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AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, **L'OREAL**, of **14, rue Royale, F-75008 Paris, France**, being the applicant in respect of Application No. **48224/93** state the following:-

The person nominated for the grant of the patent has entitlement from the actual inventors by virtue of their employment with the applicant at the time of the invention.

The person nominated for the grant of the patent is the applicant of the application listed in the declaration under Article 8 of the PCT.

The basic application listed in the declaration made under Article 8 of the PCT is the first application made in a Convention country in respect of the invention.

L'OREAL

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.....
Ian A. Scott
Registered Patent Attorney

14 February 1997
.....
(Date)

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(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 678382

(54) Title
PHOTOSTABLE FILTERING COSMETIC COMPOSITION CONTAINING A UV-A FILTER AND A FILTERING POLYMER OF THE BENZOTRIAZOLE SILICONE TYPE

(51)[5] International Patent Classification(s)
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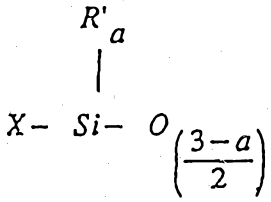
(56) Prior Art Documents
FR 2440993
EP 0392883

(57) Claim

1. Photostable filtering cosmetic composition for the protection of the skin and the hair against ultraviolet rays with wavelengths between 280 and 380 nm, characterized in that it includes, in a cosmetically acceptable vehicle containing at least one fatty phase, 0.5 to 4% by weight of 4-(tert-butyl)-4'-methoxydibenzoylmethane and 0.1 to 20%, preferably 0.5 to 15% by weight, of a filtering polymer of the benzotriazole silicone type containing at least one unit of formula:



(I)

in which

R' denotes a saturated or unsaturated C_1-C_{30} hydrocarbon group, a C_1-C_8 halogenated hydrocarbon group or a trimethylsilyloxy group;

a = 1 or 2;

X = - A - Y

.../2

where A represents an aliphatic or aromatic divalent hydrocarbon radical containing at least 2 carbon atoms and optionally containing one or more oxygen atoms;

Y represents a 2-(2'-hydroxyphenyl)benzotriazole residue optionally bearing, on one or both of the aromatic rings, one or more C_1-C_8 alkyl, C_2-C_8 alkenyl, halogen, alkoxy, carboxyl, hydroxyl or amino substituents, the weight ratio of the benzotriazole silicone to the 4-(tert-butyl)-4'-methoxydibenzoylmethane being between 1 and 10.

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(54) Title: PHOTOSTABLE FILTERING COSMETIC COMPOSITION CONTAINING A UV-A FILTER AND A FILTERING POLYMER OF THE BENZOTRIAZOLE SILICONE TYPE

(54) Titre: COMPOSITION COSMETIQUE FILTRANTE PHOTOSTABLE CONTENANT UN FILTRE UV-A ET UN POLYMERE FILTRE DU TYPE SILICONE BENZOTRIAZOLE

$$X\text{-}\overset{\overset{R'\ a}{|}}{Si}\text{-}O\ \frac{3-a}{2} \qquad (I)$$

(57) Abstract

A photostable, filtering cosmetic composition for protecting human epidermis and hair against UV rays comprises, in a cosmetically acceptable carrier having at least one fatty phase, 0.5 to 4 % by weight of 4-(tert.-butyl) 4'-methoxy dibenzoylmethane and 0.1 to 20 % by weight of a filtering polymer of the benzotriazole silicone type containing at least one unit of formula (I), where R' is a C_1-C_{30} hydrocarbon group, a C_1-C_8 halogenated hydrocarbon group or a trimethylsilyloxy group; a is 1 or 2; X = -A-Y where A is an aliphatic or aromatic bivalent hydrocarbon radical having at least 2 carbon atoms and optionally containing one or more oxygen atoms; Y is a 2-(2'-hydroxyphenyl)benzotriazole residue optionally containing one or more C_1-C_8 alkyl, C_2-C_8 alkenyl, halogen, alcoxy, carboxy, hydroxy or amino substituents, the weight ratio of the benzotriazole silicone to the 4-(tert.-butyl) 4'-methoxy dibenzoylmethane being between 1 and 10.

(57) Abrégé

L'invention concerne une composition cosmétique filtrante photostable pour la protection de l'épiderme humain et des cheveux contre les rayons UV comprenant dans un support cosmétiquement acceptable contenant au moins une phase grasse, 0,5 à 4 % en poids de 4-(tert.-butyl) 4'-méthoxy dibenzoylméthane et 0,1 à 20 % en poids d'un polymère filtre du type silicone benzotriazole comportant au moins une unité de formule (I) où R' est un groupe hydrocarboné en C_1-C_{30}, un groupe hydrocarboné halogéné en C_1-C_8 ou un groupe triméthylsilyloxy; a = 1 ou 2; X = -A-Y où A est un radical divalent hydrocarboné aliphatique ou aromatique comportant au moins 2 atomes de carbone et renfermant éventuellement un ou plusieurs atomes d'oxygène; Y est un reste 2-(2'-hydroxyphényl)benzotriazole portant éventuellement un ou plusieurs substituants alkyle en C_1-C_8, alcényle en C_2-C_8, halogène, alcoxy, carboxy, hydroxy ou amino, le rapport en poids de la silicone benzotriazole au 4-(tert.-butyl) 4'-méthoxy dibenzoylméthane étant compris entre 1 et 10.

