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(54) Title: PARTICLES CONTAINING ULTRAVIOLET ABSORBER

(57) Abstract: Provided are skin care compositions comprising (A) a particle comprising (i) a UV absorber having a λ_{max} in a range from 280 to 400 nm, and (ii) a copolymer comprising polymerized units derived from (a) 40 to 90 weight % of water-insoluble monoethylenically unsaturated monomers, (b) 10 to 60 weight % of water-soluble monoethylenically unsaturated monomers, and (c) 0.1 to less than 10 weight % of cross-linkers, and (B) a dermatologically acceptable carrier, wherein the weight ratio of ultraviolet absorber to copolymer is more than 1:2. Also provided are methods of protecting skin from UV damage comprising topically administering such compositions to the skin.

PARTICLES CONTAINING ULTRAVIOLET ABSORBER

FIELD OF THE INVENTION

This invention relates generally to particles that are useful in skin care formulations. The particles contain an ultraviolet absorbing compound and a copolymer bearing water soluble monoethylenically unsaturated compounds, water insoluble monoethylenically unsaturated compounds, and cross-linkers.

BACKGROUND

Skin care compositions contain a variety of additives that provide a wide array of benefits to the composition. Sunscreen compositions in particular contain additives that offer protection from ultraviolet ("UV") radiation, which can damage the skin. UV radiation can be classified as UVA (long wave; i.e., wavelengths of 315-400 nm) and UVB (short wave; i.e., wavelengths of 280 to 315 nm). The efficacy of sunscreen formulations is measured by its sun protection factor ("SPF"). Since both UVA and UVB forms of radiation are harmful, sunscreen formulations offer protection from both kinds of rays. One type of organic UVA absorbing compound known in the art is avobenzone (butyl methoxydibenzoylmethane). Avobenzone and other organic sunscreen actives, however, are hydrophobic and crystalline, and have been associated with poor aesthetic properties (e.g., poor sensorial feel) and undesirable staining of clothes due to their ability to chelate metal ions available in wash water during laundry cycles.

To this end, encapsulation of organic sunscreen actives has been utilized in the art. For example, U.S. Patent Application Publication No. US 2009//0311336 discloses core-shell particles including a core contains a UV absorbing compound and a shell comprised of a

polymer containing 10 to 100 weight % of multiethylenically unsaturated monomers and 0 to 90 weight % of monoethylenically unsaturated monomers. The prior art does not, however, disclose a skin care composition according to the present invention which enables increased delivery of hydrophobic crystalline organic sunscreen actives, such as avobenzone.

Accordingly, there is a need to develop new skin care compositions including organic UV absorbing compounds that enable increased loading of such compounds in formulation, while also providing improved aesthetics and reduced staining.

STATEMENT OF INVENTION

One aspect of the invention provides a skin care composition comprising (A) a particle comprising (i) a UV absorber having a λ_{max} in a range from 280 to 400 nm, and (ii) a copolymer comprising polymerized units derived from (a) 40 to 90 weight % of water-insoluble monoethylenically unsaturated monomers, (b) 10 to 60 weight % of water-soluble monoethylenically unsaturated monomers, and (c) 0.1 to less than 10 weight % of cross-linkers, and (B) a dermatologically acceptable carrier, wherein the weight ratio of ultraviolet absorber to copolymer is more than 1:2.

In another aspect, the invention provides a method for protecting skin from UV damage comprising topically administering to the skin a sunscreen composition comprising (A) a particle comprising (i) a UV absorber having a λ_{max} in a range from 280 to 400 nm, and (ii) a copolymer comprising polymerized units derived from (a) 40 to 90 weight % of water-insoluble monoethylenically unsaturated monomers, (b) 10 to 60 weight % of water-soluble monoethylenically unsaturated monomers, and (c) 0.1 to less than 10 weight % of cross-linkers,

and (B) a dermatologically acceptable carrier, and wherein the weight ratio of ultraviolet absorber to copolymer is more than 1:2.

DETAILED DESCRIPTION

The inventors have now surprisingly found that copolymers comprising polymerized units derived from water-insoluble monoethylenically unsaturated monomers and water-soluble monoethylenically unsaturated monomers allow for increased loading of organic ultraviolet absorbers in skin care compositions. Accordingly, the present invention provides in one aspect a skin care composition including a particle containing a UV absorber having a λ_{max} in a range from 280 to 400 nm, and a copolymer comprising polymerized units derived from (a) 40 to 90 weight % of water-insoluble monoethylenically unsaturated monomers, (b) 10 to 60 weight % of water-soluble monoethylenically unsaturated monomers, and (c) 0.1 to less than 10 weight % of cross-linkers, wherein the weight ratio of ultraviolet absorber to copolymer is more than 1:2, and a dermatologically acceptable carrier

In the present invention, "skin care compositions" is intended to refer to compositions for leave on application to the skin, such as lotions, creams, gels, gel creams, serums, toners, wipes, liquid foundations, make-ups, tinted moisturizer, oils, face/body sprays, topical medicines, and sunscreen compositions. "Sunscreen compositions" refers to compositions that protect the skin from UV damage. Preferably, the skin care composition is cosmetically acceptable. "Cosmetically acceptable" refers to ingredients typically used in personal care compositions, and is intended to underscore that materials that are toxic when present in the amounts typically found in personal care compositions are not contemplated as part of the present invention. The compositions of the invention may be manufactured by processes well known in the art, for

example, by means of conventional mixing, dissolving, granulating, emulsifying, encapsulating, entrapping or lyophilizing processes.

