Title: COSMETIC COMPOSITIONS WITH SILICA AEROGEL SUN PROTECTION FACTOR BOOSTERS

Abstract: A cosmetic composition for protecting keratinous substrates against UV radiation, provided in the form of a water-in-oil, or oil-in-water emulsion that includes at least one or more UV filter photoprotective compositions and at least first silica aerogel, the silica aerogel comprising particles, all in a cosmetically acceptable aqueous carrier. The composition exhibits an SPF that is greater than an SPF exhibited by an identical composition.
COSMETIC COMPOSITIONS WITH SILICA AEROGEL SUN PROTECTION FACTOR BOOSTERS

FIELD OF THE INVENTION

The present disclosure is directed to cosmetic compositions and methods of using and producing cosmetic compositions. More specifically, the present disclosure is directed to sunscreen compositions comprising a unique combination of components that provide for a high Sun Protection Factor (SPF), and to methods of making and methods of using the compositions to protect keratinous substrates, such as skin and hair, from UV radiation, the cosmetic compositions in the form of an oil-in-water type emulsion comprising a silica aerogel. The cosmetic compositions beneficially provide enhanced sun protection.

BACKGROUND OF THE INVENTION

Aging skin is the result of more than just chronological age. Skin is exposed to various environmental stresses, such as UV rays. The negative effects of exposure to ultraviolet ("UV") light are well-known. Prolonged exposure to sunlight causes damage, such as sunburn, to the skin and dries out hair making it brittle. When skin is exposed to UV light having a wavelength of from about 290 nm to about 400 nm, long-term damage can lead to serious conditions, such as skin cancer. UV light also contributes to aging by causing free radicals to form in the skin. Free radicals include, for example, singlet oxygen, hydroxyl radical, the superoxide anion, nitric oxide and hydrogen radicals. Free radicals attack DNA, membrane lipids and proteins, generating carbon radicals. These in turn react with oxygen to produce a peroxyl radical that can attack adjacent fatty acids to generate new carbon radicals. This cascade leads to a chain reaction producing lipid peroxidation products.

Damage to the cell membrane results in loss of cell permeability, increased intercellular ionic concentration, and decreased ability to excrete or detoxify waste products. The end result is a loss of skin elasticity and the appearance of wrinkles. This process is commonly referred to as photo-aging.

Sunscreens can be used to protect against UV damage and delay the signs of aging. The degree of UV protection afforded by a sunscreen composition is directly related to the amount and type of UV filters contained therein. The higher the amount of UV filters, the greater the degree of UV protection. Generally, UV sunscreen actives are utilized to provide protection from UV light. Numerous
cosmetic compositions intended for the photoprotection (UV-A and/or UV-B) of the skin have been proposed to date.

These anti-sun compositions often take the form of oil-in-water or water-in-oil emulsions, of gels, or of non-aqueous products which contain, in various concentrations, one or more insoluble and/or fat-soluble and/or water-soluble, organic and/or inorganic screening agents that are capable of selectively absorbing the harmful UV radiation. These screening agents and their amounts are selected as a function of the desired sun protection factor (SPF). The sun protection factor (SPF) mathematically expresses the ratio of the dose of UV radiation necessary to achieve the eryhematogenic threshold with the UV screening agent to the dose of UV radiation necessary to achieve the eryhematogenic threshold without the UV screening agent. Accordingly, an increasing need exists for anti-sun products having a high sun protection factor. High sun protection factors can be obtained by incorporating more screening agents in high concentrations. This cannot always be done since the addition of large quantities of screening agents considerably increases the cost of the anti-sun formulations and the risks of skin irritation.

In addition, it is also required for cosmetic products to be applied onto, for example, the skin, regardless of the purpose of photoprotection, that the irregularities on the skin, such as spots, blots, wrinkles, and fine lines, be concealed or become less distinct, and in some embodiments immediately, and that the cosmetic products have good sensorial texture, such as good spreadability, no or little formation of noodles (long, narrow aggregates formed by cosmetic products which may look like eraser dust), and moisturizing feeling.

Thus, there has been a need for a cosmetic product with good UV-shielding ability which can be achieved without increasing the amount of a UV filter or filters in the product, and good immediate optical effects to conceal the irregularities on the skin or to make them less distinct, as well as good sensorial texture.

Therefore, to provide a composition that does not suffer from one or more of the above drawbacks would be desirable in the art.

**SUMMARY OF THE INVENTION**

The present disclosure relates to sunscreen compositions that have excellent Sun Protection Factors (SPF), and exhibit good skin feel and other aesthetic properties. The inventors discovered that inclusion of a silica aerogel in a sunscreen exhibits a surprisingly significant boost to the SPF (in addition to other
beneficial properties). This allows for sunscreen compositions to be formulated that exhibit excellent sun protective properties.

In an exemplary embodiment, a composition, comprising, in a physiologically acceptable medium, a cosmetic composition comprising in a cosmetically acceptable medium:

(a) at least one UV Filter;

(b) at least one SPF booster comprising a silica aerogel, wherein the aerogel is present in an amount in the range from 0.1% to 5% by weight of the composition.

The present disclosure is also directed to a method for cosmetic treatment of keratinous tissues by applying the above-disclosed composition onto a surface of the keratinous tissue in order to achieve beneficial shielding from UV radiation.

Other features and advantages of the present invention will be apparent from the following more detailed description of the desirable embodiment which illustrates, by way of example, the principles of the invention.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1. Shows a spotting pattern for Example 1 and Comparative Example 1.

**DETAILED DESCRIPTION OF THE INVENTION**

Where the following terms are used in this specification, they are used as defined below.

The terms "a" and "the" are understood to encompass the plural as well as the singular.

"At least one" means one or more and thus may include individual components as well as mixtures/combinations.

The terms "comprising," "having," and "including" are used in their open, non-limiting sense.

The term "booster" or "SPF booster" means a compound or composition that when used in a formulation in conjunction with a UV filtering agent, increases the SPF of the formulation without increasing the amount of UV filtering agent in the formulation.
"Cosmetically acceptable" means that the item in question is compatible with any keratinous substrate. For example, "cosmetically acceptable carrier" means a carrier that is compatible with any keratinous substrate.

"Keratinous tissue," as used herein, may include but is not limited to skin, hair, and nails.

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.

The cosmetic compositions and methods of the present invention can comprise, consist of, or consist essentially of the elements and limitations of the invention described herein, as well as any additional or optional ingredients, components, or limitations described herein or otherwise useful in personal care compositions intended for topical application to keratinous tissue. The compositions, according to the instant disclosure, may be prepared according to techniques that are well known to those skilled in the art, in particular those intended for the preparation of emulsions of oil-in-water or water-in-oil type. They may be, in particular, in the form of a simple or complex emulsion (O/W, W/O, O/W/O or W/O/W emulsion), such as a cream or a milk, in the form of a gel or a cream-gel, or in the form of a lotion. Good results have been obtained with cream formulations in the form of an O/W emulsion.

It has been surprisingly discovered by the inventors that it is possible to achieve a significant enhancement of SPF by inclusion of a silica aerogel together with at least one UV filter component, whereby the silica aerogel present as a relatively small percentage by weight constitutes an SPF booster, suitable for enhanced photoprotection from light, in particular UV rays. The composition, according to the present invention, can provide (1) high UV-shielding ability without increasing the amount of the (a) UV filter(s) in the composition, (2) good optical effects, and (3) good sensorial texture. Furthermore, the methods, according to the present invention, can provide cosmetic effects based on the UV-shielding ability and optical effects of the compositions, according to the present invention. Hereinafter, the composition and the method, according to the present invention, will be explained in a more detailed manner.

The instant disclosure is directed to a cosmetic, more particularly a sunscreen composition comprising at least one silica aerogel. The at least one silica
aerogel is a SPF booster, and may be present in an amount of about 0.1, 0.5, 1, 1.5, 2, 3, 4, to about 5 wt. %, and increments therebetween, based on the total weight of the sunscreen composition. In one embodiment, the amount of booster is in an amount of about 3 wt. %, based on the total weight of the sunscreen composition. In another embodiment, the total amount of the silica aerogel is about 2 wt. %, based on the total weight of the sunscreen composition. In other embodiments, the at least one silica aerogel booster may be in a positive amount but not in excess of (no more than) about 5 wt. %, based on the total weight of the sunscreen composition.

