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(54) Title: SUNSCREEN COMPOSITION WITH POLYHYDROXY QUATERNARY AMMONIUM SALTS

(57) Abstract: A cosmetic composition is provided including a water-insoluble UV-A organic sunscreen agent having a λ_{max} ranging from 330 to 380 nm, a UV-B organic sunscreen agent having a λ_{max} ranging from 280 to 400 nm, and a photoprotective enhancing agent which is a polyhydroxy quaternary ammonium salt such as bis(dihydroxypropyl)dimethylammonium chloride, in a cosmetically acceptable carrier, and wherein the composition exhibits an SPF value which is 1 to 30 units higher than in the absence of the photoprotective enhancing agent.



SUNSCREEN COMPOSITION WITH POLYHYDROXY QUATERNARY AMMONIUM SALTS

BACKGROUND OF THE INVENTION

5 Field of the Invention

The invention concerns cosmetic compositions with enhanced photoprotection properties.

10 The Related Art

Many people dislike northern climates. There is a longing to bask in the warmth of the sun. Days at the beach find us in swimsuit attire. Many seek to turn their pale winter skin into a bronzed appearance. Others of naturally darker skin simply enjoy the refreshment of the seashore. Without protection from harmful ultraviolet radiation damage, these pleasures can
15 turn into premature aging. Skin can lose elasticity and wrinkles appear in the premature aging process. Radiation can promote erythema damage, can cause photo allergic reactions, and is implicated in skin cancers.

Protective measures are necessary. Lotions and creams formulated with sunscreens
20 can shield against ultraviolet damaging radiation. The extent of protection varies widely.

Numerous ultraviolet photoprotective (sunscreen) agents are known. Nonetheless, only a small number are both commercially available and approved by regulatory authorities. A need exists to operate with known approved commercial sunscreen agents yet formulating them to achieve more than their expected level of photoprotection.

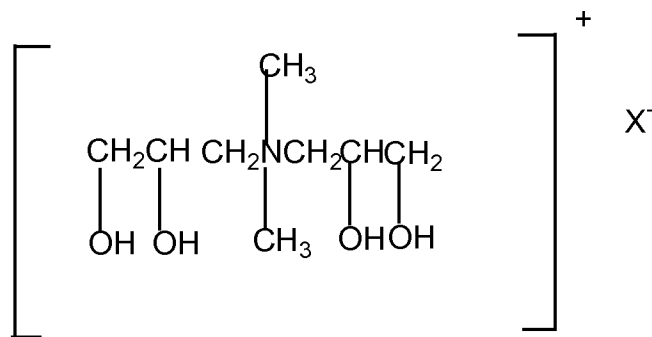
25 Representative of the art is U.S. Patent 5,961,961 (Dobkowski et al.) reporting enhancement of the photoprotective effect by utilizing relatively large particle size titanium dioxide coupled with an organic sunscreen agent. Representative organic sunscreen agents include Benzophenone-3, octyl salicylate, octyl methoxycinnamate and 2-phenylbenzimidazole-5-sulphonic acid.

30 Although the aforementioned technology is useful, there is a need to achieve higher photoprotective efficacy for cosmetics.

SUMMARY OF THE INVENTION

A cosmetic composition is provided which includes:

- 5 (i) a water-insoluble UV-A organic sunscreen agent having a λ_{\max} ranging from 330 to 380 nm;
- (ii) a UV-B organic sunscreen agent having a λ_{\max} ranging from 280 to 400 nm; and
- (iii) a photoprotective enhancing agent having the structure (I)



10

(I)

wherein X^- is selected from the group consisting of chloride, bromide, hydroxyl, sulphate, phosphate, methosulphate, carboxyl, citrate and tartrate;

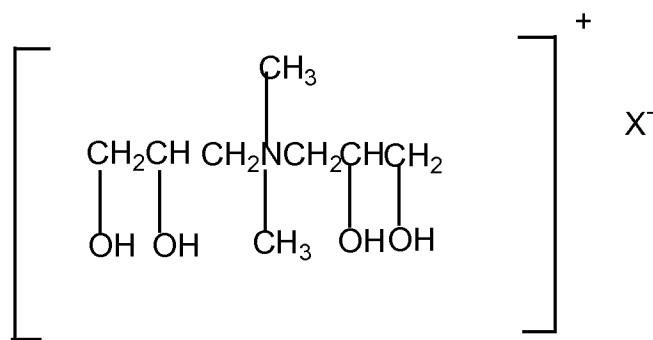
- 15 (iv) a cosmetically acceptable carrier; and wherein the composition exhibits an SPF value which is 1 to 30 units higher than in the absence of the photoprotective enhancing agent.

