

**(19) AUSTRALIAN PATENT OFFICE**

(54) Title  
Cosmetic composition comprising a dibenzoylmethane derivative and a  
2-pyrrolidinone-4-carboxy ester compound; method for the photostabilization of the  
dibenzoylmethane derivative

(51)<sup>6</sup> International Patent Classification(s)  
A61Q 17/04 (2006.01)8/35  
A61K 8/35 (2006.01) 20060101ALI2009112  
A61K 8/49 (2006.01) 3BHAU A61K  
A61Q 17/04 8/49  
20060101AFI2009112 20060101ALI2009112  
3BHAU A61K 3BHAU

(21) Application No: 2009238289 (22) Application Date: 2009.11.16

(30) Priority Data

(31) Number	(32) Date	(33) Country
0858335	2008.12.08	FR

(43) Publication Date : 2010.06.24

(43) Publication Journal Date : 2010.06.24

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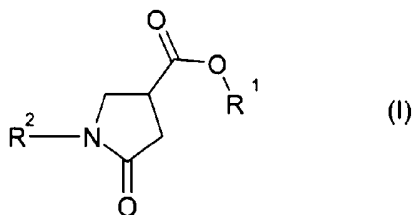
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## ABSTRACT

COSMETIC COMPOSITION COMPRISING A DIBENZOYLMETHANE  
DERIVATIVE AND A 2-PYRROLIDINONE-4-CARBOXY ESTER COMPOUND;  
METHOD FOR THE PHOTOSTABILIZATION OF THE DIBENZOYLMETHANE  
5 DERIVATIVE

The present invention relates to a composition comprising, in a cosmetically acceptable vehicle, at least one UV screening system, characterized in that it comprises:

- 10 (a) at least one dibenzoylmethane derivative and  
(b) at least one 2-pyrrolidinone-4-carboxy ester compound of following formula (I):



15

in which:

R<sup>1</sup> denotes a linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl radical,

- R<sup>2</sup> denotes a linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl radical which can comprise a C<sub>5</sub>-C<sub>6</sub> ring, the phenyl radical, the benzyl  
20 radical or the phenethyl radical.

It also relates to a method for the photostabilization with regard to radiation of at least one dibenzoylmethane derivative by an effective amount of at least one 2-pyrrolidinone-4-carboxy ester compound of  
25 formula (I).

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AUSTRALIA

Patents Act 1990

COMPLETE SPECIFICATION

Standard Patent

Applicant(s):

*L'OREAL*

Invention Title:

*Cosmetic composition comprising a dibenzoylmethane derivative and a 2-pyrrolidinone-4-carboxy ester compound; method for the photostabilization of the dibenzoylmethane derivative*

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

**COSMETIC COMPOSITION COMPRISING A DIBENZOYLMETHANE  
DERIVATIVE AND A 2-PYRROLIDINONE-4-CARBOXY ESTER  
COMPOUND; METHOD FOR THE PHOTOSTABILIZATION OF THE  
DIBENZOYLMETHANE DERIVATIVE**

5           The present invention relates to a cosmetic  
composition comprising the combination of at least one  
screening agent of the dibenzoylmethane derivative type  
and at least one 2-pyrrolidinone-4-carboxy ester  
compound of formula (I), the definition of which will  
10 be given below.

          It also relates to a process for the  
photostabilization, with regard to radiation, of at  
least one screening agent of the dibenzoylmethane  
derivative type by a specific 2-pyrrolidinone-4-carboxy  
15 ester compound of formula (I), the definition of which  
will be given below.

          The present invention also relates to the use of  
at least one specific 2-pyrrolidinone-4-carboxy ester  
compound of formula (I) in a composition comprising, in  
20 a cosmetically acceptable vehicle, at least one  
dibenzoylmethane derivative for the purpose of  
improving the effectiveness of the said composition  
with regard to UV-A rays.

          It is known that light radiation with wavelengths  
25 of between 280 nm and 400 nm makes possible browning of  
the human epidermis and that rays with wavelengths more  
particularly of between 280 and 320 nm, known under the  
name of UV-B, cause erythemas and skin burns which may  
be harmful to the development of natural tanning. For  
30 these reasons, and for aesthetic reasons, there exists  
a constant demand for means for controlling this  
natural tanning for the purpose of thus controlling the  
colour of the skin; it is thus advisable to screen out  
this UV-B radiation.