While not wishing to be bound by theory or explanation, on the skin, silica aerogel can imbibe a very high amount of sebum in its intricate internal mesh structure. The resultant interaction exhibits a super-hydrophobic behavior so called the Lotus Effect that allows for an instant sweat repellant effect. Moreover, light interacts strongly with it, producing a very strong scattering and blurring effect. In sun care products, Silica aerogel (79502 / SILICA SLYLATED / DOW CORNING) has the property of forming a film on the skin. The quality of the film is very important for sunscreens, because it influences the homogeneity of the product on the skin.

A method for treating keratinous tissue may include applying to the keratinous tissue the cosmetic composition of the present disclosure. The cosmetic composition of the present disclosure is in any desirable cosmetic form, such as, but not limited to, liquid lotions, creams, and mousses, and can be applied to keratinous tissue to provide greater hydration.

The composition, according to the present invention, may include in a physiologically acceptable medium:

(a) at least one UV filter; and

(b) at least one SPF booster comprising a silica aerogel.

Each of the various components and optional components are described below.

**AEROGEL OF SILICA**

According to various embodiments of the invention, the compositions and methods include use of an aerogel of silica.

As used here, "silica aerogels" are porous materials obtained by replacing (by drying) the liquid component of a silica gel with air. Silica aerogels are generally synthesized via a sol-gel process in a liquid medium and then dried, usually by extraction with a supercritical fluid, such as, but not limited to, supercritical carbon dioxide.
dioxide (CO₂). This type of drying makes it possible to avoid shrinkage of the pores and of the material. The sol-gel process and the various drying processes are described in detail in Brinker, C.J., and Scherer, G.W., Sol-Gel Science: New York: Academic Press, 1990.

The hydrophobic silica aerogel particles used in the present invention have a specific surface area per unit of mass (SM) ranging from about 500 to about 1500 m²/g, or alternatively from about 600 to about 1200 m²/g, or alternatively from about 600 to about 800 m²/g, and a size expressed as the mean volume diameter (D[0.5]), ranging from about 1 to about 30 µm, or alternatively from about 5 to about 25 µm, or alternatively from about 5 to about 20 µm, or alternatively from about 5 to about 15 µm. The specific surface area per unit of mass may be determined via the BET (Brunauer-Emmett-Teller) nitrogen absorption method described in the Journal of the American Chemical Society, vol. 60, page 309, February 1938, corresponding to the international standard ISO 5794/1. The BET specific surface area corresponds to the total specific surface area of the particles under consideration.

The size of the silica aerogel particles may be measured by static light scattering using a commercial granulometer such as the MasterSizer 2000 machine from Malvern. The data are processed on the basis of the Mie scattering theory. This theory, which is exact for isotropic particles, makes it possible to determine, in the case of non-spherical particles, an "effective" particle diameter. This theory is especially described in the publication by Van de Hulst, H.C., "Light Scattering by Small Particles," Chapters 9 and 10, Wiley, New York, 1957.

The silica aerogel particles used in the present invention may advantageously have a tamped (or tapped) density ranging from about 0.04 g/cm³ to about 0.10 g/cm³, or alternatively from about 0.05 g/cm³ to about 0.08 g/cm³. In the context of the present invention, this density, known as the tamped density, may be assessed according to the following protocol: 40 g of powder are poured into a measuring cylinder; the measuring cylinder is then placed on a Stav 2003 machine from Stampf Volumeter; the measuring cylinder is then subjected to a series of 2500 packing motions (this operation is repeated until the difference in volume between two consecutive tests is less than 2%); the final volume Vf of packed powder is then measured directly on the measuring cylinder. The tamped density is determined by the ratio m/Vf, in this instance 40/Vf (Vf being expressed in cm³ and m in g).
According to one embodiment, the hydrophobic silica aerogel particles used in the present invention have a specific surface area per unit of volume $S_v$ ranging from about 5 to about 60 $m^2/cm^3$, or alternatively from about 10 to about 50 $m^2/cm^3$, or alternatively from about 15 to about 40 $m^2/cm^3$. The specific surface area per unit of volume is given by the relationship: $S_v = s_{M,r}$ where $r$ is the tamped density expressed in $g/cm^3$ and $s_M$ is the specific surface area per unit of mass expressed in $m^2/g$, as defined above.

In some embodiments, the hydrophobic silica aerogel particles, according to the invention, have an oil-absorbing capacity, measured at the wet point, ranging from about 5 to about 18 ml/g, or alternatively from about 6 to about 15 ml/g, or alternatively from about 8 to about 12 ml/g. The oil-absorbing capacity measured at the wet point, noted $W_p$, corresponds to the amount of water that needs to be added to 100 g of particle in order to obtain a homogeneous paste. $W_p$ is measured according to the wet point method or the method for determining the oil uptake of a powder described in standard NF T 30-022. $W_p$ corresponds to the amount of oil adsorbed onto the available surface of the powder and/or absorbed by the powder by measuring the wet point, described below: An amount $= 2$ g of powder is placed on a glass plate, and the oil (isononyl isononanoate) is then added dropwise. After addition of 4 to 5 drops of oil to the powder, mixing is performed using a spatula, and addition of oil is continued until a conglomerate of oil and powder has formed. At this point, the oil is added one drop at a time and the mixture is then triturated with the spatula. The addition of oil is stopped when a firm, smooth paste is obtained. This paste must be able to be spread on the glass plate without cracking or forming lumps. The volume $V_s$ (expressed in ml) of oil used is then noted. The oil uptake corresponds to the ratio $V_s/m$.

The aerogels used, according to the present invention, are hydrophobic silica aerogels, preferably of silylated silica (INCI name: silica silylate). The term "hydrophobic silica" means any silica whose surface is treated with silylating agents, for example, halogenated silanes, such as alkylchlorosilanes, siloxanes, in particular dimethylsiloxanes, such as hexamethyldisiloxane, or silazanes, so as to functionalize the OH groups with silyl groups Si-Rn, for example, trimethylsilyl groups. Preparation of hydrophobic silica aerogel particles that have been surface-modified by silylation, is found in U.S. Patent No. 7,470,725, incorporated herein by reference. In one
embodiment, hydrophobic silica aerogel particles surface-modified with trimethylsilyl groups are desirable.

Suitable examples of hydrophobic silica aerogels, may include, but are not limited to, the aerogels sold under the tradenames of VM-2260 (INCI name: Silica silylate) and VM-2270 (INCI name: Silica silylate), both available from Dow Corning Corporation (Midland, Michigan). The particles of VM-2260 have a mean size of about 1000 microns and a specific surface area per unit of mass ranging from 600 to 800 m²/g. The particles of VM-2270 have a mean size ranging from 5-15 microns and a specific surface area per unit of mass ranging from 600 to 800 m²/g. Another suitable example of a hydrophobic silica aerogel may include, but is not limited to, the aerogels commercially available from Cabot Corporation (Billerica, Massachusetts) under the tradename of Aerogel TLD 201, Aerogel OGD 201 and Aerogel TLD 203, Enova Aerogel MT 1100 and Enova Aerogel MT 1200.

**UV FILTERS**

The composition, according to the present invention, may include at least one UV filter. There is no limitation to the type of the UV filter. Two or more types of UV filters may be used in combination. Thus, a single type of UV filter or a combination of different types of UV filters may be used.

The UV filter can be selected from inorganic UV filters, organic UV filters, and mixtures thereof. The composition, according to the present invention, may comprise the UV filter(s) in an amount of from 0.1 to 50% by weight, and in some embodiments from 1 to 40% by weight, and in some embodiments from 2 to 30% by weight in relation to the total weight of the composition.

**INORGANIC UV FILTERS**

The composition, according to the present invention, may comprise at least one inorganic UV filter. If two or more inorganic UV filters are used, they may be the same or different.

The inorganic UV filter used for the present invention may be active in the UV-A and/or UV-B region. The inorganic UV filter may be hydrophilic and/or lipophilic. The inorganic UV filter is in some embodiments insoluble in solvents, such as water, and ethanol commonly used in cosmetics.

It is in some embodiments desirable that the inorganic UV filter be in the form of a fine particle such that the mean (primary) particle diameter thereof ranges from 1 nm to 50 nm, and in some embodiments 5 nm to 40 nm, and in some
embodiments 10 nm to 30 nm. The mean (primary) particle size or mean (primary) particle diameter here is an arithmetic mean diameter.

