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(54) Title: SUNSCREENING EMULSION CONTAINING TWO SPECIFIC AMPHIPHILIC COPOLYMERS AND AT LEAST A LIPOPHILIC ORGANIC UV FILTER

(57) Abstract: The invention relates to a composition comprising at least one aqueous phase, one oily phase and a system for screening out UV radiation, characterized in that it contains in a cosmetically acceptable medium : (i) at least one amphiphilic copolymer A comprising at least one ethylenically unsaturated monomer containing a sulphonic group, in free form or partially or totally neutralized form, and comprising at least one hydrophobic group and (ii) at least one amphiphilic copolymer B of at least one monomer chosen from carboxylic acids possessing  $\alpha,\beta$ -ethylenic unsaturation or their esters with a monomer possessing ethylenic unsaturation comprising a hydrophobic group and (iii) at least one lipophilic organic UV screening agent.

**SUNSCREENING EMULSION CONTAINING TWO SPECIFIC AMPHIPHILIC COPOLYMERS AND AT LEAST A LIPOPHILIC ORGANIC UV FILTER**

- 5 The invention relates to a composition comprising at least one aqueous phase, one oily phase and a system for screening out UV radiation, characterized in that it contains in a cosmetically acceptable medium :
- 10 (i) at least one amphiphilic copolymer A comprising at least one ethylenically unsaturated monomer containing a sulphonic group, in free form or partially or totally neutralized form, and comprising at least one hydrophobic group and
- 15 (ii) at least one amphiphilic copolymer B of at least one monomer chosen from carboxylic acids possessing  $\alpha,\beta$ -ethylenic unsaturation or their esters with a monomer possessing ethylenic unsaturation comprising a hydrophobic group and
- (iii) at least one lipophilic organic UV screening agent.

20 It is known that light radiation with wavelengths of between 280 nm and 400 nm makes possible browning of the human epidermis and that rays with wavelengths more particularly of between 280 and 320 nm, known under the name UV-B rays, cause erythemas and skin burns which may be harmful to the development of natural tanning. For these reasons, and for aesthetic reasons, there exists a constant demand for means for controlling this natural tanning for the purpose of thus controlling the colour of the skin;

25 it is thus advisable to screen out this UV-B radiation.

30 It is also known that UV-A rays, with wavelengths of between 320 and 400 nm, which cause browning of the skin, are capable of bringing about a detrimental change in the latter, in particular in the case of sensitive skin or of skin continually exposed to solar radiation. UV-A rays cause in particular a loss in elasticity of the skin and the appearance of wrinkles, resulting in premature skin ageing. They promote the triggering of the erythematous reaction or accentuate this reaction in some subjects and can even be the cause of phototoxic or photoallergic reactions. Thus, for aesthetic and

35 cosmetic reasons, such as the preservation of the natural elasticity of the skin, for example, more and more people desire to control the effect of UV-A rays on their skin. It is therefore desirable also to screen out UV-A radiation.

40 With the aim of providing protection of the skin and keratinous substances against UV radiation, use is generally made of sun compositions comprising organic screening agents which are active in the UV-A region and which are active in the UV-B region.

45 Numerous cosmetic compositions intended for the photoprotection (UV-A and/or UV-B) of the skin have been provided to date. The aim is very

particularly to find formulations which provide the users with ready application on the skin.

5 These photoprotective compositions are usually in the form of an emulsion of oil-in-water type (which means constituted of a continuous aqueous phase and a dispersed discontinuous oily phase) or in the form of an emulsion of water-in-oil type (which means constituted of a continuous oily phase and a dispersed discontinuous aqueous phase) type, which contains, in varying concentrations, one or more standard lipophilic organic UV screening agents and/or standard hydrophilic organic UV screening agents capable of selectively absorbing harmful UV radiation, these UV screening agents (and the amounts thereof) being selected as a function of the desired sun protection factor, the sun protection factor (SPF) being expressed mathematically as the ratio of the dose of UV radiation necessary to reach the erythema-forming threshold with the UV-screening agent to the dose of UV radiation necessary to reach the erythema-forming threshold without UV-screening agent. The lipophilic organic UV sunscreens generally needs to be solubilised in the oily phase.

20 The preparation of stable emulsions comprising oils and lipophilic organic UV screening agents presents numerous difficulties, in particular when the development of strong protection is involved and thus the introduction of large amounts of lipophilic organic screening agents and of solubilizing oils is involved. This is reflected by instability of the composition, which is thus harmful to the quality of the product and to the effectiveness of the protection. Generally, this instability is overcome by the use of thickeners introduced in the composition. These difficulties in stabilizing emulsions comprising oils and lipophilic organic UV screening agents become accentuated as soon as it is a matter of obtaining compositions of very low viscosity because the level of thickening of the formulation is then intentionally limited in order to be able to maintain the viscosity at the desired level, the consequence of which is to further worsen the phenomena of instability.

35 The emulsions containing lipophilic UV organic UV screening agents solubilized in oils generally does not lead to a sufficient fresh and watery feeling on the skin after spreading and breaking of the emulsion on to the skin surface to be treated. In order to obtain such fresh and watery feeling, it is possible to add a thickening agent or a mixture of thickening agents. But certain thickening agents and mixtures of thickening agents does not allow to stabilize the emulsion or to maintain its fluidity. This instability of those emulsions is reflected by a dephasing phenomena accompanied with a greasy feeling, a shiny texture and a heavy residue (deposit of oils particles) upon the skin after application of the product.

45 Thus, the need still remains to be able to find out an appropriate thickening system in stable anti-sun emulsions containing lipophilic UV filters which

can reach a SPF superior or equal to 10, give a good fresh and watery feeling upon application on the skin, bring a very light residue, a non-shiny texture and a non-greasy effect. The consumer demands more and more for the light, less greasy and matte texture, especially in south Asia, the temperature in summer usually reaches more than 35 degree, 53% people consider themselves as shiny skin.

In the Patent FR2923716, are disclosed compositions for topical application in the form of emulsion or aqueous gel, where the aqueous phase of emulsion or aqueous gel is gelified by a (non)crosslinked hydrophobic 2-acrylamido 2-methylpropane sulfonic acid copolymers and comprises at least a filler comprising silica derivatives, silicate derivatives, and clay.

In the patents EP1353642 and EP1353633 are disclosed sun care formulations containing UV filters and an amphiphilic hydrophobically modified 2-acrylamido 2-methylpropane sulfonic acid copolymer.

In the patent EP0815828 are disclosed cosmetic formulations containing as a thickening polymer a partially or totally neutralized, crosslinked or non-crosslinked homopolymer of meth)acrylamido(C<sub>1</sub>-C<sub>4</sub>)alkylsulphonic acid.

In the patent EP 1637186 A1 is disclosed a composition, useful for skin care, skin make-up, solar protection, hydration of the skin and for the treatment of fatty skins, comprising hydrophilic progenated silica and a homopolymer of 2-acrylamido 2-methylpropane sulfonic acid

The Applicant Company has discovered, surprisingly and unexpectedly, that this object could be achieved by using (i) at least one amphiphilic copolymer A comprising at least one ethylenically unsaturated monomer containing a sulphonic group, in free form or partially or totally neutralized form, and comprising at least one hydrophobic group and (ii) at least one copolymer B resulting from the polymerization of at least one monomer (a) chosen from carboxylic acids possessing  $\alpha,\beta$ -ethylenic unsaturation or their esters with a monomer (b) possessing ethylenic unsaturation comprising a hydrophobic group in a composition comprising at least one aqueous phase, one oily phase and a system for screening out UV radiation comprising at least one organic UV screening agent..

Consequently, a subject-matter of the present invention is a composition comprising at least one aqueous phase, one oily phase and a system for screening out UV radiation, characterized in that it contains in a cosmetically acceptable medium :

(i) at least one amphiphilic copolymer A comprising at least one ethylenically unsaturated monomer containing a sulphonic group, in free form or partially or totally neutralized form, and comprising at least one hydrophobic group and

(ii) at least one amphiphilic copolymer B of at least one monomer chosen from carboxylic acids possessing  $\alpha,\beta$ -ethylenic unsaturation or their esters with a monomer possessing ethylenic unsaturation comprising a hydrophobic group and

5 (iii) at least one lipophilic organic UV screening agent.

The term "cosmetically acceptable" means compatible with the skin and/or its integuments, which has a pleasant colour, odour and feel, and which does not cause any unacceptable discomfort (stinging, tautness or redness) liable to dissuade the consumer from using this composition.

The term "lipophilic UV screening agent" is understood to mean any agent which screens out UV radiation capable of being completely dissolved in the molecular state in a fatty phase of the emulsion or else of being solubilized in the colloidal form (for example in the micelle form) in a fatty phase.

The expression "amphiphilic polymer" means any polymer comprising both a hydrophilic group and a hydrophobic group. Such polymers are also known as hydrophobic modified polymers.

The term "hydrophobic group" or "hydrophobic unit" is intended to mean a radical possessing a saturated or unsaturated and linear or branched hydrocarbon chain comprising at least 8 carbon atoms, preferably from 10 to 30 carbon atoms, in particular from 12 to 30 carbon atoms and more preferably from 18 to 30 carbon atoms.

The term "copolymer" is understood to mean both copolymers obtained from two types of monomers and those obtained from more than two types of monomers, such as terpolymers obtained from three types of monomers.

**Amphiphilic copolymers A comprising at least one ethylenically unsaturated monomer containing a sulphonic group, in free form or partially or totally neutralized form, and comprising at least one hydrophobic group**

The hydrophobic group present in those sulphonic amphiphilic copolymers of the invention preferably contains from 6 to 22 carbon atoms, even more preferably from 6 to 18 carbon atoms and more particularly from 12 to 18 carbon atoms.

Preferably, those polymers in accordance with the invention are partially or totally neutralized with a mineral base (sodium hydroxide, potassium hydroxide or aqueous ammonia) or an organic base such as mono-, di- or triethanolamine, an aminomethylpropanediol, N-methylglucamine, basic amino acids, for instance arginine and lysine, and mixtures of these compounds.

The amphiphilic sulphonic copolymers in accordance with the invention generally have a number-average molecular weight ranging from 1 000 to 20 000 000 g/mol, preferably ranging from 20 000 to 5 000 000 and even more preferably from 100 000 to 1 500 000 g/mol.

The amphiphilic sulphonic copolymers according to the invention may or may not be crosslinked. Crosslinked amphiphilic polymers are preferably chosen. When they are crosslinked, the crosslinking agents may be chosen from polyolefinically unsaturated compounds commonly used for the crosslinking of polymers obtained by free-radical polymerization.