Photostable filtering cosmetic composition containing a UV-A filter and a filtering polymer of the benzotriazole silicone type

The present invention relates to a photostable cosmetic composition intended to protect the skin and the hair from UV radiation, containing a UV-A filter and a filtering polymer of the benzotriazole silicone type, to its use for protection of the skin and the hair against UV rays and to a process for the stabilization of the UV-A filter by a benzotriazole silicone.

It is known that light radiation with wavelengths between 280 nm and 400 nm permit tanning of the human epidermis and that rays with wavelengths between 280 and 320 nm, which are known under the name UV-B, cause erythema and skin burns which may be harmful to the development of the tan; this UV-B radiation should thus be filtered out.

It is also known that UV-A rays, with wavelengths between 320 and 400 nm, which cause tanning of the skin, are liable to induce damage of the latter especially in the case of sensitive skin or skin which is continually exposed to solar radiation. UV-A rays in particular cause a loss in elasticity of the skin and the appearance of wrinkles, leading to premature ageing. They promote the triggering of the erythemal reaction or amplify this reaction in certain individuals and may even be the cause of phototoxic or photoallergic reactions. It is thus desirable also to filter out the UV-A radiation.

French Patent No. 2,440,933 describes 4-(tert-butyl)-4'-methoxydibenzoylmethane as a UV-A filter. It is proposed to combine this specific UV-A filter, sold under the name "PARSOL 1789" by the company Givaudan, with various UV-B filters for the purpose of absorbing all of the UV rays with wavelengths between 280 and 380 nm.

Unfortunately, when this UV-A filter is used alone or in combination with UV-B filters, it does not possess a photochemical stability which is satisfactory

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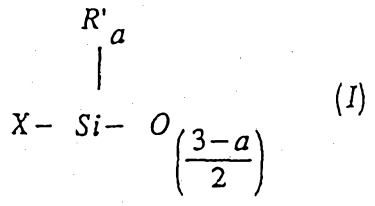
to guarantee constant protection of the skin during prolonged exposure to the sun, thereby necessitating repeated applications at close and regular intervals if it is desired to obtain effective protection of the skin against UV rays.

The Applicant has discovered that by combining, in defined proportions and in a defined weight ratio, 4-(tert-butyl)-4'-methoxydibenzoylmethane with a filtering polymer of the benzotriazole silicone type containing at least one unit of formula:



(I)

in which

R' denotes a saturated or unsaturated C_1-C_{30} hydrocarbon group, a C_1-C_8 halogenated hydrocarbon group or a trimethylsilyloxy group;

a = 1 or 2;

X = - A - Y

where A represents an aliphatic or aromatic divalent hydrocarbon radical containing at least 2 carbon atoms and optionally containing one or more oxygen atoms;

Y represents a 2-(2'-hydroxyphenyl)benzotriazole residue optionally bearing, on one or both of the aromatic rings, one or more C_1-C_8 alkyl, C_2-C_8 alkenyl, halogen, alkoxy, carboxyl, hydroxyl or amino substituents, satisfactory photochemical stability of the 4-(tert-butyl)-4'-methoxydibenzoylmethane was, surprisingly, obtained. A stabilized combination for protecting the human epidermis and hair against UV rays with wavelengths between 280 and 380 nm is thus available.

Furthermore, such a combination imparts to the filtering composition containing it, besides a good UV-A protection number and a good sun protection factor, enhanced cosmetic properties as regards the sticky effect on application and the final greasy appearance after penetration, as well as lasting properties in water, that is to say a good stability of the protection number over

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time, especially after showering or bathing.

The UV-A protection number and the sun protection factor (SPF) are determined using the in vitro method described by B.L. Diffey et al., in J.Soc. Cosmet. Chem. 40-127-133 (1989).

This method consists in determining the monochromatic protection factors every 5 nm over a wavelength range from 290 to 400 nm and in calculating, from these protection factors, the solar protection factor.

In addition to the units of formula (I), the filtering polymer may contain units of formula:

$$R'_b-Si-O_{\left(\frac{4-b}{2}\right)} \qquad (II)$$

in which R' has the same meaning as in formula (I);

b is an integer denoting 1, 2 or 3.

Hydrocarbon groups which may be mentioned are C_1-C_{30} alkyl radicals, C_2-C_{30} alkenyl radicals, cycloalkyl radicals or aromatic radicals such as phenyl or tolyl.

A halogenated hydrocarbon group which may be mentioned is the 3,3,3-trifluoropropyl radical.

In the filtering polymer consisting of moieties (I) and optionally (II), at least 40% in numerical terms of the radicals R' are methyl radicals. The total number of the units (I) and (II) is preferably less than or equal to 250 and is in particular between 2 and 50.

Such siloxane-chain filtering polymers are described in particular in European Patent Application Nos. 0,388,218 and 0,392,883.

On account of their lipophilic nature, the filters used are distributed uniformly in the conventional cosmetic vehicles containing at least one fatty phase or take the form of aqueous dispersions of lipid vesicles and may thus be applied to the skin in order to form an effective protective film.

The subject of the present invention is thus a photostable cosmetic composition which protects the skin

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or the hair against UV radiation with wavelengths between 280 and 380 nm and which comprises, in a cosmetically acceptable vehicle containing at least one fatty phase, 0.5 to 4% by weight of 4-(tert-butyl)-4'-methoxydibenzoylmethane and 0.1 to 20% by weight, preferably 0.5 to 15%, of benzotriazole silicone as defined above, the weight ratio of the benzotriazole silicone to the 4-(tert-butyl)-4'-methoxydibenzoylmethane being between 1 and 10.

The upper limit of this ratio is determined by the solubility of the filters in the fatty phase used in the composition or in the lipid phase present in the vesicle dispersion.

