Title: HIGH UV PROTECTION ALCOHOL-FREE EMULSION SYSTEM, THAT IS CLEAR ON APPLICATION

Abstract: The present invention relates to a sunscreen composition comprising: a. an aqueous phase; b. an oil phase comprising at least one cosmetically acceptable oil; c. at least one sunscreen active; and d. up to about 4.25% by weight, based on the total weight of the composition, of an emulsifier system comprising: i. from about 0.2 to 0.3% by weight of at least one ionic surfactant; ii. from about 1 to 3 % by weight of at least one nonionic surfactant having an HLB of greater than or equal to about 14; and iii. from about 1 to 3 % by weight of at least one nonionic surfactant having an HLB of less than or equal to about 10; and wherein the composition is an oil-in-water emulsion containing oil droplets having an average particle size of from about 100 to 150 nm, is alcohol-free, and appears semi-transparent to transparent upon application onto an end-user's skin.
HIGH UV PROTECTION ALCOHOL-FREE EMULSION SYSTEM,
THAT IS CLEAR ON APPLICATION

BACKGROUND OF THE INVENTION

[0001] Conventional sunscreen products generally contain ultraviolet (UV)-
filter compounds and/or particulate UV-screening compounds (collectively,
"sunscreen actives") that are solubilized, emulsified, or dispersed in a vehicle, which
is topically applied to the skin. The sunscreen actives, typically through the aid of
polymers and other ingredients included in the vehicle form a thin, protective, and
water-resistant layer on the skin.

[0002] Transparent personal care and cosmetic products have become
increasingly important to the consumer. Transparent products may be perceived as
light, clean, fresh, and cooling. Among sunscreen products, sprays are gaining
increasing consumer preference because of their convenience and ease of
application.

[0003] Currently marketed transparent sunscreen sprays are typically oil-
based or alcohol-based formulas. Alcohol-based formulas may contain more than
60% alcohol in order to dissolve the organic UV filters. Additionally, the high alcohol
content allows for easy application and quick drying. However, there are numerous
safety concerns associated with alcohol-containing formulas. Products containing
alcohols require special safety measures to be taken during production, storage, and
transport. In addition, alcohol-containing products are potentially flammable during
use. As a result, alcohol-free products are preferred by consumers because of odor,
tolerance, and safety considerations.

[0004] While oil-in-water emulsions are an alternative to alcohol- or oil-based
formulas, they are typically opaque in appearance. Obtaining transparency in a
classical oil-in-water emulsion is not easily achieved. One method of obtaining
transparent oil-in-water emulsions requires the use of high levels of surfactant which
may result in skin irritation and an unpleasant sticky feel upon application.

Additionally, high levels of surfactants in sunscreen products may cause the product
to be less water resistant. Since water resistance is critical to a sunscreen product's
efficacy, the deleterious effect on water resistance caused by high levels of
surfactants renders this solution to providing transparency unacceptable.
[0005] It is thus an object of the present invention to provide a sunscreen product that is transparent in appearance, and does not possess the above-mentioned drawbacks.

BRIEF SUMMARY OF THE INVENTION

[0006] The present invention relates to a sunscreen composition comprising:

a. an aqueous phase;

b. an oil phase comprising at least one cosmetically acceptable oil;

c. at least one sunscreen active; and

d. up to about 4.25% by weight of an emulsifier system comprising:

i. From about 0.2 to 0.3 % by weight of at least one ionic surfactant;

ii. From about 1 to 3% by weight of at least one nonionic surfactant having an HLB of greater than or equal to about 14; and

iii. From about 1 to 3 % by weight of at least one nonionic surfactant having an HLB of less than or equal to about 10, all weights being based on the total weight of the composition;

wherein the composition is an oil-in-water emulsion containing oil droplets having an average particle size of from about 100 to 150 nm, is alcohol-free, and appears semi-transparent to transparent upon application onto an end-user's skin. More particularly the invention is directed to a sunscreen composition comprising:

a. an aqueous phase;

b. an oil phase comprising from about 3 to 8% by weight of at least one cosmetically acceptable oil;

c. at least one sunscreen active; and

d. up to about 4.25% by weight of an emulsifier system comprising:

i. From about 0.2 to 0.3% by weight of at least one ionic surfactant;

ii. From about 1.5 to 2.5% by weight of at least one nonionic surfactant having an HLB of greater than or equal to about 14; and

iii. From about 1.5 to 2.5% by weight of at least one nonionic surfactant having an HLB of less than or equal to about 10, all weights being based on the total weight of the composition;
wherein the composition is an oil-in-water emulsion containing oil droplets having an average particle size of from about 100 to 150 nm, is alcohol-free, and appears semi-transparent to transparent upon application onto an end-user's skin.

