(54) Title: SUNSCREENING EMULSION CONTAINING CROSSLINKED HOMOPOLYMER OF (METH)ACRYLAMIDO(Ci-Ca)ALKYSULPHONIC ACID AND HOMOPOLYMER OF ACRYLIC ACID AT LEAST PARTIALLY NEUTRALIZED

(57) Abstract: A composition comprises 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: (a) at least one partially or totally neutralized, crosslinked or non-crosslinked homopolymer of (methyl)acrylamido(Ci-Ca)alkylsulphonic acid, and (b) at least one non-crosslinked or one crosslinked homopolymer of acrylic acid at least partially neutralized, (c) at least one lipophilic organic UV screening agent.

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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:

(a) at least one partially or totally neutralized, crosslinked or non-crosslinked homopolymer of (meth)acrylamido (Cl -C₄)alkylsulphonic acid, and

(b) at least one non-crosslinked or crosslinked homopolymer of acrylic acid at least partially neutralized

(c) at least one lipophilic organic UV screening agent.

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

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 erythermal reaction or accentuate this reaction in some subjects and can even be the cause of phototoxic or photoallergic reactions. Thus, for aesthetic and 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.

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.

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.
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 sunscreening agents generally needs to be solubilised in the oily phase.

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.

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.

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 SPF superior 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 suncare 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(Ci-C₄)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 (a) at least one partially or totally neutralized, crosslinked or non-crosslinked homopolymer of meth)acrylamido(Ci-C₄)alkylsulphonic acid, and (b) at least one non-crosslinked homopolymer of acrylic acid at least partially neutralized 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:

(a) at least one partially or totally neutralized, crosslinked or non-crosslinked homopolymer of meth)acrylamido(Ci-C₄)alkylsulphonic acid, and

(b) at least one non-crosslinked or crosslinked homopolymer of acrylic acid at least partially neutralized

(c) 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.

**HOMOPOLYMER OF METH)ACRYLAMIDO(C1-C4)ALKYLSULPHONIC ACID**

These polymers are preferably crosslinked.

Among these polymers that may especially be mentioned are:
- polyacrylamidomethanesulphonic acid,
- polyacrylamidoethanesulphonic acid,
- polyacrylamidopropanesulphonic acid,
- poly-2-acrylamido-2-methylpropanesulphonic acid,
- poly-2-methylacrylamido-2-methylpropanesulphonic acid,
- poly-2-acrylamido-n-butanesulphonic acid.

Polymers of this type and especially crosslinked and partially or totally neutralized poly-2-acrylamido-2-methylpropanesulphonic acids are known, described and prepared in document DE-A-196 25 810.

The preferred poly(meth)acrylamido (C1-C4)alkylsulphonic acids are crosslinked and at least 90% neutralized. These polymers may be crosslinked especially with a crosslinking unit containing at least two olefinic double bonds. The crosslinking units containing at least two olefinic double bonds may be chosen, for example, from dipropylene glycol diallyl ether, polyglycol diallyl ethers, triethylene glycol divinyl ether, hydroquinone diallyl ether, tetraallyloxethane or other allyl or vinyl ethers of polyfunctional alcohols, tetraethylene glycol diacrylate, triallylamine, trimethylolpropane diallyl ether, methylenebisacrylamide and divinylbenzene.

The crosslinking units containing at least two olefinic double bonds are even more particularly chosen from those corresponding to general formula (III) below:

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\[
\begin{array}{c}
  \text{H}_2\text{C} & \text{C} \quad \text{O} \quad \text{CH}_2 \\
  \text{O} & \quad \text{C} \quad \text{CH}_2 & \text{CH}_3 \\
\end{array}
\]
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in which \( R_1 \) denotes a hydrogen atom or a C1-C4 alkyl radical. The crosslinking unit may more particularly be trimethylolpropane triacrylate (Ri
The preferred poly(meth)acrylamido(Ci-C\textsubscript{4})alkylsulphonic acids are especially poly-2-acrylamido-2-methylpropanesulphonic acids that are characterized in that they comprise, randomly distributed:

a) from 90% to 99.9% by weight of units of formula (IV) below:

\[
\text{CH}_3\text{CH}\text{SO}_3^-\text{X}^+\text{CH}_3
\]

in which \(\text{X}^+\) denotes a cation or a mixture of cations,

b) from 0.01% to 10% by weight of at least one crosslinking unit containing at least two olefinic double bonds, the weight proportions being defined relative to the total weight of the polymer.