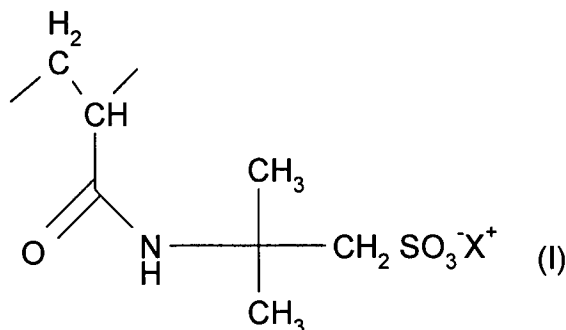
Mention may be made, for example, of divinylbenzene, diallyl ether, dipropylene glycol diallyl ether, polyglycol diallyl ethers, triethylene glycol divinyl ether, hydroquinone diallyl ether, ethylene glycol di(meth)acrylate or tetraethylene glycol di(meth)acrylate, trimethylolpropane triacrylate, methylenebisacrylamide, methylenebismethacrylamide, triallylamine, triallyl cyanurate, diallyl maleate, tetraallylethylenediamine, tetraallyloxyethane, trimethylolpropane diallyl ether, allyl (meth)acrylate, allylic ethers of alcohols of the sugar series, or other allyl or vinyl ethers of polyfunctional alcohols, and also allylic esters of phosphoric and/or vinylphosphonic acid derivatives, or mixtures of these compounds.

Methylenebisacrylamide, allyl methacrylate or trimethylolpropane triacrylate (TMPTA) will be used more particularly. The degree of crosslinking will generally range from 0.01 mol% to 10 mol% and more particularly from 0.2 mol% to 2 mol% relative to the polymer.

The ethylenically unsaturated monomers containing a sulphonic group are chosen especially from vinylsulphonic acid, styrenesulphonic acid, (meth)acrylamido(C<sub>1</sub>-C<sub>22</sub>)alkylsulphonic acids, and N-(C<sub>1</sub>-C<sub>22</sub>)alkyl(meth)acrylamido(C<sub>1</sub>-C<sub>22</sub>)alkylsulphonic acids, for instance undecylacrylamidomethanesulphonic acid, and also partially or totally neutralized forms thereof.

(Meth)acrylamido(C<sub>1</sub>-C<sub>22</sub>)alkylsulphonic acids such as, for example, acrylamidomethanesulphonic acid, acrylamidoethanesulphonic acid, acrylamidopropanesulphonic acid, 2-acrylamido-2-methylpropanesulphonic acid, methacrylamido-2-methylpropanesulphonic acid, 2-acrylamido-n-butanesulphonic acid, 2-acrylamido-2,4,4-trimethylpentanesulphonic acid, 2-methacrylamidododecylsulphonic acid or 2-acrylamido-2,6-dimethyl-3-heptanesulphonic acid, and also partially or totally neutralized forms thereof, will more preferably be used.

2-Acrylamido-2-methylpropanesulphonic acid (® AMPS), and also partially or totally neutralized forms thereof of formula (I)



in which X<sup>+</sup> denotes a proton, an alkali metal cation, an alkaline earth metal cation or the ammonium ion, it being possible for at most 10 mol% of the cations X<sup>+</sup> to be protons H<sup>+</sup> will more particularly be used.

5

The amphiphilic polymers in accordance with the invention may be chosen especially from random amphiphilic @ AMPS polymers modified by reaction with a C<sub>6</sub>-C<sub>22</sub> n-monoalkylamine or di-n-alkylamine, and such as those described in patent application WO 00/31154 (forming an integral part of the content of the description).

10

These polymers may also contain other ethylenically unsaturated hydrophilic monomers chosen, for example, from (meth)acrylic acids, β-substituted alkyl derivatives thereof or esters thereof obtained with monoalcohols or mono- or polyalkylene glycols, (meth)acrylamides, vinylpyrrolidone, maleic anhydride, itaconic acid or maleic acid, or mixtures of these compounds.

15

These same copolymers may also contain one or more ethylenically unsaturated monomers not comprising a fatty chain, such as (meth)acrylic acids, β-substituted alkyl derivatives thereof or esters thereof obtained with monoalcohols or mono- or polyalkylene glycols, (meth)acrylamides, vinylpyrrolidone, maleic anhydride, itaconic acid or maleic acid, or mixtures of these compounds.

20

These polymers are described in particular in the documents EP-A-750899, US-A-5089578 and WO-A-2002/43689 and in the following publications by Yotaro Morishima:

25

- "Self-assembling amphiphilic polyelectrolytes and their nanostructures - Chinese Journal of Polymer Science", Vol. 18, No. 40 (2000), 323-336;

30

- "Micelle formation of random copolymers of sodium 2-(acrylamido)-2-methylpropanesulphonate and a non-ionic surfactant macromonomer in water as studied by fluorescence and dynamic light scattering", *Macromolecules* 2000, Vol. 33, No. 10, 3694-3704;

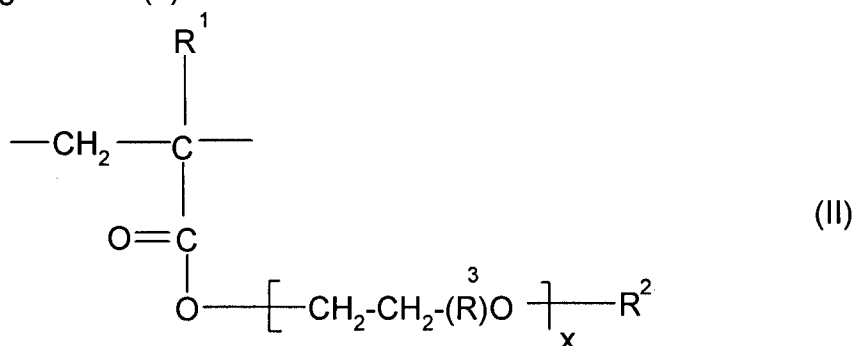
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- "Solution properties of micelle networks formed by non-ionic moieties covalently bound to a polyelectrolyte: salt effects on rheological behaviour", *Langmuir*, 2000, Vol. 16, No. 12, 5324-5332;

- "Stimuli responsive amphiphilic copolymers of sodium 2-(acrylamido)-2-

methylpropanesulphonate and associative macromonomers", Polym. Preprint, Div. Polym. Chem., 1999, 40(2), 220-221.

5 The hydrophobic monomers of these specific polymers are preferably chosen from acrylates, alkyl acrylates, acrylamides or alkylacrylamides of following formula (II):



10 in which R<sup>1</sup> and R<sup>3</sup>, which are identical or different, denote a hydrogen atom or a substantially linear or branched C<sub>1</sub>-C<sub>6</sub> alkyl radical (preferably a methyl radical); Y denotes O or NH; R<sup>2</sup> denotes a hydrocarbon radical comprising from 6 to 50 carbon atoms, more preferably from 6 to 22 carbon atoms, more preferably still from 6 to 18 carbon atoms and more particularly from 12 to 18 carbon atoms; and x denotes a number of moles of alkylene oxide and varies from 0 to 100.

15 The R<sup>2</sup> radical is preferably chosen from substantially linear C<sub>6</sub>-C<sub>18</sub> alkyl radicals (for example n-hexyl, n-octyl, n-decyl, n-hexadecyl, n-dodecyl or lauryl, or n-octadecyl or stearyl) or branched or cyclic C<sub>6</sub>-C<sub>18</sub> alkyl radicals (for example cyclododecane (C<sub>12</sub>) or adamantane (C<sub>10</sub>)); perfluorinated C<sub>6</sub>-  
 20 C<sub>18</sub> alkyl radicals (for example the group of formula -(CH<sub>2</sub>)<sub>2</sub>-(CF<sub>2</sub>)<sub>9</sub>-CF<sub>3</sub>); the cholesteryl radical (C<sub>27</sub>) or a cholesterol ester residue, such as the cholesteryl oxyhexanoate group; or polycyclic aromatic groups, such as naphthalene or pyrene. Preference is more particularly given, among these radicals, to substantially linear alkyl radicals and more particularly to the  
 25 dodecyl, n-hexadecyl or n-octadecyl radical, and to their mixtures.

According to a particularly preferred form of the invention, the monomer of formula (II) comprises at least one alkylene oxide unit (x ≥ 1) and preferably several alkylene oxide units (x > 1) constituting a polyoxyalkylene chain.  
 30 The polyoxyalkylene chain is preferably composed of ethylene oxide units and/or of propylene oxide units and more particularly still is composed of ethylene oxide units. The number of oxyalkylene units (or number of moles of alkylene oxide) generally varies from 3 to 100, more preferably from 3 to 50 and more preferably still from 7 to 25.

35 Mention may be made, among these polymers, of:  
 - crosslinked or non-crosslinked and neutralized or non-neutralized copolymers comprising from 15 to 60% by weight of ® AMPS units and



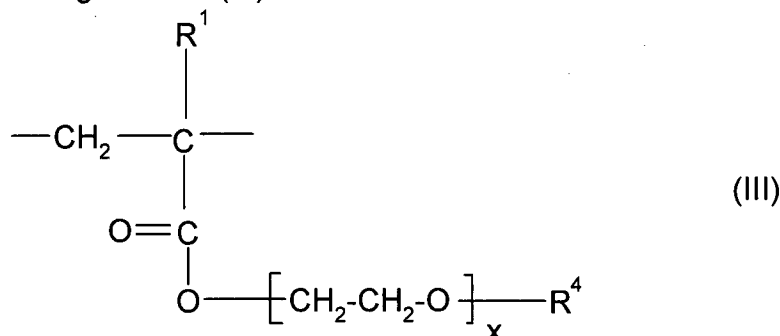
from 40 to 85% by weight of (C<sub>8</sub>-C<sub>16</sub>)alkyl(meth)acrylamide units or of (C<sub>8</sub>-C<sub>16</sub>)alkyl (meth)acrylate units, with respect to the polymer, such as those described in the document EP-A-750 899;

5 - terpolymers comprising from 10 to 90 mol% of acrylamide units, from 0.1 to 10 mol% of ® AMPS units and from 5 to 80 mol% of n-(C<sub>6</sub>-C<sub>18</sub>)alkylacrylamide units, with respect to the polymer, such as those described in the document US-A-5 089 578;

10 - non-crosslinked copolymers of partially or completely neutralized ® AMPS and of n-dodecyl, n-hexadecyl or n-octadecyl methacrylate, such as those described in the abovementioned papers by Morishima;

- crosslinked or non-crosslinked copolymers of partially or completely neutralized AMPS and of n-dodecylmethacrylamide, such as those described in the abovementioned papers by Morishima.

15 Mention may more particularly be made, as hydrophobic modified polymers, of the copolymers composed (i) of 2-acrylamido-2-methylpropanesulphonic acid units of formula (I) indicated above, in which X<sup>+</sup> is a proton, an alkali metal cation, an alkaline earth metal cation or the ammonium ion, and (ii) of units of following formula (III):



20 in which x denotes an integer varying from 3 to 100, preferably from 3 to 50 and more preferably from 7 to 25; R<sup>1</sup> has the same meaning as that indicated above in the formula (II) and R<sup>4</sup> denotes a linear or branched alkyl radical comprising from 6 to 22 carbon atoms and preferably from 10 to 22 carbon atoms.

