

679391

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Section 29

AUSTRALIA  
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**PATENT REQUEST : STANDARD PATENT**

I/We, being the person(s) identified below as the Applicant(s), request the grant of a Standard Patent to the person(s) identified below as the Nominated Person(s), for an invention described in the accompanying complete specification.

**Applicant(s) and  
Nominated Person(s):** L'OREAL

**Address:** 14, RUE ROYALE  
PARIS 75008  
FRANCE

**Invention Title:** NOVEL SUNSCREENS, PHOTOPROTECTIVE  
COSMETIC COMPOSITIONS CONTAINING THEM  
AND USES THEREOF

**Name(s) of Actual  
Inventor(s):** HERVÉ RICHARD; MADELEINE LEDUC;  
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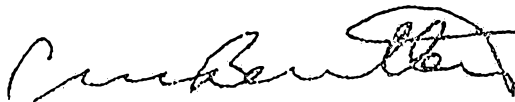
**BASIC CONVENTION APPLICATION DETAILS**

<b>Application No:</b>	<b>Country:</b>	<b>Application Date:</b>
94-13395	FR	08 November 1994

DATED: 16 October 1995

L'OREAL

GRIFFITH HACK & CO.



M. 074053 161095

Patent Attorney for and  
on behalf of the Applicant

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**NOTICE OF ENTITLEMENT**

I/We L'OREAL

of 14, RUE ROYALE  
PARIS 75008  
FRANCE

being the applicant(s) in respect of an application for a patent for an invention entitled  
NOVEL SUNSCREENS, PHOTOPROTECTIVE COSMETIC COMPOSITIONS  
CONTAINING THEM AND USES THEREOF, state the following:

1. The nominated person(s) has/have, for the following reasons, gained entitlement from the actual inventor(s):

THE NOMINATED PERSON WOULD BE ENTITLED  
TO HAVE ASSIGNED TO IT A PATENT GRANTED TO  
ANY OF THE ACTUAL INVENTORS IN RESPECT OF  
THE SAID INVENTION.

2. The nominated person(s) has/have, for the following reasons, gained entitlement from the basic applicant(s) listed on the patent request:

THE APPLICANT AND NOMINATED PERSON IS THE  
BASIC APPLICANT.

3. The basic application(s) listed on the request form is/are the first application(s) made in a Convention country in respect of the invention.

DATE: 16 October 1995

L'OREAL

GRIFFITH HACK & CO.



Patent Attorney for and  
on behalf of the applicant(s)



AU9534236

**(12) PATENT ABRIDGMENT (11) Document No. AU-B-34236/95**  
**(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 679391**

(54) Title  
**NOVEL SUNSCREENS, PHOTOPROTECTIVE COSMETIC COMPOSITIONS CONTAINING THEM AND USES THEREOF**

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(71) Applicant(s)  
 L'OREAL

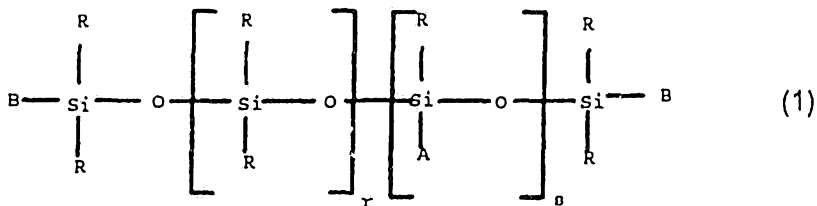
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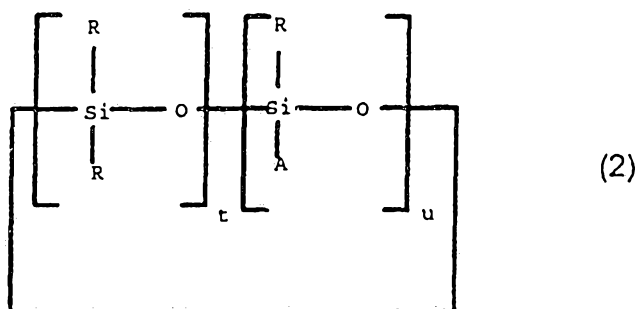
(56) Prior Art Documents  
 AU 31700/95 C07F 7/10  
 AU 34380/95 C07F 7/10  
 EP 392883

(57) Claim

1. Novel compounds of formula:



or



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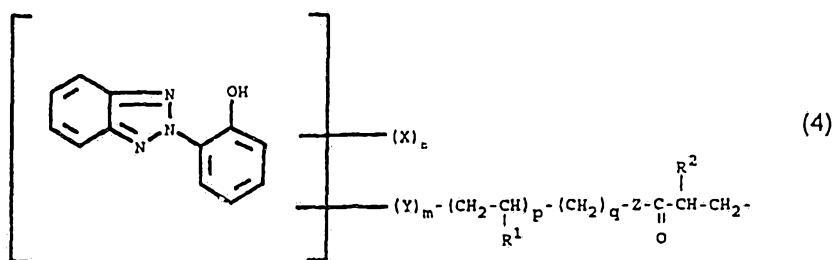
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or



in which formulae (1) to (3):

- the groups R, which may be identical or different, are chosen from C<sub>1</sub>-C<sub>10</sub> alkyl, phenyl and 3,3,3-trifluoropropyl radicals, at least 80 %, in numerical terms, of the radicals R being methyl,
- the groups B, which may be identical or different, are chosen from the above radicals R and the radical A defined below,
- the groups R', which may be identical or different, are chosen from C<sub>1</sub>-C<sub>8</sub> alkyl radicals, or phenyl radicals,
- r is an integer between 0 and 50 inclusively, and s is an integer between 0 and 20 inclusively, with the condition that if s is zero then at least one of the two symbols B denotes A,
- u is an integer between 1 and 6 inclusively, and t is an integer between 0 and 10 inclusively, it being understood that t + u is equal to or greater than 3,
- and the symbol A denotes a monovalent radical directly attached to a silicon atom and which corresponds to the following formula (4):