[0007] The present invention is also directed to a process of making a sunscreen composition by combining the above-disclosed ingredients, wherein the resultant composition is an oil-in-water emulsion containing oil droplets having an average particle size of from about 100 to 150 nm, is alcohol-free and semi-transparent to transparent in appearance during application onto an end-user's skin. More particularly the present invention is directed to a process for making a sunscreen composition comprising:

a. providing an aqueous phase;

b. providing an oil phase comprising at least one cosmetically acceptable oil;

c. providing at least one sunscreen active;

d. up to about 4.25% by weight of an emulsifier system comprising:
   i. From about 0.2 to 0.3 % by weight of at least one ionic surfactant;
   ii. From about 1 to 3% by weight of at least one nonionic surfactant having an HLB of greater than or equal to about 14; and
   iii. From about 1 to 3 % by weight of at least one nonionic surfactant having an HLB of less than or equal to about 10, all weights being based on the total weight of the composition

e. combining a. to d. to form the sunscreen composition,

the composition being an oil-in-water emulsion containing oil droplets having an average particle size of from about 100 to 150 nm, is alcohol-free, and appears semi-transparent to transparent upon application onto an end-user's skin. Even more particularly, the invention is process for making a sunscreen composition comprising:

a. providing an aqueous phase;

b. providing an oil phase comprising from about 3 to 8% by weight of at least one cosmetically acceptable oil;

c. providing at least one sunscreen active;
d. providing up to about 4.25% by weight of an emulsifier system comprising;
   i. From about 0.2 to 0.3% by weight of at least one ionic surfactant;
   ii. From about 1.5 to 2.5% by weight of at least one nonionic surfactant having an HLB of greater than or equal to about 14; and
   iii. From about 1.5 to 2.5% by weight of at least one nonionic surfactant having an HLB of less than or equal to about 10, all weights being based on the total weight of the composition; and

e. combining a. to d. to form the sunscreen composition,

wherein the composition is an oil-in-water emulsion containing oil droplets having an average particle size of from about 100 to 150 nm, is alcohol-free, and appears semi-transparent to transparent upon application onto an end-user's skin.

[0008] The present invention is also directed to a method of inhibiting UV radiation from contacting a keratinous substrate by applying the above-disclosed sunscreen composition onto a surface of the keratinous substrate.

DETAILED DESCRIPTION OF THE INVENTION

[0009] Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients and/or reaction conditions are to be understood as being modified in all instances by the term "about".

[0010] As used herein, the expression "at least one" means one or more and thus includes individual components as well as mixtures/combinations.

[0011] "Cosmetically acceptable" means compatible with any keratinous substrate. For example, "cosmetically acceptable carrier" means a carrier that is compatible with any keratinous substrate.

[0012] A "physiologically acceptable medium" means a medium which is not toxic and can be applied to the skin, lips, hair, scalp, lashes, brows, nails or any other cutaneous region of the body. The composition of the instant disclosure may especially constitute a cosmetic or dermatological composition.

[0013] The terms "semi-transparent" and "transparent" as used herein means that the emulsion contains oil droplets having an average particle size ranging from about 100 to 150 nm.
“Average particle size” as used herein is determined by dynamic light scattering using a Brookhaven Instruments DLS particle size analyzer '90 plus'.

Emulsifier System

The emulsifier system is comprised of at least one ionic surfactant, at least one nonionic surfactant having an HLB of greater than or equal to about 14, and at least one nonionic surfactant having an HLB of less than or equal to about 10.