As used herein, the term "polymer" refers to a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term "polymer" includes the terms "homopolymer," "copolymer," and "terpolymer." As used herein, the term "polymerized units derived from" refers to polymer molecules that are synthesized according to polymerization techniques wherein a product polymer contains "polymerized units derived from" the constituent monomers which are the starting materials for the polymerization reactions. As used herein, the term "(meth)acrylate" refers to either acrylate or methacrylate, and the term "(meth)acrylic" refers to either acrylic or methacrylic.

The inventive skin care compositions include particles containing copolymers comprising polymerized units derived from water-insoluble monoethylenically unsaturated momomers. In certain embodiments, the particles comprise copolymers in an amount of at least 10 weight %, preferably at least 25 weight %, and more preferably at least 50 weight %, by weight of the particle. In certain embodiments, the particles comprise copolymers in an amount of no more than 75 weight %, preferably no more than 68 weight %, and more preferably no more than 60 weight %, by weight of the particle. In certain embodiments, the weight ratio of UV absorber to copolymer is more than 1:2. In certain embodiments, the weight ratio of the UV absorber to copolymer is less than 1:1.

As used herein, the term "water-insoluble monoethylenically unsaturated monomers" refers to monoethylenically unsaturated monomers which have a water solubility of less than 5%, preferably less than 0.5%, and more preferably less than 0.1% by weight at the polymerization temperature. The polymerization temperature may be varied from about zero to the boiling point

of the reaction mixture. Suitable water-insoluble monoethylenically unsaturated monomers include, for example, styrene, substituted styrene, e.g., chlorostyrene, methylstyrene (e.g., α-methylstyrene), and ethyl styrene), non-polar C_1-C_{40} alkyl (meth)acrylates (e.g., methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-octyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, tetradecyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, and stearyl (meth)acrylate)), (meth)acrylonitrile, other (meth)acrylates (e.g., isobornyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, 2-bromoethyl (meth)acrylate, 2-phenylethyl (meth)acrylate, and 1-naphthyl (meth)acrylate)), vinyl acetate, and vinyl neodecanoate. Preferably, the water-insoluble monoethylenically unsaturated monomers comprise at least one of styrene, methyl methacrylate, and stearyl methacrylate. In certain embodiments, the inventive copolymers comprise polymerized units of water-insoluble monoethylenically unsaturated monomers in an amount of at least 40 weight %, preferably at least 50 weight %, and more preferably at least 55 weight %, by weight of the copolymer. In certain embodiments, the inventive copolymer comprise polymerized units of water-insoluble monoethylenically unsaturated monomers in an amount of no more than 90 weight %, preferably no more than 75 weight %, and more preferably no more than 60 weight %, by weight of the copolymer.

As used herein, there term "water-soluble monoethylenically unsaturated monomers" refers to monoethylenically unsaturated monomers which have a water solubility of at least 5%, preferably at least 7%, and more preferably at least 9% by weight at the polymerization temperature. The polymerization temperature may be varied from about zero to the boiling point of the reaction mixture. Suitable water-soluble monoethylenically unsaturated monomers

include, for example, polar carboxylic acid containing monomers, e.g., (meth)acrylic acids, crotonic acid, itaconic acid, fumaric acid, maleic acid, and their C_1-C_{22} alkyl poly(ethylene glycol) esters (e.g., monomers of structure $H_2C=C(R)CO_2(CH_2CH_2O)_n(CH(R')CH_2O)_mR''$), 2-hydroxyethyl methacrylate (HEMA), 2-hydroxyethyl acrylate (HEA), 2-hydroxypropyl methacrylate (HPMA), and 2-hydroxypropyl acrylate (HPA)), sulfo- and phospho- methacrylates (e.g., sulfoethyl methacrylate, sulfopropyl methacrylate, 2-acrylamido-2-methylpropane sulfonic acid, and phosphoethyl methacrylate), (meth)acrylamides (e.g., acrylamide, methacrylamide, dimethylacrylamide, and dimethylaminopropyl (meth)acrylamide)), maleic anhydride, and sodium styrene sulfonate. Preferably, the water-soluble monoethylenically unsaturated monomers comprise at least one of acrylic acid, methacrylic acid, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, acrylamide, methacrylamide, dimethylacrylamide, sulfoethyl methacrylate, sulfopropyl methacrylate, and phosphoethyl methacrylate. In certain embodiments, the inventive copolymers comprise polymerized units of water-soluble monoethylenically unsaturated monomers in an amount of at least 10 weight %, preferably at least 25 weight %, and more preferably at least 45 weight %, by weight of the copolymer. In certain embodiments, the inventive copolymer comprise polymerized units of water-soluble monoethylenically unsaturated monomers in an amount of no more than 60 weight %, preferably no more than 55 weight %, and more preferably no more than 50 weight %, by weight of the copolymer.