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in which formula (4):

- n is an integer between 0 and 3 inclusively and the groups X, which may be identical or different, are chosen from C<sub>1</sub>-C<sub>8</sub> alkyl radicals, halogens and C<sub>1</sub>-C<sub>4</sub> alkoxy radicals,

- m is 0 or 1, and Y represents -O-, -NH-, -COO-, -O(CH<sub>2</sub>)<sub>v</sub>-COO- or -(CH<sub>2</sub>)<sub>w</sub>-OCONH-, v and w being integers between 0 and 12 inclusively,

- p is 0 or 1,

- q is an integer between 0 and 12 inclusively,

- Z represents -O- or -NH-,

- R<sup>1</sup> represents hydrogen or a C<sub>1</sub>-C<sub>4</sub> alkyl radical,

- R<sup>2</sup> represents hydrogen or a methyl radical.

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COMPLETE SPECIFICATION  
STANDARD PATENT

Applicant(s):

L'OREAL

Invention Title:

NOVEL SUNSCREENS, PHOTOPROTECTIVE  
COSMETIC COMPOSITIONS CONTAINING THEM  
AND USES THEREOF

The following statement is a full description of this invention, including the best method of performing it known to me/us:

NOVEL SUNSCREENS, PHOTOPROTECTIVE COSMETIC COMPOSITIONS  
CONTAINING THEM AND USES THEREOF

The present invention relates to novel compounds of the linear or cyclic short-chain  
5 diorganosiloxane type, or of the triorganosilane type, having the common characteristic of all having at least one benzotriazole unit containing acrylate or acrylamide functionality, it being possible for these compounds to be used more particularly as organic  
10 sunscreens in cosmetic compositions intended for the protection of the skin and the hair against ultraviolet radiation. The invention also relates to the use of the said compounds in the abovementioned cosmetic application, as well as to the cosmetic compositions  
15 with enhanced properties containing them.

It is known that light radiation with wavelengths of between 280 nm and 400 nm permits tanning of the human epidermis, and that light rays with wavelengths more particularly between 280 and  
20 320 nm, known as UV-B rays, cause skin burns and erythema which may be harmful to the natural development of the tan; this UV-B radiation should thus be screened out.

It is also known that UV-A rays, with  
25 wavelengths of between 320 and 400 nm, which cause tanning of the skin, are liable to induce an adverse change in the latter, especially in the case of sensitive skin or of skin which is continually exposed

to solar radiation. UV-A rays cause in particular a loss of elasticity of the skin and the appearance of wrinkles, leading to premature skin ageing. They promote triggering of the erythematous 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 screen out UV-A radiation.

Many compounds intended for the photoprotection (UV-A and/or UV-B) of the skin have been proposed to date.

Most of these are aromatic compounds having an absorption of UV rays in the region between 280 and 315 nm, or in the region between 315 and 400 nm, or alternatively in both of these regions. They are usually formulated in antison compositions which are in the form of an emulsion of oil-in-water type (that is to say a cosmetically acceptable vehicle consisting of an aqueous dispersing continuous phase and an oily disperse discontinuous phase) and which thus contain, in various concentrations, one or more standard lipophilic and/or hydrophilic organic screening agents containing aromatic functionality, capable of selectively absorbing harmful UV radiation, these screening agents (and the amounts thereof) being selected as a function of the desired protection factor (the protection factor (PF) being expressed mathematically by the ratio of the irradiation time necessary to reach the erythema-forming threshold with



the UV screening agent to the time necessary to reach the erythema-forming threshold without UV screening agent).

Besides their screening power, these  
5 compounds with anti-UV activity should also have good cosmetic properties in the compositions which contain them, good solubility in the usual solvents and, in particular, fatty substances such as oils and fats, as well as good resistance to water and to perspiration  
10 (remanence).

Among all the aromatic compounds which have been recommended for this purpose, there may in particular be mentioned p-aminobenzoic acid derivatives, benzylidenecamphor derivatives, cinnamic  
15 acid derivatives and benzotriazole derivatives. However, some of these substances do not have all the required properties for a suitable use as UV screening agents in antisun compositions. In particular, their intrinsic screening power may be insufficient, their  
20 solubility in the various types of formulations used as regards sun protection is not always good enough (liposolubility in particular), they may not be sufficiently light-fast (photostability) and they may also have poor resistance to water and to sweat. It is  
25 also desirable for these screening substances not to penetrate into the skin.

Thus, in the more specific case of the screening substances of benzotriazole type, it has been

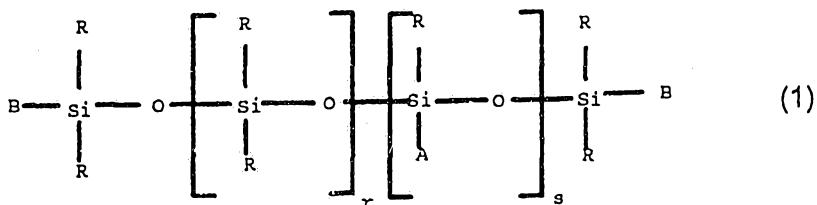
sought to obtain products having improved properties, in particular as regards their liposolubility and their cosmetic nature, by attaching the benzotriazole screening group by grafting (hydrosilylation) to a macromolecular chain of silicone type (organopolysiloxane). This technique, described in patent application EP 0,392,883 in the name of the Applicant, does admittedly lead to advantageous compounds (these products are known generally as "screening silicones"), but the liposoluble nature of these compounds may still appear to be insufficient and, in addition, in order to obtain satisfactory screening properties with products of this type, it is often necessary to use relatively large amounts of these screening polymers, which is reflected in poor cosmetic properties as regards the formulations which contain them.