The inorganic UV filter can be selected from the group consisting of silicon carbide, metal oxides which may or may not be coated, and mixtures thereof. And in some embodiments, the inorganic UV filters are selected from pigments (mean size of the primary particles: generally from 5 nm to 50 nm, and in some embodiments from 10 nm to 50 nm) formed of metal oxides, 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 that are well known per se. And in some embodiments, the inorganic UV filters are selected from titanium oxide, zinc oxide, and in some embodiments titanium oxide.

The inorganic UV filter may or may not be coated. The inorganic UV filter may have at least one coating. The coating may comprise at least one compound selected from the group consisting of alumina, silica, aluminum hydroxide, silicones, silanes, fatty acids or salts thereof (such as sodium, potassium, zinc, iron, or aluminum salts), fatty alcohols, lecithin, amino acids, polysaccharides, proteins, alkanolamines, waxes, such as beeswax, (meth)acrylic polymers, organic UV filters, and (per)fluoro compounds. It is in some embodiments desirable for the coating to include at least one organic UV filter. As the organic UV filter in the coating, a dibenzoylmethane derivative, such as butyl methoxydibenzoylmethane (Avobenzone) and 2,2'-Methylenebis[6-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-Tetramethyl-Butyl) Phenol] (Methylene Bis-Benzotriazolyl Tetramethylbutylphenol) marketed as "TINOSORB M" by BASF, may be desirable.

In a known manner, the silicones in the coating(s) may be organosilicon polymers or oligomers comprising a linear or cyclic and branched or cross-linked structure, of variable molecular weight, obtained by polymerization and/or polycondensation of suitable functional silanes and essentially composed of repeated 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 said silicon atoms via a carbon atom.

The term "silicones" also encompasses silanes necessary for their preparation, in particular alkylsilanes.
The silicones used for the coating(s) can be and in some embodiments are selected from the group consisting of alkylsilanes, polydialkylsiloxanes, and polyalkylhydrosiloxanes. And in some embodiments still, the silicones are selected from the group consisting of octyltrimethylsilane, polydimethylsiloxanes, and polymethylhydrosiloxanes.

Of course, the inorganic UV filters made of metal oxides may, before their treatment with silicones, have been treated with other surfacing agents, in particular with cerium oxide, alumina, silica, aluminum compounds, silicon compounds, or their mixtures. The coated inorganic UV filter may have been prepared by subjecting the inorganic UV filter to one or more surface treatments of a chemical, electronic, mechano-chemical, and/or mechanical nature with any of the compounds as described above, as well as polyethylenes, metal alkoxides (titanium or aluminum alkoxides), metal oxides, sodium hexametaphosphate, and those shown, for example, in Cosmetics & Toiletries, February 1990, Vol. 105, pp. 53-64.

The coated inorganic UV filters may be titanium oxides coated: with silica, such as the product "Sun veil" from Ikeda, and "Sunsil TIN 50" from Sunjin Chemical; 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" 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 aluminum stearate, such as the product "Microtitanium Dioxide MT 100 T, MT 100 TX, MT 100 Z or MT-01" from Tayca, the products "Solaveil CT-10 W" and "Solaveil CT 100" from Uniqema, and the product "Eusolex T-AVO" from Merck; with alumina and with aluminum laurate, such as the product "Microtitanium Dioxide MT 100 S" from Tayca; with iron oxide and with iron stearate, such as the product "Microtitanium Dioxide MT 100 F" from Tayca; 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", and "Microtitanium Dioxide MT 100 SAS" from Tayca; with silica, with alumina and with aluminum 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; 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; or with sodium hexametaphosphate,
such as the product "Microtitanium Dioxide MT 150 W" from Tayca. Other titanium oxide pigments treated with a silicone are, and in some embodiments $\text{TiO}_2$ treated with octyltrimethylsilane and for which the mean size of the individual particles is from 25 and 40 nm, such as that marketed under the trademark "T 805" by Degussa Silices, $\text{TiO}_2$ treated with a polydimethylsiloxane and for which the mean size of the individual particles is 21 nm, such as that marketed under the trademark "70250 Cardre UF $\text{TiO}_2\text{Si}_3"$ by Cardre, and anatase/rutile $\text{TiO}_2$ treated with a polydimethylhydroxiloxane and for which the mean size of the individual particles is 25 nm, such as that marketed under the trademark "Microtitanium Dioxide USP Grade Hydrophobic" by Color Techniques.

And in some embodiments, the following coated $\text{TiO}_2$ can be used as the coated inorganic UV filter: Stearic acid (and) Aluminum Hydroxide (and) $\text{TiO}_2$, such as the product "MT-100 TV" from Tayca, with a mean primary particle diameter of 15 nm; Dimethicone (and) Stearic Acid (and) Aluminum Hydroxide (and) $\text{TiO}_2$, such as the product "S A-TTO-S4" from Miyoshi Kasei, with a mean primary particle diameter of 15 nm; Silica (and) $\text{TiO}_2$, such as the product "MT-100 WP" from Tayca, with a mean primary particle diameter of 15 nm; Dimethicone (and) Silica (and) Aluminum Hydroxide (and) $\text{TiO}_2$, such as the product "MT-Y02" and "MT-Y-110 M3S" from Tayca, with a mean primary particle diameter of 10 nm; Dimethicone (and) Aluminum Hydroxide (and) $\text{TiO}_2$, such as the product "SA-TTO-S3" from Miyoshi Kasei, with a mean primary particle diameter of 15 nm; Dimethicone (and) Alumina (and) $\text{TiO}_2$, such as the product "UV TITAN MI 70" from Sachtleben, with a mean primary particle diameter of 15 nm; and Silica (and) Aluminum Hydroxide (and) Alginic Acid (and) $\text{TiO}_2$, such as the product "MT-100 AQ" from Tayca, with a mean primary particle diameter of 15 nm. In terms of UV filtering ability, $\text{TiO}_2$ coated with at least one organic UV filter is more desirable. For example, Avobenzone (and) Stearic Acid (and) Aluminum Hydroxide (and) $\text{TiO}_2$, such as the product "HXMT-100ZA" from Tayca, with a mean primary particle diameter of 15 nm, can be used.

The uncoated titanium oxide pigments are, for example, marketed by Tayca under the trademarks "Microtitanium Dioxide MT500B" or "Microtitanium Dioxide MT600B", by Degussa under the trademark "P 25", by Wacker under the trademark "Oxyde de titane transparent PW", by Miyoshi Kasei under the trademark
"UFTR", by Tomen under the trademark "ITS" and by Tioxide under the trademark "Tioveil AQ". The uncoated zinc oxide pigments are, for example: those marketed under the trademark "Z-cote" by Sunsmart; those marketed under the trademark "Nanox" by Elementis; and those marketed under the trademark "Nanogard WCD 2025" by Nanophase Technologies. The coated zinc oxide pigments are, for example: those marketed under the trademark "Oxide Zinc CS-5" by Toshiba (ZnO coated with polymethylhydrosiloxane); those marketed under the trademark "Nanogard Zinc Oxide FN" by Nanophase Technologies (as a 40% dispersion in Finsolv TN, C12-C15 alkyl benzoate); those marketed under the trademark "Daitopersion Zn-30" and "Daitopersion Zn-50" by Daito (dispersions in oxyethylenated polydimethylsiloxane/cyclopolydimethylsiloxane comprising 30% or 50% of zinc nano-oxides coated with silica and polymethylhydrosiloxane); those marketed under the trademark "NFD Ultrafine ZnO" by Daikin (ZnO coated with phosphate of perfluoroalkyl and a copolymer based on perfluoroalkylethyl as a dispersion in cyclopentaasiloxane); those marketed under the trademark "SPD-Z1" by Shin-Etsu (ZnO coated with a silicone-grafted acrylic polymer dispersed in cyclocdimethylsiloxane); those marketed under the trademark "Escalol Z100" by ISP (alumina-treated ZnO dispersed in an ethylhexyl methoxycinnamate/PVP-hexadecene copolymer/methicone mixture); those marketed under the trademark "Fuji ZnO-SMS-1.0" by Fuji Pigment (ZnO coated with silica and polymethylsilsesquioxane); and those marketed under the trademark "Nanox Gel TN" by Elementis (ZnO dispersed at 55% in C12-C15 alkyl benzoate with hydroxystearic acid polycondensate). The uncoated cerium oxide pigments are marketed, for example, under the trademark "Colloidal Cerium Oxide" by Rhone-Poulenc.