Another subject of the present invention is a cosmetic treatment process for the skin or the hair which is intended to protect them against the effects of UV rays with wavelengths between 280 and 380 nm, which consists in applying to the latter an effective amount of a cosmetic composition as defined above.

Another subject of the present invention consists of a process for the stabilization of 4-(tert-butyl)-4'-methoxydibenzoylmethane with regard to UV radiation using a benzotriazole silicone as defined above, in which process 0.1 to 20% by weight of benzotriazole silicone defined above is used in order to stabilize from 0.5 to 4% by weight of 4-(tert-butyl)-4'-methoxydibenzoylmethane, the weight ratio of the benzotriazole silicone to the 4-(tert-butyl)-4'-methoxydibenzoylmethane being between 1 and 10.

The cosmetic composition of the invention may be used as a composition for protecting the human epidermis or the hair against ultraviolet rays, as an antisun composition or as a make-up product.

This composition may in particular be in the form of a lotion, a thickened lotion, a gel, an oil, a vesicle dispersion, an emulsion such as a cream or milk, a powder or a solid stick, and may optionally be packaged as an aerosol and be in the form of a foam or spray.

It may contain the cosmetic adjuvants usually

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used such as fats, organic solvents, silicones, thickeners, softeners, anti-foaming agents, hydrating agents, fragrances, preserving agents, anionic, cationic, nonionic or amphoteric surfactants or mixtures thereof, fillers, sequestering agents, anionic, cationic, nonionic or amphoteric polymers or mixtures thereof, propellants, basifying or acidifying agents, dyes, metal oxide pigments of particle size between 100 nm and 20,000 nm such as iron oxides, or any other ingredient usually used in cosmetics.

The fats may consist of an oil or a wax or a mixture thereof, fatty acids, fatty acid esters, fatty alcohols, petrolatum, paraffin, lanolin, hydrogenated lanolin or acetylated lanolin.

The oils are chosen from animal, plant, mineral and synthetic oils and especially hydrogenated palm oil, hydrogenated castor oil, liquid petrolatum, paraffin oil, purcellin oil, silicone oils and isoparaffins.

The waxes are chosen from animal, fossil, plant, mineral and synthetic waxes. Bees waxes, carnauba wax, candelila wax, sugar cane wax, Japan wax, ozokerites, montan wax, microcrystalline waxes, paraffins, and silicone resins and waxes may be mentioned in particular.

The composition according to the invention may also contain metal oxide nanopigments dispersed in the fatty phase and/or in the aqueous phase.

It may also contain other lipophilic UV filters and especially UV-B filters.

The composition according to the invention may be in the form of a vesicle dispersion of amphiphilic ionic or nonionic lipids, which is prepared according to known processes. It is possible, for example, to swell the lipids in an aqueous solution in order to form spherules which are dispersed in the aqueous medium, as described in the article Bangham, Standish & Watkins, J. mol. Biol., 13, 238 (1965) or in Patents FR-2,315,991 and 2,416,008 from the Applicant. The description of the various modes of preparation will be found in "Les liposomes en biologie cellulaire et pharmacologie"

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[Liposomes in cellular biology and pharmacology], edition INSERM/John Libbery Eurotext, 1987, pages 6 to 18.

When the composition is in the form of an emulsion or a vesicle dispersion, the aqueous phase may contain water-soluble UV filters such as benzene-1,4-[di(3-methylidene-10-camphorsulfonic)] acid, 2-phenylbenzimidazole-5-sulfonic acid or 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, these acids being or not being salified.

In the case of a composition packaged as an aerosol, conventional propellants such as alkanes, fluoroalkanes and chlorofluoroalkanes are used.

When the cosmetic composition according to the invention is used for the protection of the human epidermis against UV rays, or as an antisun composition, it may be in the form of a suspension or a dispersion in solvents or fats, in the form of a vesicle dispersion or an oil, or alternatively in the form of an emulsion such as a cream or milk, or in the form of an ointment, a gel, a solid stick or an aerosol foam.

When the cosmetic composition according to the invention is used for the protection of the hair, it may be in the form of a shampoo, a lotion, a gel, an emulsion, a vesicle dispersion or a lacquer for the hair and may consist, for example, of a composition to be rinsed, to be applied before or after shampooing, before or after dyeing or bleaching, or before, during or after permanent-waving or straightening of the hair, a styling or treating lotion or gel, a lotion or gel for blow drying or hairsetting, or a composition for the permanent-waving, straightening, dyeing or bleaching of the hair.

When the composition is used as a make-up product for the eyelashes, the eyebrows or the skin, such as a treatment cream for the epidermis, a foundation, a lipstick, an eyeshadow, a blusher, a mascara or an eyeliner, it may be in solid or pasty, anhydrous or aqueous form, such as oil-in-water or water-in-oil emulsions, vesicle dispersions or alternatively

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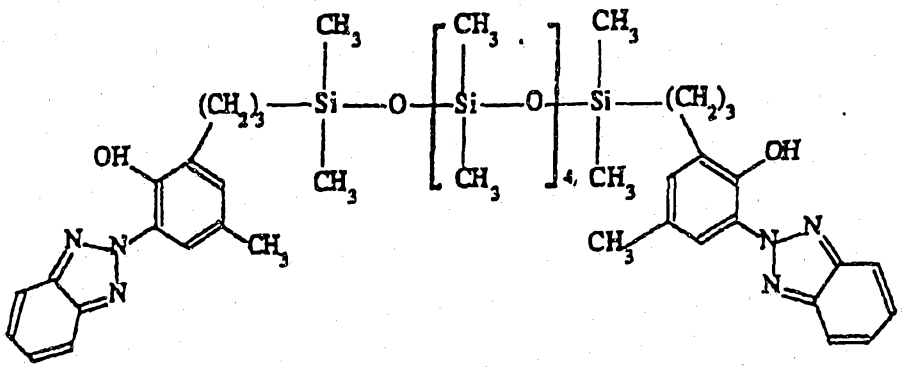
suspensions.