\(\text{X}^+\) is preferably selected from a proton \((\text{H}^+\)), an alkali metal cation, a cation equivalent to that of an alkaline-earth metal, or an ammonium ion. Ammonium ion is particularly preferred.

The crosslinked and neutralized poly-2-acrylamido-2-methylpropanesulphonic acid used preferably comprises from 98% to 99.5% by weight of units of formula (III) and from 0.5% to 2% by weight of crosslinking units, the crosslinking unit preferably being trimethylolpropane triacrylate.

The crosslinked and partially or totally neutralized poly-2-acrylamido-2-methylpropanesulphonic acids are generally known under the name "Ammonium Polyacrylamido-2-methylpropanesulphonate" or "Ammonium Polyacryldimethyltauramide" (INCI name).

A product that is particularly preferred according to the invention is the one sold by the company Clariant under the trade name ® Hostacerin AMPS, which is a crosslinked poly-2-acrylamido-2-methylpropanesulphonic acid partially neutralized with ammonia.

The crosslinked poly(meth)acrylamido(Ci-C\textsubscript{4})alkylsulphonic acids may be obtained according to the known preparation process comprising the following steps:

(a) the 2-(meth)acrylamido(Ci-C\textsubscript{4})alkylsulphonic acid monomer in free form is dispersed or dissolved in a solution of tert-butanol or in a solution of
water and tert-butanol;
(b) the monomer solution or dispersion obtained in (a) is neutralized with one or more mineral or organic bases, preferably aqueous ammonia, in an amount producing a degree of neutralization of the sulphonic acid functions of the polymer ranging from 0 to 100%;
(c) the crosslinking monomer(s) is(are) added to the solution or dispersion obtained in (b);
(d) a standard free-radical polymerization is performed in the presence of free-radical initiators at a temperature ranging from 10 to 150°C, the polymer precipitating in the tert-butanol-based solution or dispersion.

The amount of poly(meth)acrylamido(Ci-C_j)alkylsulphonic acid 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.

HOMOPOLYMERS OF ACRYLIC ACID.

The homopolymers of acrylic acid according to the invention may be present in the composition under a non particular form or in a particular form.

When they are under a particular form, their average size, under hydrated form is preferentially inferior or equal to 10 µm and more preferably inferior or equal to 5 µm. Under dry state or non hydrated state, their average size inferior por equal to 2 µm and more preferably inferior or equal to 1 µm.

The non-crosslinked and crosslinked homopolymers of acrylic acid according to the invention are preferably selected from polyacrylates of an alkaline-earth metal such as sodium polyacrylates de sodium and potassium polyacrylates. The Sodium Polyacrylate is particulary preferred.

The non-crosslinked and crosslinked homopolymers of acrylic acid according to the invention are preferably neutralized in an amount ranging from 5 to 80 %.

According to a particular form of the invention, homopolymers of acrylic acid will be non crosslinked.

According to a particular form of the invention, homopolymers of acrylic acid will be crosslinked. The crosslinking may be obtainind according to a well-known method for a skilled man in the art, particularly in the description of the document US 6,197,283 or the description of the US 6,444,785 which mention suitable crosslinking agents.

These polymers may be crosslinked especially with a crosslinking unit
containing at least two olefinic double bonds. The crosslinking units containing at least two olefinic double bonds may be chosen, for example, from dipropylene glycol diallyl ether, polyglycol diallyl ethers, triethylene glycol divinyl ether, hydroquinone diallyl ether, tetraallyloxyethane or other allyl or vinyl ethers of polyfunctional alcohols, tetraethylene glycol diacrylate, triallylamine, trimethylolpropane diallyl ether, methylenebisacrylamide and divinylbenzene.