Suitable ionic surfactants for use in the present invention include, but are not limited to:

- alkali metal salts of dicetyl phosphate and of dimyristyl phosphate;
- alkali metal salts of cholesterol sulphate;
- alkali metal salts of cholesterol phosphate;
- lipoamino acids and their salts, such as mono and disodium acylglutamates, for instance the disodium salt of N-stearoyl-L-glutamic acid sold under the trade name AMISOFT® HS 21P by the company Ajinomoto;
- sodium salts of phosphatidic acid;
- phospholipids;
- alkylsulphonic derivatives, in particular of formula (I):

\[
R-\text{CH-CO-O-}(\text{CH}_2-\text{CH}_2-\text{CO})\cdot\text{CH}_3 \\
\mid \\
\text{SO}_3\text{M}
\]

(1)

in which R represents C16-C22 alkyl radicals, in particular the C16H33 and C18H37 radicals taken as a mixture or separately, and M is an alkali metal or alkaline earth metal, such as sodium; and mixtures thereof.

Particularly preferred ionic surfactants are sodium stearoyl glutamate and disodium stearoyl glutamate.

The ionic surfactant will typically be employed in an amount of from about 0.2 to about 0.3% by weight, based on the total weight of the composition.
[0019] Suitable nonionic surfactants having an HLB greater than or equal to about 14 include, but are not limited to, polysorbate 60, polysorbate 20, polysorbate 21, polysorbate 40, polysorbate 80, and mixtures thereof.

[0020] A particularly preferred polysorbate is polysorbate 60.

[0021] The at least one nonionic surfactant having an HLB of greater than or equal to about 14 will typically be employed in an amount of from about 1.0 to 3.0% by weight, preferably from about 1.25 to 2.75% by weight, and most preferably from about 1.5 to 2.5% by weight, based on the total weight of the composition.

[0022] Suitable nonionic surfactants having an HLB of less than or equal to about 10 include, but are not limited to, polyglycerides, polysorbate 61, polysorbate 65, polysorbate 81, polysorbate 85, and mixtures thereof.

[0023] Particularly preferred nonionic surfactants having an HLB of less than or equal to about 10 include polysorbate 61 and polyglyceryl-2 laurate.

[0024] The at least one nonionic surfactant having an HLB of less than or equal to about 10 will typically be employed in an amount of from about 1 to 3% by weight, preferably from about 1.25 to 2.75% by weight, and most preferably from about 1.5 to 2.5% by weight, based on the total weight of the composition.

[0025] The emulsifier system will typically be present in the composition in an amount of from about 4.25% by weight, based on the total weight of the composition.

[0026] It is imperative that the emulsifier system be employed in the above-disclosed amounts so that the oil droplets present in the composition possess the desired average particle size. Without intending to be bound by theory, it is believed that the average particle size of the oil droplets is what facilitates the composition having a semi-transparent to transparent appearance during application onto an end-user's skin.

Oil Phase

[0027] The oil phase of the present invention is comprised of at least one oil.

[0028] Suitable oils include, but are not limited to:

- mineral oils, such as hexadecane, isohexadecane and liquid paraffin;
- animal or plant oils formed by fatty acid esters of polyols, in particular liquid triglycerides, for example sunflower oil, corn oil, soybean oil, avocado oil,
jojoba oil, marrow oil, grapeseed oil, sesame oil, hazelnut oil, fish oils, glyceryl
tricaprylylstearyl, purcellin oil, or liquid jojoba wax;

- natural or synthetic essential oils such as, for example, eucalyptus oil,
lavandin oil, lavender oil, vetivier oil, litsea cubeba oil, lemon oil, sandalwood
oil, rosemary oil, camomile oil, savory oil, nutmeg oil, cinnamon oil, hyssop oil,
caraway oil, orange oil, geraniol oil, cade oil and bergamot oil;

- synthetic oils such as parleam oil, polyolefins and liquid carboxylic acid esters;

- halogenated oils, in particular fluorocarbons, such as fluoroamines, for
example perfluorotributylamine, fluorinated hydrocarbons, for example
perfluoro-decahydronaphthalene, fluoroesters and fluoroethers;

- volatile and non-volatile silicone oils;