35           It is also known that UV-A rays, with wavelengths

of between 320 and 400 nm, which cause browning of the skin, are capable of bringing about a detrimental change in the latter, in particular in the case of sensitive skin or of skin continually exposed to solar radiation. UV-A rays cause in particular a loss in the elasticity of the skin and the appearance of wrinkles, resulting in premature skin ageing. They promote the triggering of the erythema reaction or accentuate this reaction in some subjects and can even be the cause of phototoxic or photoallergic reactions. Thus, for aesthetic and cosmetic reasons, such as the preservation of the natural elasticity of the skin, for example, increasingly people desire to control the effect of UV-A rays on their skin. It is therefore desirable also to screen out UV-A radiation.

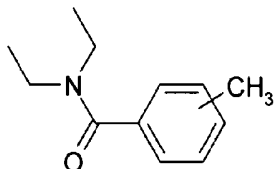
With the aim of providing protection of the skin and keratinous substances against UV radiation, use is generally made of sunscreen compositions comprising organic screening agents which are active in the UV-A region and which are active in the UV-B region. The majority of these screening agents are fat-soluble.

In this respect, a particularly advantageous family of UV-A screening agents is currently composed of dibenzoylmethane derivatives and in particular 4-tert-butyl-4'-methoxydibenzoylmethane, this being because these exhibit a high intrinsic absorption power. These dibenzoylmethane derivatives, which are now products well known per se as screening agents active in the UV-A region, are described in particular in French Patents FR-A 2 326 405 and FR-A 2 440 933, and in European Patent Application EP-A 0 114 607; furthermore, 4-tert-butyl-4'-methoxydibenzoylmethane is currently provided for sale under the trade name of "Parsol 1789 ®" by DSM Nutritional Products.

Unfortunately, it is found that dibenzoylmethane derivatives are products which are relatively sensitive

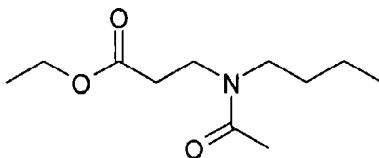
to ultraviolet radiation (in particular UV-A radiation), that is to say, more specifically, that they exhibit an unfortunate tendency to decompose more or less rapidly under the action of the latter. Thus, this substantial lack of photochemical stability of dibenzoylmethane derivatives in the face of the ultraviolet radiation to which they are by nature intended to be subjected does not make it possible to guarantee continuous protection during prolonged exposure to the sun, so that repeated applications at regular and close intervals of time have to be carried out by the user in order to obtain effective protection of the skin against UV rays.

It is known that, in Patent EP 717 982, amide compounds have a photostabilizing effect on dibenzoylmethane derivatives and more particularly N,N-disubstituted amidated oils, such as the compound N,N-diethyl-3-methylbenzamide with the structure:



20

or ethyl N-butyl-N-acetylaminopropionate of formula:



25

such as the product sold under the trade name R3535 by

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the company Merck. These amidated oils have been described in particular in Application US2007141014 as solvents in cosmetic formulations of active principles which are difficult to dissolve in oils, such as UV screening agents, flavone derivatives, chromone derivatives, aryloximes and parabens.

However, this stabilization is obtained in the presence of 20 to 30% of the latter compound, which exhibits a high solvating power for all the starting materials involved in producing the formulations, the consequence of which is reflected by a destabilization of the compositions, rendering unsuitable for use the compositions comprising such a combination.

Patent US 6 528 068 also discloses sun compositions comprising amidated oils which are neutral esters of N-acylamino acid comprising a linear or branched long-chain C<sub>6</sub>-C<sub>22</sub> acyl group, such as Isopropyl Lauroyl Sarcosinate (Eldew SL 205 from Ajinomoto), in combination with organic UV screening agents which are difficult to dissolve in the oils commonly used in sun formulations. The combination of these amidated oils with a dibenzoylmethane derivative, such as 4-tert-butyl-4'-methoxydibenzoylmethane, does not make it possible to obtain a completely satisfactory dibenzoylmethane photostability.

The photostabilization of dibenzoylmethane derivatives with regard to UV radiation by amidated compounds thus constitutes, at the present time, a problem which has not yet been completely satisfactorily solved.