DETAILED DESCRIPTION OF THE INVENTION

Now it has been found that photoprotection of sunscreen agents can be enhanced by
 20 combining a cocktail of two or more different types of the sunscreen agents with a photoprotective enhancing agent which is a polyhydroxy quaternary ammonium salt.

The photoprotective enhancing agent has the general structure as noted below:

3



(I)

wherein X⁻ is selected from the group consisting of chloride, bromide, hydroxyl, sulphate, phosphate, methosulphate, carboxyl, citrate and tartrate. Most preferred as structure (I) is bis(dihydroxypropyl)dimethylammonium chloride.

5

Amounts of the polyhydroxy quaternary ammonium salt may range from 0.05 to 5%, or from 0.1 to 1%, or from 1 to 3%, and may also be from 0.1 to 0.5% by weight of the composition.

Cosmetic compositions of the present invention may include the following types of
 10 organic sunscreen agents. A first of these is a water-insoluble UV-A sunscreen agent having a λ_{max} between 330 and 380 nm. Particularly the λ_{max} will range from 340 to 360 nm, and optimally at 360 nm. In this category of sunscreen agent, the preferred materials are 4,4'-t-butyl methoxydibenzoylmethane known as Avobenzene (available as Parsol 1789®), 2-hydroxy-4-methoxybenzophenone known as Benzophenone-3 and as Oxybenzone,
 15 terephthalylidene dicamphor sulfonic acid (available as Mexoryl SX) and combinations thereof.

Amounts of the water-insoluble UV-A sunscreen agent may range from 1 to 8%, optimally from 2 to 3% by weight of the composition.

A second of the sunscreen agents is a water-insoluble or water soluble UV-B sunscreen
 20 agent having a λ_{max} ranging between 280 and 400 nm. More particularly the λ_{max} may range from 280 to 320 nm, and optimally at 305 nm.

A large variety of water-insoluble substances may be utilized as the UV-B sunscreen agent. Illustrative are 2-ethylhexyl p-methoxycinnamate, octyldimethyl p-aminobenzoic acid,

digalloyltriolate, ethyl 4-[bis(hydroxypropyl)]aminobenzoate, 2-ethylhexyl-2-cyano-3,3-diphenylacrylate, octylsalicylate, glyceryl p-aminobenzoate, 3,3,5-trimethylcyclohexylsalicylate, methylanthranilate, p-dimethylaminobenzoic acid or aminobenzoate, 2-ethylhexyl p-dimethylaminobenzoate, bis-ethylhexyloxyphenol methoxyphenol triazine, methylene bis-
5 benzotriazolyl tetramethylbutylphenol, dimethicodiethylbenzal malonate, isoamyl methoxycinnamate, octyl triazone, and mixtures thereof.

Amounts of the water-insoluble UV-B sunscreen agent may range from 1 to 8%, preferably from 3 to 6%, and optimally about 5% by weight of the composition. Most preferred is 2-ethylhexyl p-methoxycinnamate.

10 Not only water-insoluble but also water soluble UV-B sunscreen agents separately or in combination may be utilized. An especially useful water-soluble sunscreen agent for this purpose is 2-phenylbenzimidazole-5-sulfonic acid and salt forms (available as Ensulizole®). Amounts of the water-soluble sunscreen agent may range from 1 to 8%, preferably from 2 to 3%, and optimally about 3% by weight of the composition.

15 When the water-soluble sunscreen agent is in salt form, advantageously the salt may be a metallic counter ion selected from sodium and potassium or an ammonium counter ion including triethanolammonium. Most preferred is a mixture of sodium and potassium counter ions, which when present may be found in a relative molar ratio sodium to potassium of 0.5:2 to 2:1, preferably 0.8:2 to 1.5:1, more preferably from 0.8:1 to 1:1.

20 Advantageously but not necessarily the amount of UV-A to UV-B sunscreen agent may range from 1:5 to 1:1, more preferably from 1:4 to 2:5 by weight of the composition.

Increase in the SPF of the composition by the photoprotective enhancing agent over the same formula without the photoprotective enhancing agent should range from 1 to 30, preferably from 2 to 15, and optimally from 3 to 10 units.