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

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

Mention may also be made of mixtures of metal oxides, in particular, of titanium dioxide and of cerium dioxide, including a mixture of equal weights of...
titanium dioxide coated with silica and of cerium dioxide coated with silica marketed by Ikeda under the trademark "Sunveil A", and also a mixture of titanium dioxide and of zinc dioxide coated with alumina, with silica and with silicone, such as the product "M 261" marketed by Kemira, or coated with alumina, with silica and with glycerol, such as the product "M 211" marketed by Kemira.

Coated inorganic UV filters are desirable, because the UV filtering effects of the inorganic UV filters can be enhanced. In addition, the coating(s) may help uniformly or homogeneously disperse the UV filters in the composition, according to the present invention.

ORGANIC UV FILTERS

The composition, according to the present invention, may comprise at least one organic UV filter. If two or more organic UV filters are used, they may be the same or different.

The organic UV filter used for the present invention may be active in the UV-A and/or UV-B region. The organic UV filter may be hydrophilic and/or lipophilic.

The organic UV filter may be solid or liquid. The terms "solid" and "liquid" mean solid and liquid, respectively, at 25°C under 1 atm.

The organic UV filter can be selected from the group consisting of anthranilic compounds; dibenzoylmethane compounds; cinnamic compounds; salicylic compounds; camphor compounds; benzophenone compounds; β,β-diphenylacrylate compounds; triazine compounds; benzotriazole compounds; benzalmonate compounds; benzimidazole compounds; imidazoline compounds; bis-benzoazolyl compounds; p-aminobenzoic acid (PABA) compounds; methylenebis(hydroxyphenylbenzotriazole) compounds; benzoazole compounds; screening polymers and screening silicones; dimers derived from a-alkylstyrene; 4,4-diarylbutfadienes compounds; guaiazulene and derivatives thereof; rutin and derivatives thereof; flavonoids; bioflavonoids; oryzanol and derivatives thereof; quinic acid and derivatives thereof; phenols; retinol; cysteine; aromatic amino acids; peptides having an aromatic amino acid residue; and mixtures thereof.

Mention may be made, as examples of the organic UV filter(s), of those denoted below under their INCI names, and mixtures thereof. Anthranilic compounds: Menthyl anthranilate, marketed under the trademark "Neo Heliopan MA" by Haarmann and Reimer. Dibenzoylmethane compounds: Butyl methoxydibenzoylmethane, marketed in particular under the trademark "Parsol 1789"
by Hoffmann-La Roche; and isopropyl dibenzoylmethane. Cinnamic compounds: Ethylhexyl methoxycinnamate, marketed in particular under the trademark "Parsol MCX" by Hoffmann-La Roche; isopropyl methoxycinnamate; isopropanoxy methoxycinnamate; isoamyl methoxycinnamate, marketed under the trademark "Neo Heliopan E 1000" by Haarmann and Reimer; cinoxate (2-ethoxyethyl-4-methoxy cinnamate); DEA methoxycinnamate; diisopropyl methylcinnamate; and glyceryl ethylhexanoate dimethoxycinnamate. Salicylic compounds: Homosalate (homomentyl salicylate), marketed under the trademark "Eusolex HMS" by Rona/EM Industries; ethylhexyl salicylate, marketed under the trademark "Neo Heliopan OS" by Haarmann and Reimer; glycol salicylate; butyloctyl salicylate; phenyl salicylate; dipropyleneglycol salicylate, marketed under the trademark "Dipsal" by Scher; and TEA salicylate, marketed under the trademark "Neo Heliopan TS" by Haarmann and Reimer. Camphor compounds, in particular, benzylidencamphor derivatives: 3-benzylidene camphor, manufactured under the trademark "Mexoryl SD" by Chimex; 4-methylbenzylidene camphor, marketed under the trademark "Eusolex 6300" by Merck; benzylidene camphor sulfonic acid, manufactured under the trademark "Mexoryl SL" by Chimex; camphor benzalkonium methosulfate, manufactured under the trademark "Mexoryl SO" by Chimex; terephthalylidene dicamphor sulfonic acid, manufactured under the trademark "Mexoryl SX" by Chimex; and polyacrylamidomethyl benzylidene camphor, manufactured under the trademark "Mexoryl SW" by Chimex. Benzophenone compounds: Benzophenone-1 (2,4-dihydroxybenzophenone), marketed under the trademark "Uvinul 400" by BASF; benzophenone-2 (Tetrahydroxybenzophenone), marketed under the trademark "Uvinul D50" by BASF; Benzophenone-3 (2-hydroxy-4-methoxybenzophenone) or oxybenzone, marketed under the trademark "Uvinul M40" by BASF; benzophenone-4 (hydroxymethoxy benzophonene sulfonic acid), marketed under the trademark "Uvinul MS40" by BASF; benzophenone-5 (Sodium hydroxymethoxy benzophenone Sulfonate); benzophenone-6 (dihydroxy dimethoxy benzophenone) marketed under the trademark "Helisorb 11" by Norquay; benzophenone-8, marketed under the trademark "Spectra-Sorb UV-24" by American Cyanamid; benzophenone-9 (Disodium dihydroxy dimethoxy benzophenonedisulfonate), marketed under the trademark "Uvinul DS-49" by BASF; and benzophenone- 12, and n-hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate (UVINUL A+ by BASF). β,β-Diphenylacrylate compounds: Octocrylene, marketed in particular under the
trademark "Uvinul N539" by BASF; and Etocrylene, marketed in particular under the trademark "Uvinul N35" by BASF. Triazine compounds: Diethylhexyl butamido triazone, marketed under the trademark "Uvasorb HEB" by Sigma 3V; 2,4,6-tris(dineopentyl 4'-aminobenzalmalonate)-s-triazine, bis-ethylhexyloxyphenol methoxyphenyl triazone marketed under the trademark «TINOSORB S .. by CIBA GEIGY, and ethylhexyl triazone marketed under the trademark «UVTNUL T150 .. by BASF. Benzotriazole compounds, in particular, phenylbenzotriazole derivatives: 2-(2H-benzotriazole-2-yl)-6-dodecyl-4-methylpheno, branched and linear; and those described in USP 5240975. Benzalalnate compounds: Dineopentyl 4'-methoxybenzalmalonate, and polyorganosiloxane comprising benzalalnate functional groups, such as polysilicone-1 5, marketed under the trademark "Parsol SLX" by Hoffmann-LaRoche. Benzimidazole compounds, in particular, phenylbenzimidazole derivatives: Phenylbenzimidazole sulfonic acid, marketed in particular under the trademark "Eusolex 232" by Merck, and disodium phenyl dibenzimidazole tetralsulfonate, marketed under the trademark "Neo Heliopan AP" by Haarmann and Reimer. Imidazoline compounds: Ethylhexyl dimethoxybenzylidene dioximimidazoline propionate. Bis-benzoazolyl compounds: The derivatives as described in EP-669,323 and U.S. Pat. No. 2,463,264. Para-aminobenzoic acid compounds: PABA (p-aminobenzoic acid), ethyl PABA, Ethyl dihydroxypropyl PABA, pentyl dimethyl PABA, ethylhexyl dimethyl PABA, marketed in particular under the trademark "Escalol 507" by ISP, glyceryl PABA, and PEG-25 PABA, marketed under the trademark "Uvinul P25" by BASF. Methylene bis-(hydroxyphenylbenzotriazol) compounds, such as 2,2'-methylenebis[6-(2H-benzotriazol-2-yl)-4-methyl-phenol] marketed in the solid form under the trademark "Mixxim BB/200" by Fairmount Chemical, 2,2'-methylenebis[6-(2H-benzotriazol-2-yl)-4-(1, 3,3-tetramethylbutyl)phenol] marketed in the micronized form in aqueous dispersion under the trademark "Tinosorb M" by BASF, or under the trademark "Mixxim BB/1 00" by Fairmount Chemical, and the derivatives as described in U.S. Pat. Nos. 5,237,071 and 5,166,355, GB-2,303,549, DE-1 97,261,84, and EP-893,1 19, and Drometrizole trasiloxane, marketed under the trademark "Silatrizole" by Rhodia Chimie or- "Mexoryl XL" by L'Oreal. Benzoxazole compounds: 2,4-bis[5-l(dimethylpropyl)benzoxazol-2-yl-(4-phenyl)imino]- 6-(2-ethylhexyl)imino-l,3,5-triazine, marketed under the trademark of Uvasorb K2A by Sigma 3V. Screening polymers and screening silicones: The silicones described in WO 93/04665. Dimers derived from a-alkylstyrene: The dimers
described in DE-1 9855649. 4,4-Diarylbutadiene compounds: l,l-dicarboxy(2,2'-dimethylpropyl)-4,4-diphenylbutadiene.