The invention will be better illustrated by the non-limiting examples below.

EXAMPLE 1

An oil-in-water antisun emulsion having the following composition is prepared:

- 4-tert-Butyl-4'-methoxydibenzoylmethane 2 g
- Polydimethylsiloxane containing 2-(3'-trimethylene-2'-hydroxy-5'-methylphenyl)benzotriazole grafts corresponding to the Patent Application EP 0 392,883, of formula 6 g



- Mixture of cetyl/stearyl alcohol and oxyethylenated cetyl/stearyl alcohol containing 33 mol of ethylene oxide, sold under the name "SINNOWAX AO" by the company Henkel 7 g
- Mixture of non-autoemulsifiable glycol mono- and distearate 2 g
- Cetyl alcohol 1.5 g
- Polydimethylsiloxane sold under the name DC 200-350 CST by the company Dow Corning 1.5 g
- Capric and caprylic acid triglycerides sold under the name MIGLYOL 812 by the company Huls 15 g
- Glycerol 20 g
- Preserving agents qs
- Sequestering agent 0.1 g
- Water qs 100 g

EXAMPLE 2

An antisun oil of the following composition is prepared:

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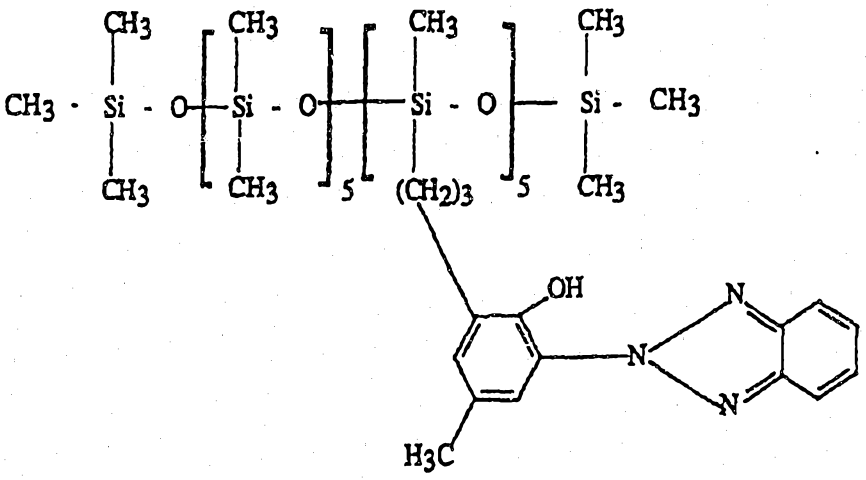
- 4-tert-Butyl-4'-methoxydibenzoylmethane 3 g
- Polydimethylsiloxane containing the 2-(3'-trimethylene-2'-hydroxy-5'-methylphenyl)benzotriazole graft of Example 1 of Application EP-A-0,392,883, of formula : 8 g

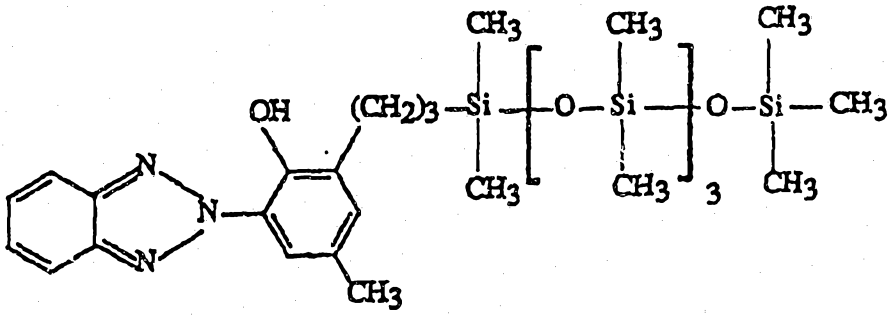


- Titanium oxide nanopigment sold under the name TiO_2 MOTG by the company Tioxide 5 g AM
- Diisopropyl adipate qs 100 g

EXAMPLE 3

An antisun emulsion having the following composition is prepared:

- 4-tert-Butyl-4'-methoxydibenzoylmethane 1 g
- Polydimethylsiloxane containing the 2-(3'-trimethylene-2'-hydroxy-5'-methylphenyl)benzotriazole graft of Example 1 of Application EP-A-0,388,218, of formula : 5 g



- Sorbitan monostearate 5 g
- Hydrophobic pyrogenous silica sold under

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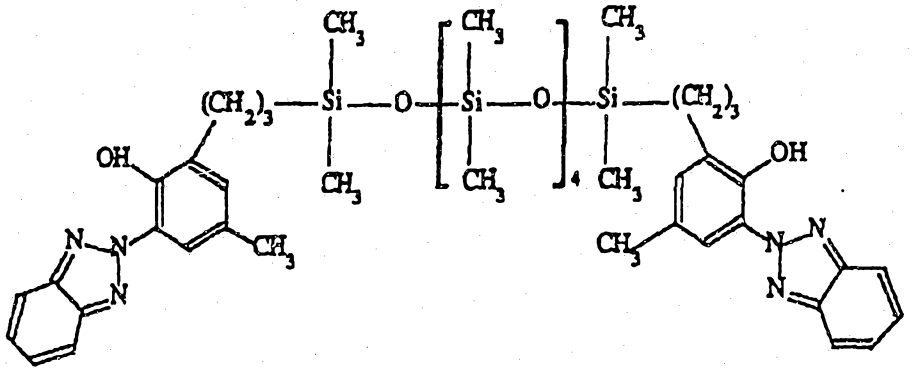
the name AEROSIL R 972 by the company Degussa 0.5 g