25 Cosmetic compositions of the present invention may be but are not limited to cream or lotion form.

Also present in the compositions will be a cosmetically acceptable carrier. Carriers may be present in amounts ranging from 5 to 98%, preferably from 20 to 95%, optimally from 40 to 80% by weight of the cosmetic compositions. Water is the most common carrier for this

invention. Oily carriers in the presence of water and an emulsifier will form emulsion systems as carriers. These systems may either be water-in-oil or oil-in-water emulsions. Besides water, suitable carrier classes include fatty acids, silicones, polyhydric alcohols, fatty alcohols, hydrocarbons, triglycerides and thickening powders.

5 Fatty acids may be selected from stearic acid, oleic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, palmitic acid, behenic acid and mixtures thereof. Amounts may range from 1 to 50%, preferably from 8 to 30%, and optimally from 10 to 25% by weight of the composition.

Concentrations of the silicone may range from about 5% to about 60%, more
10 preferably from about 5% to about 40%, by weight of the composition. These silicone fluids may be organic, silicone-containing or fluorine-containing, volatile or non-volatile, polar or non-polar.

Particularly preferred volatile silicone oils are cyclic volatile silicones wherein the repeating unit ranges from 3 to 5; and linear silicones wherein the repeating unit ranges from
15 1 to 7. Highly preferred examples of volatile silicone oils include cyclomethicones of varying viscosities, e.g., Dow Corning 200, Dow Corning 244, Dow Corning 245, Dow Corning 344, and Dow Corning 345, (commercially available from Dow Corning Corp.); SF-1204 and SF-1202 Silicone Fluids, GE 7207 and 7158 (commercially available from G.E. Silicones) and SWS-03314 (commercially available from SWS Silicones Corp).

20 Hydrocarbons may be useful as cosmetically acceptable carriers for compositions of this invention. They may include mineral oil, petrolatum and polyalpha-olefins. Examples of preferred volatile hydrocarbons include polydecanes such as isododecane and isodecane (e.g., Permethyl-99A which is available from Presperse Inc.) and the C7-C8 through C12-C15 isoparaffins (such as the Isopar Series available from Exxon Chemicals).

25 Polyhydric alcohols may serve as carriers. Illustrative of this group are propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,3-butylene glycol, isoprene glycol, ethoxylated glycerol, propoxylated glycerol and mixtures thereof. Most preferred is glycerol known also as glycerin.

Fatty alcohols may also be useful carriers. The term "fatty" refers to carbon chain lengths ranging from 10 to 30 carbon atoms. Illustrative of this category are lauryl alcohol, cetyl alcohol, stearyl alcohol, isostearyl alcohol and combinations thereof.

Triglycerides are another group of materials useful as carriers. Illustrative but not limiting
5 are sunflower seed oil, cotton oil, canola oil, soybean oil, castor oil, borage oil, olive oil, shea butter, jojoba oil and mixtures thereof. Mono- and di- glycerides may also be useful. Illustrative of these categories are glyceryl monostearate and glyceryl distearate.

The carriers can comprise one or more thickening agents, preferably from 0.05% to 10%, more preferably from 0.1% to 5%, and even more preferably from 0.25% to 4%, by weight for the
10 composition.

Cosmetic compositions of the present invention may contain a variety of optional components to enhance physical properties and performance.

The optional components, when incorporated into the cosmetic compositions, should be suitable for use in contact with human keratinous tissue without undue toxicity, incompatibility,
15 instability, allergic response, and the like within the scope of sound judgment. The *CTFA Cosmetic Ingredient Handbook*, Second Edition (1992) describes a wide variety of nonlimiting cosmetic and pharmaceutical ingredients commonly used in the skin care industry, which are suitable for use in the compositions of the present invention. Examples of these classes include: abrasives, absorbents, aesthetic components such as fragrances, pigments, colorings/colorants,
20 essential oils, skin sensates, astringents, etc. (e.g. clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate), anti-acne agents, anti-caking agents, antifoaming agents, antimicrobial agents, antioxidants, biological additives, buffering agents, bulking agents, chelating agents, chemical additives, colorants, cosmetic astringents, cosmetic biocides, denaturants, drug astringents, external analgesics, film forming polymers, opacifying
25 agents, pH adjusters, propellants, reducing agents, sequestrants, skin bleaching and lightening agents, skin conditioning agents, skin soothing and/or healing agents and derivatives, skin treating agents, thickeners, and vitamins and derivatives thereof.

A safe and effective amount of an anti-oxidant/radical scavenger may be added in amounts from 0.01% to 10%, more preferably from 0.1% to 5% by weight of the composition.