It is in some embodiments desirable that the organic UV filter(s) be selected from the group consisting of: butyl methoxydibenzoylmethane, ethylhexyl methoxycinnamate, homosalate, ethylhexyl salicylate, octocrylene, phenylbenzimidazole sulfonic acid, benzophenone-3, benzophenone-4, benzophenone-5, n-hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate, l,r-(l,4-piperazinediyl)bis[l-[2-(4-diethylamino)-2-hydroxybenzoyl]phenyl]-methanone 4-methylbenzylidene camphor, terephthalylidene dicamphor sulfonic acid, disodium phenyl dibenzimidazole tetrasulfonate, ethylhexyl triazine, bis-ethylhexyloxyphenol methoxyphenyl triazine, diethylhexyl butamido triazone, 2,4,6-tris(dineopentyl 4'-aminobenzalmalonate)-s-triazine, 2,4,6-tris(diisobutyl 4'-aminobenzalmalonate)-s-triazine, 2,4-bis-(n-butyl 4'-aminobenzalmalonate)-6- [(3 - { 1,3,3 -3 -tetramethyl- 1 - [(trimethylsilyloxy) - disiloxanyl]propyl}amino)-s-triazine, 2,4,6-tris-(di-phenyl)-triazine, 2,4,6-tris(ter-phenyl)-triazine, methylene bis-benzotriazolyl tetramethylbutylphenol, drometrizole trisiloxane, polysilicone-15, dineopentyl 4'-methoxybenzalmalonate, l,l-dicarboxy(2,2'-dimethylpropyl)-4,4-diphenylbutadiene, 2,4-bis[5-(dimethylpropyl)benzoxazol-2-yl-(4-phenylimino)-6-(2-ethylhexylimino)-l,3,5-triazine, camphor benzylkonium methosulfate, and mixtures thereof.

**SUPPLEMENTAL SPF BOOSTERS**

The composition, according to the present invention, comprises at least one SPF booster. If two or more SPF boosters are used, they may be the same or different.

The term "SPF booster" means a compound or composition that, when used in a formulation in conjunction with a UV screening agent, increases the SPF value of the formulation without increasing the amount of the UV screening agent in the formulation. It is desirable that the SPF booster be in the form of a particle, and in some embodiments a spherical particle. It is furthermore in some embodiments desirable that the SPF booster be selected from hollow particles, in particular hollow latex particles.

In one embodiment, the supplemental SPF boosters include hollow latex particles. The hollow latex particles suitable for use with the invention have a particle size which ranges generally from 100 to 380 nm, and in some embodiments from 150 to 375 nm, and in some embodiments from 190 to 350 nm, and more
particularly from 251 to 325 nm, the particle size being a volume-average particle size measured by a Brookhaven BI-90 photon correlation spectrometer.

For a given particle size, the hollow latex particles, according to the invention, must, in general, possess a maximum hollow fraction. The hollow latex particles in some embodiments contain a void fraction of 0.1 % to 50% and in some embodiments of 5% to 50%. The void fractions are determined by comparing the volume occupied by the latex particles after having been compacted from a diluted dispersion in a centrifuge, relative to the volume of non-void particles in the same composition.

Hollow latex particles, according to the invention, may be obtained from particles comprising at least one polymer for the core and at least one polymer for the shell. The core polymer and the shell polymer may be obtained from a single polymerization step or from a sequence of polymerization steps.

Typically, the hollow latex particles are provided as part of an aqueous dispersion that is generally stabilized with at least one emulsifier.

The hollow latex particles, according to the invention, may be prepared by the conventional techniques of emulsion polymerization. Such processes are described especially in patents U.S. 4,427,836, U.S. 4,469,825, U.S. 4,594,363, U.S. 4,677,003, U.S. 4,920,160, and U.S. 4,970,241 or by the conventional techniques of polymerization that are described in the following patents and patent applications: EP267726, EP331421, U.S. 490,229, and U.S. 5,157,084. The monomers used for the shell of the latex particles are and, in some embodiments, constituted of one or more unsaturated nonionic ethylenic units. Optionally one or more monoethylenically unsaturated monomers containing at least one carboxylic acid group may be polymerized in the shell. The monomers constituting the shell are selected such that they exhibit a glass transition temperature (Tg) which is sufficiently high to withstand the void of the hollow latex particle. And in some embodiments the glass transition temperature is greater than 50°C, and in some embodiments greater than 60°C, and in some embodiments still greater than 70°C. This temperature Tg may be determined by DSC (differential scanning calorimetry).

The monomers used in the emulsion polymerization in the core polymer of the latex particles of the invention are and in some embodiments constituted of one or more monoethylenically unsaturated monomers containing at least one carboxylic acid group. And in some embodiments the core comprises at least 5% by
weight of monoethylenically unsaturated monomers containing at least one carboxylic acid group, relative to the total weight of the core monomers.

The core polymer may, for example, be obtained by emulsion homopolymerization of the monoethylenically unsaturated monomer containing at least one acid group or by copolymerization of two or three monoethylenically unsaturated monomers containing at least one acid group. And, in some embodiments, the monoethylenically unsaturated monomer containing at least one acid group is copolymerized with one or more ethylenically unsaturated nonionic monomers.

The core polymer or the shell polymer may, for example, be obtained by emulsion homopolymerization of the monoethylenically unsaturated monomer containing at least one acid group or by copolymerization of two or three monoethylenically unsaturated monomers containing at least one acid group. And, in some embodiments, the monoethylenically unsaturated monomer containing at least one acid group is copolymerized with one or more ethylenically unsaturated nonionic monomers.

The core polymer or the shell polymer may contain from 0.1 % to 20% by weight, and, in some embodiments, from 0.1 % to 3% by weight, of polyethylenically unsaturated monomers, such as ethylene glycol di(meth)acrylate, allyl (meth)acrylate, 1 ,3-butanediol di(meth)acrylate, diethylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, or divinylbenzene, relative to the total weight of the core monomers. Alternatively, the core polymer or the shell polymer may optionally contain from 0.1 % to 60% by weight of butadiene, relative to the total weight of the core monomers.

The monoethylenically unsaturated monomers containing at least one carboxylic acid group include, for example: acrylic acid, methacrylic acid, acryloyloxypropionic acid, (meth)acryloyloxypropionic acid, itaconic acid, aconitic acid, maleic acid or maleic anhydride, fumaric acid, crotonic acid, monomethyl maleate, monomethyl fumarate, and monomethyl itaconate.

In an embodiment, the monomer is selected from acrylic acid and methacrylic acid. The monoethylenically unsaturated nonionic monomers include, for example: styrene, vinyl toluene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile, (meth)acrylamide, C1-C20 alkyl esters of (meth)acrylic acid, and C3-C20 alkenyl esters of (meth)acrylic acid, such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, benzyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, and stearyl (meth)acrylate. According to the invention, the term "(meth)acrylic" will denote the general expression encompassing both methacrylic or acrylic. The term "(meth)acrylate" will denote the general expression encompassing both methacrylate or acrylate.
The void part of the core of the latex particles is, in some embodiments, produced by swelling the core with a swelling agent comprising one or more volatile compounds. The agent penetrates the shell in order to swell the core. The volatile components of the swelling agent may be subsequently removed by drying the latex particles, thus creating a void within the particles. The agent is, in some embodiments, an aqueous base. Mention may be made, for example, of ammonia, ammonium hydroxide, alkali metal hydroxides, such as sodium hydroxide, and volatile amines, such as trimethylamine or triethylamine.

The hollow latex particles may be introduced into the composition of the invention with the swelling agent. In that case, the volatile compounds are removed when the composition is dried. The hollow latex particles may also be added to the composition after the volatile compounds of the swelling agent have been removed.

The hollow latex particles which can be used, according to the invention, are those described in patent U.S. 5,663,213 and patent application EP1 092421.