- polyolefins, in particular poly-α-olefins, and more particularly those of
hydrogenated or nonhydrogenated polybutene type, and preferably
hydrogenated or nonhydrogenated polyisobutene type;

- esters of mono-, di-, tri- or tetracarboxylic acids, in particular alkyl palmitates,
such as ethyl palmitate, isopropyl palmitate, 2-ethylhexyl palmitate, 2-
octyldodecyl palmitate; alkyl myristates, such as isopropyl myristate, butyl
myristate, cetyl myristate, 2-octyldodecyl myristate; alkyl stearates, such as
hexyl stearate, butyl stearate or isobutyl stearate; alkyl malates, such as
dioctyl malate; alkyl laurates, such as hexyl laurate and 2-hexyldodecyl laurate,
isononyl isononanoate, or cetyl octanoate; and mixtures thereof.

[0029] The oil phase will typically be employed in an amount of from about
1 to 15% by weight, preferably from about 2 to 10% by weight, and more preferably
from about 3% to 8% by weight, based on the total weight of the composition.

Sunscreen Actives

[0030] Suitable UV-screening agents include, but are not limited to, cinnamic
derivatives; anthranilates; salicylic derivatives; dibenzoylmethane derivatives;
camphor derivatives; benzophenone derivatives; β,β-diphenylacrylate derivatives;
triazine derivatives; benzotriazole derivatives; benzalmalonate derivatives, especially
those cited in patent US5624663; benzimidazole derivatives; imidazolines; bis-
benzoazolyl derivatives as described in patents EP669323 and US2463264; p-
aminobenzoic acid (PABA) derivatives; methylene bis(hydroxyphenylbenzotriazole)
derivatives as described in applications US5237071, US5166355, GB2303549, DE19726184 and EP893119; benzoxazole derivatives as described in patent applications EP0832642, EP1027883, EP1300137 and DE10162844; screening polymers and screening silicones such as those described especially in patent application WO 93/04665; dimers derived from α-alkylstyrene such as those described in patent application DE 19855649; 4,4-diarylbutadienes such as those described in patent applications EP0967200, DE19746654, DE19755649, EP-A-1008586, EP1133980 and EP1133981, merocyanine derivatives such as those described in patent applications WO 04/006878, WO 05/058269 and WO 06/032741; and mixtures thereof.

[0031] As examples of complementary organic photoprotective agents, mention may be made of those denoted herein below under their INCI name:

**Cinnamic derivatives:**

- Ethylhexyl Methoxycinnamate sold in particular under the trade name "Parsol® MCX" by DSM Nutritional Products, Isopropyl Methoxycinnamate, Isoamyl Methoxycinnamate sold under the trade name "Neo Heliopan® E 1000" by Symrise, DEA Methoxyccinnamate, Diisopropyl Methylcinnamate, Glyceryl Ethylhexanoate Dimethoxyccinnamate.

**Dibenzoylmethane derivatives:**

- Butyl Methoxydibenzoylmethane sold especially under the trade name "Parsol® 1789" by DSM, Isopropyl Dibenzoylmethane.

**para-Aminobenzoic acid derivatives:**

- PABA, Ethyl PABA, Ethyl Dihydroxypropyl PABA, Ethylhexyl dimethyl PABA sold in particular under the name “Escalol™ 507” by ISP, Glyceryl PABA, PEG-25 PABA sold under the name "Uvinul® P25" by BASF.

**Salicylic derivatives:**

- Homosalate sold under the name “Eusolex® HMS” by Rona/EM Industries, Ethylhexyl Salicylate sold under the name “Neo Heliopan® OS” by Symrise, Dipropylene Glycol Salicylate sold under the name “Dipsal™” by Scher, TEA Salicylate sold under the name “Neo Heliopan® TS” by Symrise.