The copolymers of the invention also include a crosslinker, such as a monomer having two or more non-conjugated ethylenically unsaturated groups, i.e., a multiethylenically unsaturated monomer, or ionic cross-linkers. Suitable multiethylenically unsaturated monomers include, for example, di- or tri-allyl ethers and di- or tri-(meth)acrylyl esters of diols or polyols

(e.g., trimethylolpropane diallyl ether, trimethylolpropane triacrylate, ethylene glycol dimethacrylate), di- or tri-allyl esters of di- or tri-acids, (e.g. diallyl phthalate), allyl (meth)acrylate, divinyl sulfone, triallyl phosphate, and divinylaromatics (e.g., divinylbenzene). Suitable ionic cross-linkers include, for example, calcium acetate, zinc acetate, and zinc oxide. In certain embodiments, the inventive copolymers comprise polymerized units of crosslinker monomers in an amount of less than 10 weight %, preferably less than 7 weight %, and more preferably no more than 5 weight %. In certain embodiments, the inventive copolymer comprise polymerized units of crosslinker monomers in an amount of at least 0.1 weight %, preferably at least 1 weight %, and more preferably at least 3 weight %.

Polymer molecular weights can be measured by standard methods such as, for example, size exclusion chromatography or intrinsic viscosity. In certain embodiments, the copolymer particles of the present invention have a weight average molecular weight (M_w) of 1,000,000 or less, preferably 500,000 or less, more preferably 350,000 or less, and even more preferably 190,000 or less, as measured by gel permeation chromatography. In certain embodiments, the copolymer particles have a M_w of 50,000 or more, preferably 100,000 or more, and more preferably 180,000 or more, as measured by gel permeation chromatography.

The inventive particles contain at least one UV absorbers having a λ_{max} in a range of from 280 to 400 nm. In certain embodiments, the particles contain at least one UV-A absorber, i.e., a UV absorber having a λ_{max} in a range of from 315 to 400 nm. In certain embodiments, the particles contain at least one UV-B absorber, i.e., a UV absorber having a λ_{max} in a range of from 280 to 315 nm. In certain embodiments, the particles contain at least UV-A absorber and at least one UV-B absorber. Preferably, the UV absorbers have an extinction coefficient at λ_{max} of at least 3,000 L/cm-mol, more preferably at least 4,000 L/cm-mol, and even more preferably at

least 5,000 L/cm-mol. Preferably, the UV absorbers are organic compounds, i.e., those containing carbon and having at most trace levels of metals, and in certain preferred embodiments are aromatic compounds. Suitable UV absorbers include, for example, aminobenzoic acid, avobenzone, cinoxate, dioxybenzone, homosalate, menthyl anthranilate, octocrylene, octyl methoxycinnamate, octyl salicylate, oxybenzone, Padimate O, phenylbenzimidazole sulfonic acid, sulisobenzone, and trolamine salicylate. In certain embodiments, the UV absorber comprises avobenzone. In certain embodiments, the UV absorber comprises homosalate (3,3,5-trimethylcyclohexyl salicylate). In certain embodiments, the particles in the inventive skin care compositions comprise UV absorbers in an amount of at least 25 weight %, preferably at least 30 weight %, and more preferably at least 35 weight %, by weight of the particle. In certain embodiments, the particles comprise copolymers in an amount of no more than 90 weight %, preferably no more than 75 weight %, and more preferably no more than 50 weight %, by weight of the particle.

Visible dyes having a λ_{max} in the visible range, i.e., above 400 nm, are not considered UV absorbers for purposes of this invention. In some embodiments, the particle is substantially free of any visible dyes. As used herein, the term "substantially free of any visible dyes" refers to particles containing less than 1 weight %, preferably less than 0.5 weight %, more preferably less than 0.2 weight %, and even more preferably less than 0.1 weight % visible dyes by weight of the particle.

The diameters of the particles of the inventive skin care compositions may be characterized by light scattering measurements on a multimodal emulsion. In certain embodiments, the particles have an average diameter at least 20 nm, preferably at least 125 nm, and more preferably at least 250 nm. In certain embodiments, the particles have an average

diameter of no more than 5,000 nm, preferably no more than 2,500 nm, and more preferably no more than 700 nm. In certain embodiments, the particles included in the inventive skin care compositions are of an occluded morphology.