According to one particular embodiment of the invention, the hollow latex particles used will be those constituted of a copolymer of styrene and (meth)acrylic acid or one of its alkyl esters under the INCI name Styrene/Acrylates Copolymer, such as the product sold under the tradename Sunspheres™ Powder by the company Rohm & Haas, which is an aqueous dispersion containing 86% of Styrene/Acrylates Copolymer in a mixture of 11% of PEG-8 Laurate, 2.5% of water, and 0.5% of Sodium Dodecylbenzenesulfonate.

Another example of the SPF booster, which is typically capable of reflecting UV light, is glass microspheres. Typically, the glass microspheres used in the compositions of the invention are essentially homogeneous and essentially uniform in sphericity and have a mean particle size of between about 5 μm and 70 μm, such as from about 10 μm to 20 μm. Glass microspheres useful in the present invention include hollow microspheres of calcium aluminum borosilicate (commercially available from Presperse Inc. under the tradename LUXSIL®), sodium borosilicate particulates (commercially available from PQ Corporation under the tradename Q-CEL 570), and calcium/sodium borosilicate hollow microspheres (commercially available from 3M under the tradenames ES 22 and IK), calcium/sodium borosilicate microspheres (commercially available from 3M's under the tradename Scotchlite™ K20 product). Another example of the SPF booster is
porous silica in the form of microparticles, in particular, spherical microparticles. The spherical microparticles of porous silica, in accordance with the invention and in some embodiments, have a mean particle size ranging from 0.5 to 20 µm and more particularly from 3 to 15 µm. They, in some embodiments, have a specific surface ranging from 50 to 1,000 m²/g and more particularly from 150 to 800 m²/g.

They, in some embodiments, 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-1500 from Ikeda Corporation, and Sylosphere from Fuji Silysia.

It is, in some embodiments, desirable that the SPF booster be made from at least one material selected from the group consisting of (co)polymers of (meth)acrylic acid, (meth)acrylates, and/or styrene; glass; silica; and mixtures thereof. As the (co)polymers of (meth)acrylic acid, (meth)acrylates, and/or styrene, mention may be made of poly(meth)acrylates, such as PMMA, a copolymer of (meth)acrylic acid and (meth)acrylates, and a copolymer of (meth)acrylic acid, (meth)acrylates, and styrene.

The composition, according to the present invention, may comprise the SPF booster in an amount of from 0.1 to 10% by weight, and in some embodiments from 0.3 to 8% by weight, and, in some embodiments, from 0.5 to 5% by weight in relation to the total weight of the composition. In the composition of the present invention, the SPF booster may be employed in an amount equal to, or smaller than, the amount of the (a) UV filter present in the composition.

Typically, the ratio of the (c) SPF booster to the (a) UV filter is in the range of from about 0.5:1 to about 1:20, such as from about 0.1:1 to about 1:5.

**AQUEOUS PHASE**

The composition, according to the present invention, may include at least one aqueous phase.

The aqueous phase present in the cosmetic composition may include glycerin, water, and other aqueous phase ingredients. The aqueous phase of the cosmetic composition is at a concentration, by weight, of about 20% to about 85%, or alternatively about 25% to about 80%, or alternatively about 30% to about 75% based upon weight of the cosmetic composition.
HYDRATING AGENT

The aqueous phase present in the cosmetic composition, according to the disclosure, may include a hydrating agent at a concentration, by weight, of about 1% to about 50%, or alternatively about 5% to about 40%, or alternatively about 10% to about 30% based upon weight of the composition.

Suitable examples of the hydrating agent, include polyols, for example, glycerol, glycols, such as butylene glycol, propylene glycol, isoprene glycol, dipropylene glycol, hexylene glycol and polyethylene glycols, sorbitol, sugars, such as glucose, and mixtures thereof. According to one desirable embodiment of the invention, the polyol chosen is glycerol, dipropylene glycol or mixtures thereof, or a mixture of glycerol and/or of dipropylene glycol and of one or more other polyols especially chosen from those indicated above: butylene glycol, propylene glycol, isoprene glycol, hexylene glycol, polyethylene glycols, sorbitol, sugars, methylpropanediol and 1,3-propanediol and mixtures thereof. A particularly suitable polyol for use with the present invention is glycerin.

In one embodiment, glycerin is incorporated in the cosmetic composition at levels greater than 5% or alternatively, greater than 10%, by weight, of the cosmetic composition.

WATER

The aqueous phase present in the cosmetic composition, according to the disclosure, may include water at a concentration, by weight, of about 30% to about 85%, or alternatively about 35% to about 80% or alternatively about 40% to about 70%, based upon weight of the composition. The water used may be sterile demineralized water and/or a floral water, such as rose water, cornflower water, chamomile water or lime water, and/or a natural thermal or mineral water, such as, for example: water from Vittel, water from the Vichy basin, water from Uriage, water from La Roche Posay, water from La Bourboule, water from Enghien-les-Bains, water from Saint Gervais-les-Bains, water from Neris-les-Bains, water from Allevar-les-Bains, water from Digne, water from Maizieres, water from Neyrac-les-Bains, water from Lons-le-Saunier, water from Eaux Bonnes, water from Rochefort, water from Saint Christau, water from Les Fumades, water from Tercis-les-Bains or water from Avene. The water phase may also comprise reconstituted thermal water, that is to say a water comprising trace element, such as zinc, copper, magnesium, etc., reconstituting the characteristics of a thermal water.
PRESERVATIVE SYSTEM

The aqueous phase present in the cosmetic composition, according to the disclosure, may include a preservative system at a concentration, by weight of about 0.1% to about 3%, or alternatively about 0.5% to about 2.5% or alternatively about 1% to about 2.0%, based upon weight of the composition. In a desirable embodiment, the preservative system may include organic acids, parabens, formaldehyde donors, phenol derivatives, quaternary ammoniums, alcohols, isothiazolones, and combinations thereof.

Examples of organic acid preservative systems include, but are not limited to, sodium benzoate, potassium sorbate, benzoic acid and dehydroacetic acid, sorbic acid, and combinations thereof. A desirable organic acid preservative system may include a mixture of sodium benzoate and potassium sorbate.

Examples of paraben preservative systems include, but are not limited to, alkyl para-hydroxybenzoates, wherein the alkyl radical has from 1, 2, 3, 4, 5 or 6 carbon atoms and, in some embodiments, from 1 to 4 carbon atoms e.g., methyl para-hydroxybenzoate (methylparaben), ethyl para-hydroxybenzoate (ethylparaben), propyl para-hydroxybenzoate (propylparaben), butyl para-hydroxybenzoate (butylparaben) and isobutyl para-hydroxybenzoate (isobutylparaben).

Examples of formaldehyde donor preservative systems include, but are not limited to, 1,3-Dimethylol-5,5-dimethylhydantoin (DMDM hydantoin), imidazolidinyl urea, gluteraldehyde, and combinations thereof.

Examples of quaternary ammonium preservative systems include, but are not limited to, benzalkonium chloride, methene ammonium chloride, benzethonium chloride, and combinations thereof.

Examples of alcohol preservative systems include, but are not limited to, ethanol, benzyl alcohol, dichlorobenzyl alcohol, phenoxyethanol, and combinations thereof.

Examples of isothiazolone preservative systems include, but are not limited to, methylchloroisothiazolinone, methylisothiazolinone, and combinations thereof.

Other suitable preservatives for preservative systems include, but are not limited to, chloracetamide, triclosan and iodopropynyl butylcarbamate, pyridine derivatives (e.g., pyrithione and zinc pyrithione), chlorphenesin, phenyl mercuric salts, phenoxyethanol, and other known preservative systems.
OIL PHASE

The oil phase present in the cosmetic composition, according to the disclosure, may include a silicone polymer, an emulsifying crosslinked siloxane elastomer, a hydrophobic silica, and a co-emulsifier.

SILICONE POLYMER

The oil phase present in the cosmetic composition, according to the disclosure, may include silicone polymer at a concentration, by weight, of about 1% to about 40%, or alternatively about 5% to about 35%, or alternatively about 10% to about 30%, based upon weight of the composition. Suitable examples of silicone polymers include, but are not limited to, polydimethylsiloxane (dimethicone), a mixture of dimethicone and dimethiconol, decamethylcyclopentasiloxane (D5), cyclomethicone (mixture of D4, D5 and D6), and combinations thereof.