**β,β-Diphenylacrylate derivatives:**

- Octocrylene sold in particular under the trade name “Uvinul® N539” by BASF, Etocrylene sold in particular under the trade name “Uvinul® N35” by BASF.
Benzophenone derivatives:

- Benzophenone-1 sold under the trade name “Uvinit® 400” by BASF,
Benzophenone-2 sold under the trade name “Uvinul® D50” by BASF,
Benzophenone-3 or Oxybenzone sold under the trade name “Uvinit® M40” by
BASF, Benzophenone-4 sold under the trade name “Uvinit® MS40” by BASF,
Benzophenone-5, Benzophenone-6 sold under the trade name “Helisorb® 11”
by Norquay, Benzophenone-8 sold under the trade name “Spectra-Sorb
UV-24” by American Cyanamid, Benzophenone-9 sold under the trade name
“Uvinit® DS-49” by BASF, Benzophenone-12, n-Hexyl 2-(4-diethylamino-2-
hydroxybenzoyl)benzoate sold under the trade name “Uvinit® A+” or as a
mixture with octyl methoxycinnamate under the trade name “Uvinit® A+B”
by BASF.

Benzylidenecamphor derivatives:

- 3-Benzylidene Camphor manufactured under the name “Mexoryl™ SD” by
Chimex, 4-Methylbenzylidene Camphor sold under the name “Eusolex® 6300”
by Merck, Benzylidene Camphor Sulfonic Acid manufactured under the name
“Mexoryl™ SL” by Chimex, Camphor Benzalkonium Methosulfate
manufactured under the name “Mexoryl™ SO” by Chimex, Terephthalidene
Dicamphor Sulfonic Acid manufactured under the name “Mexoryl™ SX” by
Chimex, Polyacrylamidomethyl Benzylidene Camphor manufactured under
the name “Mexoryl™ SW” by Chimex.

Phenylbenzimidazole derivatives:

- Phenylbenzimidazole Sulfonic Acid sold in particular under the trade name
“Eusolex® 232” by Merck, Disodium Phenyl Dibenzimidazole Tetrakisulfonate
sold under the trade name “Neo Heliopan® AP” by Symrise.

Phenylbenzotriazole derivatives:

- Drometrizole Trisiloxane sold under the name “Silatrizole” by Rhodia Chimie,
Methylene bis-Benzotriazolyl Tetramethylbutyl-phenol sold in solid form under
the trade name “MIXXIM BB/100” by Fairmount Chemical, or in micronized
form as an aqueous dispersion under the trade name “Tinosorb M” by Ciba
Specialty Chemicals.

Triazine derivatives:
bis-Ethylhexyloxyphenol Methoxyphenyl Triazine sold under the trade name “Tinosorb® S” by BASF, Ethylhexyl Triazone sold in particular under the trade name “Uvinul® T150” by BASF, Diethylhexyl Butamido Triazone sold under the trade name “Uvasorb® HEB” by Sigma 3V, 2,4,6-tris(dineopentyl 4'-aminobenzalmalonate)s-triazine, 2,4,6-tris(diisobutyl 4'-aminobenzalmalonate)s-triazine, 2,4-bis(dineopentyl 4'-aminobenzalmalonate)-6-(n-butyl 4'-aminobenzoate)-s-triazine, symmetrical triazine screening agents described in patent US 6,225,467, patent application WO 2004/085412 (see compounds 6 and 9) or the document "Symmetrical Triazine Derivatives" IP.COM Journal, IP.COM Inc., West Henrietta, NY, US (20 September 2004), especially 2,4,6-tris(biphenyl)-1,3,5-triazines (in particular 2,4,6-tris(biphenyl-4-yl)-1,3,5-triazine and 2,4,6-tris(terphenyl)-1,3,5-triazine, which is included in patent applications WO 06/035000, WO 06/034982, WO 06/034991, WO 06/035007, WO 2006/034992 and WO 2006/034985).

Anthranilic derivatives:
- Menthyld Anthranilate sold under the trade name “Neo Heliopan® MA” by Symrise.

Imidazoline derivatives:
- Ethylhexyl Dimethoxybenzylidene Dioxoimidazoline Propionate.

Benzalmonate derivatives:
- Polyorganosiloxane containing benzalmonate functions, for instance Polysilicone-15, sold under the trade name “Parsol® SLX” by DSM Nutritional Products.

4,4-Diarylbutaadiene derivatives:
- 1,1-dicarboxy(2,2'-dimethylpropyl)-4,4-diphenylbutadiene.