In certain embodiments, the inventive skin care composition includes the particles described herein in an amount of at least 0.001 weight %, at least 0.1 weight %, or at least 1 weight %, by weight of the composition. In certain embodiments, the inventive skin care compositions comprise the particles described herein in an amount of no more than 20 weight %, no more than 15 weight %, or no more than 7.5 weight %, by weight of the composition.

Suitable polymerization techniques for preparing the particles contained in the inventive skin care compositions include, for example, miniemulsion polymerization, as described, e.g., in G.H. Al-Ghamdi et al., *J. Appl. Poly. Sci.*, vol. 101, pp. 3479-3486 (2006), or Landfester, K., *Macromol. Rapid. Commun.*, vol. 22, pp. 896-936 (2001), and references cited therein, using an ultrasonic or high-pressure homogenizer, preferably with sufficient power to create 200 nm droplets. Aqueous emulsion polymerization processes typically are conducted in an aqueous reaction mixture, which contains at least one monomer and various synthesis adjuvants, such as the free radical sources, buffers, and reductants in an aqueous reaction medium. In certain embodiments, a chain transfer agent may be used to limit molecular weight. The aqueous reaction medium is the continuous fluid phase of the aqueous reaction mixture. Surfactants suitable for conventional emulsion polymerization are also suitable for miniemulsion polymerization. In certain embodiments, the polymerization is performed at temperatures in the range of from 20 to 100°C. In certain embodiments, the solids content of the polymerization mixture is in a range of from 20 to 60 weight %, preferably from 20 to 60 weight %, more preferably from 25 to 55 weight %, and even more preferably from 30 to 50 weight %. In certain

embodiments, the aqueous reaction medium has a pH of less than or equal to 5, and preferably having a pH of less than or equal to 5.

The inventive skin care compositions also include a dermatologically acceptable carrier. Such material is typically characterized as a carrier or a diluent that does not cause significant irritation to the skin and does not negate the activity and properties of active agent(s) in the composition. Examples of dermatologically acceptable carriers that are useful in the invention include, without limitation, water, such as deionized or distilled water, emulsions, such as oil-in-water or water-in-oil emulsions, alcohols, such as ethanol, isopropanol or the like, glycols, such as propylene glycol, glycerin or the like, creams, aqueous solutions, oils, ointments, pastes, gels, lotions, milks, foams, suspensions, powders, or mixtures thereof. The aqueous solutions may contain cosolvents, e.g., water miscible cosolvents. Suitable water miscible cosolvents include, for example, methanol, ethanol, propanol, acetone, ethylene glycol ethyl ethers, propylene glycol propyl ethers, and diacetone alcohol. In some embodiments, the composition contains from about 99.99 to about 50 percent by weight of the dermatologically acceptable carrier, based on the total weight of the composition. The pH of the skin care composition may be in the range of 5 to 8.

The inventive skin care compositions may also include particulate scatterers. Suitable particulate scatterers include, for example, SUNSPHERES Polymer (available from The Dow Chemical Company), solid UV absorbers (e.g., bemotrizinol and bisoctrizole), and inorganic metal oxides. Suitable inorganic metal oxides include, for example, zinc oxide (ZnO) and titanium dioxide (TiO_2). In certain embodiments, the inorganic metal oxide particles are pigment grade ZnO or pigment grade TiO_2. In certain embodiments, the inorganic metal oxide particles are transparent ZnO or transparent TiO_2. Most inorganic metal oxides used in sunscreen

formulations produce a cosmetically undesirable white appearance caused by light scattering. Thus, as used herein, the term "transparent" inorganic metal oxide sunscreen particle refers to inorganic metal oxide particles produced by a variety of processing conditions which render compositions containing such particles as clear, or more transparent than pigment grade, upon application. Suitable ZnO particles include, for example, those commercially available under the trade names Z-COTE from BASF Corporation, ZINCLEAR IM from Antaria Limited, and Z-CLEAR from Actifirm. Suitable TiO_2 particles include, for example, those commercially available under the trade names TIPAQUE and TTO-51(A) from Ishiharra Sangyo Kaisha, Ltd., T-COTE from BASF Corporation, UFTR (from Miyoshi Kasei), and SOLAVEIL CLARUS from Uniquema. In certain embodiments, the skin care compositions include inorganic metal oxide particles in an amount of at least 0.1 weight %, and no more than 5 weight %, by weight of the composition.

The skin care compositions of the invention may also include other ingredients known in the art of sunscreen formulations including, for example, a thickener, emollients, an emulsifier, a humectant, a surfactant, a suspending agent, a film forming agent, a lower monoalcoholic polyol, a high boiling point solvent, a propellant, a mineral oil, silicon feel modifiers, or mixtures thereof. The amount of optional ingredients effective for achieving the desired property provided by such ingredients can be readily determined by one skilled in the art.