Anti-oxidants/radical scavengers may be employed such as ascorbic acid (vitamin C) and its salts, ascorbyl esters of fatty acids, ascorbic acid derivatives (e.g. magnesium ascorbyl phosphate), tocopherol (vitamin E), tocopherol sorbate, tocopherol acetate, other esters of tocopherol, butylated hydroxy benzoic acids and their salts, 6-hydroxy-2,5,7,8-
5 tetramethylchroman-2-carboxylic acid (commercially available under the tradename Trolor®), amines (e.g. N,N-diethylhydroxylamine, amino-guanidine), nordihydroguaiaretic acid, bioflavonoids, amino acids, cassia plant and extracts, silymarin, tea extracts, and grape skin/seed extracts. Preferred anti-oxidants/radical scavengers are selected from esters of tocopherol, more preferably tocopherol acetate.

10 The cosmetic compositions may optionally comprise a flavonoid compound. Flavonoids are disclosed in U.S. Patents 5,686,082 and 5,686,367 herein incorporated by reference. Examples of flavonoids particularly suitable flavones, isoflavones, coumarins, chromones, discoumarols, chromanones, chromanols, isomers (e.g. cis/trans isomers) thereof, and mixtures thereof.

15 Preferred for use are flavones and isoflavones, in particular daidzein (7,4'-dihydroxy isoflavone), genistein (5,7,4'-trihydroxy isoflavone), equol (7,4'-dihydroxy isoflavan), 5,7-dihydroxy-4'-methoxy isoflavone, soy isoflavones (a mixture extracted from soy), and mixtures thereof. Flavonoid compounds useful herein are commercially available from a number of sources, e.g., Indofine Chemical Company, Inc., Stearoids, Inc., and Aldrich Chemical
20 Company, Inc. The herein described flavonoid compounds are preferably present in from 0.01% to 20%, more preferably from 0.1% to 10%, and even more preferably from 0.5% to 5% by weight.

Anti-inflammatory agents useful herein include allantoin and compounds of the Licorice (the plant genus/species Glycyrrhiza glabra) family, including glycyrrhetic acid, glycyrrhizic acid,
25 and derivatives thereof (e.g. salts and esters).

The compositions may comprise a skin lightening agent. When used, the compositions preferably comprise from 0.1% to 10%, more preferably from 0.2% to 5%, also preferably from 0.5% to 2%, by weight of the composition, of a skin lightening agent. Suitable skin lightening agents include niacinamide, kojic acid, arbutin, tranexamic acid, placental extract, ascorbic acid
30 and derivatives thereof (e.g. magnesium ascorbyl phosphate, sodium ascorbyl phosphate, ascorbyl glucoside, and ascorbyl tetraisopalmitates). Other skin lightening materials suitable for

use herein include Actiwhite® (Cognis), Emblica® (Rona), Azeloglicina (Sinerga) and extracts (e.g. mulberry extract).

The compositions may comprise an antimicrobial or antifungal active. Such actives are capable of destroying microbes, preventing the development of microbes or preventing the pathogenic action of microbes. A safe and effective amount of an antimicrobial or antifungal active may be added to the present compositions, preferably, from 0.001% to 10%, more preferably from 0.01% to 5%, and even more preferably from 0.05% to 2% by weight of the composition.

Preferred examples of these actives include those selected from the group consisting of salicylic acid, benzoyl peroxide, 3-hydroxy benzoic acid, glycolic acid, lactic acid, 4-hydroxy benzoic acid, acetyl salicylic acid, 2-hydroxybutanoic acid, 2-hydroxypentanoic acid, 2-hydroxyhexanoic acid, cis-retinoic acid, trans-retinoic acid, retinol, phytic acid, N-acetyl-L-cystein, lipoic acid, azelaic acid, arachidonic acid, benzoylperoxide, tetracycline, ibuprofen, naproxen, hydrocortisone, acetaminophen, resorcinol, phenoxyethanol, phenoxypropanol, phenoxyisopropanol, 2,4,4'-trichloro-2'-hydroxy diphenyl ether, 3,4,4'-trichlorocarbanilide, octopirox, ciclopirox, lidocaine hydrochloride, clotrimazole, climbazole, miconazole, ketoconazole, neocycin sulfate, and mixtures thereof.