25 The hydrophobic modified polymers of this type are in particular those described in the abovementioned papers by Morishima, for which x = 25, R<sup>1</sup> denotes methyl and R<sup>4</sup> represents n-dodecyl, or those described in the document WO-A-02/43689, for which x = 8 or 25, R<sup>1</sup> denotes methyl and R<sup>4</sup> represents n-hexadecyl (C<sub>16</sub>), n-octadecyl (C<sub>18</sub>) or n-dodecyl (C<sub>12</sub>), or their mixtures. The polymers for which X<sup>+</sup> denotes sodium or ammonium are more particularly preferred.

35 The preferred hydrophobic modified polymers which can be used in the composition in accordance with the invention can be obtained according to conventional radical polymerization processes in the presence of one or more initiators, such as, for example, azobisisobutyronitrile (AIBN),

azobisdimethylvaleronitrile, 2,2'-azobis[2-amidinopropane] hydrochloride (ABAH), organic peroxides, such as dilauryl peroxide, benzoyl peroxide, tert-butyl hydroperoxide, and the like, inorganic peroxide compounds, such as potassium persulphate or ammonium persulphate, or H<sub>2</sub>O<sub>2</sub>, optionally in the presence of reducing agents.

These hydrophobic modified polymers can be obtained in particular by radical polymerization in a tert-butanol medium, from which they precipitate. It is possible, using polymerization by precipitation from tert-butanol, to obtain a distribution in the size of the particles of the polymer which is particularly favourable to the uses thereof.

The reaction can be carried out at a temperature of between 0 and 150°C, preferably between 10 and 100°C, either at atmospheric pressure or under reduced pressure. It can also be carried out under an inert atmosphere and preferably under nitrogen.

These preferred hydrophobic modified polymers are in particular those described in the document EP-1 069 142 and especially those obtained by polymerization of 2-acrylamido-2-methylpropanesulphonic acid or one of its sodium or ammonium salts with an ester of (meth)acrylic acid and

- of a C<sub>10</sub>-C<sub>18</sub> alcohol oxyethylenated with 8 mol of ethylene oxide (Genapol® C-080 from Clariant),
- of a C<sub>11</sub> oxo alcohol oxyethylenated with 8 mol of ethylene oxide (Genapol® UD-080 from Clariant),
- of a C<sub>11</sub> oxo alcohol oxyethylenated with 7 mol of ethylene oxide (Genapol® UD-070 from Clariant),
- of a C<sub>12</sub>-C<sub>14</sub> alcohol oxyethylenated with 7 mol of ethylene oxide (Genapol® LA-070 from Clariant),
- of a C<sub>12</sub>-C<sub>14</sub> alcohol oxyethylenated with 9 mol of ethylene oxide (Genapol® LA-090 from Clariant),
- of a C<sub>12</sub>-C<sub>14</sub> alcohol oxyethylenated with 11 mol of ethylene oxide (Genapol® LA-110 from Clariant),
- of a C<sub>16</sub>-C<sub>18</sub> alcohol oxyethylenated with 8 mol of ethylene oxide (Genapol® T-080 from Clariant),
- of a C<sub>16</sub>-C<sub>18</sub> alcohol oxyethylenated with 15 mol of ethylene oxide (Genapol® T-150 from Clariant),
- of a C<sub>16</sub>-C<sub>18</sub> alcohol oxyethylenated with 11 mol of ethylene oxide (Genapol® T-110 from Clariant),
- of a C<sub>16</sub>-C<sub>18</sub> alcohol oxyethylenated with 20 mol of ethylene oxide (Genapol® T-200 from Clariant),
- of a C<sub>16</sub>-C<sub>18</sub> alcohol oxyethylenated with 25 mol of ethylene oxide (Genapol® T-250 from Clariant),
- of a C<sub>18</sub>-C<sub>22</sub> alcohol oxyethylenated with 25 mol of ethylene oxide and/or of an iso-C<sub>16</sub>-C<sub>18</sub> alcohol oxyethylenated with 25 mol of ethylene oxide.

The mol% concentration of the units of formula (I) and of the units of

formula (III) in the polymers according to the invention varies according to the cosmetic application desired and the rheological properties desired for the formulation. It can vary between 0.1 and 99.9 mol%.

5 Preferably, for the most hydrophobic polymers, the molar proportion of units of formula (I) or (III) varies from 50.1 to 99.9%, more particularly from 70 to 95% and more particularly still from 80 to 90%.

10 Preferably, for the polymers which are not very hydrophobic, the molar proportion of units of formula (I) or (III) varies from 0.1 to 50%, more particularly from 5 to 25% and more particularly still from 10 to 20%.

The distribution of the monomers in the polymers of the invention can be, for example, alternating, block (including multiblock) or random.

15 Mention may in particular be made, as hydrophobic modified polymers of this type, of the copolymer of ammonium salt of 2-acrylamido-2-methylpropanesulphonic acid and of ethoxylated C<sub>12</sub>-C<sub>14</sub> alkyl methacrylate (noncrosslinked copolymer obtained from ® Genapol LA-070 and from ®  
20 AMPS) (CTFA name: Ammonium Acryloyldimethyltaurate/Laureth-7 Methacrylate Copolymer) sold under the name ® Aristoflex LNC by Clariant, and the crosslinked copolymer of ammonium salt of 2-acrylamido-2-methylpropanesulphonic acid and of ethoxylated (25 EO) stearyl  
25 methacrylate (copolymer which is preferably crosslinked with trimethylolpropane triacrylate and obtained from Genapol T-250 and from ®AMPS) (CTFA name: Ammonium Acryloyldimethyltaurate/Steareth-25 Methacrylate Crosspolymer) sold under the name ® Aristoflex HMS by Clariant.

30 The most preferred amphiphilic copolymer A is the copolymer of ammonium salt of 2-acrylamido-2-methylpropanesulphonic acid and of ethoxylated (25 EO) stearyl methacrylate (CTFA name: Ammonium Acryloyldimethyltaurate/Steareth-25 Methacrylate Crosspolymer) sold under the name Aristoflex HMS by Clariant.

35 The amount of amphiphilic copolymer A in active material preferably ranges from 0.1% to 10% by weight, preferentially from 0.2% to 5% by weight and better still from 0.5% to 2% by weight relative to the total weight of the composition.

40 **Amphiphilic copolymer B of at least one monomer (a) chosen from carboxylic acids possessing  $\alpha,\beta$ -ethylenic unsaturation or their esters with at least one monomer (b) possessing ethylenic unsaturation comprising a hydrophobic group**

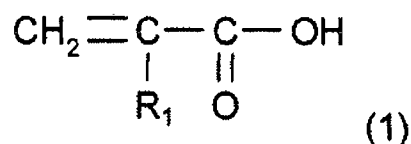
45 Their chemical structure more particularly comprises at least one hydrophilic unit and at least one hydrophobic unit. The term "hydrophobic

group" or "hydrophobic unit" is intended to mean a radical possessing a saturated or unsaturated and linear or branched hydrocarbon chain comprising at least 8 carbon atoms, preferably from 10 to 30 carbon atoms, in particular from 12 to 30 carbon atoms and more preferably from 18 to 30 carbon atoms.

The preferred copolymers are chosen from copolymers resulting from the polymerization:

a) of at least one monomer of following formula (1):

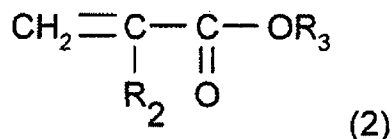
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in which  $\text{R}_1$  denotes H or  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ , that is to say acrylic acid, methacrylic acid or ethacrylic acid monomers, and

b) of at least one monomer of unsaturated carboxylic acid ( $\text{C}_{10}$ - $\text{C}_{30}$ )alkyl ester type which corresponds to the monomer of following formula (2):

15



in which  $\text{R}_2$  denotes H or  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$  (that is to say, acrylate, methacrylate or ethacrylate units) and preferably H (acrylate units) or  $\text{CH}_3$  (methacrylate units) and  $\text{R}_3$  denotes a  $\text{C}_{10}$ - $\text{C}_{30}$  and preferably  $\text{C}_{12}$ - $\text{C}_{22}$  alkyl radical.

20

The ( $\text{C}_{10}$ - $\text{C}_{30}$ )alkyl esters of unsaturated carboxylic acids are preferably chosen from lauryl acrylate, stearyl acrylate, decyl acrylate, isodecyl acrylate, dodecyl acrylate and the corresponding methacrylates, such as lauryl methacrylate, stearyl methacrylate, decyl methacrylate, isodecyl methacrylate and dodecyl methacrylate, and their mixtures.

25

According to a preferred embodiment, these thickening polymers are crosslinked.

30

Use will more particularly be made, among the thickening polymers of this type, of copolymers resulting from the polymerization of a mixture of monomers comprising:

(i) acrylic acid,

(ii) an ester of formula (2) described above in which  $\text{R}_2$  denotes H or  $\text{CH}_3$  and  $\text{R}_3$  denotes an alkyl radical having from 12 to 22 carbon atoms,

35

(iii) and a crosslinking agent which is a well-known copolymerizable polyethylenic unsaturated monomer, such as diallyl phthalate, allyl

(meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate and methylenebisacrylamide.

Use will more particularly be made, among copolymers of this type, of those composed of 95 to 60% by weight of acrylic acid (hydrophilic unit), 4 to 40% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate (hydrophobic unit) and 0 to 6% by weight of crosslinking polymerizable monomer or else of those composed of 98 to 96% by weight of acrylic acid (hydrophilic unit), 1 to 4% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate (hydrophobic unit) and 0.1 to 0.6% by weight of crosslinking polymerizable monomer, such as those described above.

Preference is very particularly given according to the present invention, among the said polymers above, to acrylate/C<sub>10</sub>-C<sub>30</sub> alkyl acrylate copolymers (INCI name: Acrylates/C<sub>10</sub>-C<sub>30</sub> Alkyl Acrylate Crosspolymer), such as the products sold by Lubrizol under the trade names ® Pemulen TR1, ® Pemulen TR2, ® Carbopol 1382 and ® Carbopol EDT 2020 and more preferably still ® Pemulen TR-2.

The amphiphilic copolymers B are preferably present in the composition according to the invention, in active material preferably ranges from 0.1% to 10% by weight, preferentially from 0.2% to 5% by weight and better still from 0.5% to 2% by weight relative to the total weight of the composition.

#### 25 LIPOPHILIC ORGANIC UV SCREENING AGENTS.

The lipophilic organic screening agents are chosen in particular from from anthranilates; cinnamic derivatives; salicylic derivatives; camphor derivatives; benzophenone derivatives; β,βdiphenylacrylate derivatives; triazine derivatives ; benzotriazole derivatives; benzalmalonate derivatives, especially those mentioned in patent US5624663; benzimidazole derivatives; imidazolines; bis-benzazolyl derivatives as described in patents EP 669 323 and US 2 463 264; p-aminobenzoic acid (PABA) derivatives; methylenebis(hydroxyphenylbenzotriazole) derivatives as described in patent applications US 5 237 071, US 5 166 355, GB 2 303 549, DE 197 26 184 and EP 893 119; benzoxazole derivatives as described in patent applications EP 0 832 642, EP 1 027 883, EP 1 300 137 and DE 101 62 844; screening polymers and screening silicones such as those described especially in patent application WO 93/04665; alkylstyrene-based dimers, such as those described in patent application DE 198 55 649; 4,4-diarylbutadienes such as those described in patent applications EP 0 967 200, DE 197 46 654, DE 197 55 649, EP-A-1 008 586, EP 1 133 980 and EP 133 981; merocyanin derivatives such as those described in patent applications WO 04/006 878, WO 05/058 269 and WO 45 06/032 741; and mixtures thereof.