In point of fact, the Applicant Company has now just discovered, surprisingly, that, by combining the abovementioned dibenzoylmethane derivatives with a specific 2-pyrrolidinone-4-carboxy ester compound of formula (I) which will be defined in detail below, it is possible to further improve in a substantial and

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noteworthy way the photochemical stability (or photostability) of these same dibenzoylmethane derivatives and their effectiveness in the UV-A region. The compositions comprising such a combination also  
5 result, after application, in a more homogeneous distribution of the dibenzoylmethane screening agent.

This discovery forms the basis of the present invention.

Thus, in accordance with one of the subject-  
10 matters of the present invention, a composition is now provided comprising, in a cosmetically acceptable vehicle, at least one UV screening system, characterized in that it comprises:

- (a) at least one dibenzoylmethane derivative and
- 15 (b) at least one 2-pyrrolidinone-4-carboxy ester compound of formula (I), the definition of which will be given below.

Another subject-matter of the invention is also a method for improving the chemical stability with regard  
20 to UV radiation of at least one dibenzoylmethane derivative which consists in combining the said dibenzoylmethane derivative with an effective amount of at least one 2-pyrrolidinone-4-carboxy ester compound of formula (I), the definitions of which will be given  
25 below.

Another subject-matter of the present invention is the use of at least one 2-pyrrolidinone-4-carboxy ester compound of formula (I) in a composition comprising, in a cosmetically acceptable vehicle, at least one  
30 dibenzoylmethane derivative with the aim of improving the effectiveness of the said composition with regard to UV-A rays.

Other characteristics, aspects and advantages of the invention will become apparent on reading the

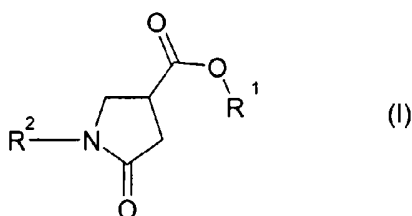


detailed description which will follow.

"Cosmetically acceptable" is understood to mean compatible with the skin and/or its superficial body growths, exhibiting a pleasant colour, a pleasant odour and a pleasant feel, and not causing unacceptable discomfort (smarting, tightness, redness) liable to dissuade the consumer from using this composition.

"Effective amount" is understood to mean an amount sufficient to produce a notable and significant improvement in the photostability of the dibenzoylmethane derivative or derivatives in the cosmetic composition. This minimum amount of 2-pyrrolidinone-4-carboxy ester compound of formula (I), which can vary according to the nature of the vehicle selected for the composition, can be determined without any difficulty by means of a conventional test for measuring photostability, such as that given in the examples below.

The 2-pyrrolidinone-4-carboxy ester compounds in accordance with the invention are chosen from those corresponding to the following general formula (I):



in which:

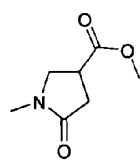
R<sup>1</sup> denotes a linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl radical,

R<sup>2</sup> denotes a linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl radical which can comprise a C<sub>5</sub>-C<sub>6</sub> ring, the phenyl radical, the benzyl radical or the phenethyl radical.

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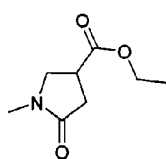
In the formula (I), mention may in particular be made, among the alkyl groups, of the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-octyl, 2-ethylhexyl, dodecyl, hexadecyl, cyclohexyl or methylcyclohexyl groups.

Among the compounds of formula (I), use will more particularly be made of the following products (a) to (oo):



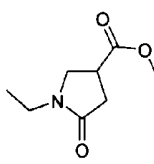
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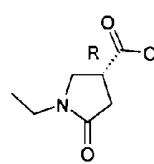
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(c)

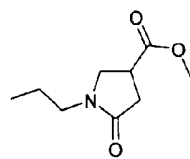
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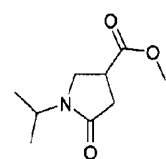
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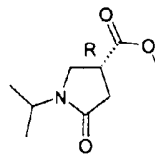
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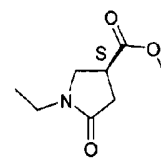
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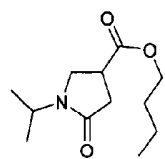
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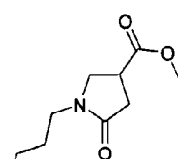
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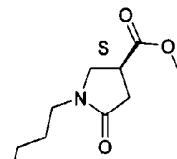
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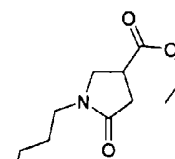
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(k)