The compositions may comprise a conditioning agent selected from the group consisting of humectants, moisturizers, or skin conditioners. A variety of these materials can be employed and each can be present at a level of from 0.01% to 40%, more preferably from 0.1% to 30%, and even more preferably from 0.5% to 15% by weight of the composition. These materials include, but are not limited to, guanidine; urea; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g. ammonium and quaternary alkyl ammonium); aloe vera in any of its variety of forms (e.g., aloe vera gel); polyhydroxy compounds such as sorbitol, mannitol, glycerol, hexanetriol, butanetriol, propylene glycol, butylene glycol and hexylene glycol; polyethylene glycols; sugars and starch derivatives (e.g. alkoxylated glucose, fructose, sucrose, trehalose); hyaluronic acid; lactamide monoethanolamine; acetamide monoethanolamine; sucrose polyester; petrolatum; and mixtures thereof.

The cosmetic compositions include but are not limited to lotions, milks, mousses, serums, sprays, aerosols, foams, sticks, pencils, gels, creams and ointments. The compositions

Silicone Oil	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Isopropyl Myristate	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Methyl Paraben	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Propyl Paraben	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Water	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100

EXAMPLE 9

Photoprotective effects were evaluated on a model system wherein the lamellar oil phase of an aqueous emulsion had the formulas outlined in Table II.

5 TABLE II

Component	Formula (Wt. % Active)						
	A	B	C	D	E	F	G
Stearic Acid	1.58	1.58	1.58	1.58	1.58	1.58	1.58
Glyceryl Monostearate	0.81	0.81	0.81	0.81	0.81	0.81	0.81
Cetyl Alcohol	0.47	0.47	0.47	0.47	0.47	0.47	0.47
PEG-100 Stearate	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Avobenzene	1.50	1.50	1.50	1.50	1.50	1.50	--
2-Ethylhexylmethoxycinnamate	3.00	3.00	3.00	--	--	--	--
2-Phenylbenzimidazole-5-sulfonic salt (in aqueous phase)	--	--	--	3.00	3.00	3.00	--
Bis(dihydroxypropyl)-dimethylammonium chloride	--	2.00	--	--	2.00	--	2.00
Dihydroxypropyl-trimethylammonium chloride	--	--	2.00	--	--	2.00	--

Procedure

SPF Measurements

Sun protection factor (SPF) was measured in vitro using an Optometrics SPF 290 instrument. The test procedure required calibration of the monochromator and sample stage of the Optometrics SPF 290 instrument. Thereafter the instrument was calibrated with a blank sample quartz plate (10 cm x 10 cm and 3 mm thickness). Calibration zeros the UV detector. Formulas were applied and spread uniformly onto a plate to leave a film of 2 mg/cm². The film was left to dry for 30 minutes. Subsequently an SPF reading was taken on the dried film using three measurements on different parts of the coated quartz plate and recording an average value. For the present experiments the wavelength is the peak maximum at 305 to 360 nm.

Results

The SPF in vitro results on the formulas detailed under Table II are recorded in Table III below.

TABLE III

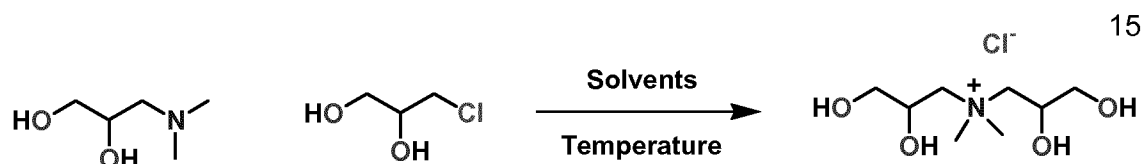
Formula	SPF (2 mg/cm ²)
A	17
B	23
C	20
D	10
E	18
F	11
G	2.4

5

Evident from the results is that the presence of bis(dihydroxypropyl)dimethylammonium chloride enhanced photoprotection. Compare Formula A with B and D with E which show an increase of from 6 to 8 units of SPF in the presence of the photoprotective enhancing agent. A compound similar to the enhancer of this invention, dihydroxypropyltrimethylammonium chloride, 10 was much less effective at improving the SPF. Compare results of Formula B versus C and Formula E versus F.

EXAMPLE 10

Synthesis of Bis-(2,3-dihydroxypropyl) dimethylammonium Chloride



General Procedure: Dimethylaminopropanediol (20 g, 0.168 moles) and 3-Chloropropane-1,2-diol (18.5 g, 0.168 moles) were stirred in ethanol (40 mL) at 70 °C until the reaction is 20 complete. The reaction was monitored by LCMS. Upon completion, the reaction was allowed to cool and the solution was poured to a mixture of acetone:methyl-tert-butyl ether (2:1, 300 mL) to oil out the product. The Supernatant was decanted and product was washed with a

mixture of acetone/ methyl-tert-butyl ether (2 x 300 mL). The oil obtained was dried over high vacuum followed by freeze drying to obtain colorless oil/semisolid (> 90% yield). The pure product was characterized using ^1H NMR, ^{13}C NMR, and MS. Details on characterization as follows.