- Benzene-1,4-di(3-methylidene-10-camphor-sulfonic) acid 3 g
- Triethanolamine qs pH7
- Benzoate of C_{12}-C_{15} alcohols sold under the name "FINSOLV TN" by the company Witco 15 g
- Purified water qs 100 g

EXAMPLE 4

A day cream for the face having the following composition is prepared:

- 4-tert-Butyl-4'-methoxydibenzoylmethane 1.5 g
- Polydimethylsiloxane containing 2-(3'-trimethylene-2'-hydroxy-5'-methylphenyl)benzotriazole grafts according to the Patent Application EP 0 392,883, of formula 1.5 g



- Mixture of cetyl/stearyl alcohol and oxyethylenated cetyl/stearyl alcohol containing 33 mol of ethylene oxide, sold under the name "SINNOWAX AO" by the company Henkel 7 g
- Mixture of non-autoemulsifiable glycol mono- and distearate 2 g
- Cetyl alcohol 1.5 g
- Polydimethylsiloxane sold under the name DC 200-350 CST by the company Dow Corning 1.5 g
- Capric and caprylic acid triglycerides sold under the name MIGLYOL 812 by the company Huls 15 g
- Glycerol 20 g
- Preserving agents qs

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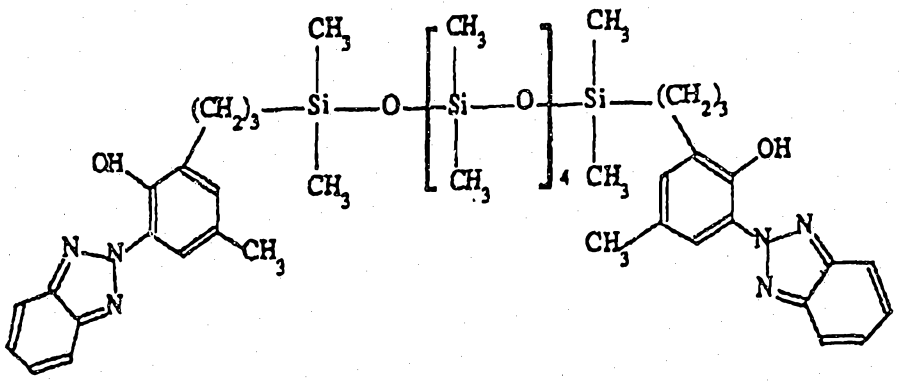
- Sequestering agent 0.1 g
- Water qs 100 g

EXAMPLE 5

Hair-protecting lotion:

- 4-tert-Butyl-4'-methoxydibenzoylmethane 0.5 g
- Silicone containing 2-(3'-trimethylene-2'-hydroxy-5'-methylphenyl) benzotriazole grafts of formula (silicone B): 2 g

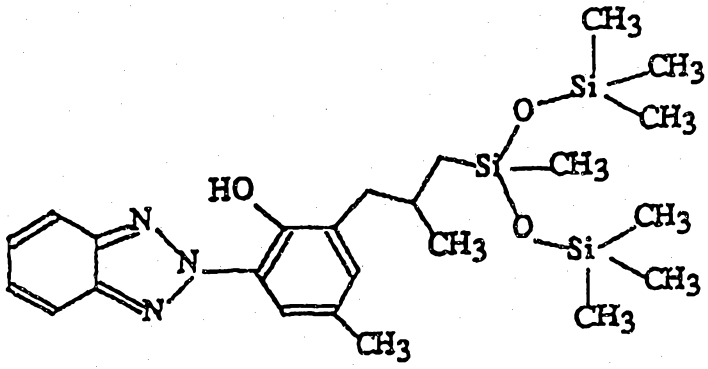


- Benzoate of C_{12}/C_{15} alcohols, sold under the name "FINSOLV TN" by the company Witco 12 g
- Ethyl alcohol qs 100 g

EXAMPLE 6

Oil-in-water antisun emulsion:

- 4-tert-Butyl-4'-methoxydibenzoylmethane 1.75 g
- Silicone containing a 2-[3'-(2"-methyltrimethylene)-2'-hydroxy-5'-methylphenyl]benzotriazole graft of formula (silicone C): 5 g



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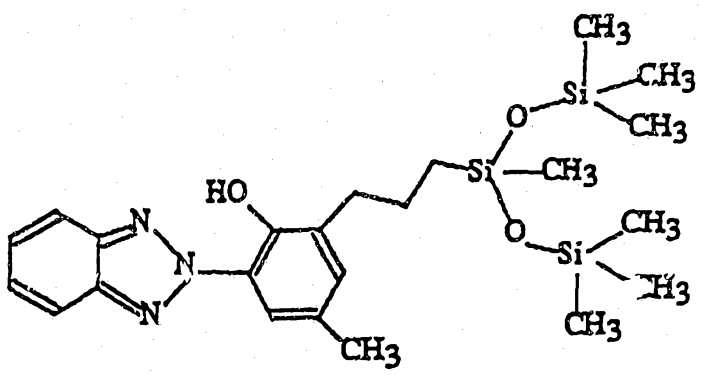
- Mixture of cetyl/stearyl alcohol and oxyethylenated cetyl/stearyl alcohol containing 33 mol of ethylene oxide, sold under the name "SINNOWAX AO" by the company Henkel		8	g
- Mixture of non-autoemulsifiable glyceryl mono- and distearate		2	g
- Cetyl alcohol		2	g
- Diisopropyl adipate		10	g
- Liquid petrolatum		5	g
- Glycerol		10	g
- Preserving agents	qs		
- Water	qs	100	g