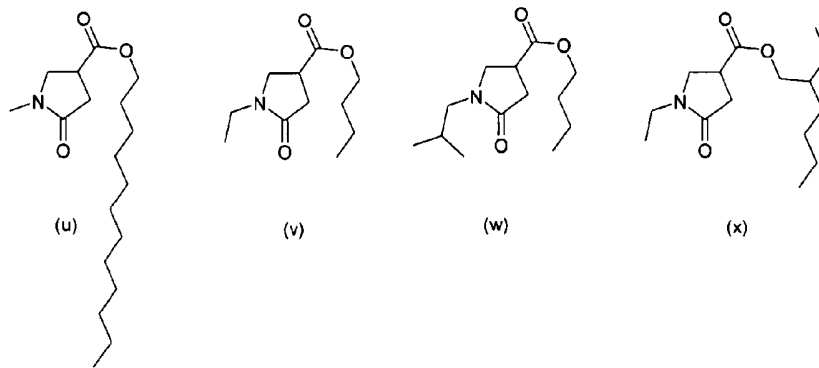
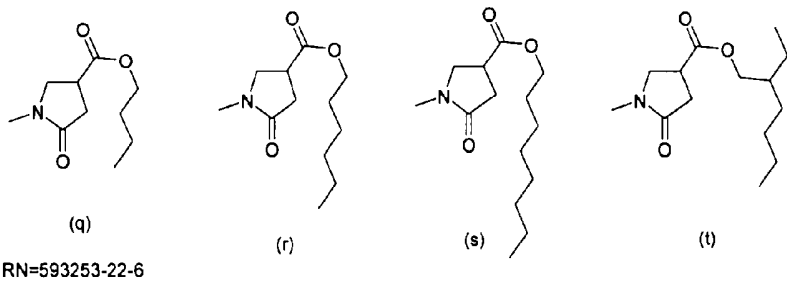
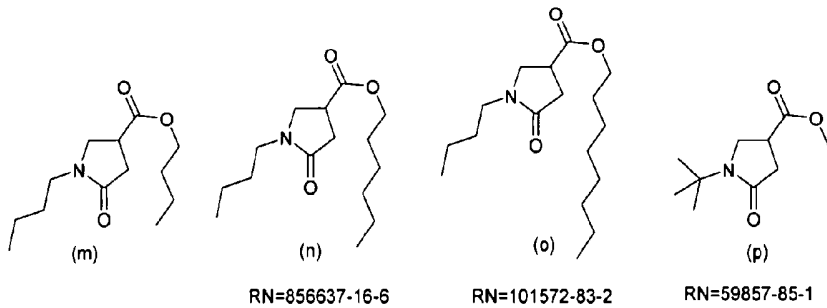
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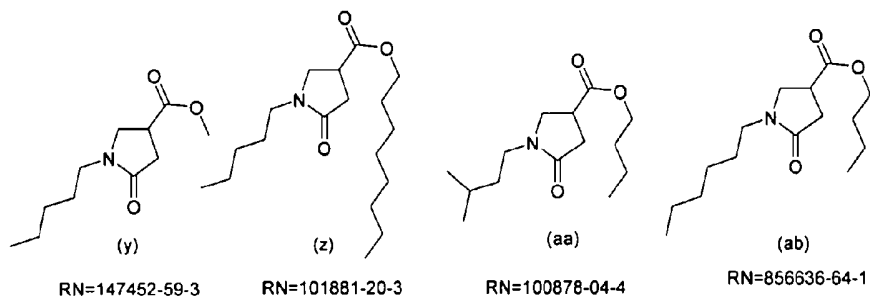
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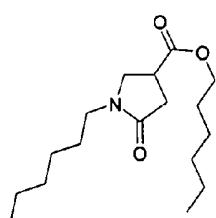
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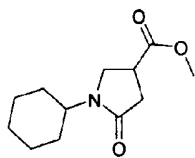
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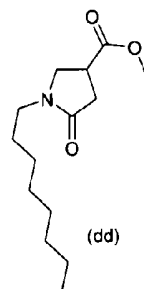
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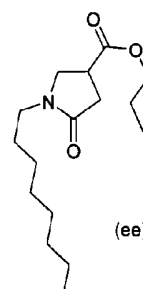
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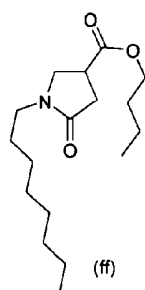
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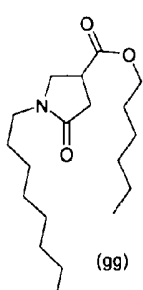
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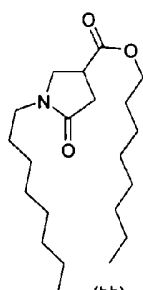
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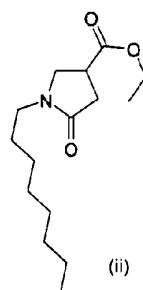
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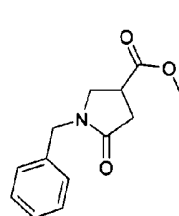
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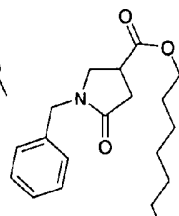
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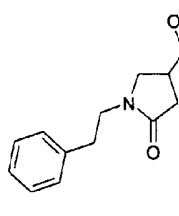