5 Analytical Instrumentation used:

LC MS: The MS of the compound was recorded using a Micromass Quattro Ultima LCMS system with Mass Lynx 4.1 software equipped with Agilent 1100 LC system. A solution of 50ppm was infused in the LCMS system using 50:50 Methanol: 5mM HCOOH as the mobile phase and ESI positive source.

- 10 **NMR:** A sample (144mg) was dissolved in D_2O (650 mL) and analyzed by ^1H and ^{13}C NMR using a Varian Eft-60 NMR Spectrometer (60 MHz) and the data processed using Nuts Pro (2D Professional version, Acorn NMR).

Characterization of Bis-(2.3-dihydroxypropyl) dimethylammonium Chloride:

^1H NMR (D_2O , 60 MHz) δ 3.22 (s, 6H, CH_3), 3.48 (s, 4H, CH_2), 3.57 (s, 4H, CH_2), 4.2 (bm, 2H,
15 -CH),

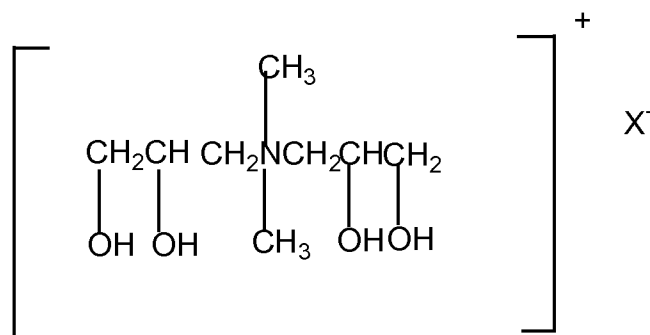
^{13}C NMR (D_2O) δ 52.72 (CH_3s), 63.55 ($-\text{CH}_2$), 65.97 ($-\text{CH}$), 67.24 ($-\text{CH}_2\text{s}$)

LCMS (M-Cl) 194.25 (calcd), 194.22 (observed).

The above description is presented to enable a person skilled in the art to make and use the invention, and is provided in the context of a particular application and its
20 requirements. Various modifications to the preferred embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments and applications without departing from the spirit and scope of the invention. Thus, this invention is not intended to be limited to the embodiments shown, but is to be accorded the widest scope consistent with the principles and features disclosed herein.

Claims

1. A cosmetic composition comprising:
- (i) a water-insoluble UV-A organic sunscreen agent having a λ_{\max} ranging from 330 to 380 nm;
 - (ii) a UV-B organic sunscreen agent having a λ_{\max} ranging from 280 to 400 nm; and
 - (iii) a photoprotective enhancing agent having the structure (I)



(I)

wherein X⁻ is selected from the group consisting of chloride, bromide, hydroxyl, sulphate, phosphate, methosulphate, carboxyl, citrate and tartrate;

- (iv) a cosmetically acceptable carrier; and wherein the composition exhibits an SPF value which is 1 to 30 units higher than in the absence of the photoprotective enhancing agent.
2. The composition according to claim 1 wherein the water-insoluble UV-A organic sunscreen agent is Avobenzone or Benzophenone-3.
 3. The composition according to claim 1 or claim 2 wherein the UV-B organic sunscreen agent is 2-ethylhexylmethoxycinnamate.
 4. The composition according to claim 1 or claim 2 wherein the UV-B sunscreen agent is 2-phenylbenzimidazole-5-sulfonic acid or salt thereof.

5. The composition according to any one of claims 1 to 4 wherein the photoprotective enhancing agent is present in an amount from 0.05 to 5%, preferably in an amount from 1 to 3% by weight of the composition.
6. The composition according to any one of claims 1 to 5 wherein the UV-A organic sunscreen agent is present in an amount from 1 to 8% by weight of the composition.
7. The composition according to any one of claims 1 to 6 wherein the UV-B organic sunscreen agent is present in an amount from 1 to 8% by weight of the composition.
8. The composition according to any one of claims 1 to 7 wherein the polyhydroxy quaternary ammonium salt is bis(dihydroxypropyl)dimethylammonium chloride.