Other additives may be included in the compositions of the invention such as, but not limited to, abrasives, absorbents, aesthetic components such as fragrances, pigments, colorings/colorants, essential oils, skin sensates, astringents (e.g., clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate), preservatives, anti-caking agents, a foam building agent, antifoaming agents, antimicrobial agents (e.g., iodopropyl

butylcarbamate), antioxidants, binders, biological additives, buffering agents, bulking agents, chelating agents, chemical additives, colorants, cosmetic astringents, cosmetic biocides, denaturants, drug astringents, external analgesics, film formers or materials, e.g., polymers, for aiding the film-forming properties and substantivity of the composition (e.g., copolymer of eicosene and vinyl pyrrolidone), opacifying agents, pH adjusters, propellants, reducing agents, sequestrants, skin bleaching and lightening agents (e.g., hydroquinone, kojic acid, ascorbic acid, magnesium ascorbyl phosphate, ascorbyl glucosamine), skin-conditioning agents (e.g., humectants, including miscellaneous and occlusive), skin soothing and/or healing agents (e.g., panthenol and derivatives (e.g., ethyl panthenol), aloe vera, pantothenic acid and its derivatives, allantoin, bisabolol, and dipotassium glycyrrhizinate), skin treating agents, and vitamins (e.g., Vitamin C) and derivatives thereof. The amount of option ingredients effective for achieving the desired property provided by such ingredients can be readily determined by one skilled in the art.

As noted above, skin care compositions of the present invention are highly effective as SPF and UV absorption boosters. Accordingly, the skin care compositions of the present invention are useful for the treatment and protection of skin, including, for example, protection from UV damage. Thus, in one aspect the present invention provides that the skin care compositions may be used in a method for protecting skin from UV damage comprising topically administering to the skin a composition comprising topically administering to the skin the inventive skin care compositions described herein, namely, a skin care composition comprising (A) a particle comprising (i) a UV absorber having a λ_{max} in a range from 280 to 400 nm, and (ii) a copolymer comprising polymerized units derived from (a) 25 to 75 weight % of water-insoluble monoethylenically unsaturated monomers, and (b) 2 to 75 weight % of water-soluble

monoethylenically unsaturated monomers, and (B) a dermatologically acceptable carrier, and wherein the weight ratio of ultraviolet absorber to copolymer is less than 1:1.

In practicing the methods of the invention, the skin care compositions are generally administered topically by applying or spreading the compositions onto the skin. A person of ordinary skill in the art can readily determine the frequency with which the compositions should be applied. The frequency may depend, for example, on the level of exposure to UV light that an individual is likely to encounter in a given day and/or the sensitivity of the individual to UV light. By way of non-limiting example, administration on a frequency of at least once per day may be desirable.

Some embodiments of the invention will now be described in detail in the following Examples.

EXAMPLES

Example 1

Preparation of Exemplary and Comparative Particles Including Avobenzone and Copolymer

Exemplary particles in accordance with the present invention and comparative particles contain the components recited in Table 1.

Table 1. Exemplary and Comparative Copolymer Particles

Sample	Monomer (wt % in total solid)	Avobenzone (wt % in total solid)	Stability
P1	60% (50 STY / 45 MAA / 5 ALMA)	40%	Stable
P2	60% (50 STY / 45 MAA / 5 DVB)	40%	Stable
P3	60% (55 STY / 45 MAA // 3 calcium acetate)	40%	Stable

P4	50% (50 STY / 45 MAA / 5 ALMA)	50%	Stable
P5	50% (45 STY / 50 MAA / 5 ALMA)	50%	Stable
P6	60% (50 STY / 45 AA / 5 ALMA)	40%	Stable
PA*	60% (45 STY / 45 MAA / 10 ALMA)	40%	Unstable

STY = styrene
MAA = methacrylic acid
ALMA = allyl methacrylate
DVB = divinylbenzene
AA = acrylic acid
*Comparative

For particle P1, 6.45 grams of Aerosol A-102 surfactant (31% active) and 91 grams of DI water were added to a 500 mL round bottom flask equipped with a y-tube and condenser, thermocouple, and y-tube with attached bump trap. In a separate container 40 grams of Avobenzone is dissolved in 30 grams of styrene, 27 grams of methacrylic acid, and 3 grams of allyl methacrylate at 35°C and then added to the 500 mL round bottom flask and sonicated for 2 minutes with the Misonix brand lab sonicator at 100% power setting. The contents of the reactor are then stirred at 400 rpm with a lab mixer. The resulting sonicated emulsion is then heated to 90°C with a heating mantle and then 1.8 grams of sodium persulfate dissolved in 6 grams of water is added to the contents of the flask with stirring along with 2.0 grams of anhydrous sodium acetate dissolved in 8 grams of water. The batch is held at 2 minutes at 85°C until the exotherm begins at which point the heating mantle is removed from the flask. Five minutes after the reaction peak temperature of 98°C the batch is air cooled to room temperature. Stability was evaluated by monitoring the samples for formation of gelation at room temperature.