EXAMPLE 7

Water-in-oil antisun emulsion:

- 4-tert-Butyl-4'-methoxydibenzoylmethane		1	g
- Silicone containing a 2-(3'-trimethylene-2'-hydroxy-5'-methylphenyl)benzotriazole graft of formula (silicone A):		2	g



- Mixture (hydroxystearate and isostearate of sorbitol and of glycerol) oxypropylenated with 2 mol of propylene oxide and oxyethylenated with 3 mol of ethylene oxide, sold under the name "ARLACEL 780" by the company ICI		6	g
- Liquid petrolatum		10	g
- Capric and caprylic acid triglycerides sold under the name "MIGLYOL 812" by the company Huls		5	g

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- beta-Hydroxyoctacosanyl 12-hydroxystearate sold under the name "ELFACOS C26" by the company AKZO 3 g
- Mixture of cyclopentadimethylsiloxane, cyclotetradimethylsiloxane and cyclohexadimethylsiloxane, sold under the name "DC 345 FLUID" by the company Dow Corning 3 g
- Glycerol 5 g
- Magnesium sulfate 0.7 g
- Preserving agents qs
- Water qs 100 g

Modes of preparation of silicones A, B and C

Silicone A

A mixture of 3-allyl-2-hydroxy-5-methylphenylbenzotriazole (5 g, 18 meq), bis(trimethylsiloxy)methylsilane (Petrarch Systems Inc., B 2497, 4.2 g, 18 meq as SiH) and cyclovinylmethylsiloxane complexed with platinum (Petrarch, PC085, 5 µl) in dry toluene (8 ml) at 60-70°C is heated to 40°C, with stirring and under nitrogen. The mixture is left stirring at 40°C until the SiH groups have disappeared (absence of a peak at 2180 cm^{-1} in infrared), which is equivalent to 2 hours. The solvent is evaporated off. The brown oil obtained is chromatographed on a column of silica (150 g, eluent: heptane/dichloromethane 80/20). After removal of the head fractions, the expected product is obtained in the form of a white powder (6 g, yield = 65%).

- ^{13}C NMR Spectrum ($CDCl_3$): spectrum in accordance with the formula.
- ^{29}Si NMR Spectrum ($CDCl_3$): spectrum in accordance with the formula.
- UV (Ethanol) λ_{max} = 303 nm, ϵ_{max} = 16,000
  λ_{max} = 342 nm, ϵ_{max} = 15,300.
- Analysis for $C_{23}H_{37}N_3O_3Si_3$

	C	H	N	Si
Calculated	56.63	7.65	8.61	17.27
Found	57.01	7.71	8.66	16.94

m.p. = 68°C.

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Silicone B

1,1,3,3,5,5,7,7,9,9,11,11-Dodecamethylhexasiloxane (50 g, 232 meq as SiH) is added dropwise over one hour to a solution of 3-allyl-2-hydroxy-5-methylphenylbenzotriazole (61.6 g, 232 meq) and cyclovinylmethylsiloxane complexed with platinum (Petrarch PC085, 50 µl) in dry toluene (150 ml) at 80-90°C, under nitrogen and with stirring. The mixture is left stirring at 80°C until the SiH groups have disappeared (absence of a peak at 2180 cm^{-1} in infrared), which is equivalent to 4 hours. The solvent is evaporated off. The orange-colored viscous oil obtained (103 g) is purified on a column of silica (500 g, eluent heptane/dichloromethane 9/1 in order to remove the monomers and then heptane/dichloromethane/AcOH 90/9.8/0.2 to give the expected product in the form of a white wax (70 g, yield = 63%).

- ^{13}C NMR Spectrum ($CDCl_3$): spectrum in accordance with the formula.
- ^{29}Si NMR Spectrum ($CDCl_3$): spectrum in accordance with the formula.
- UV (Ethanol) λ_{max} = 302 nm, ϵ_{max} = 30,200
  λ_{max} = 340 nm, ϵ_{max} =27,700.
- Analysis for $C_{44}H_{68}N_6O_7Si_6$

	C	H	N	Si
Calculated	54.96	7.13	8.74	17.52
Found	54.90	7.12	8 81	17.11

m.p. = 38°C.

Silicone C

bis(Trimethylsiloxy)methylsilane (Petrarch Systems Inc., B 2497, 75.4 g, 322 meq as SiH) is added dropwise over 1 hour 15 minutes to a solution of 3-methallyl-2-hydroxy-5-methylphenylbenzotriazole (90 g, 322 meq) and cyclovinylmethylsiloxane complexed with platinum (Petrarch PC 085, 0.3 ml) in dry toluene (130 ml) at 80°C, under nitrogen and with stirring. The mixture is left stirring at 80°C until the starting benzotriazole has disappeared, which is equivalent to 4 hours. The solvent is evaporated off. The brown oil obtained is

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crystallized from ethanol to give the expected product in the form of an off-white powder (97 g, yield = 60%).