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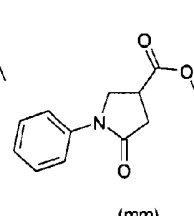


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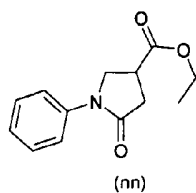
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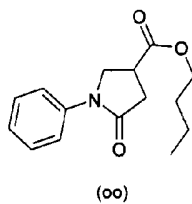


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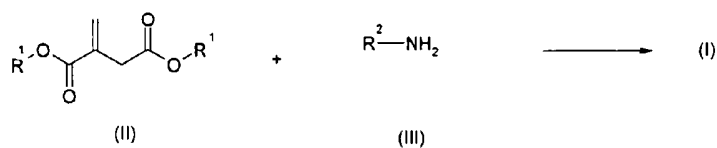


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Preference will more particularly be given to the compounds (j), (l), (m) and (n).

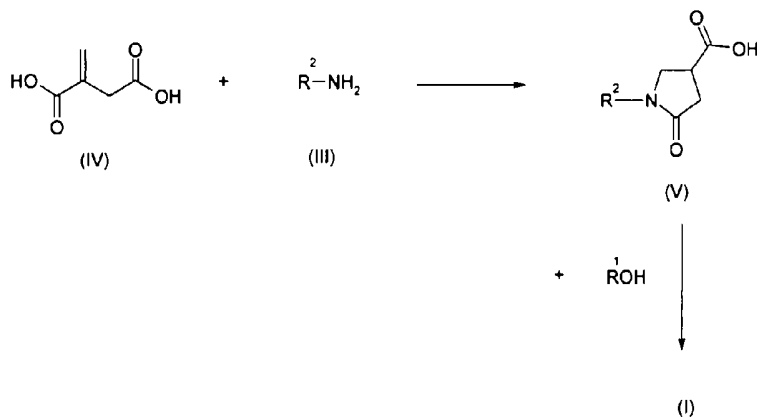
- 5 The derivatives of formula (I), the syntheses of which are described in the following papers: J. Org. Chem., 26, pages 1519-24 (1961); Tetrahedron Asymmetric, 12 (23), pages 3241-9 (2001); J. Industrial & Engineering Chem., 47, pages 1572-8 (1955); J. Am. Chem. Soc., 60, pages 402-6 (1938); and in Patents EP 0 069 512, US 2 811 496 (1955), US 2 826 588, US 3 136 620, FR 2 290 199 and FR 2 696 744, can be easily obtained:

- 15 - either by the condensation of a diester of itaconic acid of formula (II) with a primary amine of formula (III), with or without solvent, at a temperature of between 20°C and 150°C, according to the following scheme:



- 25 - or in 2 stages starting from itaconic acid of formula (IV) by condensation with the primary amine of formula (III) in or not in the presence of a solvent, in order to give the intermediate acid of formula (V), followed by an esterification of this acid of formula (V) in the

presence of an excess of alcohol of formula (VI),  
according to the following scheme:



5

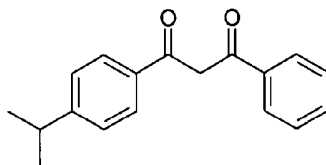
The 2-pyrrolidinone-4-carboxy ester compounds of  
formula (I) in accordance with the invention are  
preferably present in the compositions at contents of  
0.01 to 20% by weight and more preferably of 0.1 to 10%  
10 by weight, with respect to the total weight of the  
composition.