Particles P2-P5 and PA were prepared substantially as described above, with the appropriate changes in monomer amounts as recited in Table 1.

Example 2

Particle Size Analysis of Exemplary Particles

Particle sizes of P1 and P3 samples as prepared in Example 1 above were measured using static light scattering by a Hydro2000 Mastersizer (Malvern Inc.). Sample aliquots of 25 mL were prepared by diluting the emulsions with deionized water 20 to 50 times of the emulsion volume. The aliquots were then added dropwise into the mixer chamber on the Mastersizer where the samples became further diluted and homogenized. Three sequential measurements were taken on each sample. The particle size distribution profile with trimodal peaks was obtained with diameters corresponding to the 10^{th}, 50^{th}, and 90^{th} percentile, as shown in Table 2.

Table 2. Particle Size Distribution

Sample	D(0.1)	D(0.5)	D(0.9)
P1	62 nm	165 nm	972 nm
P3	65 nm	265 nm	666 nm

The particle exhibited a broad poly-modal particle size ranging from 20 nm to 1000 nm.

Example 3

Determination of Fraction of Amorphous Avobenzone in Exemplary Particles

Pure avobenzone is a crystalline solid at room temperature, but becomes an amorphous solid when incorporated into the particles of the inventive skin care compositions. The fraction of amorphous avobenzone in P1 and P3 samples as prepared in Example 1 above was determined. The sample was dried under vacuum at room temperature. Once dried, 7.6 mg of the sample was hermetically sealed in an aluminum Tzero pan. The sample was used for a modulated differential scanning calorimetry (mDSC) measurement using a TA Instruments

D2000 DSC equipped with a liquid nitrogen cooling system, where the heat flow between the sample and the environment immediately surrounding the sample was recorded. When a crystalline solid melts during the temperature range, the melting temperature (T_m, in unit of °C) and the specific heat of fusion (ΔH_m, in unit of J/g) were recorded. The ratio between ΔH_m (avobenzone) and ΔH_m (particle) yields the percentage of crystalline avobenzone in the exemplary sample, as shown in Table 3.

Table 3. Melting Temperature and Heat of Fusion UV Absorber and Inventive Particle

Sample	**T_m (°C)**	**ΔH_m (J/g)**
Avobenzone	84	77.2
P1	79	0.82
P3	70	0.22

Using this information, the percentage of amorphous (non-crystalline) avobenzone in the total avobenzone in P1 and P3 can be calculated by the following equation:

$$\%_{amor} = (1 - (\Delta H_{m(avobenzone)} / \Delta H_{m(P1)}) \times 100\%$$

Accordingly, the samples were determined to contain 99% and 100% amorphous (non-crystalline) avobenzone in samples P1 and P3, respectively.

Example 4

UV Absorber Leakage Study

Encapsulation stability against leakage of UV absorber avobenzone from exemplary samples was measured. Leakage of avobenzone from each sample was measured via the cyclodextrin (CD) extraction method: 100-400 mg of each sample and 5 mL of DI water (for extraction test at pH 6) or 0.5M pH 8 EGTA buffer solution (for extraction test at pH 8) were

added into a 25 mL vial and mixed with a rotator for 30 minutes. 5 mL of cyclodextrin solution (50% by weight, Cavasol W7M TL, available from Wacker Chemical) was added into the mixture and mixed with a rotator for 16 hours. The mixed sample was centrifuged at 100,000 rpm at 25°C for 15 minutes, and the upper clear phase was removed for HPLC analysis (avobenzone detection set at 360 nm). The percentage of leaked avobenzone was calculated as the ratio of detected avobenzone levels verses the total theoretical avobenzone level.

The results of the heat-aging leakage study were conducted by placing the samples into a force convection oven at 50°C are shown in Table 4.

Table 4. Leakage of Avobenzone Under Heat-Aging Conditions (at pH 6)

Sample	0 Days	14 Days
P1	8.1%	16.1%
P3	9.9%	14.3%

The results of pH dependent extraction at a pH of 6 and 8 are shown in table 5.

Table 5. Leakage of Avobenzone Under pH Extraction

Sample	CD Extraction at pH 6	CD Extraction at pH 8
P1	8.1%	16.1%
P3	9.1%	14.3%

The results indicate that exemplary particles prepared in accordance with the present invention demonstrate an ability to hold avobenzone under various stress conditions.

Example 5

Preparation of Skin Care Formulations

Exemplary and comparative skin care formulations contain the components recited in Table 6.