- ^{13}C NMR Spectrum ($CDCl_3$): spectrum in accordance with the formula.
- ^{29}Si NMR Spectrum ($CDCl_3$): spectrum in accordance with the formula.
- UV (Ethanol) λ_{max} = 303 nm, ϵ_{max} = 16,300
  λ_{max} = 343 nm, ϵ_{max} = 15,600.
- Analysis for $C_{24}H_{39}N_3O_3Si_3$

	C	H	N	Si
Calculated	57.44	7.83	8.37	16.79
Found	57.35	7.76	8.09	16.51

m.p. = 49°C.

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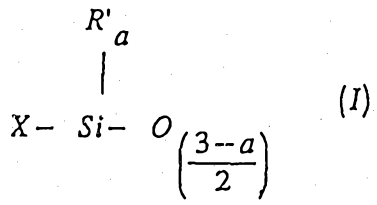
CLAIMS

1. Photostable filtering cosmetic composition for the protection of the skin and the hair against ultraviolet rays with wavelengths between 280 and 380 nm, characterized in that it includes, in a cosmetically acceptable vehicle containing at least one fatty phase, 0.5 to 4% by weight of 4-(tert-butyl)-4'-methoxydibenzoylmethane and 0.1 to 20%, preferably 0.5 to 15% by weight, of a filtering polymer of the benzotriazole silicone type containing at least one unit of formula:



(I)

in which

R' denotes a saturated or unsaturated C_1-C_{30} hydrocarbon group, a C_1-C_8 halogenated hydrocarbon group or a trimethylsilyloxy group;

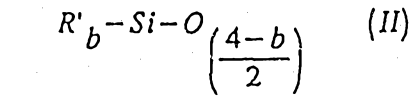
a = 1 or 2;

X = - A - Y

where A represents an aliphatic or aromatic divalent hydrocarbon radical containing at least 2 carbon atoms and optionally containing one or more oxygen atoms;

Y represents a 2-(2'-hydroxyphenyl)benzotriazole residue optionally bearing, on one or both of the aromatic rings, one or more C_1-C_8 alkyl, C_2-C_8 alkenyl, halogen, alkoxy, carboxyl, hydroxyl or amino substituents, the weight ratio of the benzotriazole silicone to the 4-(tert-butyl)-4'-methoxydibenzoylmethane being between 1 and 10.

2. Composition according to Claim 1, characterized in that the benzotriazole silicone includes, in addition to the units of formula (I), units of formula:



(II)

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in which R' has the same meaning as in Claim 1 and b is an integer denoting 1, 2 or 3, at least 40% of the radicals R' being methyl radicals.

3. Cosmetic composition according to Claim 1 or 2, characterized in that it constitutes a composition for protecting the human epidermis or an antisun composition and is in the form of a lotion, a thickened lotion, a gel, an oil, a vesicle dispersion, a cream, a milk, a powder, a solid stick, a foam or a spray.

4. Cosmetic composition according to Claim 1 or 2, characterized in that it constitutes a make-up composition for the eyelashes, the eyebrows or the skin and is in solid or pasty, anhydrous or aqueous form, in the form of an emulsion, a suspension or a vesicle dispersion.

5. Cosmetic composition according to Claim 1 or 2, which is used for protection of the hair against ultraviolet rays, characterized in that it is in the form of a shampoo, a lotion, a gel, an emulsion, a vesicle dispersion or a lacquer for the hair.

6. Composition according to any one of Claims 1 to 5, in the form of an emulsion or vesicle dispersion of ionic or nonionic amphiphilic lipids, characterized in that it contains a water-soluble UV filter chosen from benzene-1,4-[di(3-methylidene-10-camphorsulfonic)] acid, 2-phenylbenzimidazole-5-sulfonic acid and 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, which may or may not be salified and which are present in the aqueous phase.

7. Cosmetic composition according to any one of Claims 1 to 6, characterized in that it additionally includes cosmetic adjuvants chosen from fats, organic solvents, silicones, thickeners, softeners, lipophilic UV-B sunscreen agents, anti-foaming agents, hydrating agents, fragrances, preserving agents, anionic, cationic, nonionic or amphoteric surfactants or mixtures thereof, fillers, sequestering agents, anionic, cationic, nonionic or amphoteric polymers or mixtures thereof, propellants, basifying or acidifying agents, dyes and metal oxide pigments of particle size between 100 nm and 20,000 nm.

8. Composition according to any one of Claims 1 to 7,

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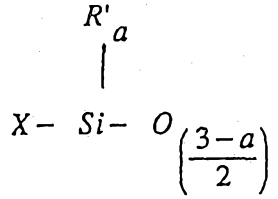
characterized in that it additionally contains metal oxide nanopigments dispersed in the fatty phase and/or in the aqueous phase.

9. Cosmetic treatment process for the skin and the hair for protecting them against the effects of UV rays with wavelengths between 280 and 380 nm, characterized in that it consists in applying an effective amount of a filtering cosmetic composition as defined in any one of Claims 1 to 8.

10. Process for the stabilization of 4-(tert-butyl)-4'-methoxydibenzoylmethane with regard to UV radiation, characterized in that there is added 0.1 to 20%, and preferably 0.5 to 15% by weight, of a filtering polymer of the benzotriazole silicone type containing at least one unit of formula:



(I)

in which

R' denotes a saturated or unsaturated C_1-C_{30} hydrocarbon group, a C_1-C_8 halogenated hydrocarbon group or a trimethylsilyloxy group;

a = 1 or 2;

X = - A - Y

where A represents an aliphatic or aromatic divalent hydrocarbon radical containing at least 2 carbon atoms and optionally containing one or more oxygen atoms;

Y represents a 2-(2'-hydroxyphenyl)benzotriazole residue optionally bearing, on one or both of the aromatic rings, one or more C_1-C_8 alkyl, C_2-C_8 alkenyl, halogen, alkoxy, carboxyl, hydroxyl or amino substituents to 0.5 to 4% by weight of 4-(tert-butyl)-4'-methoxydibenzoylmethane; the weight ratio of the benzotriazole silicone to the 4-(tert-butyl)-4'-methoxydibenzoylmethane being between 1 and 10.