According to a preferred embodiment of the invention, the composition will contain at least one UVA lipophilic organic screening agent and at least one UVB lipophilic organic screening agent and/or at least one UVA and UVB lipophilic organic screening agent.

5

As examples of UVA lipophilic organic UV screening agent, can be cited :

Dibenzoylméthane derivatives :

10 Butyl Methoxydibenzoylméthane sold in particular under the trade name «® PARSOL 1789 » by DSM Nutritional Products, Inc ;

Aminobenzophenone derivatives :

15 n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)-benzoate sold in particular under the trade name « © UVINUL A + » by BASF ;  
1,1'-(1,4-piperazinediyl)bis[1-[2-[4-(diethylamino)-2-hydroxybenzoyl]phenyl]-methanone (CAS 919803-06-8)

Anthranilates derivatives

20 - Menthyl anthranilate vendu notamment sous le nom commercial « ® NEO HELIOPAN MA » par SYMRISE ;

4,4-diarylbutadienes derivatives :

1,1-dicarboxy (2,2'-diméthyl-propyl)-4,4-diphénylbutadiène ;

25 Merocyanine derivatives :

Octyl-5-N,N-diéthylamino-2-phénysulfonyl-2,4-pentadiénoate ;

According to a preferred embodiment of the invention, the UVA lipophilic organic screening agent will be selected from :

30 Butyl Méthoxydibenzoylméthane ;

n- Hexyl 2-(4-diéthylamino-2-hydroxybenzoyl)-benzoate ;

As examples of UVB lipophilic organic UV screening agent, can be cited :

35 Para-aminobenzoate derivatives :

- Ethyl PABA ;  
- Ethyl Dihydroxypropyl PABA ;  
- Ethylhexyl Diméthyl PABA (® ESCALOL 507 de ISP) ;

40 Salicylic derivatives :

Homosalate sold in particular under the trade name « ® Eusolex HMS » by Rona/EM Industries ;

Ethylhexyl Salicylate old in particular under the trade name « ® NEO HELIOPAN OS » by SYMRISE ;

45 Dipropylèneglycol Salicylate old in particular under the trade name « ® DIPSAL » by SCHER ;

TEA Salicylate old in particular under the trade name « ® NEO HELIOPAN

TS » by SYMRISE.

Cinnamic derivatives

- Ethylhexyl Méthoxycinnamate sold in particular under the trade name  
5 « ® PARSOL MCX » by DSM Nutritional Products, Inc. ;  
Isopropyl Méthoxy cinnamate ;  
Isoamyl Méthoxy cinnamate sold in particular under the trade name  
« ® NEO HELIOPAN E 1000 » by SYMRISE ;  
Diisopropyl Méthylcinnamate ;  
10 Cinnoxate ;  
Glycéryl Ethylhexanoate Diméthoxycinnamate ;

$\beta,\beta'$ -diphénylacrylate derivatives :

- Octocrylène, sold in particular under the trade name « ® UVINUL N539 »  
15 par BASF ;  
Etocrylène, sold in particular under the trade name « ® UVINUL N35 » par  
BASF ;

Benzylidene camphor derivatives :

- 20 3-Benzylidene camphor manufactured in particular under the trade name  
« ® MEXORYL SD » by CHIMEX ;  
Méthylbenzylidene Camphor sold in particular under the trade name « ®  
EUSOLEX 6300 » by MERCK ;  
Polyacrylamidométhyl Benzylidene Camphor manufactured in particular  
25 under the trade name « ® MEXORYL SW » by CHIMEX ;

Triazine derivatives :

- Ethylhexyl triazone manufactured in particular under the trade name «  
® UVINUL T150 » by BASF ;  
30 Diéthylhexyl Butamido Triazone manufactured in particular under the trade  
name « ® UVASORB HEB » by SIGMA 3V ;  
2,4,6-tris(4'-amino benzalmalonate de dinéopentyle)-s-triazine ;  
2,4,6-tris(4'-amino benzalmalonate de diisobutyle)-s- triazine ;  
2,4-bis(4'-amino benzalmalonate de dinéopentyle)-6-(4'-aminobenzoate de  
35 n-butyle)-s-triazine ;  
2,4-bis(4'-amino benzoate de n-butyle)-6-(aminopropyltrisiloxane)-s-  
triazine ;  
Symetrical triazine filters as described in the patent US 6,225,467, WO  
2004/085412 (see compounds 6 et 9) or the document « Symetrical  
40 Triazine Derivatives » IP.COM Journal, IP.COM INC WEST HENRIETTA,  
NY, US (20 septembre 2004) in particular 2,4,6-tris-(biphényl)-1,3,5-triazine  
(ie la 2,4,6-tris(biphényl-4-yl)-1,3,5-triazine) and 2,4,6-tris(terphenyl)-1,3,5-  
triazine, as described in the international applications WO 06/035000,  
WO 06/034982, WO 06/034991, WO 06/035007, WO 2006/034992, WO  
45 2006/034985).

Imidazoline derivatives :

Ethylhexyl Diméthoxybenzylidene Dioxoimidazoline Propionate,

Benzmalonate derivatives :

- 5 Benzmalonate function containing Polyorganosiloxanes as Polysilicone-15 sold in particular under the trade name « ® PARSOL SLX » by DSM Nutritional Products, Inc. ;  
Di-neopentyl 4'-méthoxybenzmalonate ;
- 10 According to a preferred embodiment of the invention, the UVB lipophilic organic screening agent will be selected from :
- Ethylhexylsalicylate ;
  - Homosalate
  - Octocrylene ;

15

As examples of lipophilic organic UVA and UVB screening agents, can be cited :

Benzophenone derivatives :

- 20 Benzophenone-1 sold in particular under the trade name « ® UVINUL 400 » by BASF ;  
Benzophenone-2 sold in particular under the trade name « ® UVINUL D50 » by BASF ;  
Benzophenone-3 or Oxybenzone sold in particular under the trade name  
25 « ® UVINUL M40 » par BASF ;  
Benzophénone-6 sold in particular under the trade name « ® HELISORB 11 » by Norquay ;  
Benzophenone-8 sold in particular under the trade name « Spectra-Sorb UV-24 » by American Cyanamid ;  
30 Benzophenone-10 ;  
Benzophenone-11 ;  
Benzophenone-12 ;

Benzotriazole derivatives :

- 35 - Drometrizole Trisiloxane sold in particular under the trade name « ® SILATRIZOLE » by RHODIA CHIMIE or manufactured under the trade name « ® MEROXYL XL » by CHIMEX ;  
- Méthylene bis-Benzotriazolyl Tétraméthylbutylphénol, sold in particular  
40 under the trade name « ® MIXXIM BB/100 » par FAIRMOUNT CHEMICAL  
or under the micronized form in aqueous aqueuse notamment sold in particular under the trade name « ® TINOSORB M » by CIBA SPECIALTY CHEMICALS ;

Bis-résorcinyl triazines

- 45 Bis-Ethylhexyloxyphenol Méthoxyphenyl Triazine sold in particular under the trade name « TINOSORB S » by CIBA SPECIALTY CHEMICALS;



Benzoxazole derivatives :

2,4-bis-[5-1(diméthylpropyl)benzoxazol-2-yl-(4-phenyl)-imino]-6-(2-ethylhexyl)-imino-1,3,5-triazine sold in particular under the trade name Uvasorb K2A by Sigma 3V ;

5

According to a preferred embodiment of the invention, the UVA and UVB lipophilic organic screening agents will be selected from :

- Drométrizole Trisiloxane ;
- Méthylène bis-Benzotriazolyl Tétraméthylbutylphénol ;
- Bis-Ethylhexyloxyphénol Méthoxyphenyl Triazine.

10

The lipophilic organic UV screening agents are preferably present in amounts ranging from 0.01 to 30 % by weight relative to the total weight of the composition and more preferably 0.1 to 20 %.

15

ADDITIONNAL UV FILTERS

According to one embodiment of the invention, the compositions may further contain at least one hydrophilic organic UV sunscreen agent and/or one inorganic UV screening agent.

20

The hydrophilic organic UV sunscreen agents may be UVA hydrophilic UV sunscreen agents, UVB hydrophilic UV sunscreen agents or UVA and UVB hydrophilic UV sunscreens agents

25

The term "hydrophilic UV screening agent" is understood to mean any agent which screens out UV radiation capable of being completely dissolved in the molecular state in an aqueous phase of the emulsion or else of being solubilized in the colloidal form (for example in the micelle form) in an aqueous phase.

30

As examples of UVA hydrophilic organic suncreening agent, can be cited :

Terephtalylidene Dicamphor Acide Sulfonic Acid manufactured in particular under the trade name « ® MEXORYL SX » par CHIMEX, Disodium Phenyl Dibenzimidazo tetra-sulfonate sold in particular under the trade name « ® NEO HELIOPAN AP » by SYMRISE.

35

The most preferred UVA hydrophilic UV suncreening agent is Terephtalylidène Dicamphor Acide Sulfonic Acid.

40

As examples of UVB hydrophilic organic screening agent, can be cited :

p-aminobenzoïc acid derivatives as :

45

PABA,  
Glyceryl PABA et  
PEG-25 PABA sold in particular under the trade name « UVINUL P25 » by

BASF.

Phenylbenzimidazole Sulfonic Acid sold in particular under the trade name « ® EUSOLEX 232 » by MERCK,

Ferulic acid,

5 Salicylic acid,

DEA methoxycinnamate,

Benzylidene Camphor Sulfonic Acid manufactured in particular under the trade name « ® MEXORYL SL » par CHIMEX,

10 Benzalkonium Methosulfate Camphor manufactured in particular under the trade name « ® MEXORYL SO » par CHIMEX.

The most preferred UVB hydrophilic sunscreens agent is Phenylbenzimidazole Sulfonic Acid.

15 As examples of UVA and UVB hydrophilic organic sunscreens agent, can be cited :

Benzophenone derivatives comprising at least one sulphonic radical as Benzophenone-4 sold in particular under the trade name « ® UVINUL MS 20 40 » by BASF,

Benzophenone-5 and

Benzophenone-9.

25 The organic hydrophilic UV screening agents are preferably present in amounts ranging from 0.01 to 30 % by weight relative to the total weight of the composition and more preferably 0.1 to 20 %.