Table 6. Sunscreen Formulations

	Trade Name	INCI Name	C1 (wt%)	C2 (wt%)	E1 (wt%)	E2 (wt%)	E3 (wt%)	E4 (wt%)
A	DI water	--	75.22	73.57	62.59	59.04	62.59	59.04
A	ACULYN 33[1]	Acrylates copolymer	3.33	6.23	3.33	6.23	3.33	6.23
A	Glycerin (99%)	Glycerin	1.00	1.00	1.00	1.00	1.00	1.00
A	Versenen 220[1]	Tetrasodium EDTA	0.10	0.10	0.10	0.10	0.10	0.10
A	P1 (19.2% avobenzone in emulsion)	--	0	0	15.63	15.63	0	0
A	P3 (19.2% avobenzone in emulsion)	--	0	0	0	0	15.63	15.63
A	Triethanolamine (99%)	Triethanolamine	0.85	1.10	0.85	3.00	0.85	3.00
B	Parsol 1789[2] (avobenzone)	Butyl Methoxydibenzoylmethane	3	3	0	0	0	0
B	HallBrite HS USP[3]	Homosalate	2.25	2.25	2.25	2.25	2.25	2.25
B	Uvinul N 539 T[4]	Octocrylene	2.25	2.25	2.25	2.25	2.25	2.25
B	Dermol 25L[5]	C12-15 Alkyl Lactate	2.00	2.00	2.00	2.00	2.00	2.00
B	GANEX V-220[6]	VP/Eicosene Copolymer	1.50	0	1.50	0	1.50	0

B	Dow Corning 345 Fluid[7]	Cyclopentasiloxane and Cyclohexasiloxane	2.00	2.00	2.00	2.00	2.00	2.00
B	Rita TN[8]	C12-15 Alkyl Benzoate	5.00	5.00	5.00	5.00	5.00	5.00
B	Stearic Acid	Stearic Acid	1.50	1.50	1.50	1.50	1.50	1.50
	Total		100	100	100	100	100	100

[1] Available from the DOW Chemical Company
[2] Available from DSM Nutritional Products Ltd.
[3] Available from HallStar
[4] Available from BASF Corporation
[5] Available from Alzo International
[6] Available from Ashland Inc.
[7] Available from Dow Corning
[8] Available from Rita Corporation

The sunscreen formulations were prepared by mixing all components in Table 6. The aqueous phase (Phase A) and oil phase (Phase B) were separately mixed with an overhead mixer (Eurostar 60) while heating each to 75°C. The two phases were then mixed and cooled with stirring to form an emulsion.

Example 6

Anti-Staining Study of Exemplary Skin Care Formulation

The anti-staining properties of formulations as prepared in Example 5 were measured according to the following protocol. Cotton fabric (Testfabrics, Inc. #493) was cut into cloths (8 cm x 11 cm). 0.3 g of skin care formulations were "painted" onto the cotton cloth using a Plexiglas template with a 5 cm diameter opening and a china bristle brush (#10). The cloths were allowed to air dry at room temperature overnight. The dry stained cloths were laundered in a six pot Terg-o-meter (United States Testing Co.) in warm tap water at 35°C for 12 min with 1 g/L detergent (Arm & Hammer, Clean Burst) with 3 min cold tap water rinsing. After the

rinsing, the cloths were left for drying at room temperature for 48 hours. The Yellowness Index (b*) was measured by spectrocolorimeter (Colorgard System 1000) for remaining stain.

The change in Yellowness Index was calculated based on the following equation:

$$\Delta b^* = b^* - b^*_{Control\text{-}0}$$

The percent increase in anti-staining performance based on the Yellowness Index was calculated based on the following equation:

$$\%\Delta b^* = ((\Delta b^*_{Control\text{-}a} - \Delta b^*_{E1}) / B^*_{Control\text{-}a}) \times 100\%$$

where the variables are as shown in Table 7.

Table 7. Anti-Staining Performance of Exemplary Skin Care Formulation

Sample	b*	Δb*	%Δb*
Control-0 (clean cloth)	2.82	--	--
Control-a (free avobenzone)	7.40	4.58	--
E1	7.09	4.27	6.88%
E3	6.14	3.32	27.51%

The results of the anti-staining measurements demonstrate that exemplary skin care formulations prepared in accordance with the present invention provide anti-staining properties as compared with free UV absorber.

Example 7

SPF Boost Study

The SPF value of exemplary formulations as prepared in Example 5 were measured using an *in vitro* technique substantially according to the following protocol in compliance with the COLIPA 2007 method:

Initially, the weight of a roughened PMMA substrate (purchased from SCHÖNBERG GmbH & Co. KG, Hamburg / Germany,) is measured. The batch to be tested is then deposited on the substrate and then quickly leveled with a 7 micron draw down bar to achieve a thin, uniform layer. The layer is allowed to dry for about 20 minutes, and the weight of the substrate plus dry uniform layer is determined. The UV absorption of dry uniform layer is measured using a LABSPHERE UV-2000S spectrometer at multiple points on the layer.