11. Process according to Claim 10, characterized in that the benzotriazole silicone includes, in addition to

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the units of formula (I), units of formula:

$$R'_b-Si-O_{\left(\frac{4-b}{2}\right)} \qquad (II)$$

in which R' has the same meaning as in Claim 10 and b is an integer denoting 1, 2 or 3, at least 40% of the radicals R' being methyl radicals.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FR 93/00886

A. CLASSIFICATION OF SUBJECT MATTER

IPC5 A61K 7/42; A61K7/48; A61K7/06

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)

IPC5 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 392 883 (L'OREAL) 17 October 1990 cited in the application see claims 1-19	1-11
Y	FR,A,2 440 933 (L. GIVAUDAN & CIE) 6 June 1980 cited in the application see page 1, line 13 - page 2, line 26; claims 1-7	1-11
A	EP,A,0 365 370 (L'OREAL) 25 April 1990 see claims 1-16	1-11
A,P	FR,A,2 680 683 (L'OREAL) 5 March 1993 see page 13, line 1 - page 14, line 9; claims 1-18	1-11

☐ 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 document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 December 1993 (07.12.93)	04 January 1994 (04.01.94)
Name and mailing address of the ISA/ EUROPEAN PATENT OFFICE Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. FR 9300886
SA 79180

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 07/12/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0392883	17-10-90	FR-A-	2642968	17-08-90
		AU-B-	639439	29-07-93
		AU-A-	4970390	23-08-90
		CA-A-	2010162	15-08-90
		JP-A-	2282319	19-11-90
		US-A-	5089250	18-02-92
FR-A-2440933	06-06-80	CH-A-	642536	30-04-84
		DE-A,C	2945125	29-05-80
		GB-A,B	2038807	30-07-80
		NL-A-	7907446	16-05-80
		US-A-	4387089	07-06-83
		JP-C-	1352832	11-12-86
		JP-A-	55066535	20-05-80
		JP-B-	61016258	28-04-86
EP-A-0365370	25-04-90	FR-A-	2636530	23-03-90
		AU-B-	628840	24-09-92
		AU-A-	4015889	01-03-90
		JP-A-	2142719	31-05-90
FR-A-2680683	05-03-93	WO-A-	9304665	18-03-93

EPO FORM P0479

RAPPORT DE RECHERCHE INTERNATIONALE

Demande Internationale No PCT/FR 93/00886

I. CLASSEMENT DE L'INVENTION (si plusieurs symboles de classification sont applicables, les indiquer tous) 7

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB

CIB 5 A61K7/42; A61K7/48; A61K7/06

II. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE

Documentation minimale consultée 8

Système de classification	Symboles de classification
CIB 5	A61K

Documentation consultée autre que la documentation minimale dans la mesure où de tels documents font partie des domaines sur lesquels la recherche a porté 9

III. DOCUMENTS CONSIDERES COMME PERTINENTS 10

Catégorie °	Identification des documents cités, avec indication, si nécessaire, 12 des passages pertinents 13	No. des revendications visées 14
Y	EP,A,0 392 883 (L'OREAL) 17 Octobre 1990 cité dans la demande voir revendications 1-19	1-11
Y	FR,A,2 440 933 (L. GIVAUDAN & CIE) 6 Juin 1980 cité dans la demande voir page 1, ligne 13 - page 2, ligne 26; revendications 1-7	1-11
A	EP,A,0 365 370 (L'OREAL) 25 Avril 1990 voir revendications 1-16	1-11
A,P	FR,A,2 680 683 (L'OREAL) 5 Mars 1993 voir page 13, ligne 1 - page 14, ligne 9; revendications 1-18	1-11

° Catégories spéciales de documents cités: 11

"A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent

"E" document antérieur, mais publié à la date de dépôt international ou après cette date

"L" document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)

"O" document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens

"P" document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée

"T" document ultérieur publié postérieurement à la date de dépôt international ou à la date de priorité et n'appartenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention

"X" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive

"Y" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier.

"&" document qui fait partie de la même famille de brevets

IV. CERTIFICATION

Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale
07 DECEMBRE 1993	04.01.94
Administration chargée de la recherche internationale	**Signature du fonctionnaire autorisé**
OFFICE EUROPEEN DES BREVETS	SIATOU E.

ANNEXE AU RAPPORT DE RECHERCHE INTERNATIONALE RELATIF A LA DEMANDE INTERNATIONALE NO.

FR 9300886
SA 79180

La présente annexe indique les membres de la famille de brevets relatifs aux documents brevets cités dans le rapport de recherche internationale visé ci-dessus. –
Lesdits membres sont contenus au fichier informatique de l'Office européen des brevets à la date du
Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office européen des brevets. 07/12/93

Document brevet cité au rapport de recherche	Date de publication	Membre(s) de la famille de brevet(s)		Date de publication
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		AU-B-	639439	29-07-93
		AU-A-	4970390	23-08-90
		CA-A-	2010162	15-08-90
		JP-A-	2282319	19-11-90
		US-A-	5089250	18-02-92
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		AU-B-	628840	24-09-92
		AU-A-	4015889	01-03-90
		JP-A-	2142719	31-05-90
FR-A-2680683	05-03-93	WO-A-	9304665	18-03-93

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