Benzoxazole derivatives:
- 2,4-bis[5-(1-dimethylpropyl)benzoxazol-2-yl-(4-phenylimino)-6-(2-ethylhexyl)imino]-1,3,5-triazine sold under the name Uvasorb® K2A by Sigma 3V, and mixtures thereof.

Preferred organic screening agents are chosen from:
- Ethylhexyl Methoxycinnamate, Ethylhexyl Salicylate,
Home salate, Butyl Methoxydibenzoylmethane, Octocrylene, Phenylbenzimidazole Sulfonic Acid, Benzophenone-3, Benzophenone-4, Benzophenone-5, n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate, 4-Methylbenzylidene Camphor, Terephthalylidene Dicamphor Sulfonic Acid, Disodium Phenyl Dibenzimidazole Tetrasulfonate, Methylene Bis-Benzotriazolyl Tetramethylbutylphenol, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Ethylhexyl triazine, Diethylhexyl Butamido Triazone, 2,4,6-Tris(dineopentyl 4′-aminobenzalmonate)-s-triazine, 2,4,6-Tris(diisobutyl 4′-aminobenzalmonate)-s-triazine, 2,4-Bis(dineopentyl 4′-aminobenzalmonate)-6-(n-butyl 4′-aminobenzoate)-s-triazine, 2,4,6-Tris(biphenyl-4-yl)-1,3,5-triazine, 2,4,6-Tris(terphenyl)-1,3,5-triazine, Drometrizole Trisiloxane, Polysilicone-15, 1,1-dicarboxy(2,2′-dimethylpropyl)-4,4-diphenylbutadiene, 2,4-bis[5-1(dimethylpropyl)benzoxazol-2-yl-(4-phenyl)imino]-6-(2-ethylhexyl)imino-1,3,5-triazine, and mixtures thereof.

The sunscreen actives according to the invention are typically present in the composition in an amount ranging from about 25 to 40% by weight, preferably from about 25% to 35% by weight, and most preferably from about 25 to 30% by weight, based on the total active weight of the composition, if a composition having an SPF of from about 50 to 100 is desired.

On the other hand, if a composition having an SPF of from about 15 to about 50 is desired, the sunscreen actives will be employed in an amount ranging from about 10 to 25% by weight, preferably from about 12% to 25% by weight, and most preferably from about 15 to 25% by weight, based on the total active weight of the composition.

Optional Solvents

The composition may optionally comprise at least one solvent. The at least one solvent may be chosen from:

- glycols, such as glycerol, propylene glycol, 1,3 butylene glycol, caprylyl glycol, dipropylene glycol or polyethylene glycols comprising from 4 to 16 ethylene oxide units, and preferably from 8 to 12;

- glycol ethers, such as phenoxyethanol, di(ethylene glycol) ethyl ether, also known as ethoxy diglycol, 2-(2-ethoxyethoxy)ethanol, diglycol monoethyl ether, ethyl diethylene glycol, ethylene diglycol monoethyl ether, di(ethylene glycol)
ethyl ether, methoxyisopropanol, PPG-2 methyl ether, PPG-3 methyl ether, propylene glycol butyl ether, PPG-2 butyl ether, phenoxysopropyl, butoxyethanol, butoxydiglycol, methoxydiglycol, PPG-3 butyl ether, PPG-2 propyl ether, propylene glycol propyl ether, or dipropylene glycol dimethyl ether; and mixtures thereof.

[0036] The at least one solvent may be employed in an amount of from about 0.25 to 15 % by weight, preferably from about 1 to 10 % by weight, and more preferably from about 2 to 8 % by weight, based on the total weight of the composition.

[0037] The composition of the invention may also contain adjuvants, and in particular water-soluble or liposoluble active agents having a cosmetic or dermatological activity. By way of examples of active agents, mention may be made of vitamins and their derivatives, such as vitamin E and its esters, for instance vitamin E acetate, vitamin C and its esters, B vitamins, vitamin A alcohol or retinol and its esters, such as vitamin A palmitate, vitamin A acid or retinoic acid and its derivatives, provitamins such as panthenol and niacinamide, ergocalciferol, antioxidants, essential oils, humectants, sunscreens, moisturizers, proteins, ceramides and pseudoceramides, and DHEA and its derivatives and biological precursors. As adjuvants, mention may also be made of sequestering agents, preserving agents, fillers, softeners, dyestuffs (pigments or dyes) and fragrances.