According to a particular form of the invention, homopolymers of acrylic acid may be a mixture of a non crosslinked, homopolymer of acrylic acid and of a crosslinked homopolymer of acrylic acid and of:

As examples of homopolymers of acrylic acid, we can mention:
- sodium polyacrylates under INCI name SODIUM POLYACRYLATE as those sold under the commercial name Cosmedia SP® containing 90 % of dry material and 10 % of water, or Cosmedia SPL® under the form of inverse emulsion containing about 60 % of dry material, an oil (Hydrogenated Polydecene) and a surfactant (PPG-5 Laureth-5) having the INCI NAME SODIUM ACRYLATE (AND) POLYHYDROGENATED POLYDECENE (AND) PPG-5 LAURETH-5, both sold by the company;
- partially neutralized sodium polyacrylates de sodium under the form of inverse emulsion with a polar oil (ie : Capric/Caprylic Triglerides) as the product under the INCI name : CAPRYLIC/CAPRIC TRIGLYCERIDE (and) SODIUM ACRYLATES COPOLYMER and sold under the commercial name Luvigel® EM by the company BASF ; and
- their melanges.

The homopolymers of acrylic acid are preferably present in the composition according to the invention, in an amount ranging from 0.05 to 2 % by weight relative to the total weight of the composition and more preferably ranging from 0.1 to 1 %.

**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; p,p-diphenylacrylate derivatives; triazine derivatives ; benzotriazole derivatives; benzalmalonate derivatives, especially those mentioned in patent US 5 624 663; 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
screening polymers and screening silicones such as those described especially in patent application WO 93/04665; alkylstyrene-based dinners, 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 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.

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

Dibenzoylmethane derivatives:
Butyl Methoxydibenzoylmethane sold in particular under the trade name «® PARSOL 1789 » by DSM Nutritional Products, Inc;

Aminobenzophenone derivatives:
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 91 9803-06-8)

Anthranilates derivatives
- Menthol anthranilate vendu notamment sous le nom commercial « ® NEO HELIOPAN MA » par SYMRISE;

4,4-diarylbutadienes derivatives:
1,1'-dicarboxy (2,2'-dimethyl-propyl)-4,4-diphenylbutadiene;

Merocyanine derivatives:
Octyl-5-N,N-diethylamino-2-phenylsulfonyle-2,4-pentadienoate;

According to a preferred embodiment of the invention, the UVA lipophilic organic screening agent will be selected from:
Butyl Methoxydibenzoylmethane;
n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)-benzoate;

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

Para-aminobenzoate derivatives:
- Ethyl PABA;
- Ethyl Dihydroxypropyl PABA;
- Ethylhexyl Dimethyl PABA (® ESCALOL 507 de ISP);
Salicylic derivatives:
Homosalate sold in particular under the trade name «® Eusolex HMS » by Rona/EM Industries;
Ethylhexyl Salicylate sold in particular under the trade name «® NEO HELIOPAN OS » by SYMRISE;
Dipropylene glycol Salicylate sold in particular under the trade name «® DIPSAL » by SCHER;
TEA Salicylate sold in particular under the trade name «® NEO HELIOPAN TS » by SYMRISE.

Cinnamic derivatives
Ethylhexyl Methoxycinnamate sold in particular under the trade name «® PARSOL MCX » by DSM Nutritional Products, Inc.;
Isopropyl Methoxy cinnamate;
Isoamyl Methoxy cinnamate sold in particular under the trade name «® NEO HELIOPAN E1000 » by SYMRISE;
Diisopropyl Methylcinnamate;
Cinnoxate;
Glyceryl Ethylhexanoate Dimethoxycinnamate;

β,β′-diphenylacrylate derivatives:
Octocrylene, sold in particular under the trade name «® UVINUL N539 » par BASF;
Etocrylene, sold in particular under the trade name «® UVINUL N35 » par BASF;

Benzylidene camphor derivatives:
3-Benzylidene camphor manufactured in particular under the trade name «® MEXORYL SD » by CHIMEX;
Methylbenzylidene Camphor sold in particular under the trade name «® EUSOLEX 6300 » by MERCK;
Polyacrylamidomethyl Benzylidene Camphor manufactured in particular under the trade name «® MEXORYL SW » by CHIMEX;