According to one preferred embodiment of the invention, the compositions contain the following mixture of UVA and UVB screening agents ;

30 Butylmethoxydibenzoylmethane, Octocrylene, Homosalate and Phenylbenzimidazole Sulfonic Acid

According to another embodiment of the invention, the compositions contain the following mixture of UVA and UVB screening agents ;

35 n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)-benzoate, Ethylhexyl Méthoxycinnamate, Terephthalylidene Dicamphor Sulfonic Acid and Ethylhexyl Triazone.

40 According to the most preferred embodiment of the invention, the compositions contain the following mixture of UVA and UVB screening agents ;

Butylmethoxydibenzoylmethane, Bis-Ethylhexyloxyphénol Méthoxyphenyl Triazine, Homosalate, Drometrizole Trisiloxane and Phenylbenzimidazole Sulfonic Acid .

45

According to one embodiment of the invention, the compositions may further contain at least one inorganic UV screening agent.

The additional inorganic UV screening agents are preferably chosen from coated or uncoated metal oxide pigments, such as, for example, pigments formed of titanium oxide (amorphous or crystalline in the rutile and/or anatase form), iron oxide, zinc oxide, zirconium oxide or cerium oxide, which are all UV photoprotective agents well known per se.

The pigments may or may not be coated.

The coated pigments are pigments which have been subjected to one or more surface treatments of chemical, electronic, mechanochemical and/or mechanical nature with compounds such as described, for example, in *Cosmetics & Toiletries*, February 1990, Vol. 105, pp. 53-64, such as amino acids, beeswax, fatty acids, fatty alcohols, anionic surfactants, lecithins, sodium, potassium, zinc, iron or aluminium salts of fatty acids, metal alkoxides (titanium or aluminium alkoxides), polyethylene, silicones, proteins (collagen, elastin), alkanolamines, silicon oxides, metal oxides or sodium hexametaphosphate.

In a known way, the silicones are organosilicon polymers or oligomers comprising a linear or cyclic and branched or crosslinked structure, of variable molecular weight, obtained by polymerization and/or polycondensation of suitably functionalized silanes and essentially composed of a repetition of main units in which the silicon atoms are connected to one another via oxygen atoms (siloxane bond), optionally substituted hydrocarbon radicals being connected directly to the said silicon atoms via a carbon atom.

The term "silicones" also encompasses the silanes necessary for their preparation, in particular alkylsilanes.

The silicones used for the coating of the pigments suitable for the present invention are preferably chosen from the group consisting of alkylsilanes, polydialkylsiloxanes and polyalkylhydrosiloxanes. More preferably still, the silicones are chosen from the group consisting of octyltrimethylsilane, polydimethylsiloxanes and polymethylhydrosiloxanes.

Of course, the pigments formed of metal oxides may, before their treatment with silicones, have been treated with other surfacing agents, in particular with cerium oxide, alumina, silica, aluminium compounds, silicon compounds or their mixtures.

The coated pigments are, for example, titanium oxides coated:  
- with silica, such as the product "Sunveil" from Ikeda and the product "Eusolex T-AVO" from Merck  
- with silica and with iron oxide, such as the product "Sunveil F" from Ikeda,  
- with silica and with alumina, such as the products "Microtitanium Dioxide

MT 500 SA" and "Microtitanium Dioxide MT 100 SA" from Tayca, "Tioveil" from Tioxide and "Mirasun TiW 60" from Rhodia,

- with alumina, such as the products "Tipaue TTO-55 (B)" and "Tipaue TTO-55 (A)" from Ishihara and "UVT 14/4" from Kemira,

5 - with alumina and with aluminium stearate, such as the product "Microtitanium Dioxide MT 100 TV", "MT 100 TX", "MT 100 Z" or "MT-01" from Tayca and the products "Solaveil CT-10 W", "Solaveil CT 100" and "Solaveil CT 200" from Uniqema,

10 - with silica, with alumina and with alginic acid, such as the product "MT-100 AQ" from Tayca,

- with alumina and with aluminium laurate, such as the product "Microtitanium Dioxide MT 100 S" from Tayca,

- with iron oxide and with iron stearate, such as the product "Microtitanium Dioxide MT 100 F" from Tayca,

15 - with zinc oxide and with zinc stearate, such as the product "BR351" from Tayca,

- with silica and with alumina and treated with a silicone, such as the products "Microtitanium Dioxide MT 600 SAS", "Microtitanium Dioxide MT 500 SAS" or "Microtitanium Dioxide MT 100 SAS" from Tayca,

20 - with silica, with alumina and with aluminium stearate and treated with a silicone, such as the product "STT-30-DS" from Titan Kogyo,

- with silica and treated with a silicone, such as the product "UV-Titan X 195" from Kemira or the product SMT-100 WRS from Tayca,

25 - with alumina and treated with a silicone, such as the products "Tipaue TTO-55 (S)" from Ishihara or "UV Titan M 262" from Kemira,

- with triethanolamine, such as the product "STT-65-S" from Titan Kogyo,

- with stearic acid, such as the product "Tipaue TTO-55 (C)" from Ishihara,

- with sodium hexametaphosphate, such as the product "Microtitanium Dioxide MT 150 W" from Tayca.

30

Other titanium oxide pigments treated with a silicone are, for example, TiO<sub>2</sub> treated with octyltrimethylsilane, such as that sold under the trade name "T 805" by Degussa Silices, TiO<sub>2</sub> treated with a polydimethylsiloxane, such as that sold under the trade name "70250 Cardre UF TiO<sub>2</sub>SI3" by Cardre, 35 or anatase/rutile TiO<sub>2</sub> treated with a polydimethylhydrosiloxane, such as that sold under the trade name "Microtitanium Dioxide USP Grade Hydrophobic" by Color Techniques.

40 The uncoated titanium oxide pigments are, for example, sold by Tayca under the trade names "Microtitanium Dioxide MT 500 B" or "Microtitanium Dioxide MT600 B", by Degussa under the name "P 25", by Wacker under the name "Oxyde de titane transparent PW", by Miyoshi Kasei under the name "UFTR", by Tomen under the name "ITS" and by Tioxide under the name "Tioveil AQ".

45

The uncoated zinc oxide pigments are, for example:

- those sold under the name "Z-cote" by Sunsmart;

- those sold under the name "Nanox" by Elementis;
- those sold under the name "Nanogard WCD 2025" by Nanophase Technologies.

5 The coated zinc oxide pigments are, for example:

- those sold under the name "Z-cote HP1" by Sunsmart (ZnO coated with dimethicone);
- those sold under the name "Oxide zinc CS-5" by Toshiba (ZnO coated with polymethylhydrosiloxane);
- 10 - those sold under the name "Nanogard Zinc Oxide FN" by Nanophase Technologies (as a 40% dispersion in Finsolv TN, C12-C15 alkyl benzoate);
- those sold under the name "Daitopersion Zn-30" and "Daitopersion Zn-50" by Daito (dispersions in oxyethylenated polydimethylsiloxane/cyclopolymethylsiloxane comprising 30% or 50% of zinc oxides coated with silica and polymethylhydrosiloxane);
- 15 - those sold under the name "NFD Ultrafine ZnO" by Daikin (ZnO coated with phosphate of perfluoroalkyl and copolymer based on perfluoroalkylethyl as a dispersion in cyclopentasiloxane);
- those sold under the name "SPD-Z1" by Shin-Etsu (ZnO coated with silicone-grafted acrylic polymer dispersed in cyclodimethylsiloxane);
- 20 - those sold under the name "Escalol Z100" by ISP (alumina-treated ZnO dispersed in the ethylhexyl methoxycinnamate/PVP-hexadecene copolymer/methicone mixture);
- those sold under the name "Fuji ZnO-SMS-10" by Fuji Pigment (ZnO coated with silica and polymethylsilsesquioxane);
- 25 - those sold under the name "Nanox Gel TN" by Elementis (ZnO dispersed at 55% in C12-C15 alkyl benzoate with hydroxystearic acid polycondensate).

30 The uncoated cerium oxide pigments are sold, for example, under the name "Colloidal Cerium Oxide" by Rhône-Poulenc.

The uncoated iron oxide pigments are, for example, sold by Arnaud under the names "Nanogard WCD 2002 (FE 45B)", "Nanogard Iron FE 45 BL AQ",  
35 "Nanogard FE 45R AQ" or "Nanogard WCD 2006 (FE 45R)", or by Mitsubishi under the name "TY-220".

The coated iron oxide pigments are, for example, sold by Arnaud under the names "Nanogard WCD 2008 (FE 45B FN)", "Nanogard WCD 2009 (FE  
40 45B 556)", "Nanogard FE 45 BL 345" or "Nanogard FE 45 BL", or by BASF under the name "Oxyde de fer transparent".

Mention may also be made of mixtures of metal oxides, in particular of titanium dioxide and of cerium dioxide, including the mixture of equal  
45 weights of titanium dioxide coated with silica and of cerium dioxide coated with silica sold by Ikeda under the name "Sunveil A", and also the mixture of titanium dioxide and of zinc dioxide coated with alumina, with silica and

with silicone, such as the product "M 261" sold by Kemira, or coated with alumina, with silica and with glycerol, such as the product "M 211" sold by Kemira.

- 5 The inorganic UV screening agents are preferably present in amounts ranging from 0.01 to 30 % by weight relative to the total weight of the composition and more preferably 0.1 to 20 %.

### **SPHERICAL MICROPARTICLES OF POROUS SILICA**

10 According to a particular form of the invention, the compositions may further contain spherical microparticles of porous silica in order to optimize the stability, the light residue, the matte effect and the non-greasy feeling onto the skin.

15 The spherical microparticles of porous silica in accordance with the invention preferably have a mean particle size ranging from 0.5 to 20  $\mu\text{m}$  and more particularly from 3 to 15  $\mu\text{m}$ .

20 They preferably have a specific surface ranging from 50 to 1 000  $\text{m}^2/\text{g}$  and more particularly from 150 to 800  $\text{m}^2/\text{g}$ .

They preferably have a specific pore volume ranging from 0.5 to 5  $\text{ml}/\text{g}$  and more particularly from 1 to 2  $\text{ml}/\text{g}$ .

25 By way of example of microbeads of porous silica, it is possible to use the following commercial products:

Silica Beads SB 150 from Myoshi  
Sunsphere H-51 from Asahi Glass  
30 Sunsil 130 from Sunjin  
Spherica P-1500 from Ikeda Corporation  
Sylosphere from Fuji Silysia

35 The spherical microparticles of porous silica in accordance with the present invention are used in the compositions in accordance with the invention at concentrations preferably ranging from 0.1 to 10% by weight relative to the total weight of the composition and more particularly from 0.2 to 5% by weight.

### **OTHER ADDITIVES**

40 The compositions in accordance with the present invention can additionally comprise conventional cosmetic adjuvants chosen in particular from oils, waxes, organic solvents, softening agents, humectants, opacifiers,  
45 stabilizing agents, emollients, silicones, antifoaming agents, fragrances, preservatives, anionic, cationic, nonionic, zwitterionic or amphoteric surfactants, active principles, fillers, polymers, propellants, basifying or

acidifying agents or any other ingredient commonly used in the cosmetics and/or dermatological field.