The present invention is directed towards overcoming the above problems by proposing novel compounds, of screening silicone type, containing a benzotriazole unit, which have improved properties, in particular as regards their solubility in fatty substances and their cosmetic properties.

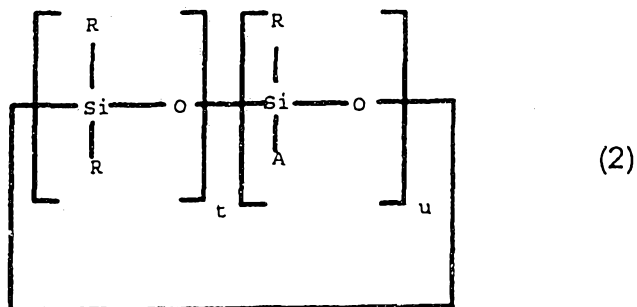
Even more precisely, it was found, according to the present invention, that by combining, in particular by a hydrosilylation reaction, one or more specific benzotriazole derivatives, namely, more precisely, benzotriazole acrylates or acrylamides, with

a specific linear or cyclic silicone chain or with a specific silane, it was possible to arrive at novel compounds of the screening silicone type, obviating the drawbacks of the screening silicones of the prior art, these novel compounds having in particular very good screening properties, both in the UV-A range and in the UV-B range, very good solubility in the usual organic solvents and in particular in fatty substances such as oils, as well as excellent cosmetic properties, making them particularly suitable for use as sunscreens in, or for the preparation of, cosmetic compositions intended for the protection of the skin and/or the hair against ultraviolet radiation.

The first subject of the present invention is thus novel compounds which are characterized in that they correspond to one of the following formulae (1) to (3):



or



or



in which formulae (1) to (3):

5 - the groups R, which may be identical or different, are chosen from C<sub>1</sub>-C<sub>10</sub> alkyl, phenyl and 3,3,3-trifluoropropyl radicals, at least 80 %, in numerical terms, of the radicals R being methyl,

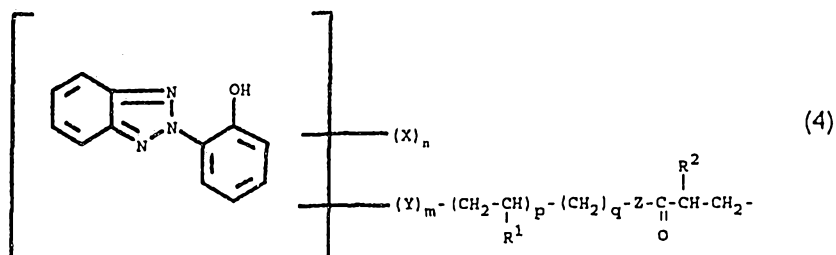
10 - the groups B, which may be identical or different, are chosen from the above radicals R and the radical A defined below,

- the groups R', which may be identical or different, are chosen from C<sub>1</sub>-C<sub>8</sub> alkyl radicals, or phenyl radicals,

15 - r is an integer between 0 and 50 inclusively, and s is an integer between 0 and 20 inclusively, with the condition that if s is zero then at least one of the two symbols B denotes A,

20 - u is an integer between 1 and 6 inclusively, and t is an integer between 0 and 10 inclusively, it being understood that t + u is equal to or greater than 3,

- and the symbol A denotes a monovalent radical directly attached to a silicon atom and which corresponds to the following formula (4):



in which formula (4):

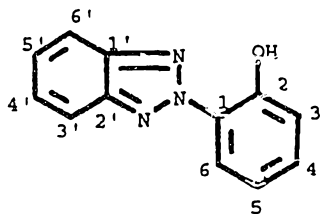
- 5                   - n is an integer between 0 and 3 inclusively and the groups X, which may be identical or different, are chosen from C<sub>1</sub>-C<sub>8</sub> alkyl radicals, halogens and C<sub>1</sub>-C<sub>4</sub> alkoxy radicals,
- m is 0 or 1, and Y represents -O-, -NH-,
- 10                   -COO-, -O(CH<sub>2</sub>)<sub>v</sub>-COO- or -(CH<sub>2</sub>)<sub>w</sub>-OCONH-, v and w being integers between 0 and 12 inclusively,
- p is 0 or 1,
- q is an integer between 0 and 12 inclusively,
- 15                   - Z represents -O- or -NH-,
- R<sup>1</sup> represents hydrogen or a C<sub>1</sub>-C<sub>4</sub> alkyl radical,
- R<sup>2</sup> represents hydrogen or a methyl radical.

In the above formulae (1) to (3), A thus

20 represents the group derived from benzotriazole which, after attaching to the short starting silicone-containing chain or to the starting silane, imparts

absorbent properties to the compounds of linear diorganosiloxane type (formula (1)) or cyclic diorganosiloxane type (formula (2)) or of triorganosiloxane type (formula (3)) both with respect to UV-A and UV-B radiation. As indicated above, and as emerges from the definition of formula (4) given above, this group necessarily has either one acrylate function ( $Z = O$ ) or one acrylamide function ( $Z = NH$ ) which is provided by the chain unit which ensures anchoring of the benzotriazole to the silicone chain or to the silane.