EMULSIFYING CROSSLINKED SILOXANE ELASTOMERS

The oil phase present in the cosmetic composition, according to the disclosure, may include an emulsifying crosslinked siloxane elastomer at a concentration, by weight, of about 3% to about 20%, or alternatively about 4% to about 15%, or alternatively about 5% to about 10%, based upon weight of the composition. Examples of suitable emulsifying crosslinked siloxane elastomers, include, but are not limited to, substituted or unsubstituted dimethicone/copolyol crosspolymer, dimethicone and dimethicone/PEG-1 0/1 5 crosspolymers, substituted or unsubstituted dimethicone/polyglycerol crosspolymer, dimethicone and dimethicone/polyglycerol-3 crosspolymer. Such suitable emulsifying crosslinked siloxane elastomers are sold or made, for example, under the names of "KSG-21 0" a polyether-modified cross polymer with an INCI name of dimethicone (and) dimethicon/PEG-1 0/1 5 crosspolymer, and "KSG-71 0" a polyglycerin-modified cross polymer with and INCI name of dimethicone (and) dimethicone/polyglycerol-3 crosspolymer, both available from ShinEtsu Silicones of America, Inc. (Akron, OH).

EMULSIFIER

When present, an emulsifier may be selected from self-emulsifying polyether silicone elastomers, polyglyceryl silicone elastomers, polyether dimethicone copolymers, and mixtures thereof. The self-emulsifying silicone elastomers may include functional groups selected from the group consisting of polyglyceryl, polyethylene glycol, or polypropylene glycol. Suitable examples of commercially available self-emulsifying silicone elastomer water-in-oil emulsifiers, include, but are
not limited to, dimethicone (and) dimethicone/PEG-1 0/1 5 crosspolymer, sold under
the tradename KSG-21 0, and dimethicone (and) dimethicone/polyglycerin-3 crosspolymer, sold under the tradename of KSG-71 0, both available from Shin-Etsu. Examples of emulsifiers may also include, but are not limited to, PEG-1 0 dimethicone sold under the tradename KF-601 7 from ShinEtsu, dimethicone (and) PEG/PPG-18/1 8 dimethicone sold under the tradename ES-5226 DM from Dow Corning Corporation, PEG-9 polydimethylsiloxoethyl dimethicone (and) PEG-9 available under the tradename KF-6028, and lauryl PEG-9 polydimethylsiloxoethyl dimethicone available under the tradename KF-6038, both available from ShinEtsu. In certain particular embodiments, the emulsifier may be selected from stearic acid, glyceryl stearate, and PEG-1 0 0 stearate.

The emulsifier is advantageously present at a concentration of about 0.1 % to about 20%, or alternatively about 0.5% to about 10%, or alternatively about 1% to about 5% by weight, based upon the weight of the composition.

HYDROPHOBIC SILICA

An oil phase when present in the cosmetic composition, according to the disclosure, may include a hydrophobic silica at a concentration, by weight, of about 0.1 % to about 5%, or alternatively about 0.5% to about 4% or alternatively about 0.6% to about 2%, based upon weight of the composition. If the hydrophobic silica concentration exceeds 5% by weight of the cosmetic composition, then the cosmetic composition becomes gritty, which is undesirable to users.

As used herein, hydrophobic silica may include hydrophobic fumed silica, hydrophobic precipitation-process silica, hydrophobic aerogels of silica. After substitution with alkyl groups, hydrophobic silica products are classified according to the different substitution groups into silylated silica, dimethyl-silylated silica, trimethyl-silylated silica and polydimethylsiloxane-silylated silica.

Suitable examples of hydrophobic fumed silica, include, but are not limited to, the commercial products AEROSIL® R202, AEROSIL® R972, AEROSIL® R805, AEROSIL® R8200, AEROSIL® R974, AEROSIL® R81 2S and AEROSIL® R81 2 available from Evonik Degussa GmbH through the subsidiary North America Evonik Degussa Corporation (Piscataway, New Jersey).

CO-EMULSIFIER

The oil phase present in the cosmetic composition, according to the disclosure, may include a co-emulsifier at a concentration, by weight, of about 0.01 %
to about 1%, or alternatively about 0.05% to about 0.9%, or alternatively about 0.1% to about 0.8%, based upon weight of the composition. If the co-emulsifier concentration exceeds 1%, by weight, of the cosmetic composition, then the cosmetic composition may still form an emulsion, but the desirable transformative effect of cream changing to droplets upon rubbing is lost.

Suitable examples of co-emulsifiers include polyether substituted linear or branched polysiloxane copolymers. One desirable co-emulsifier is PEG-10 dimethicone available under the tradename of ES-5612 from Dow Corning Corporation (Midland, Michigan), or KF-6017 from ShinEtsu (Akron, Ohio). Another desirable co-emulsifier is dimethicone (and) PEG/PPG-18/18 dimethicone available under the tradename of ES-5226 DM from Dow Corning Corporation (Midland, Michigan) Other suitable co-emulsifiers include, PEG-9 polydimethylsiloxylslyethyldimethicone available under the tradename KF-6028 and PEG-9, lauryl PEG-9 polydimethylsiloxylslyethyldimethicone available under the tradename KF-6038, both available from ShinEtsu (Akron, Ohio). In certain embodiments, the co-emulsifier is potassium cetyl phosphate.

**OPTIONAL INGREDIENTS**

The compositions, in accordance with the present invention, may also comprise one or more standard cosmetic adjuvants chosen from oils, waxes, organic solvents, fillers, ionic or nonionic, hydrophilic or lipophilic thickeners, softeners, humectants, opacifiers, stabilizers, emollients, silicones, antifoams, fragrances, preserving agents, surfactants, active agents, coloring agents, cationic polymers, propellants, neutralizing or pH-adjusting agents (e.g., citric acid, triethylamine (TEA) and sodium hydroxide), conditioning or softening agents (e.g., panthenol and allantoin), extracts, such as botanical extracts, free-radical scavengers, keratolytic agents, vitamins (e.g., Vitamin E and derivatives thereof), anti-elastase and anti-collagenase agents, peptides, fatty acid derivatives, steroids, trace elements, extracts of algae and of planktons, enzymes and coenzymes, flavonoids and ceramides, hydroxy acids and mixtures thereof, and enhancing agents. These ingredients may be soluble or dispersible in whatever phase or phases is/are present in the cosmetic composition (i.e., aqueous and/or fatty (oil) phase) or any other ingredient usually used in cosmetics and/or dermatology. Additives and adjuvants may be present in the compositions in amounts generally ranging from about 0.01% to about 10% by weight.
Needless to say, a person skilled in the art will take care to select the optional adjuvant(s) added to the composition, according to the invention, such that the advantageous properties intrinsically associated with the composition, in accordance with the invention, are not, or are not substantially, adversely affected by the envisaged addition.

Needless to say, those skilled in the art will take care to select the optional additional compound(s) mentioned above and/or the amounts thereof such that the advantageous properties intrinsically associated with the compositions, in accordance with the invention, are not, or are not substantially, adversely affected by the envisaged addition(s). Those skilled in the art will choose said active agent(s) according to the desired effect on the skin, hair, eyelashes, eyebrows, or nails.

The following examples are intended to further illustrate the present invention. They are not intended to limit the invention in any way. Unless otherwise indicated, all parts are by weight.

**EXAMPLES**

The comparative and inventive sunscreen compositions were prepared according to the following method incorporating the components as listed in Table 1, and the SPF compared:

1) Weigh RMs from Phase A1, Start heating under Rayneri turbine; 2) When the temperature is around 80°C, turn off the heater and when is around 70°C add Phases A3 and A4; 3) Weigh RMs from B1, B2 and B3 together in another vessel; 4) When Phase A is around 65°C, pour Phase B very slowly while turning up to 1500rpm; 5) Stop the heating and let emulsionate for 10 minutes; 6) Slowly add Phase C while starting the cooling; 7) When the temperature is under 40°C, add MPs from Phase D one by one; 8) Add Phase E; 9) Add RMs from Phase F; 10) When the temperature is under 30°C, add RMs from Phase G, Stir for 15 more minutes.

The SPF was determined using the in vitro method described by B. L. DIFFEY et al., in J. Soc. Cosmet. Chem. 40 127-1 33 (1989); this method consists in determining the monochromatic protection factors in a range of wavelengths from 290 nm to 400 nm and in calculating from them the sun protection factor according to a given mathematical equation. The measurement was carried out with a step of 1 nm on a UV-1000S apparatus from the company Labsphere, 2 mg/cm² of product being spread on the Transpore® strip.
There is a gain of 328.66% in SPF of Comparative Example 1 in relation with Example 1, as can be seen in the table below.