- Of course, a person skilled in the art will take care to choose the optional  
5 additional compound or compounds mentioned above and/or their amounts  
so that the advantageous properties intrinsically attached to the  
compositions in accordance with the invention are not, or not substantially,  
detrimentally affected by the envisaged addition or additions,.
- 10 Mention may be made, among organic solvents, for example, of lower  
alcohols and polyols. The latter can be chosen from glycols and glycol  
ethers, such as ethylene glycol, propylene glycol, butylene glycol,  
dipropylene glycol or diethylene glycol.
- 15 The compositions in accordance with the invention generally comprise at  
least one oily phase that contains at least one oil, especially a cosmetic oil.  
The term "oil" means a fatty substance that is liquid at room temperature  
(25°C).
- 20 As oils that may be used in the composition of the invention, it is possible to  
use, for example, hydrocarbon-based oils of animal origin, such as  
perhydro-squalene (or squalane); hydrocarbon-based oils of plant origin,  
such as caprylic/capric acid triglycerides, for instance those sold by the  
25 company Stearineries Dubois or those sold under the names Miglyol 810,  
812 and 818 by the company Dynamit Nobel, or alternatively oils of plant  
origin, for instance sunflower oil, corn oil, soybean oil, marrow oil,  
grapeseed oil, sesameseed oil, hazelnut oil, apricot oil, macadamia oil,  
arara oil, coriander oil, castor oil, avocado oil, jojoba oil and shea butter oil;  
30 synthetic oils; silicone oils, for instance volatile or non-volatile  
polymethylsiloxanes (PDMS) containing a linear or cyclic silicone chain,  
which are liquid or pasty at room temperature; fluoro oils, such as partially  
hydrocarbon-based and/or silicone-based fluoro oils, for instance those  
described in document JP-A-2 295 912; ethers, such as dicaprylyl ether  
35 (CTFA name: Dicaprylyl ether); esters, for instance C12-C15 fatty alkyl  
benzoates (Finsolv TN from Finetex); arylalkyl benzoates, for instance 2-  
phenylethyl benzoate (X-Tend 226 from ISP); and amidated oils, for  
instance isopropyl N-lauroylsarcosinate (Eldew SL-205 from Ajimoto);  
mixtures thereof.
- 40 The oily phase may also comprise one or more fatty substances chosen,  
for example, from fatty alcohols (cetyl alcohol, stearyl alcohol or cetearyl  
alcohol), fatty acids (stearic acid) or waxes (paraffin, polyethylene wax,  
carnauba wax or beeswax). The oily phase may contain lipophilic gelling  
agents, surfactants or organic or mineral particles. The oily phase may  
45 preferably represent from 2% to 70% by weight of oil relative to the total  
weight of the composition.

According to a particular form of the invention, liquid organic lipophilic UV filters at room temperature may be used as the oils constituting the oily phase of the emulsion. As example of liquid lipophilic UV filters, can be mentioned Octocrylene, Ethylhexyl Methoxycinnamate, Homosalate, Ethylhexyl Salicylate and their mixtures.

Mention may be made, as wax, for example, of carnauba wax, beeswax, hydrogenated castor oil, polyethylene waxes and polymethylene waxes, such as that sold under the name Cirebelle 303 by Sasol.

The compositions according to the invention can be prepared according to techniques well known to a person skilled in the art. They can be provided in particular in the form of a simple or complex (O/W, W/O, O/W/O or W/O/W) emulsion, such as a cream, a milk. They can optionally be packaged as an aerosol and be provided in the foam or spray form.

Preferably, the compositions according to the invention are provided in the form of an oil-in-water or water-in-oil emulsion and more preferably in the form of an oil-in-water emulsion.

The emulsification processes which can be used are of the paddle or propeller, rotor-stator and HPH type.

It is also possible, by HPH (between 50 and 800 bar), to obtain stable dispersions with drop sizes which may be as low as 100 nm.

The emulsions generally comprise at least one emulsifying surfactant chosen from amphoteric, anionic, cationic or nonionic emulsifying surfactants, used alone or as a mixture. The emulsifiers are appropriately chosen according to the emulsion to be obtained (W/O or O/W emulsion).

Mention may be made, as emulsifying surfactants which can be used for the preparation of the W/O emulsions, for example, of alkyl esters or ethers of sorbitan, of glycerol or of sugars; or silicone surfactants, such as dimethicone copolyols, for example the mixture of cyclomethicone and of dimethicone copolyol sold under the name "DC 5225 C" by Dow Corning, and alkyl dimethicone copolyols, such as lauryl methicone copolyol, sold under the name "Dow Corning 5200 Formulation Aid" by Dow Corning, or cetyl dimethicone copolyol, such as the product sold under the name Abil EM 90R by Goldschmidt and the mixture of cetyl dimethicone copolyol, of polyglycerol (4 mol) isostearate and of hexyl laurate sold under the name Abil WE O9 by Goldschmidt. It is also possible to add thereto one or more coemulsifiers which, advantageously, can be chosen from the group consisting of polyol alkyl esters.

Mention may in particular be made, as polyol alkyl esters, of polyethylene glycol esters, such as PEG-30 dipolyhydroxystearate, such as the product



sold under the name Arlacel P135 by ICI.

5 Mention may be made, as glycerol and/or sorbitan esters, for example, of polyglycerol isostearate, such as the product sold under the name Isolan GI 34 by Goldschmidt; sorbitan isostearate, such as the product sold under the name Arlacel 987 by ICI; sorbitan glyceryl isostearate, such as the product sold under the name Arlacel 986 by ICI, and their mixtures.

10 Mention may be made, for the O/W emulsions, for example, as emulsifying surfactants, of nonionic emulsifiers, such as oxyalkylenated (more particularly polyoxyethylenated) esters of fatty acids and of glycerol; oxyalkylenated esters of fatty acids and of sorbitan; oxyalkylenated (oxyethylenated and/or oxypropylenated) esters of fatty acids, such as the PEG-100 stearate/glyceryl stearate mixture sold, for example, by ICI under the name Arlacel 165; oxyalkylenated (oxyethylenated and/or oxypropylenated) ethers of fatty alcohols; esters of sugars, such as sucrose stearate; or ethers of fatty alcohol and of sugar, in particular alkyl polyglucosides (APGs), such as decyl glucoside and lauryl glucoside, sold, for example, by Henkel under the respective names Plantaren 2000 and 20 Plantaren 1200, cetearyl glucoside, optionally as a mixture with cetearyl alcohol, sold, for example, under the name Montanov 68 by Seppic, under the name Tegocare CG90 by Goldschmidt and under the name Emulgade KE3302 by Henkel, and arachidyl glucoside, for example in the form of the mixture of arachidyl and behenyl alcohols and of arachidyl glucoside sold 25 under the name Montanov 202 by Seppic. According to a specific embodiment of the invention, the mixture of the alkyl polyglucoside as defined above with the corresponding fatty alcohol can be in the form of a self-emulsifying composition, for example as described in the document WO-A-92/06778.

30 When an emulsion is involved, the aqueous phase of the latter can comprise a nonionic vesicular dispersion prepared according to known processes (Bangham, Standish and Watkins, J. Mol. Biol., 13, 238 (1965), FR 2 315 991 and FR 2 416 008).

35 When it is an emulsion, the aqueous phase of the said emulsion may comprise a nonionic vesicular dispersion prepared according to known processes (Bangham, Standish and Watkins, J. Mol. Biol. 13, 238 (1965), FR 2 315 991 and FR 2 416 008).

40 According to one particular embodiment of the invention, the oil-in-water emulsions may comprise only 1% by weight or less of emulsifying surfactants, and may even be free of emulsifying surfactants, while at the same time being stable on storage. In this case, they may be stabilized via 45 various techniques such as the use of the hydrophilic or lipophilic thickeners such as those of patent EP 864 320, amphiphilic polymers such as those mentioned in patent EP 1 093 796 or in patent application WO

02/44231, and solid particles (Pickering-type emulsions) such as the emulsions mentioned in patent applications WO 98/42300, WO 98/42301, EP 98/7001, EP 98/7002, EP 98/7003, EP 98/7004, EP 98/7005, EP 98/7006, EP 98/7007, EP 98/7008, WO 2000/07548, WO 2000/07549 and EP 99/2233.

The compositions according to the invention have applications in a large number of treatments, in particular cosmetic treatments, of the skin, lips and hair, including the scalp, in particular for protecting and/or caring for the skin, lips and/or hair and/or for making up the skin and/or lips.

Another subject-matter of the present invention is composed of the use of the compositions according to the invention as defined above in the manufacture of products for the cosmetic treatment of the skin, lips, nails, hair, eyelashes, eyebrows and/or scalp, in particular of care products, sun protection products and make-up products.

The cosmetic compositions according to the invention can, for example, be used as make-up product.

The cosmetic compositions according to the invention can, for example, be used as care product and/or sun protection product for the face and/or body with a liquid to semi-liquid consistency, such as lotions, milks, relatively smooth creams, creams. They can optionally be packaged as an aerosol and be provided in the form of a foam or of a spray.

According to a particular form of the invention, the compositions may be fluid emulsions.

The term "fluid emulsion" is understood to mean any emulsion not existing in a solid form. Its viscosity can be measured using a Rheomat 180 viscometer at 25°C with a measuring body 2 at a rotational speed of 200 rpm after rotating for 10 minutes and is less than 900 mPa.s, more preferably less than 700 mPa.s, more preferably ranging from 150 to 650 mPa.s.

The compositions according to the invention in the form of vaporizable fluid lotions in accordance with the invention are applied to the skin or hair in the form of fine particles by means of pressurizing devices. The devices in accordance with the invention are well known to a person skilled in the art and comprise nonaerosol pumps or "atomizers", aerosol containers comprising a propellant and aerosol pumps using compressed air as propellant. The latter are described in Patents US 4 077 441 and US 4 850 517 (forming an integral part of the content of the description).

The compositions packaged as an aerosol in accordance with the invention generally comprise conventional propellants, such as, for example,

hydrofluorinated compounds, dichlorodifluoromethane, difluoroethane, dimethyl ether, isobutane, n-butane, propane or trichlorofluoromethane. They are preferably present in amounts ranging from 15 to 50% by weight, with respect to the total weight of the composition.

5

The compositions according to the invention can, in addition, also comprise additional cosmetic and dermatological active principles.

Mention may be made, among active principles, of:

- 10 - vitamins (A, C, E, K, PP, and the like) and their derivatives or precursors, alone or as mixtures;
- antiaging agents;
  - antioxidants;
  - agents for combating free radicals;
  - 15 - antiglycation agents;
  - smoothing agents;
  - NO-synthase inhibitors;
  - agents which stimulate the synthesis of dermal or epidermal macromolecules and/or which prevent their decomposition;
  - 20 - agents which stimulate the proliferation of fibroblasts;
  - agents which stimulate the proliferation of keratinocytes;
  - dermo-decontracting agents;
  - tightening agents;
  - matifying agents;
  - 25 - keratolytic agents;
  - desquamating agents;
  - moisturizing agents, such as, for example, polyols, such as glycerol, butylene glycol or propylene glycol;
  - agents which act on the energy metabolism of the cells;
  - 30 - insect repellents;
  - substance P or substance CRGP antagonists;
  - agents for combating hair loss and/or for the regrowth of the hair;
  - antiwrinkle agents;
  - agents which modulate the pigmentation of the skin or hair;
  - 35 - astringent agents;
  - sebum-regulating agents or antiseborrhoeics.