[0038] The amounts of these various adjuvants are those conventionally used in the field under consideration, and are, for example, from 0.01% to 20% of the total weight of the composition. These adjuvants and the concentrations thereof should be such that they do not modify the property desired for the composition of the invention.

EXAMPLES

Table 1: Inventive Examples --Oil in water emulsions

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<th>Ingredients</th>
<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
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<td>Droplets (nm)</td>
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<td>132</td>
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<tr>
<td>Stable Emulsion</td>
<td>Yes</td>
<td>Yes</td>
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Table 2: Comparative Examples
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<td>PEG-8</td>
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<td>DISODIUM EDTA</td>
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<td><strong>Phase C</strong></td>
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<td><strong>Average Particle Size of Oil Droplets (nm)</strong></td>
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<td>measured at time=0</td>
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<tr>
<td><strong>Stable Emulsion</strong></td>
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In making each of the examples in Tables 1 and 2, the following procedure was used. Phases A and B were heated to 50°C. Phase B was added to phase A and homogenized with a high speed mixer for 15 minutes at 4500 rpm. The resulting emulsion was passed two times through a high pressure homogenizer at 700 bar. Phase C was added to the emulsion and mixed with an overhead blade for 10 minutes.

A Brookhaven Instruments DLS particle size analyzer '90 plus' was then used to measure the effective particle size of the emulsions. The samples were diluted with deionized water and measurements run for 2 minutes, at ambient temperature. The "effective diameter" was reported.

Examples 6 and 7 demonstrate the criticality of the emulsifier system. When the emulsifier system fails to correspond to the inventive emulsifier system, the composition yields an unstable emulsion which is neither semi-transparent nor transparent.
WHAT IS CLAIMED IS:

1. A process for making a sunscreen composition comprising:
   a. providing an aqueous phase;
   b. providing an oil phase comprising at least one cosmetically acceptable oil;
   c. providing at least one sunscreen active;
   d. providing up to about 4.25% by weight, based on the total weight of the composition, of an emulsifier system comprising:
      i. from about 0.2 to 0.3% by weight of at least one ionic surfactant;
      ii. from about 1 to 3% by weight of at least one nonionic surfactant having an HLB of greater than or equal to about 14; and
      iii. from about 1 to 3% by weight of at least one nonionic surfactant having an HLB of less than or equal to about 10; and
   e. combining a. to d. to form the sunscreen composition,

wherein the composition is an oil-in-water emulsion containing oil droplets having an average particle size of from about 100 to 150 nm, is alcohol-free, and appears semi-transparent to transparent upon application onto an end-user's skin.

2. The process of claim 1 wherein the oil phase is employed in an amount of from about 1 to 15%, preferably 2 to 10%, by weight, based on the weight of the composition.

3. The process according to anyone of the preceding claims wherein the nonionic surfactant having an HLB of greater than or equal to about 14 is employed in an amount of from 1.25 to 2.75%, by weight, based on the weight of the composition.

4. The process according to anyone of the preceding claims wherein the nonionic surfactant having an HLB of less than or equal to about 10 is employed in an amount of from about 1.25 to 2.75%, by weight, based on the weight of the composition.

5. The process according to anyone of the preceding claims further comprising providing a solvent in an amount of from about 0.25 to 15%, preferably 1 to 10%, by weight, based on the weight of the composition.
6. A process for making a sunscreen composition comprising:
   a. Providing an aqueous phase;
   b. Providing an oil phase comprising from about 3 to 8% by weight of at
      least one cosmetically acceptable oil;
   c. Providing at least one sunscreen active;
   d. Providing up to about 4.25% by weight of an emulsifier system
      comprising;
      i. From about 0.2 to 0.3% by weight of at least one ionic surfactant;
      ii. From about 1.5 to 2.5% by weight of at least one nonionic
          surfactant having an HLB of greater than or equal to about 14;
      and
      iii. From about 1.5 to 2.5% by weight of at least one nonionic
           surfactant having an HLB of less than or equal to about 10, all
           weights being based on the total weight of the composition; and
   e. combining a. to d. to form the sunscreen composition,

wherein the composition is an oil-in-water emulsion containing oil droplets
having an average particle size of from about 100 to 150 nm, is alcohol-free,
and appears semi-transparent to transparent upon application onto an end-
user’s skin.