As emerges from formula (4) given above, the anchoring of the chain unit  $-(Y)_m-(CH_2-CHR^1)_p-(CH_2)_q-Z-CO-CHR^2-CH_2-$  to the benzotriazole unit, which thus ensures connection of the said benzotriazole unit to the silicon atom of the silicone-containing chain or of the silane, may, according to the present invention, take place in all the available positions offered by the two aromatic rings of the benzotriazole:



This anchoring preferably takes place in position 3, 4, 5 (aromatic ring bearing the hydroxyl function) or 4' (benzene ring adjacent to the triazolyl

ring), and even more preferably in position 3, 4 or 5.

Similarly, the substituent unit X may be anchored in all the other positions available within the benzotriazole. However, this anchoring preferably  
5 takes place in position 3, 4, 4', 5 and/or 6.

In the above formulae (1) to (3), the alkyl radicals may be linear or branched and chosen in particular from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-amyl, isoamyl,  
10 neopentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl and tert-octyl radicals. The preferred alkyl radicals R, R' and B according to the invention are the methyl, ethyl, propyl, n-butyl, n-octyl and 2-ethylhexyl radicals. Even more preferably, the radicals R, R' and B are all  
15 methyl radicals.

Among the compounds of formulae (1) to (3) above, it is preferred to use those corresponding to formula (1) or to formula (2), that is to say linear or cyclic short-chain diorganosiloxanes.

20 Among the linear or cyclic diorganosiloxanes falling within the scope of the present invention, the random derivatives or well-defined block derivatives having at least one, and more preferably all of the characteristics below are more particularly preferred:

25 - R is alkyl and, even more preferably, is methyl,

- B is alkyl and, even more preferably, methyl (in the case of the linear compounds of

formula (1)),

- r is between 0 and 3 inclusively; s is between 0 and 3 inclusively (in the case of the linear compounds of formula (1)),

5 - t + u is between 3 and 5 (in the case of the cyclic compounds of formula (2)),

- n is non-zero and preferably equal to 1 or 2, and X is then chosen from methyl, tert-butyl or C<sub>1</sub>-C<sub>4</sub> alkoxy, in particular methoxy,

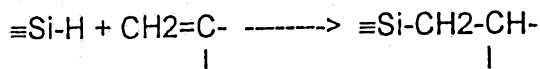
10 - m is non-zero and Y represents -O- or -NH-

- p is non-zero and R<sup>1</sup> is H

- q is between 0 and 3 inclusively

- Z represents -O- or -NH-

In order to prepare the silicone-containing  
15 screening agents of formula (1) and (2), it is possible, according to a first method (Method 1), to follow a standard procedure using a hydrosilylation reaction of the type

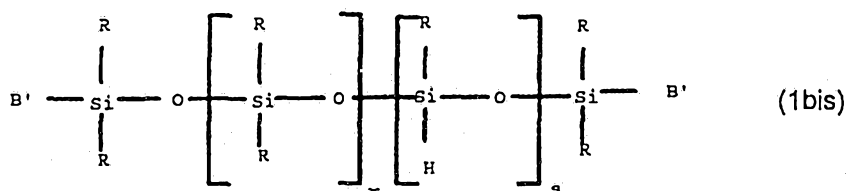


starting with the corresponding silicone in which, for  
20 example, all the radicals A are hydrogen atoms. This starting silicone is referred to hereinbelow as derivative containing SiH; the SiH groups may be present in the chain and/or at the ends of the silicone chain. These derivatives containing SiH are well-known  
25 products in the silicone industry and are generally



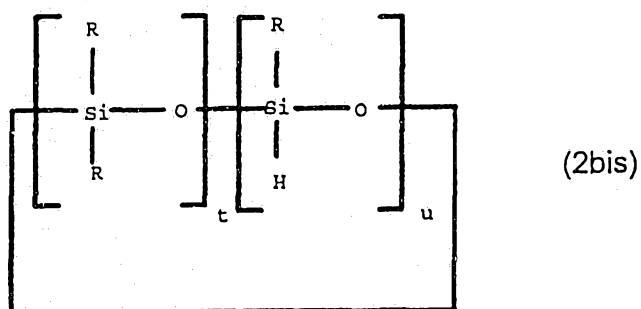
commercially available. They are described, for example, in American patents US-A-3,220,972, US-A-3,697,473 and US-A-4,340,709.

This derivative containing SiH may thus be represented either by the following formula (1bis):



in which R, r and s have the meanings given above for formula (1) and the radicals B', which may be identical or different, are chosen from the radicals R and a hydrogen atom,

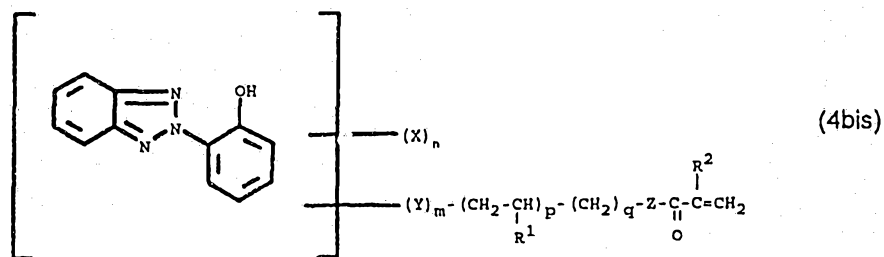
or by the following formula (2bis):



in which R, t and u have the meanings given above for formula (2).

