties were then evaluated in accordance with the following criteria.

- Dispersion Stability

OK: capsules were evenly dispersed in the composition.
NG: capsules were floating or precipitated in the composition.

- Color Evolution

OK: the color did not change or slightly changed into light brown.
NG: the color changed into brown.

The results are shown in Table 1.

Table 1

| Ingredients | | Ex. 1 | Comp. Ex. 1 | Comp. Ex. 2 | Comp. Ex. 3 |
|---|---|---|---|---|---|
| Dispersed Phase | Isopropyl Lauroyl Sarcosinate | 0.522 | 0.522 | 0.522 | 0.522 |
| | Octyldodecanol | 0.087 | 0.087 | 0.087 | 0.087 |
| | Glycine Soya (Soybean) Oil | 3.150 | 3.150 | 3.150 | 3.150 |
| | Retinol | 0.2 | 0.2 | 0.2 | 0.2 |
| | Butylparaben | 0.131 | 0.131 | 0.131 | 0.131 |
| | Tocopherol | 0.261 | 0.261 | 0.261 | 0.261 |
| | Water | 2.853 | 2.853 | 2.853 | 2.853 |
| | Agar | 0.032 | 0.032 | 0.032 | 0.032 |
| | Alginate | 0.015 | 0.015 | 0.015 | 0.015 |
| Continuous Phase | Water | qs100 | qs100 | qs100 | qs100 |
| | Ascorbic Acid | 12 | - | 12 | 12 |
| | Pentylene Glycol | 3 | 3.5 | 3 | 3 |
| | Sodium Hydroxide | 2.7 | - | 2.7 | 2.7 |
| | Propanediol | 1.254 | 1.254 | 1.254 | 1.254 |
| | Glucosylrutin (And) Rutin | 0.9 | 0.9 | - | 0.9 |
| | Hydroxypropyl Guar Hydroxypropyltrimonium Chloride | 0.7 | 0.7 | 0.7 | - |
| | Hydroxyacetophenone | 0.536 | 0.536 | 0.536 | 0.536 |
| | Xanthan Gum (And) Ceratonia Siliqua (Carob) Gum | 0.308 | 0.304 | 0.308 | 0.308 |
| | Caprylyl/Capryl Glucoside (and) Polyglyceryl-10 Isostearate (and) Sodium Dilauramidoglutamide Lysine | 0.3 | 0.3 | 0.3 | 0.3 |
| | Chlorphenesin | 0.279 | 0.279 | 0.279 | 0.279 |
| | Caprylyl Glycol | 0.205 | 0.205 | 0.205 | 0.205 |
| | Fragrance | 0.1 | 0.1 | 0.1 | 0.1 |
| | Niacinamide | 0.097 | 0.097 | 0.097 | 0.097 |
| | Trisodium Ethylenediamine Disuccinate | 0.062 | 0.062 | 0.062 | 0.062 |
| | PPG-6-Decyltetradeceth-30 | 0.05 | 0.05 | 0.05 | 0.05 |
| | Caffeine | 0.039 | 0.039 | 0.039 | 0.039 |
| | Tris(Tetramethylhydroxypiperidinol) Citrate | 0.039 | 0.039 | 0.039 | 0.039 |
| Retinol Residual Rate (%) | 55°C, 2 weeks | OK | NG | OK | OK |
| | UV rays (765W/m$^2$), 24 hours | OK | OK | NG | OK |
| Ascorbic Acid Residual Rate (%) | 55°C, two weeks | OK | - | OK | OK |
| | UV rays (765W/m$^2$), 24 hours | OK | - | OK | OK |
| Dispersion Stability at 55°C, 2 weeks | | OK | OK | NG | NG |
| Color Evolution at 55°C, 2 weeks | | OK | OK | OK | OK |

The composition according to Example 1 which included the ingredients (a) to (d) explained above, maintained a stable dispersion form without floating or precipitation of the dispersed phases, and could maintain the retinoid therein at a sufficient residual rate even under light exposure and at high temperature.

On the other hand, the composition according to Comparative Example 1, which did not include the ingredient (c) could not maintain the ingredient (a) at a sufficient residual rate at the high temperature.

The composition according to Comparative Example 2 which did not include the ingredient (b), could not maintain the ingredient (a) at a sufficient residual rate under UV ray irradiation.

The composition according to Comparative Example 3 which did not include the ingredient (d), could not maintain the dispersion form and the capsules floated in the composition.