The percent solids of the layer is measured using an OHAUS MB45 solids analyzer. Using the weight of the dry film, and the solids content of the layer, the weight, and consequently the density of the original wet layer immediately after deposition can be calculated. Using this information, the SPF can be calculated by the following equation:

$$SPF = \frac{\int_{290nm}^{400nm} E(\lambda)S(\lambda)\partial\lambda}{\int_{290nm}^{400nm} E(\lambda)S(\lambda)10^{(-A(\lambda))}\partial\lambda}$$

Where $E(\lambda)$ = spectral irradiance of the Standard Sun Spectrum; $S(\lambda)$ = erythemal action spectrum at wavelength λ; and $A(\lambda)$ = corrected spectral absorbance at wavelength λ (a correction factor is calculated to extrapolate the data to establish what the absorbance would be at a wet layer density of 2.0 mg/cm^2 (using the original wet layer immediately after deposition).

The results of the SPF measurements are shown in Table 8 as percent SPF improvement from a composition with no particles having an SPF of 9 and formulated to pH 7.5.

Table 8. SPF Performance of Exemplary Skin Care Formulations

Sample	SPF Boost (%)
C2	100
E2	348

E4	386

The results demonstrate that exemplary skin care formulations prepared in accordance with the present invention provide a SPF boost value significantly higher than comparative formulations.

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WHAT IS CLAIMED IS:

1. A skin care composition comprising:

(A) a particle comprising

(i) a UV absorber having a λ_{max} in a range from 280 to 400 nm, and

(ii) a copolymer comprising polymerized units derived from (a) 40 to 90 weight % of water-insoluble monoethylenically unsaturated monomers, (b) 10 to 60 weight % of water-soluble monoethylenically unsaturated monomers, and (c) 0.1 to less than 10 weight % of cross-linkers; and

(B) a dermatologically acceptable carrier,

wherein the weight ratio of UV absorber to copolymer is more than 1:2.

2. The skin care composition of claim 1, wherein the UV absorber is present in the particle in an amount of from 25 to 90 weight %, and the copolymer is present in the particle in an amount of from 10 to 75 weight %.

3. The skin care composition of claim 1, wherein the polymer comprises polymerized units derived from (a) 40 to 75 weight % of water-insoluble monoethylenically unsaturated monomers, (b) 25 to 60 weight % of water-soluble monoethylenically unsaturated monomers, and (c) 0.1 to 5 weight % of cross-linkers.

4. The skin care composition of claim 1, wherein the water-insoluble monoethylenically unsaturated monomers comprise at least one of styrene, substituted styrene, and non-polar C_1-C_{40} alkyl (meth)acrylates.

5. The skin care composition of claim 1, wherein the water-soluble monoethylenically unsaturated monomers comprise at least one of acrylic acid, methacrylic acid, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, acrylamide, methacrylamide, dimethylacrylamide, sulfoethyl methacrylate, sulfopropyl methacrylate, and phosphoethyl methacrylate.

6. The skin care composition of claim1, wherein the cross-linkers comprise at least one of allyl methacrylate, allyl acrylate, trimethylolpropane trimethacrylate, trimethylolpropane diallyl ether, and divinylbenzene.

7. The skin care composition of claim 1, wherein the UV absorber has a λ_{max} in a range from 315 to 400 nm, and wherein the particle further comprises a second ultraviolet absorbing compound having a λ_{max} in a range from 280 to 315 nm.

8. The skin care composition of claim 1, wherein the UV absorber comprises avobenzone.

9. The skin care composition of claim 1, wherein the particle is of an occluded morphology and has an average diameter in a range of from 20 nm to 5,000 nm.

10. A method of protecting skin from UV damage comprising topically administering to the skin a sunscreen composition comprising:

(A) a particle comprising

(i) a UV absorber having a λ_{max} in a range from 280 to 400 nm, and

(ii) a copolymer comprising polymerized units derived from (a) 40 to 90 weight % of water-insoluble monoethylenically unsaturated monomers, (b) 10 to 60 weight % of water-soluble monoethylenically unsaturated monomers, and (c) 0.1 to less than 10 weight % of cross-linkers; and

(B) a dermatologically acceptable carrier,

wherein the weight ratio of UV absorber to copolymer is more than 1:2.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/038883

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61Q17/04 A61K8/04 A61K8/02 A61K8/35 A61K8/81
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)
A61Q A61K

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, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 051 963 A1 (HOFFMANN LA ROCHE [CH]) 15 November 2000 (2000-11-15)	1-10
Y	claims page 1, paragraph 6 pages 9-10; examples	1-10

X	US 2010/284950 A1 (MUELLER STEFAN [DE] ET AL) 11 November 2010 (2010-11-11)	1,2,4,5, 7,9,10
Y	claims page 6, paragraph 46 page 6, paragraph 65-66 page 14; compound 104 page 15; example A6 UV Mix 4; page 16, paragraph 215	1-10

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 August 2016	12/08/2016

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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PCT/US2016/038883

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