**TABLE 2**

<table>
<thead>
<tr>
<th>PHASE</th>
<th>INGREDIENT</th>
<th>EX. 1</th>
<th>COMP. EX. 1</th>
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<tbody>
<tr>
<td>A1</td>
<td>GLYCERYL STEARATE (AND) PEG-100 STEARATE</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>A1</td>
<td>STEARIC ACID</td>
<td>1.5</td>
<td>1.5</td>
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<td>A1</td>
<td>POTASSIUM CETYL PHOSPHATE</td>
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</tr>
<tr>
<td>A1</td>
<td>BUTYL METHOXYDIBENZOYL METHANE</td>
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<td>5</td>
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<tr>
<td>A1</td>
<td>ETHYLHEXYL SALICYLATE</td>
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<td>5</td>
</tr>
<tr>
<td>A1</td>
<td>ETHYLHEXYL TRIAZONE</td>
<td>1.5</td>
<td>1.5</td>
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<tr>
<td>A1</td>
<td>OCTOCRYLENE</td>
<td>5</td>
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<td>HOMOSALATE</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>A1</td>
<td>CAPRYLGLYCOL</td>
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<td>0.5</td>
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<tr>
<td>A1</td>
<td>SYNTHETIC WAX</td>
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<td>1</td>
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<tr>
<td>A3</td>
<td>TITANIUM DIOXIDE (AND) ALUMINUM HYDROXIDE (AND) STEARIC ACID</td>
<td>2.5</td>
<td>2.5</td>
</tr>
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<td>A4</td>
<td>PHENOXYETHANOL</td>
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<td>A4</td>
<td>TRIETHANOLAMINE</td>
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<td>TOCOPHEROL</td>
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<tr>
<td>B1</td>
<td>WATER</td>
<td>17.5</td>
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<td>GLYCERIN</td>
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<tr>
<td>B2</td>
<td>DISODIUM EDTA</td>
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<td>TRIETHANOLAMINE</td>
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<td>TEREPTHALYLIDENE DICAMPHOR SULFONIC ACID</td>
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<tr>
<td>C</td>
<td>WATER</td>
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<td>E</td>
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<tr>
<td>F</td>
<td>ZEA MAYS (CORN) STARCH</td>
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<td>FRAGRANCE</td>
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<tr>
<td>G</td>
<td>ALCOHOL</td>
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<tr>
<td>G</td>
<td>SILICA SILYATE</td>
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<tr>
<td></td>
<td>TOTAL</td>
<td>100</td>
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There is a gain of 328.66% in SPF of Comparative Example 1 in relation with Example 1, as can be seen in the table below.
<table>
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<th>COMPOSITION</th>
<th>COMP EX. 1</th>
<th>EX. 1</th>
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<td>AVERAGE SPF</td>
<td>23.06</td>
<td>98.85</td>
<td>328.66%</td>
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The data shows that the sunscreen composition containing a silica aerogel SPF booster together with a UV Filter exhibited a significant and unexpected improvement in UV-absorption and SPF compared to an equivalent composition without silica aerogel booster.

While the invention has been described with reference to a desirable embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.
SET OF CLAIMS

1. A cosmetic composition for protecting keratinous substrates against UV radiation, the composition in the form of an oil in water emulsion and comprising, in a cosmetically acceptable aqueous carrier:

   (a) at least one UV filter; and

   (b) at least one SPF booster compound comprising a first silica aerogel, the silica aerogel comprising particles, the silica aerogel present in an amount in the range from 0.1 % to 5% by weight of the composition,

   wherein the composition exhibits an SPF that that represents a gain in protection of about 330% greater than a SPF exhibited by an identical composition lacking the aerogel.

2. The composition of claim 1, the silica aerogel particles having surface area per unit of mass (SM) ranging from about 500 to about 1500 m$^2$/g, and a size expressed as the mean volume diameter (D[0.5]), ranging from about 1 to about 30 µm.

3. The composition of claim 1, the silica aerogel particles comprising in amounts not greater than 5% weight of the composition.

4. The composition of claim 1, the silica aerogel selected from VM-2260 (INCI name: Silica silylate), VM-2270 (INCI name: Silica silylate), Aerogel TLD 201 , Aerogel OGD 201 and Aerogel TLD 203, Enova Aerogel MT 1100 and Enova Aerogel MT 1200, and combinations of these.

5. The composition of claim 1, the at least one UV filter photoprotective composition comprising one or more inorganic, organic, and combinations of inorganic and organic UV filters.

6. The composition of claim 4, comprising one or more UV filters selected titanium dioxide, zinc oxide, iron oxide, an anthranilate UV-screening agent; a cinnamic UV-screening agent; a dibenzoylmethane UV-screening agent; a salicylic UV-screening agent, a camphor UV-screening agent; a triazine UV-screening agent; a benzotriazole UV-screening agent; a benzimidazole UV-screening agent; an imidazoline UV-screening agent; a p-aminobenzoic acid (PABA) UV-screening agent; a methylenebis(hydroxyphenylbenzotriazole) UV-screening agent; a benzoazole UV-screening agent; a polymer UV-screening agent, a silicone UV-screening agent; an a-alkylstylene dimer UV-screening agent; a 4,4-diarylbutadiene UV-screening agent; ethylhexyl salicylate, ethylhexyl methoxycinnamate,
octocrylene, phenylbenzimidazole sulphonic acid, benzophenone-3, benzophenone-4, benzophenone-5, n-hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate, 4-methylbenzylidene camphor, terephthalylidene dicamphor sulphonic, disodium phenyl dibenzimidazole tetra-sulphonate, 2,4,6-tris (diisobutyl 4'-aminobenzaldehyde)-s-triazine, anisotriazine, ethylhexyl triazone, diethylhexyl butamido triazone, methylene bis-benzotriazolyl tetramethylbutylphenol, drometrizole trisiloxane, polysilicone-1,1-dicarboxy (2,2'-dimethyl-propyl)-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 and combinations thereof.

7. The composition of claim 1, the at least one UV filter comprising from 0.1% to 30%, by weight, of said composition.

8. The composition of claim 1, further comprising at least one cosmetic additive or adjuvant selected from water-soluble or water-miscible solvents or co-solvents, dispersion enhancing agents, hydrating agents, emulsifiers, moisturizers, colorants, fillers, antioxidants (e.g., EDTA, BHT, tocopherol), essential oils, fragrances, dyes, neutralizing or pH-adjusting agents (e.g., citric acid, triethanolamine (TEA) and sodium hydroxide), conditioning or softening agents (e.g., panthenol and allantoin) and extracts, such as botanical extracts, free-radical scavengers, keratolytic agents, vitamins (e.g., Vitamin E and derivatives thereof), anti-elastase and anti-collagenase agents, peptides, fatty acid derivatives, steroids, trace elements, extracts of algae and of planktons, enzymes and coenzymes, flavonoids and ceramides, hydroxy acids and mixtures thereof, and enhancing agents and mixtures and combinations of these, and present in amounts generally ranging from about 0.01% to about 10%, by weight.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/25 A61Q17/04
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
A61K A61Q

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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| X         | FR 2 986 423 Al (OREAL [FR])
9 August 2013 (2013-08-09)
page 20, line 11 - page 21, line 37
page 22, lines 30-48
page 36, lines 17-18
page 40, lines 10-15; examples 1-5 | 1-8 |
| X         | Wo 2014/203913 Al (OREAL [FR]; TAKANUKI MAYUMI [JP]; SUDA MARI [JP])
24 December 2014 (2014-12-24)
page 19, lines 35-41; claims 1-9; table 1 | 1-8 |
| A         | Wo 2013/068236 Al (OREAL [FR]; FAGEOIN LAURE [FR]; LEMAL MATHILDE [FR])
16 May 2013 (2013-05-16)
claims 1-9, 13-15 | 1-8 |

Further documents are listed in the continuation of Box C. See patent family annex.

* 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

Date of the actual completion of the international search
7 July 2016
Date of mailing of the international search report
25/07/2016

Name and mailing address of the ISA:
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Tel.: (+31-70) 340-2040,
Fax: (+31-70) 340-2016

Authorized officer
Uhl, Martin
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