# CLAIMS

1. A dispersion composition comprising a continuous phase and a plurality of dispersed phases, comprising:
   (a) at least one retinoid;
   (b) at least one compound which is capable of providing a solution thereof with a transmittance of 10% or less, preferably 5% or less, and more preferably 2% or less, for light with a wavelength of from 290 to 420 nm, along a light path length of 10 mm, the concentration of the compound in the solution being 0.9% by weight relative to the total weight of the solution;
   (c) at least one hydrophilic antioxidant agent other than the ingredient (b); and
   (d) at least one cationic polymer.

2. The composition according to Claim 1, wherein the (a) retinoid is present in the dispersed phases.

3. The composition according to Claim 1 or 2, wherein the (b) compound, (c) hydrophilic antioxidant agent, and (d) cationic polymer are present in the continuous phase.

4. The composition according to any one of the preceding claims, where the (a) retinoid is retinol.

5. The composition according to any one of the preceding claims, wherein the amount of the (a) retinoid(s) in the composition ranges from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 1% by weight, relative to the total weight of the composition.

6. The composition according to any one of the preceding claims, wherein the (b) compound is selected from polyphenols, preferably quercetin, isoquercetin, rutin, glucosylrutin, and a mixture thereof.

7. The composition according to any one of the preceding claims, wherein the amount of the (b) compound in the composition ranges from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight, relative to the total weight of the composition.

8. The composition according to any one of the preceding claims, wherein the (c) hydrophilic antioxidant agent is selected from ascorbic acid, ascorbic acid salts, and combination thereof.

9. The composition according to any one of the preceding claims, wherein the amount of the (c) hydrophilic antioxidant agent(s) in the composition ranges from 1% to 30% by weight, preferably from 5% to 20% by weight, and more preferably from 10% to 15% by weight, relative to the total weight of the composition.

10. The composition according to any one of the preceding claims, wherein the (d) cationic polymer is selected from cationic polysaccharides, preferably non-cellulose-based cationic polysaccharides, more preferably cationic gums, in particular cationic

galactomannan gums.

11. The composition according to any one of the preceding claims, wherein the amount of the (d) cationic polymer in the composition ranges from 0.01% to 10% by weight, preferably from 0.05% to 5% by weight, and more preferably from 0.1% to 2% by weight, relative to the total weight of the composition.

12. The composition according to any one of Claims 3 to 11, wherein the continuous phase is an aqueous continuous phase.

13. The composition according to any one of the preceding claims, wherein the dispersed phases comprise capsules.

14. The composition according to any one of the preceding claims, wherein the amount of the dispersed phases in the composition ranges from 0.1% to 30% by weight, preferably from 1% to 20% by weight, more preferably from 3% to 15% by weight, and even more preferably from 5% to 10% by weight relative to the total weight of the composition.

15. A cosmetic process for treating a keratin substance such as skin, comprising the step of applying the composition according to any one of the preceding claims to the keratin substance.

# INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2023/045166

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. A61K8/04 A61K8/49 A61K8/60 A61K8/67 A61K8/73
A61Q19/00

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 A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | DATABASE GNPD [Online]<br>MINTEL;<br>30 November 2010 (2010-11-30),<br>anonymous: "Clear Anti-Acne Serum",<br>XP093071427,<br>Database accession no. 1447770 | 1,4,6,8,<br>10,15 |
| Y | the whole document<br>----- | 1-15 |
| X | DATABASE GNPD [Online]<br>MINTEL;<br>6 February 2019 (2019-02-06),<br>anonymous: "Cucumber and Aloe Silk Mask",<br>XP055965356,<br>Database accession no. 6310613 | 1,4,6,<br>10,15 |
| Y | the whole document<br>----- | 1-15 |
|  | -/-- |  |

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

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|---|---|
| Date of the actual completion of the international search<br>5 March 2024 | Date of mailing of the international search report<br>19/03/2024 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Heller, Dorothée |

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# INTERNATIONAL SEARCH REPORT

| International application No |
|---|
| PCT/JP2023/045166 |

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| Y | WO 2022/006054 A1 (OREAL [FR]; FAIG JONATHAN JAMES [US] ET AL.)<br>6 January 2022 (2022-01-06)<br>page 1, line 8 - line 10<br>page 2, line 12 - line 22<br>page 4, line 9 - line 17<br>page 7, line 17ff<br>page 23, line 28ff<br>page 33, line 22ff<br>page 34, line 32ff<br>page 35, line 1 - line 2; claims; examples<br>----- | 1-15 |
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| Y | US 2019/380934 A1 (LE MAIRE MARIELLE [FR] ET AL) 19 December 2019 (2019-12-19)<br>paragraphs [0001], [0021], [0041], [0065], [0066], [0208], [0214]; claims; examples<br>----- | 1-15 |

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**Information on patent family members**

International application No

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