Mention may in particular be made, among the  
dibenzoylmethane derivatives, without implying a  
limitation, of:

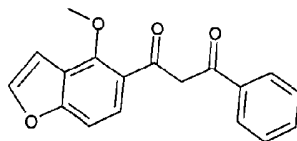
- 15 - 2-methyldibenzoylmethane,  
- 4-methyldibenzoylmethane,  
- 4-isopropyldibenzoylmethane,  
- 4-(tert-butyl)dibenzoylmethane,  
- 2,4-dimethyldibenzoylmethane,  
20 - 2,5-dimethyldibenzoylmethane,  
- 4,4'-diisopropyldibenzoylmethane,  
- 4,4'-dimethoxydibenzoylmethane,

- 4-(tert-butyl)-4'-methoxydibenzoylmethane,
  - 2-methyl-5-isopropyl-4'-methoxydibenzoylmethane,
  - 2-methyl-5-(tert-butyl)-4'-methoxydibenzoylmethane,
  - 2,4-dimethyl-4'-methoxydibenzoylmethane,
- 5 - 2,6-dimethyl-4-(tert-butyl)-4'-methoxydibenzoylmethane.

Use will in particular be made, among the abovementioned dibenzoylmethane derivatives, of 4-isopropylidibenzoylmethane, sold under the name of  
10 "Eusolex 8020" by Merck, which corresponds to the following formula:



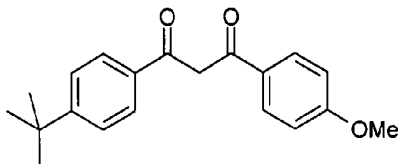
- 15 Mention may also be made of 1-(4-methoxy-1-benzofuran-5-yl)-3-phenylpropane-1,3-dione, provided for sale by Quest under the name of Pongamol, of formula:



20

- Preference is very particularly given to the use of 4-(tert-butyl)-4'-methoxydibenzoylmethane or Butyl Methoxy Dibenzoylmethane, provided for sale under the  
25 trade name of "Parsol 1789" by DSM Nutritional

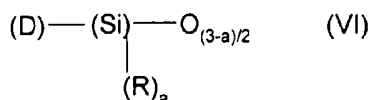
Products; this screening agent corresponds to the following formula:



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The dibenzoylmethane derivative or derivatives can be present in the compositions in accordance with the invention at contents which preferably vary from 0.01 to 10% by weight and more preferably from 0.1 to 6% by weight, with respect to the total weight of the composition.

According to a particularly preferred form of the invention, use will additionally be made, in the compositions of the invention, of a silicated s-triazine compound substituted by two aminobenzoate or aminobenzamide groups of following general formula (VI) or one of its tautomeric forms:



20

in which:

- R, which are identical or different, represent a linear or branched C<sub>1</sub>-C<sub>30</sub> alkyl radical which is optionally halogenated or unsaturated, a C<sub>6</sub>-C<sub>12</sub> aryl radical, a C<sub>1</sub>-C<sub>10</sub> alkoxy radical, a hydroxyl radical or the trimethylsilyloxy group;

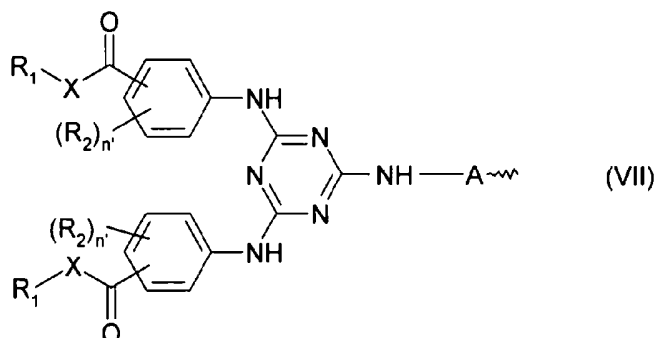
- a = 0 to 3; in addition to the units of formula



-A-(Si)(R)<sub>a</sub>(O)<sub>(3-a)/2</sub>, the organosiloxane can comprise units of formula: (R)<sub>b</sub>-(Si)(O)<sub>(4-b)/2</sub>, in which:

R has the same meaning as in the formula (II) and b = 1, 2 or 3;

- 5 - the group (D) denotes an s-triazine compound of following formula (VII):



10 where

- X represents -O- or -NR<sub>3</sub>-, with R<sub>3</sub> representing hydrogen or a C<sub>1</sub>-C<sub>5</sub> alkyl radical,