Thazine derivatives:
Ethylhexyl triazone manufactured in particular under the trade name «® UVINUL T150 » by BASF;
Diethylhexyl Butamido Triazone manufactured in particular under the trade name «® UVASORB HEB » by SIGMA 3V;
2,4,6-ths(4′-amino benzalmalonate de dineopentyle)-s-triazine;
2,4,6-tris(4′-amino benzalmalonate de diisobutyle)-s-triazine;
2,4-bis(4′-amino benzalmalonate de dineopentyle)-6-(4′-aminobenzoate de n-butyle)-s-triazine;
2,4-bis(4′-amino benzoate de n-butyle)-6-(aminopropyltrisiloxane)-s-triazine;
Symmetrical triazine filters as described in the patent US 6,225,467, WO 2004/085412 (see compounds 6 et 9) or the document « Symmetrical
Triazine Derivatives » IP.COM Journal, IP.COM INC WEST HENRIETTA, NY, US (20 septembre 2004) in particular 2,4,6-tris-(biphenyl)-1,3,5-triazine (ie la 2,4,6-tris(biphenyl-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 2006/034985).

Imidazoline derivatives:
Ethylhexyl Dimethoxybenzylidene Dioxoimidazoline Propionate,

Benzalmalonate derivatives:
Benzalmalonate function containing Polyorganosiloxanes as Polysilicone-15 sold in particular under the trade name «® PARSOL SLX » by DSM Nutritional Products, Inc.;

Di-neopentyl 4’-methoxybenzalmalonate;

According to a preferred embodiment of the invention, the UVB lipophilic organic screening agent will be selected from:
- Ethylhexylsalicylate;
- Homosalate;
- Octocrylene;

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

Benzophenone derivatives:
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 «® UVINUL M40 » par BASF;
Benzophenone-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;
Benzophenone-1 0;
Benzophenone-1 1;
Benzophenone-1 2;

Benzothazole derivatives:
- Drometrizole Trisiloxane sold in particular under the trade name «® SILATRIZOLE » by RHODIA CHIMIE or manufactured under the trade name «® MEROXYL XL » by CHIMEX;
- Methylene bis-Benzotriazoyl Tetramethylbutylphenol, sold in particular under the trade name «® MIXXIM BB/1 0 0 » 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-resorcinyl triazines

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

Benzoxazole derivatives:

2,4-bis-[5-1(dimethyl propyl)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;

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

- Drometrizole Trisiloxane;
- Methylene bis-Benzotriazolyl Tetramethylbutylphenol;
- Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine.

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%.

ADDITIONAL 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.

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

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 a aqueous phase of the emulsion or else of being solubilized in the colloidal form (for example in the micelle form) in an aqueous phase.

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

Terephthalylidene 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;

The most preferred UVA hydrophilic organic suncreening agent is Terephthalylidene Dicamphor Acide Sulfonic Acid.
As examples of UVB hydrophilic organic screening agent, can be cited:

- p-aminobenzoic acid derivatives as: 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,
- Salicylic acid,
- DEA methoxycinnamate,
- Benzylidene Camphor Sulfonic Acid manufactured in particular under the trade name «® MEXORYL SL» par CHIMEX,
- Benzalkonium Methosulfate Camphor manufactured in particular under the trade name «® MEXORYL SO» par CHIMEX.

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

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

- Benzophenone derivatives comprising at least one sulphonic radical as Benzophenone-4 sold in particular under the trade name «® UVINUL MS 40» by BASF,
- Benzophenone-5 and Benzophenone-9.

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: Butylmethoxydibenzoylmethane, Octocrylene, Homosalate and Phenylbenzimidazole Sulfonic Acid.

According to one preferred embodiment of the invention, the compositions contain the following mixture of UVA and UVB screening agents: n-Hexyl 2-(4-diethylamo-2-hydroxybenzoyl)-benzoate, Ethylhexyl Methoxycinnamate, Terephtalylidene Dicamphor Sulfonic Acid and Ethylhexyl Triazone.

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 "Tipaque TTO-55 (B)" and "Tipaque TTO-55 (A)" from Ishihara and "UVT 14/4" from Kemira,
- 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,
- with silica, with alumina and with alginic acid, such as the product "MT-100 AQ" from Tayca,
- with alumina and with aluminium laureate, 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,
- 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,
- 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,
- with alumina and treated with a silicone, such as the products "Tipaque 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 "Tipaque TTO-55 (C)" from Ishihara,
- with sodium hexametaphosphate, such as the product "Microtitanium Dioxide MT 150 W" from Tayca.