7. A sunscreen composition comprising:
   a. an aqueous phase;
   b. an oil phase comprising at least one cosmetically acceptable oil;
   c. at least one sunscreen active; and
   d. up to about 4.25% by weight, based on the total weight of the
      composition, of an emulsifier system comprising;
      i. from about 0.2 to 0.3% by weight of at least one ionic surfactant;
      ii. from about 1 to 3% by weight of at least one nonionic surfactant
          having an HLB of greater than or equal to about 14; and
      iii. from about 1 to 3% by weight of at least one nonionic surfactant
           having an HLB of less than or equal to about 10; and

wherein the composition is an oil-in-water emulsion containing oil droplets
having an average particle size of from about 100 to 150 nm, is alcohol-free,
and appears semi-transparent to transparent upon application onto an end-user’s skin.

8. The composition of the preceding claim wherein the oil phase is employed in an amount of from about 1 to 15%, preferably 2 to 10%, by weight, based on the weight of the composition.

9. The composition according to anyone of claims 7 or 8 wherein the nonionic surfactant having an HLB of greater than or equal to about 14 is employed in an amount of from about 1.25 to 2.75%, by weight, based on the weight of the composition.

10. The composition according to anyone of claims 7 to 9 wherein the nonionic surfactant having an HLB of less than or equal to about 10 is employed in an amount of from about 1.25 to 2.75% by weight, based on the weight of the composition.

11. The composition according to anyone of claims 7 to 10 further comprising providing a solvent in an amount of from about 0.25 to 15%, preferably 1 to 10%, by weight, based on the weight of the composition.

12. A sunscreen composition according to anyone of claims 7 to 11 comprising:
   a. an aqueous phase;
   b. an oil phase comprising from about 3 to 8% by weight of at least one cosmetically acceptable oil;
   c. at least one sunscreen active; and
   d. up to about 4.25% by weight of an emulsifier system comprising:
      i. From about 0.2 to 0.3% by weight of at least one ionic surfactant;
      ii. From about 1.5 to 2.5% by weight of at least one nonionic surfactant having an HLB of greater than or equal to about 14; and
      iii. From about 1.5 to 2.5% by weight of at least one nonionic surfactant having an HLB of less than or equal to about 10, all weights being based on the total weight of the composition;
wherein the composition is an oil-in-water emulsion containing oil droplets having an average particle size of from about 100 to 150 nm, is alcohol-free, and appears semi-transparent to transparent upon application onto an end-user's skin.

13. A process for inhibiting UV rays from contacting a keratinous substrate comprising applying the composition of any one of claims 7 to 12 onto a surface of the keratinous substrate.
**INTERNATIONAL SEARCH REPORT**

**INTERNATIONAL APPLICATION NO**
PCT/EP2015/072445

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### A. CLASSIFICATION OF SUBJECT MATTER

INV. A61K8/44  A61K8/49  A61Q17/04

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### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61K  A61Q

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

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

EPO-Internal, WPI Data

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### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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### Date of the actual completion of the international search

3 November 2015

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### Date of mailing of the international search report

13/11/2015

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### Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk

Tel. (+31-70) 340-3040, Fax: (+31-70) 340-3016

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### Authorized officer

Skulj, Primoz
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<td>US 2012128601 A1</td>
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<td>CN 102197022 A</td>
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<td>JP 2012506392 A</td>
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<td>KR 20110073541 A</td>
<td>29-06-2011</td>
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<td>US 2012128601 A1</td>
<td>24-05-2012</td>
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<td>29-04-2010</td>
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<td>DE 602005001028 T2</td>
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<td>ES 2285656 T3</td>
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<td>FR 2872033 A1</td>
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