A standard hydrosilylation reaction is thus carried out on this SiH-containing derivative of formula (1bis) or (2bis), performed in the presence of a catalytically effective amount of a platinum

catalyst, on an organic benzotriazole derivative of following formula (4bis):



in which X, Y, Z, R<sup>1</sup>, R<sup>2</sup>, n, m, p and q have the meanings given above for formula (4).

5                    Suitable processes for the preparation of the above products of formula (4bis) are described in particular in patents US-4,316,033 and US-4,328,346. Moreover, some of these products are commercially available. In particular, 2-(2'-hydroxy-5-

10 methacrylyloxyethylphenyl)-2H-benzotriazole is sold under the trade name "Norbloc 7966®" by the company Noramco. In addition, the details of the operating conditions to follow in order to give the

15 hydrosilylation reaction between the compounds of formula (1bis) or (2bis) above and the compound of formula (4bis) above are given in the abovementioned patent application EP-0,392,883, the teaching of which is, in this respect, included in its entirety in the present description by way of reference.

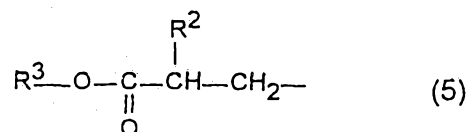
20                    As regards the preparation of the screening agents of triorganosilane type of formula (3) given above, the process may be performed as indicated above,

still by hydrosilylation reaction between a starting silane of formula  $(R')_3Si-H$  (formula (3bis)), in which  $R'$  has the same meaning as for the compound of formula (3), and an organic benzotriazole derivative of formula (4bis) defined above.

Compounds of formula (4bis) which are particularly suitable for use within the context of the present invention are, in particular:

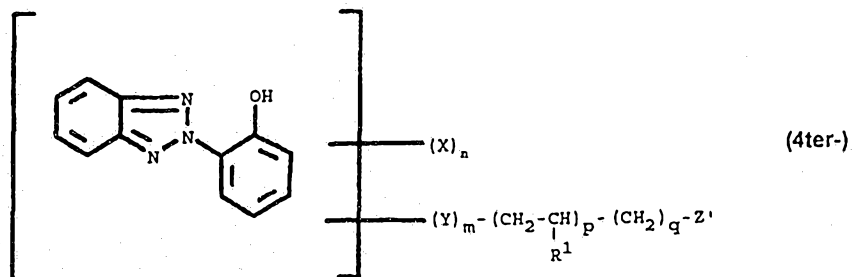
- 10 a) 2-(2'-hydroxy-5'-methacrylyloxyethylphenyl)-2H-benzotriazole
- b) 5-methoxy-2-(2'-hydroxy-4'-methacrylyloxyphenyl)-2H-benzotriazole
- c) 5-methoxy-2-(2'-hydroxy-3'-tert-butyl-5'-methacrylyloxyethylphenyl)-2H-benzotriazole
- 15 d) 5-methyl-2-(2'-hydroxy-5'-methacrylyloxyethylphenyl)-2H-benzotriazole
- e) 5-methacrylyloxyethyl-2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-2H-benzotriazole.

20 Another possible synthetic route (Method 2) which is suitable for the preparation of the silicone-containing screening agents of formulae (1) and (2) consists in starting with the derivatives corresponding to formula (1) or (2) in which all the radicals A are replaced by the radical of formula (5):



in which R<sup>2</sup> has the same meaning as above and R<sup>3</sup> is a hydrogen atom or a methyl or ethyl radical.

The alcohol, the phenol or the amine corresponding to formula (4ter-):



5 in which X, Y, R<sup>1</sup>, n, m, p and q have the meanings given above for formula (4) and Z' represents -OH or -NH<sub>2</sub>, is then reacted with this carboxylic siloxane derivative.

Compared with the screening silicones of the prior art as are defined in the abovementioned patent application EP 0,392,863, the screening silicones according to the invention thus have one or more essential structural differences, which are the source of their noteworthy properties: the silicone-containing chains, on which the benzotriazole unit or units are grafted, are firstly much shorter; next, the unit derived from the benzotriazole still carries at least one acrylate or acrylamide function.

As indicated above, the compounds of formulae (1) to (3) above have excellent intrinsic screening power with regard to UV-A and UV-B ultraviolet radiation. In addition, on account of their highly

liposoluble nature, the compounds of formulae (1) to (3) above may be used in high concentrations, thereby imparting very high protection factors to the final compositions; moreover, they distribute themselves  
5 uniformly in standard cosmetic vehicles containing at least one fatty phase or one cosmetically acceptable organic solvent, and may thus be applied to the skin or the hair in order to constitute an effective protective film. Finally, they have very good cosmetic properties,  
10 namely, in particular, that these products are less sticky and afford more softness when compared with the screening silicones of the prior art.

The subject of the present invention is thus also a cosmetic composition comprising, in a  
15 cosmetically acceptable vehicle preferably containing at least one fatty phase or one organic solvent, an effective amount of at least one compound of formulae (1) to (3) defined above.

The compounds of formulae (1) to (3) are  
20 generally present in proportions of between 0.1 % and 20 % by weight, preferably of between 0.5 % and 10 % by weight, relative to the total weight of the composition.

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

This composition may in particular be in the

form of a lotion, a thickened lotion, a gel, a cream, a milk, a powder or a solid stick and may optionally be packaged as an aerosol and be in the form of a foam or a spray.

5                   It may contain the cosmetic adjuvants usually used in the field, such as fatty substances, organic solvents, silicones, thickeners, softeners, complementary sunscreens, anti-foaming agents, moisturizing agents, fragrances, preserving agents, 10 surfactants, fillers, sequestering agents, anionic, cationic, nonionic or amphoteric polymers or mixtures thereof, propellants, basifying or acidifying agents, dyes, pigments or nanopigments, in particular those intended to provide a complementary photoprotective effect by physically blocking out ultraviolet 15 radiation, or any other ingredient usually used in cosmetics, in particular for the manufacture of antison compositions.