Other titanium oxide pigments treated with a silicone are, for example, TiO2 treated with octyltrimethylsilane, such as that sold under the trade name "T 805" by Degussa Silices, TiO2 treated with a polydimethylsiloxane, such as that sold under the trade name "70250 Cardre UF TiO2Sl3" by Cardre, or anatase/rutile TiO2 treated with a polydimethylhydroxiloxane, such as that sold under the trade name "Microtitanium Dioxide USP Grade Hydrophobic" by Color Techniques.

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".

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.

The coated zinc oxide pigments are, for example:
- those sold under the name "Z-cote HP" by Sunsmart (ZnO coated with dimethicone);
- those sold under the name "Oxide zinc CS-5" by Toshibi (ZnO coated with polymethylhydrosiloxane);
- 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 oxyethylated polydimethylsiloxane/cyclo-polydimethylsiloxane comprising 30% or 50% of zinc oxides coated with silica and polymethylhydrosiloxane);
- 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);
- 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);
- those sold under the name "Nanox Gel TN" by Elementis (ZnO dispersed at 55% in C12-C15 alkyl benzoate with hydroxystearic acid polycondensate).

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

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**

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.

The spherical microparticles of porous silica in accordance with the invention preferably have a mean particle size ranging from 0.5 to 20 µm and more particularly from 3 to 15 µm.

They preferably have a specific surface ranging from 50 to 1 000 m²/g and more particularly from 150 to 800 m²/g.

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

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
- Sunsil 130 from Sunjin
- Spherica P-1 500 from Ikeda Corporation
- Sylosphere from Fuji Silysia

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**

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, 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 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.

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.

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).

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 perhydrosqualene (or squalane); hydrocarbon-based oils of plant origin, such as 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, or alternatively oils of plant origin, for instance sunflower oil, corn oil, soybean oil, marrow oil, grapeseed oil, sesame seed oil, hazelnut oil, apricot oil, macadamia oil, arara oil, coriander oil, castor oil, avocado oil, jojoba oil and shea butter oil; 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 (CTFA name: Dicaprylyl ether); esters, for instance C12-C15 fatty alkyl benzoates (Finsolv TN from Finetex); aylalkyl 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.

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 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 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 in particular 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 copolyls, for example the mixture of cycodimethicone and of dimethicone copolyl sold under the name "DC 5225 C" by Dow Corning, and alkyl dimethicone copolyls, such as lauryl methicone copolyl, sold under the name "Dow Corning 5200 Formulation Aid" by Dow Corning, or cetyl dimethicone copolyl, such as the product sold under the name Abil EM 90R by Goldschmidt and the mixture of cetyl dimethicone copolyl, 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 P 135 by ICI.

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.

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 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 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.

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).

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).

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 various techniques such as the use of the hydrophilic or lipophilic thickeners such as those of patent EP 864 320, amphiphilic polymers such

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.

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:
- 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;
- antglycation agents;
- smoothing agents;
- NO-synthase inhibitors;
- agents which stimulate the synthesis of dermal or epidermal macromolecules and/or which prevent their decomposition;
- agents which stimulate the proliferation of fibroblasts;
- agents which stimulate the proliferation of keratinocytes;
- dermo-decontracting agents;
- tightening agents;
- matifying agents;
- 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;
- 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;
- 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.

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.
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.

**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.

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.

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 hydrogenocarbonates.

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-dihydroxypyrazolin-5-one derivatives, such as described in Patent Application EP 903 342. Use will preferably be made of DHA.

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

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.

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.

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;
- 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 (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.
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.

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).