Of course, a person skilled in the art will take care to choose the optional additional compound or compounds mentioned above and/or their amounts so that the advantageous properties intrinsically attached to the compositions in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions.

40

A person skilled in the art will choose the said active principle or principles according to the effect desired on the skin, hair, eyelashes, eyebrows or nails.

45

In addition, the composition can comprise at least one ingredient, such as fillers having a soft focus effect or agents which promote the natural colouring of the skin, intended to supplement the biological effect of these active principles or to contribute an immediate visual antiaging effect.

5

### **OTHER ADDITIONAL INGREDIENTS**

In addition, the composition can comprise at least one additional ingredient intended to contribute an immediate visual effect. Mention may in particular be made of agents which promote the naturally pink colouring of the skin.

10

Mention may be made, as agents which promote the naturally pink colouring of the skin, for example, of self-tanning agents, that is to say an agent which, applied to the skin, in particular to the face, makes it possible to obtain a tanning effect with an appearance more or less similar to that which can result from prolonged exposure to the sun (natural tanning) or under a UV lamp.

15

Mention may in particular be made, as examples of self-tanning agents, of: dihydroxyacetone (DHA), erythulose, and the combination of a catalytic system formed of: manganese and/or zinc salts and oxides, and alkali metal and/or alkaline earth metal hydrogencarbonates.

20

25

The self-tanning agents are generally chosen from mono- or polycarbonyl compounds, such as, for example, isatin, alloxan, ninhydrin, glyceraldehyde, mesotartaric aldehyde, glutaraldehyde, erythulose, pyrazoline-4,5-dione derivatives, such as described in Patent Applications FR 2 466 492 and WO 97/35842, dihydroxyacetone (DHA) or 4,4-dihydropyrazolin-5-one derivatives, such as described in Patent Application EP 903 342. Use will preferably be made of DHA.

30

The DHA can be used in the free and/or encapsulated form, for example encapsulated in lipid vesicles, such as liposomes, described in particular in Application WO 97/25970.

35

Generally, the self-tanning agent is present in an amount ranging from 0.01 to 20% by weight and preferably in an amount of between 0.1 and 10% of the total weight of the composition.

40

Use may also be made of other dyes which make it possible to modify the colour produced by the self-tanning agent. These dyes can be chosen from synthetic or natural direct dyes.

45

These dyes can be chosen, for example, from red or orange dyes of the fluoran type, such as those described in Patent Application FR 2 840 806.

Mention may be made, for example, of the following dyes:

- tetrabromofluorescein or eosin, known under the CTFA name: CI 45380 or Red 21;
- phloxine B, known under the CTFA name: CI 45410 or Red 27;
- 5 - diiodofluorescein, known under the CTFA name: CI 45425 or Orange 10;
- dibromofluorescein, known under the CTFA name: CI 45370 or Orange 5;
- the sodium salt of tetrabromofluorescein, known under the CTFA name: CI 45380 (Na salt) or Red 22;
- the sodium salt of phloxine B, known under the CTFA name: CI 45410
- 10 (Na salt) or Red 28;
- the sodium salt of diiodofluorescein, known under the CTFA name: CI 45425 (Na salt) or Orange 11;
- erythrosine, known under the CTFA name: CI 45430 or Acid Red 51;
- phloxine, known under the CTFA name: CI 45405 or Acid Red 98.
- 15 These dyes can also be chosen from anthraquinones, caramel, carmine, carbon black, azulene blues, methoxsalen, trioxsalen, guaiazulene, chamazulene, rose bengal, eosin 10B, cyanosine or daphinine.

20 These dyes can also be chosen from indole derivatives, such as monohydroxyindoles, such as described in Patent FR 2 651 126 (i.e.: 4-, 5-, 6- or 7-hydroxyindole), or dihydroxyindoles, such as described in Patent EP-B-0 425 324 (i.e.: 5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole, 3-methyl-5,6-dihydroxyindole or 2,3-dimethyl-5,6-dihydroxyindole).

25 The examples which follow serve to illustrate the invention, but without having any limiting character. In these examples, the amounts of the ingredients of the compositions are given as % by weight, with respect to the total weight of the composition.

<b>Ingrédients</b>	<b>Ex 1 *</b>	<b>Ex 2 *</b>	<b>Ex 3 *</b>
Butylmethoxy Dibenzoylmethane (® PARSOL 1789)	1	1	1
Homosalate (® UVINUL T150)	6	6	6
BIS-ETHYLHEXYLOXYPHENOL METHOXYPHENYL TRIAZINE (®TINOSORB S)	1,2	1,2	1,2
Drometrizole Trisiloxane	1	1	1
Dimethicone	2	2	2
Phenylbenzimidazole Sulfonic Acid (® EUSOLEX 232)	1.5	1.5	1.5
Gomme de Xanthane (KELTROL CG-T - CP KELCO)	0.2	-	-
Carbomer (CARBOPOL 980 POLYMER - LUBRIZOL)	-	0.15	-
POLYACRYLAMIDE (and) C13-14 ISOPARAFFIN (and) LAURETH-7 (SEPIGEL 305- SEPPIC)	-	-	1
Acrylates/C <sub>10</sub> -C <sub>30</sub> Alkyl Acrylate Crosspolymer (PEMULEN TR2 - Lubrizol)	0.3	0.3	0.3
Sodium Stearoyl Glutamate (® AMISOFT HS 11 PF - Ajinomoto)	0.3	0.3	0.3
PENTASODIUM ETHYLENEDIAMINE TETRAMETHYLENE PHOSPHONATE (Dequest 2046 - Thermphos)	0.3	0.3	0.3
Spherical microparticles of porous silica (5µm) (® SUNSPHERE H51 - AGC-SI TEH)	3	3	3
Triéthanolamine	1.49	1.49	1.49
Propyleneglycol	3	3	3
Preservatives	0,8	0,8	0,8
Water	qsp 100	qsp 100	qsp 100

\* out of invention

<b>Ingrédients</b>	<b>Ex 4</b>
Butylmethoxy Dibenzoylmethane (® PARSOL 1789)	1
Homosalate (® UVINUL T150)	6
BIS-ETHYLHEXYLOXYPHENOL      METHOXYPHENYL TRIAZINE (®TINOSORB S)	1,2
Drometrizole Trisiloxane	1
Dimethicone	2
Phenylbenzimidazole Sulfonic Acid (® EUSOLEX 232)	1.5
Ammonium                      Acryloyldimethyltaurate/Steareth-25 Methacrylate Crosspolymer sold under the name ® Aristoflex HMS by Clariant	0.35
Acrylates/C <sub>10</sub> -C <sub>30</sub> Alkyl Acrylate Crosspolymer (PEMULEN TR2 –Lubrizon)	0.3
Sodium Stearoyl Glutamate (® AMISOFT HS 11 PF – Ajinomoto)	0.3
PENTASODIUM                                      ETHYLENEDIAMINE TETRAMETHYLENE PHOSPHONATE (Dequest 2046 – Thermphos)	0.3
Spherical microparticles of porous silica (5µm) (® SUNSPHERE H51 – AGC-SI TEH)	3
Triéthanolamine	1.49
Propyleneglycol	3
Preservatives	0,8
Water	qsp 100

5 All the compositions 1 to 4 have a viscosity in the same range 290-322 mPa.s measured using a Rheomat 180 viscometer at 25°C with a measuring body 2 at a rotational speed of 200 rpm after rotating for 10 minutes . The different mixtures of polymers were used for each formula in a sufficient amount to obtain the viscosity in the same range as above defined.

10 For the compositions 1 to 4, a stability test and a sensorial test were carried out.

#### **Stability protocol:**

15 This stability protocol contains T0 and T2 Months check.  
T2 Months have 4 °C, 37 °C, 45 °C and room temperature (RT).  
T0 means 24 hours after the trial.  
T2 Months means 2 months after T0.  
T2 Months is the accelerated stability studies.

Aspect of the composition, pH, presence of oil on the surface, viscosity, microscope and centrifugation were observed.

**Sensorial test protocol:**

5

A sensorial test was carried out on 10 experts who evaluated the different formulations according to the following criteria with values on a schedule from 1 to 5.:

10

Watery effect on application on the hand and face : Score 1 watery, score 5 not watery. For watery, under 3 consider watery feeling, above and equal 4 means not watery, from 3 (including equal 3) to 4 consider medium watery. In this invention, score under 3 (not including equal 3), watery is acceptable.

15

Fresh feeling on application on the hand and face : Score 1 fresh, score 5 not fresh. Under 3 consider fresh, above and equal 4 consider not fresh, from 3 (including equal 3) to 4 consider medium fresh. In this invention, score under 3 (not including equal 3), fresh feeling is acceptable.

20

Film skin after application score : 1 light film, score 5 heavy film. Under and equal 3 consider light film, above and equal 4 consider heavy finish, from 3 (including equal 3) to 4 consider medium film. In this invention, score under 3 (not including equal 3), film on skin is light and acceptable.

25

The average score will be calculated.

Each product is applied to the hand and to the face, and evaluated both ways.

30

The definition of watery is the ability to create an immediate sensation of water, the watery sensation is evaluated tactilely, when applying 0.5ml if the product on the upper surface of the hand (and face), from the first circular movement.

35

The definition of fresh is the ability to create an immediate sensation of coolness, the refreshing sensation is evaluated tactilely, when applying 0.5ml if the product on the upper surface of the hand (and face), from the first circular movement.

40

The definition of a light or heavy film is evaluated tactilely, after application 0.5 ml of the product to the hand (and face).

45

For the composition 4, the following are also evaluated for each of the compositions:



(1) the in vivo SPF on 5 subjects according to the international method published by Colipa/ CTFA SA/JCIA (May 2006)

(2) the UV-APPD PF on 5 subjects according to the recommendations of the JCIA (version of 15/11/1995).