                  Among the organic solvents, there may be 20 mentioned lower alcohols and polyols such as ethanol, isopropanol, propylene glycol, glycerol and sorbitol.

                  The fatty substances may consist of an oil or of a wax or mixtures thereof, fatty acids, fatty acid esters, fatty alcohols, petrolatum, paraffin, lanolin, 25 hydrogenated lanolin or acetylated lanolin. The oils may be chosen from animal, plant, mineral or synthetic oils and, in particular, hydrogenated palm oil, hydrogenated castor oil, liquid petrolatum, liquid

paraffin, purcellin oil, volatile or non-volatile silicone oils, and isoparaffins.

When the cosmetic composition according to the invention is more particularly intended for protection of the human epidermis against UV rays or as an antisen composition, it may be in the form of a suspension or a dispersion in solvents or fatty substances, or alternatively in the form of an emulsion (in particular of O/W or W/O type, but preferably of O/W type) such as a cream or a milk, or in the form of a vesicle dispersion, a salve, a gel, a solid stick or an aerosol foam. The emulsions may additionally contain anionic, nonionic, cationic or amphoteric surface-active agents.

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

When the cosmetic composition according to the invention is used as a make-up product for the eyelashes, the eyebrows, the skin or the hair, such as

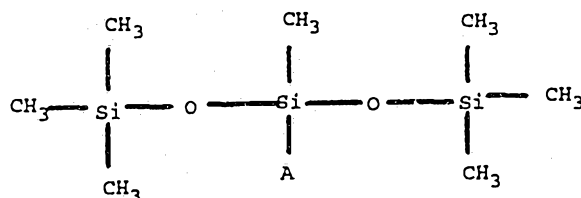
a skin-treatment cream, a foundation, a stick of lipstick, an eye shadow, a blusher, an eye-liner, a mascara or a colouring gel, it may be in solid or pasty and anhydrous or aqueous form, such as oil-in-water or water-in-oil emulsions, suspensions or gels.

The subject of the invention is also a process for the protection of the skin and the hair against ultraviolet radiation, in particular solar radiation, which consists in applying to the skin or the hair an effective amount of the cosmetic composition defined above, or of a compound of formula (1), (2) or (3) as defined above.

The examples which follow illustrate the invention without, however, limiting the scope thereof.

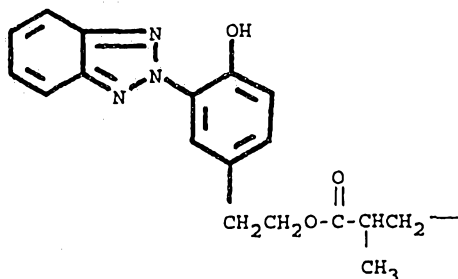
EXAMPLE 1

This example illustrates the preparation (according to Method 1) of a compound in accordance with the invention, of formula:



in which A represents:





(this product corresponds to a compound of formula (1)  
 for which  $R = B = \text{CH}_3$ ;  $r = 0$ ;  $s = 1$ ;  $n = 0$ ;  $m = 0$ ;  
 $p = 0$ ;  $q = 2$ ;  $Z = 0$ ;  $R^2 = \text{CH}_3$ )

30 g of 2-(2'-hydroxy-5-  
 5 methacrylyloxyethylphenyl)-2H-benzotriazole ("Norbloc  
 7966®") and 50 ml of toluene are loaded into a reactor.  
 The mixture is brought to 80°C, under nitrogen. The  
 hydrosilylation catalyst (complex containing 3-3.5 % of  
 Pt in cyclovinylmethylsiloxane, from Hüls Petrarch  
 10 PC085: 100  $\mu\text{l}$ ) is added, followed by 24.5 g of  
 heptamethyltrisiloxane. After 67 hours at 80°C under  
 nitrogen, with 50  $\mu\text{l}$  additions of catalyst every 12  
 hours, the reaction medium is concentrated and  
 chromatography is then carried out on silica under  
 15 pressure (eluent: heptane with a 0-50 % gradient of  
 $\text{CH}_2\text{Cl}_2$ ). 5.1 g of the desired final product, which is in  
 the form of a pale yellow oil, are thus recovered.

The UV absorption characteristics (measured  
 in ethanol) of this product are as follows:

20  $\lambda_{\text{max}}$  : 337 nm  $\epsilon_{\text{max}}$  : 17 500  
 $\lambda_{\text{max}}$  : 298 nm  $\epsilon_{\text{max}}$  : 14 550

This product may thus be used very

effectively as a sunscreen which is active in the UV-A and UV-B range.