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.
<table>
<thead>
<tr>
<th>Ingrédients</th>
<th>Ex 1 *</th>
<th>Ex2 *</th>
<th>Ex3*</th>
<th>Ex4 *</th>
<th>Ex5</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)-benzoate (® UVINUL A+)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ethylhexyl Triazone (® UVINUL T150)</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Ethylhexyl methoxycinnamate (® PARSOL MCX)</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Dimethicone</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Caprylic/Capric Triglycéride</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Terephthalidene Dicamphor Sulfonic Acid</td>
<td>3</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>ACRYLAMIDE/SODIUM ACRYLOYLDIMETHYLTAURATE COPOLYMER (and) ISOHEDADECANE (and) POLYSORBATE 80 (® SIMULGEL 600- Seppic)</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ACRYLATES/C-10-C30 ALKYL ACRYLATE CROSSPOLYMER (CARBOPOL ULTREZ 20 POLYMER – LUBRIZOL)</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Carbomer</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Ammonium Polyacryldimethyltauramide ((® HOSTACERIN AMPS – Clariant)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
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<tr>
<td>Sodium Polyacrylate (® COSMEDIA SP – Cognis)</td>
<td>1.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
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<tr>
<td>Sodium Stearoyl Glutamate (® AMISOF 11 PF – Ajinomoto)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Triéthanolamine</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
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<tr>
<td>Propyleneglycol</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
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<tr>
<td>Conservateurs</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Eau</td>
<td>qsp 100</td>
<td>qsp 100</td>
<td>qsp 100</td>
<td>qsp 100</td>
<td>qsp 100</td>
</tr>
</tbody>
</table>

(*) out of invention

All the compositions 1 to 5 have a viscosity in the same range 330-410 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 polymer or the mixture of polymers were used for each formula in a sufficient amount to obtain the viscosity in the same range as above defined.
The compositions 6 and 7 have a viscosity in the same range 330-410 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 polymer or the mixture of polymers were used for each formula in a sufficient amount to obtain the viscosity in the same range as above defined.
For all the compositions 1 to 8, the stability was observed according to the following protocol:

**Stability protocol:**

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**

For all the compositions 1 to 8, 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:
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.

Fresh feeling on application on the hand and face: score 1 fresh, score 5 not fresh. For fresh feeling, 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.

Film skin after application score: 1 light film, score 5 heavy film. For film on skin, 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.

The average score will be calculated.

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

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

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

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

<table>
<thead>
<tr>
<th>Exemples</th>
<th>Stability</th>
<th>Watery effect</th>
<th>Fresh effect</th>
<th>Film after application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex1 (out of invention)</td>
<td>stable</td>
<td>3.5</td>
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<td>EX7 (invention)</td>
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5 Only the formulations 5, 7 and 8 containing the association of a homopolymer of meth)acrylamido (Ci-C₄)alkylsulphonic acid and a homopolymer of acrylic acid at least partially neutralized have a good stability and leads on application onto the skin a fresh feeling, a light film and a watery effect.
For the compositions 7 and 8, the following are evaluated:

1. the viscosity, 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.

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

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

The results are shown in the following table:

<table>
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<tr>
<th>Exemples</th>
<th>Viscosity</th>
<th>SPF</th>
<th>PPD</th>
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<tr>
<td>EX7</td>
<td>402/418 mPa.s</td>
<td>12.7 ± 2.6</td>
<td>4.7 ± 0.9</td>
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<tr>
<td>EX8</td>
<td>418/434 mPa.s</td>
<td>24.1 ± 3.5</td>
<td>5.9 ± 1.1</td>
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CLAIMS

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:
   characterized in that it contains in a cosmetically acceptable medium:
   (a) at least one partially or totally neutralized, crosslinked or non-crosslinked homopolymer of (meth)acrylamido \((\text{C}_1-\text{C}_4)\)alkylsulphonic acid, and
   (b) at least one non-crosslinked or crosslinked homopolymer of acrylic acid at least partially neutralized,
   (c) at least one lipophilic organic UV screening agent.

2. Composition according to claim 1, wherein the homopolymer of (meth)acrylamido \((\text{C}_1-\text{C}_4)\)alkylsulphonic acid is a crosslinked poly-2-acrylamido-2-methylpropanesulphonic acid, characterized in that it comprises, randomly distributed:

   a) from 90% to 99.9% by weight of units of formula (IV) below:

   \[
   \begin{align*}
   &\text{O} \quad \text{NH} \quad \text{C} \quad \text{CH}_3 \\
   &\text{CH}_3 \quad \text{CH}_2\text{SO}_3^- \quad X^+ \\
   \end{align*}
   \]

   in which \(X^+\) denotes a cation or a mixture of cations and preferably selected from a proton (H\(^+\)), an alkali metal cation, a cation equivalent to that of an alkaline-earth metal or an ammonium ion and more preferably ammonium ion,

   b) from 0.01% to 10% by weight of at least one crosslinking unit containing at least two olefinic double bonds,
   the weight proportions being defined relative to the total weight of the polymer.