5

The results are shown in the following table :

**RESULTS :**

10

<b>Exemples</b>	<b>Stability</b>	<b>Watery effect</b>	<b>Fresh effect</b>	<b>Film</b>
<b>Ex1*</b>	unstable	2.5	2.5	2
<b>Ex2*</b>	stable	3	3.5	2
<b>Ex3*</b>	unstable	3	3.5	3
<b>Ex4 (invention)</b>	stable	1.5	1.5	1

\* out of invention

<b>Exemple</b>	<b>SPF</b>	<b>PPD</b>
<b>Ex4 (invention)</b>	18.4 +/- 3.3	5.0 +/- 1.4

15

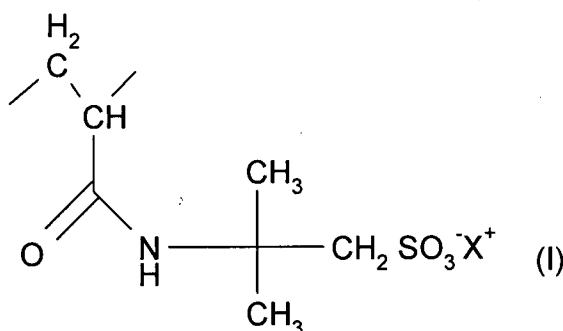
Only the composition 4 according to the invention containing the amphiphilic copolymer A : Ammonium Acryloyldimethyltaurate/Steareth-25 Methacrylate Crosspolymer and the amphiphilic copolymer B : Acrylates/C<sub>10</sub>-C<sub>30</sub> Alkyl Acrylate Crosspolymer gives a good sun protection,

20

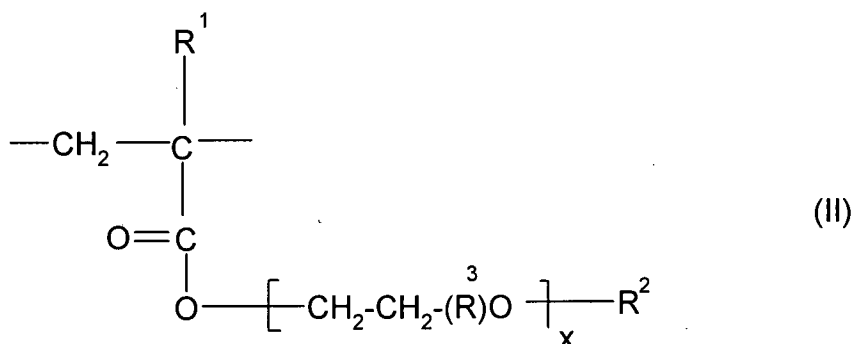
a pleasant watery and fresh effect and gives a light film on the skin.

**CLAIMS**

- 5 **1.** Composition comprising at least one aqueous phase, one oily phase and a system for screening out UV radiation, characterized in that it contains in a cosmetically acceptable medium :
- 10 (i) at least one amphiphilic copolymer A comprising at least one ethylenically unsaturated monomer containing a sulphonic group, in free form or partially or totally neutralized form, and comprising at least one hydrophobic group and
- 15 (ii) at least one amphiphilic copolymer B of at least one monomer chosen from carboxylic acids possessing  $\alpha,\beta$ -ethylenic unsaturation or their esters with a monomer possessing ethylenic unsaturation comprising a hydrophobic group and
- (iii) at least one lipophilic organic UV screening agent.
- 2.** Composition according to claim 1, wherein the amphiphilic copolymer A is a copolymer of 2-acrylamido-2-methylpropanesulphonic acid in free form or partially or totally neutralized forms of formula (I)



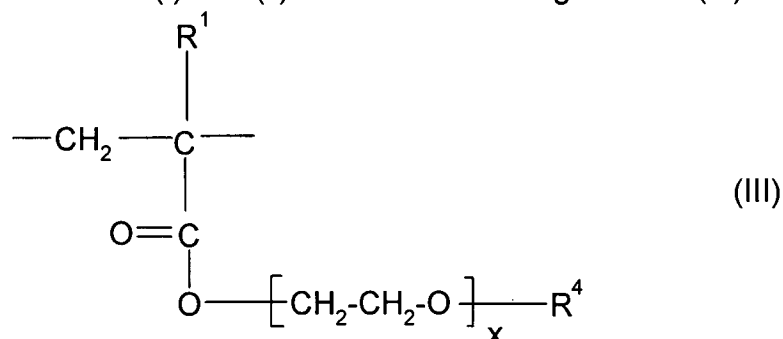
- 25 in which  $\text{X}^+$  denotes a proton, an alkali metal cation, an alkaline earth metal cation or the ammonium ion and a hydrophobic monomer of formula (II) :



- 30 in which  $\text{R}^1$  and  $\text{R}^3$ , which are identical or different, denote a hydrogen atom or a substantially linear or branched  $\text{C}_1\text{-C}_6$  alkyl radical (preferably a methyl radical);  $\text{Y}$  denotes O or NH;  $\text{R}^2$  denotes a hydrocarbon radical comprising from 6 to 50 carbon atoms, more preferably from 6 to 22 carbon

atoms, more preferably still from 6 to 18 carbon atoms and more particularly from 12 to 18 carbon atoms; and x denotes a number of moles of alkylene oxide and varies from 0 to 100.

- 5 **3.** Composition according to claim 2, wherein the amphiphilic copolymer A is a copolymer composed (i) of 2-acrylamido-2-methylpropanesulphonic acid units of formula (I) and (ii) of units of following formula (III):



- 10 in which x denotes an integer varying from 3 to 100, preferably from 3 to 50 and more preferably from 7 to 25; R<sup>1</sup> has the same meaning as that indicated in the formula (II) and R<sup>4</sup> denotes a linear or branched alkyl radical comprising from 6 to 22 carbon atoms and preferably from 10 to 22 carbon atoms.

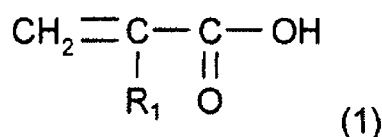
- 15 **4.** Composition according to any one of claims 1 to 3, wherein the amphiphilic copolymer A is selected from :

- a non-crosslinked copolymer of 2-acrylamido-2-methylpropanesulphonic acid and of ethoxylated C<sub>12</sub>-C<sub>14</sub> alkyl methacrylate (noncrosslinked copolymer
- 20 - a crosslinked copolymer of ammonium salt of 2-acrylamido-2-methylpropanesulphonic acid and of ethoxylated (25 EO) stearyl methacrylate.

- 25 **5.** Composition according to any one of claims 1 to 4, wherein the amphiphilic copolymer A is a crosslinked copolymer of ammonium salt of 2-acrylamido-2-methylpropanesulphonic acid and of ethoxylated (25 EO) stearyl methacrylate.

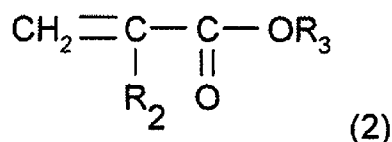
- 30 **6.** Composition according to any one of claims 1 to 5, wherein the amphiphilic copolymer B is chosen from copolymers resulting from the polymerization:

- a) of at least one monomer of following formula (1):



- 35 in which R<sub>1</sub> denotes H or CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>, that is to say acrylic acid,

methacrylic acid or ethacrylic acid monomers, and  
 b) of at least one monomer of unsaturated carboxylic acid (C<sub>10</sub>-C<sub>30</sub>)alkyl ester type which corresponds to the monomer of following formula (2):



5 in which R<sub>2</sub> denotes H or CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> (that is to say, acrylate, methacrylate or ethacrylate units) and preferably H (acrylate units) or CH<sub>3</sub> (methacrylate units) and R<sub>3</sub> denotes a C<sub>10</sub>-C<sub>30</sub> and preferably C<sub>12</sub>-C<sub>22</sub> alkyl radical.

10 **7.** Composition according to claim 6, wherein the amphiphilic copolymer B is chosen from copolymers resulting from the polymerization of a mixture of monomers comprising:

- (i) acrylic acid,
- (ii) an ester of formula (2) in which R<sub>2</sub> denotes H or CH<sub>3</sub> and R<sub>3</sub> denotes an alkyl radical having from 12 to 22 carbon atoms,
- (iii) and a crosslinking agent which is a copolymerizable polyethylenic unsaturated monomer, preferably selected from diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate and methylenebisacrylamide.

20 **8.** Composition according to claim 7, wherein the amphiphilic copolymer B is composed of 95 to 60% by weight of acrylic acid, 4 to 40% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate and 0 to 6% by weight of crosslinking polymerizable monomer or else of those composed of 98 to 96% by weight of acrylic acid,  
 25 1 to 4% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate and 0.1 to 0.6% by weight of crosslinking polymerizable monomer.

30 **9.** Composition according to any one of claims 1 to 8, wherein the lipophilic organic screening agent is chosen from anthranilates; cinnamic derivatives; salicylic derivatives; camphor derivatives; benzophenone derivatives; β,βdiphenylacrylate derivatives; triazine derivatives ; benzotriazole derivatives ; benzmalonate derivatives; benzimidazole derivatives; imidazolines ; bis-benzazolyl derivatives ; p-aminobenzoic acid (PABA) derivatives; methylenebis(hydroxyphenylbenzotriazole) derivatives ;  
 35 screening polymers and screening silicones ; α-alkylstyrene-based dimmers ; 4,4-diarylbutadienes ; merocyanin derivatives and mixtures thereof.

40 **10.** Composition according to any one of claims 1 to 6, containing at least one UVA lipophilic organic screening agent and at least one UVB lipophilic organic screening agent and/or at least one UVA and UVB lipophilic organic screening agent.

- 11.** Composition according to claim 10, wherein  
(i) the UVA lipophilic organic screening agent is selected from :  
Butyl Méthoxydibenzoylméthane ;  
5 n- Hexyl 2-(4-diéthylamino-2-hydroxybenzoyl)-benzoate ;  
(ii) the UVB lipophilic organic screening agent is selected from :  
Ethylhexylsalicylate ;  
Homosalate  
Octocrylene ;  
10 (iii) the UVA and UVB lipophilic organic screening agent is selected from :  
Drométrizole Trisiloxane ;  
Méthylène bis-Benzotriazolyl Tétraméthylbutylphénol ;  
Bis-Ethylhexyloxyphénol Méthoxyphenyl Triazine.
- 12.** Composition according to any one of claims 1 to 11, further containing  
15 at least a hydrophilic organic UV sunscreen agent and/or an inorganic UV  
sunscreen.
- 13.** Composition according to any one of claims 1 to 12, containing a  
20 mixture of UVA and UVB screening agents selected from :  
(1) Butylmethoxydibenzoylmethane, Octocrylene, Homosalate and  
Phenylbenzimidazole Sulfonic Acid ;  
(2) Butylmethoxydibenzoylmethane, Bis-Ethylhexyloxyphénol  
Méthoxyphenyl Triazine, Homosalate, Drométrizole Trisiloxane and  
25 Phenylbenzimidazole Sulfonic Acid and more preferably the following  
mixture :  
(3) n-Hexyl 2-(4-diéthylamino-2-hydroxybenzoyl)-benzoate, Ethylhexyl  
Méthoxycinnamate, Terephtalylidene Dicapmor Sulfonic Acid and  
Phenylbenzimidazole Sulfonic Acid.
- 14.** Composition according to any one of claims 1 to 13, further containing  
30 spherical microparticles of porous silica.
- 15.** Composition according to any one of claims 1 to 14, in the form of an  
35 oil-in-water or water-in-oil emulsion and preferably in the form of an oil-in-  
water emulsion.
- 16.** Composition according to any one of claims 1 to 15, characterized in  
40 that it is a fluid emulsion.