EXAMPLE 2

This example illustrates the preparation, but  
5 this time according to Method 2, of the same compound as that of Example 1 above.

a) First step:

34.24 g of ethyl methacrylate containing a spatula-tipful of 4-hydroxyanisole are brought to 80°C,  
10 under nitrogen, in a reactor. The hydrosilylation catalyst (complex containing 3-3.5 % of Pt in cyclovinylmethylsiloxane, from Hüls Petrarch PC085 : 200 µl) is added thereto, followed by dropwise addition, over 30 minutes, of 73.42 g of  
15 heptamethyltrisiloxane. After stirring for 3 hours at 80°C under nitrogen, the medium is concentrated, the acrylate and the siloxane in excess are evaporated off and a pale yellow oil is thus recovered. This oil is then distilled under vacuum. The fraction distilling at  
20 48-52°C at 20 mmHg corresponds to the desired derivative of formula (1) in which:  $R = B = CH_3$ ;  $r = 0$ ;  $s = 1$ ; and A is the radical of formula (5) with  $R^2 = \text{methyl}$  and  $R^3 = \text{ethyl}$ .

b) Second step:

25 340 ml of toluene, 20 g of the derivative prepared in the above step and 12.7 g of 2-(2'-hydroxy-5'-hydroxyethylphenyl)-2H-benzotriazole (i.e. a derivative of formula (4tert) in which  $n = 0$ ;  $m = 0$ ;

p = 1; R<sup>1</sup> = H; q = 0 and Z' = OH) are loaded into a reactor fitted with Dean-Stark apparatus. 0.5 g of p-toluenesulphonic acid is added and the mixture is heated at reflux for 20 hours with removal of the ethanol formed. The reaction medium is concentrated and chromatography is then carried out on silica under pressure (eluent: heptane with a 0-50 % gradient of CH<sub>2</sub>Cl<sub>2</sub>). 9.8 g of the desired final product, which corresponds with the product prepared in Example 1, are thus recovered.

### EXAMPLE 3

A concrete formulation of an antison cosmetic composition in accordance with the invention, namely an antison cream, is illustrated here.

15	-	Compound of Example 1	5 g
	-	Mixture of cetylstearyl alcohol and cetylstearyl alcohol oxyethylenated with 33 mol of EO ("SINNOWAX AO" from Henkel)	7 g
20	-	Mixture of non-self-emulsifiable glyceryl mono- and distearate	2 g
	-	Cetyl alcohol	1.5 g
	-	C <sub>12</sub> -C <sub>15</sub> alkyl benzoate ("FINSOLV TN" from Witco)	20 g
	-	Polydimethylsiloxane	1.5 g
25	-	Glycerol	17.5 g
	-	Fragrance, preserving agent	qs
	-	Water	qs 100 g

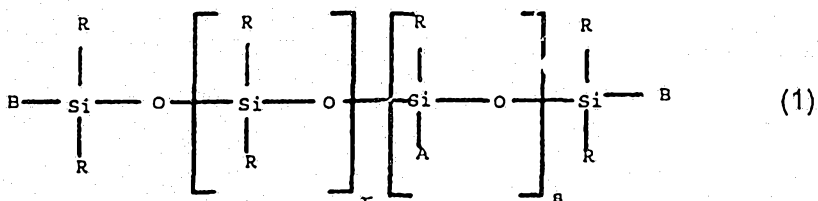
This cream is prepared according to the

standard techniques for the preparation of emulsions, by dissolving the screening agent in the fatty phase containing the emulsifying agents, heating this fatty phase to about 70-80°C and adding, with vigorous stirring, the water which has been heated to the same temperature. Stirring is maintained for 10 to 15 minutes and, after allowing to cool with moderate stirring, the fragrance and preserving agent are then finally added at about 40°C.

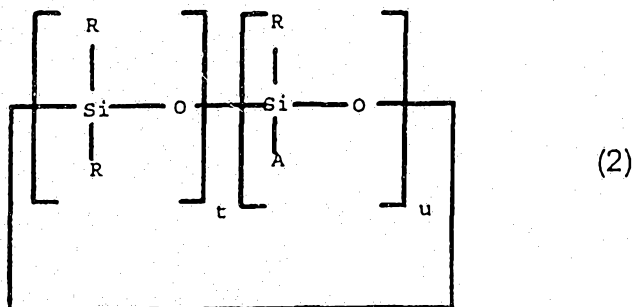


THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Novel compounds of formula:



or



or



in which formulae (1) to (3):

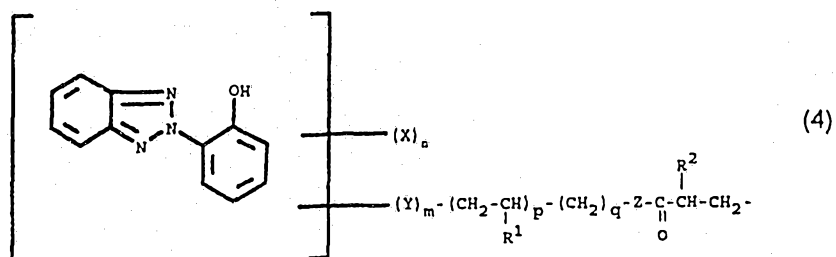
- the groups R, which may be identical or different, are chosen from C<sub>1</sub>-C<sub>10</sub> alkyl, phenyl and 3,3,3-trifluoropropyl radicals, at least 80 %, in numerical terms, of the radicals R being methyl,
- the groups B, which may be identical or different, are chosen from the above radicals R and the radical A defined below,
- the groups R', which may be identical or different, are chosen from C<sub>1</sub>-C<sub>8</sub> alkyl radicals, or

phenyl radicals,

- r is an integer between 0 and 50  
inclusively, and s is an integer between 0 and 20  
inclusively, with the condition that if s is zero then  
5 at least one of the two symbols B denotes A,

- u is an integer between 1 and 6  
inclusively, and t is an integer between 0 and 10  
inclusively, it being understood that t + u is equal to  
or greater than 3,

10 - and the symbol A denotes a monovalent  
radical directly attached to a silicon atom and which  
corresponds to the following formula (4):



in which formula (4):

- n is an integer between 0 and 3 inclusively  
15 and the groups X, which may be identical or different,  
are chosen from C<sub>1</sub>-C<sub>8</sub> alkyl radicals, halogens and C<sub>1</sub>-C<sub>4</sub>  
alkoxy radicals,

- m is 0 or 1, and Y represents -O-, -NH-,  
-COO-, -O(CH<sub>2</sub>)<sub>v</sub>-COO- or -(CH<sub>2</sub>)<sub>w</sub>-OCONH-, v and w being  
20 integers between 0 and 12 inclusively,

- p is 0 or 1,

- q is an integer between 0 and 12

inclusively,

- Z represents -O- or -NH-,

- R<sup>1</sup> represents hydrogen or a C<sub>1</sub>-C<sub>4</sub> alkyl radical,

5 - R<sup>2</sup> represents hydrogen or a methyl radical.