3. Composition according to claim 2, wherein the crosslinked and neutralized poly-2-acrylamido-2-methylpropanesulphonic acid comprises from 98% to 99.5% by weight of units of formula (IV) and from 0.5% to 2% by weight of crosslinking units, the crosslinking unit preferably being trimethylolpropane triacrylate.

4. Composition according to any one of claims 1 to 3, wherein the homopolymer of acrylic acid is selected from polyacrylates of an alkaline-earth metal such as sodium polyacrylates and potassium polyacrylates and
preferably is a sodium polyacrylate.

5. Composition according to any one of claims 1 to 4, wherein the homopolymer of acrylic acid is neutralized in an amount ranging from 5 to 80 %.

6. Composition according to any one of claims 1 to 5, wherein the lipophilic organic screening agent is chosen from anthranilates; cinnamic derivatives; salicylic derivatives; camphor derivatives; benzophenone derivatives; p,p'-diphenylacrylate derivatives; triazine derivatives; benzotriazole derivatives; benzaldehyde derivatives; benzimidazole derivatives; imidazolines; bis-benzazolyl derivatives; p-aminobenzoic acid (PABA) derivatives; methylenebis(hydroxyphenylbenzotriazole) derivatives; screening polymers and screening silicones; a-alkylstyrene-based dimmers; 4,4-diarylmethylenebutadienes; merocyanin derivatives and mixtures thereof.

7. 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.

8. Composition according to claim 7, wherein (i) the UVA lipophilic organic screening agent is selected from: Butyl Methoxydibenzoylmethane; n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)-benzoate; (ii) the UVB lipophilic organic screening agent is selected from: Ethylhexylsalicylate; Homosalate; Octocrylene; (iii) the UVA and UVB lipophilic organic screening agent is selected from: Drometrizole Trisiloxane; Methylene bis-Benzotriazolyl Tetramethylbutylphenol; Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine.

9. Composition according to any one of claims 1 to 8, further containing at least a hydrophilic organic UV sunscreen agent and/or an inorganic UV sunscreen.

10. Composition according to any one of claims 1 to 9, containing a mixture of UVA and UVB screening agents selected from: (1) Butylmethoxydibenzoylmethane, Octocrylene, Homosalate and Phenylbenzimidazole Sulfonic Acid; (2) Butylmethoxydibenzoylmethane, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Homosalate and Phenylbenzimidazole Sulfonic Acid; (3) n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)-benzoate, Ethylhexyl...
Methoxycinnamate, Terephtalyldene Dicamphor Sulfonic Acid and Phenylbenzimidazole Sulfonic Acid.

11. Composition according to any one of claims 1 to 11, further containing spherical microparticles of porous silica.

12. Composition according to any one of claims 1 to 12, in the form of an oil-in-water or water-in-oil emulsion and preferably in the form of an oil-in-water emulsion.

13. Composition according to any one of claims 1 to 13, characterized in that it is a fluid emulsion.
INTERNATIONAL SEARCH REPORT

International application No. PCT/CN2012/072509

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet
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)

IPC:A61Q 17/-, A61Q 1/-, A61K 8/-

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

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

EPDOC, WPI, CNPAT, CNKI: acrylamido, methylpropane, AMPS, sunscreen, UV, cosmetical, acrylic, amphiphilic, homopolymer, crosslink, acrylate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>US5607664A (L’OREAL) 04 Mar. 1997 (04.03.1997) claim 1</td>
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Further documents are listed in the continuation of Box C.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 30 May 2012 (30.05.2012)

Date of mailing of the international search report 21 Jun. 2012 (21.06.2012)

Name and mailing address of the ISA/CN
The State Intellectual Property Office, the P.R.China
6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088
Facsimile No. 86-10-62019451

Authorized officer YUAN, Haibin
TelephoneNumber No. (86-10)82246919

Form PCT/ISA/210 (second sheet) (July 2009)
## INTERNATIONAL SEARCH REPORT

### Information on patent family members

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Form PCT/ISA /210 (patent family annex) (July 2009)
INTERNATIONAL SEARCH REPORT

Continuation of: A. CLASSIFICATION OF SUBJECT MATTER

A61K 8/81 (2006.01)i
A61Q 17/04 (2006.01)m
A61Q 1/00 (2006.01)m