2. Novel compounds according to Claim 1, corresponding to formula (1) or to formula (2), characterized in that the radicals R are alkyl radicals.

10 3. Novel compounds according to Claim 2, characterized in that the radicals R are methyl, ethyl, propyl, n-butyl, n-octyl or 2-ethylhexyl radicals.

4. Novel compounds according to Claim 3, characterized in that the radicals R are methyl  
15 radicals.

5. Novel compounds according to any one of the preceding claims, corresponding to formula (1), characterized in that the radicals B are alkyl radicals.

20 6. Novel compounds according to Claim 5, characterized in that the radicals B are methyl, ethyl, propyl, n-butyl, n-octyl or 2-ethylhexyl radicals.

7. Novel compounds according to Claim 6, characterized in that the radicals B are methyl  
25 radicals.

8. Novel compounds according to any one of the preceding claims, corresponding to formula (1), characterized in that r is between 0 and 3 inclusively,

and  $s$  is between 0 and 3 inclusively.

9. Novel compounds according to any one of Claims 1 to 4, corresponding to formula (2), characterized in that  $t + u$  is between 3 and 5  
5 inclusively.

10. Novel compounds according to Claim 1, corresponding to formula (3), characterized in that the radicals  $R'$  are alkyl radicals chosen from the methyl, ethyl, propyl, *n*-butyl, *n*-octyl and 2-ethylhexyl  
10 radicals.

11. Novel compounds according to Claim 10, characterized in that the radicals  $R'$  are methyl radicals.

12. Novel compounds according to any one of the  
15 preceding claims, characterized in that  $n$  is non-zero, preferably equal to 1 or 2, and  $X$  is chosen from methyl, *tert*-butyl and  $C_1$ - $C_4$  alkoxy, in particular methoxy.

13. Novel compounds according to any one of the  
20 preceding claims, characterized in that  $m$  is non-zero and  $Y$  represents -O- or -NH-.

14. Novel compounds according to any one of the preceding claims, characterized in that  $p$  is non-zero and  $R^1$  is hydrogen.

25 15. Novel compounds according to any one of the preceding claims, characterized in that  $q$  is between 0 and 3 inclusively.

16. Novel compounds according to any one of the



preceding claims, characterized in that the chain unit  $-(Y)_m-(CH_2-CHR^1)_p-(CH_2)_q-Z-CO-CHR^2-CH_2-$  is anchored onto the benzotriazole unit in position 3, 4, 4' or 5 of the latter.

5

17. Novel compounds according to Claim 16, characterized in that the said anchoring takes place in position 3, 4 or 5.

10 18. Novel compounds according to any one of the preceding claims, characterized in that the substituent X is anchored onto the benzotriazole unit position(s) 3, 4, 4', 5 and/or 6 of the latter.

15 19. Compounds of formulae (1)-(3) as defined in any one of Claims 1 to 18, when used as sunscreens which are active in the UV-A and UV-B region.

20 20. Cosmetic composition, in particular for screening out ultraviolet rays, characterized in that it comprises, in a cosmetically acceptable vehicle, an effective amount of at least one of the compounds defined in any one of Claims 1 to 18.

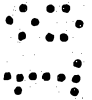
25 21. Cosmetic composition according to Claim 20, characterized in that the said cosmetically acceptable vehicle contains at least one fatty phase or one organic solvent.

30



22. - Cosmetic composition according to Claim 21,  
characterized in that the said vehicle is in the form of  
an emulsion of oil-in-water or water-in-oil type,  
5 preferably of oil-in-water type.

23. Cosmetic composition according to any one of



Claims 20 to 22, characterized in that the content of screening compound(s) is between 0.1 and 20 % by weight relative to the total weight of the composition.

24.           Cosmetic composition according to Claim 23,  
5 characterized in that the said content is between 0.5 and 10 % by weight.

25.           Process for protecting the skin and/or the hair against ultraviolet radiation, in particular solar radiation, characterized in that it consists in  
10 applying to the skin and/or the hair an effective amount of at least one compound or of at least one composition as are defined in any one of the preceding claims.

DATED THIS 16TH DAY OF OCTOBER 1995

L'OREAL

By its Patent Attorneys:

GRIFFITH HACK & CO

Fellows Institute of Patent  
Attorneys of Australia

ABSTRACT

NOVEL SUNSCREENS, PHOTOPROTECTIVE COSMETIC COMPOSITIONS  
CONTAINING THEM AND USES THEREOF

The invention relates to novel compounds of the linear or cyclic short-chain diorganosiloxane type or of the triorganosilane type, having the common characteristic of all having at least one benzotriazole unit containing acrylate or acrylamide functionality, it being possible for these compounds to be used more particularly as organic sunscreens in cosmetic compositions intended for the protection of the skin and the hair against ultraviolet radiation (UV-A and UV-B). The invention also relates to the use of the said compounds in the abovementioned cosmetic application, as well as to the cosmetic compositions with enhanced properties containing them.