- R<sub>1</sub> represents a linear or branched C<sub>1</sub>-C<sub>30</sub> alkyl radical which is optionally unsaturated and which can comprise  
15 a silicon atom, a C<sub>5</sub>-C<sub>20</sub> cycloalkyl group, optionally substituted by 1 to 3 linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl radicals, the -(CH<sub>2</sub>CHR<sub>4</sub>-O)<sub>m</sub>R<sub>5</sub> group or the

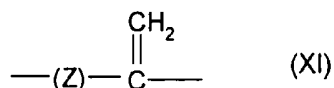
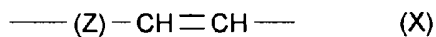
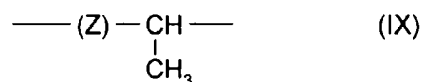
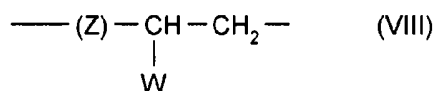
-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-O-R<sub>6</sub> group,

- R<sub>4</sub> represents hydrogen or methyl; it being possible  
20 for the (C=O)XR<sub>1</sub> group to be in the ortho, meta or para position with respect to the amino group,

- R<sub>5</sub> represents hydrogen or a C<sub>1</sub>-C<sub>8</sub> alkyl group,

- R<sub>6</sub> represents hydrogen or a C<sub>4</sub>-C<sub>8</sub> alkyl group,

- m is an integer ranging from 2 to 20,
- n' = 0 to 2,
- R<sub>2</sub>, which are identical or different, represent a hydroxyl radical, a linear or branched C<sub>1</sub>-C<sub>8</sub> alkyl radical or a C<sub>1</sub>-C<sub>8</sub> alkoxy radical, it being possible for two adjacent R<sub>2</sub> groups on the same aromatic nucleus to together form an alkylidenedioxy group in which the alkylidene group comprises 1 or 2 carbon atoms,
- A is a divalent radical chosen from methylene,
- [CH(Si(CH<sub>3</sub>)<sub>3</sub>)]-, ethylene or a group corresponding to one of the following formulae (VIII), (IX), (X) or (XI):

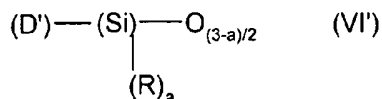


20 in which:

- Z is a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>10</sub> alkylene diradical which is optionally substituted by a hydroxyl radical or oxygen atoms and which can optionally comprise an amino group,
- W represents a hydrogen atom, a hydroxyl radical or a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>8</sub> alkyl radical.

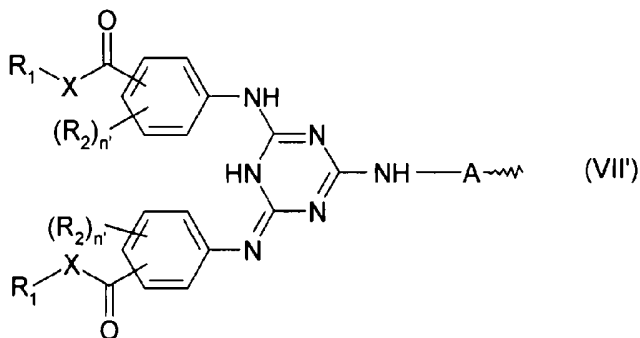
It should be noted that the derivatives of formula (VI) can be used in their tautomeric forms and more particularly in the tautomeric form of following formula (VI'):

5



in which the group (D') denotes an s-triazine compound of following formula (VII'):

10



The preferred s-triazine derivatives are those for which, in the formula (VII) or (VII'), at least one and more preferably still all of the following characteristics are met:

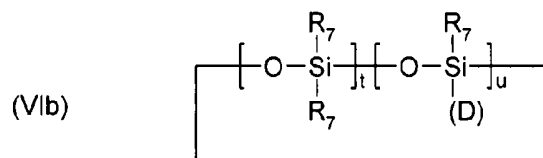
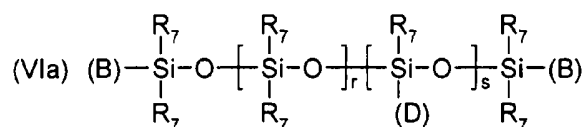
- 15
- R is methyl,
  - a = 1 or 2,
  - X is O,
  - 20 R<sub>1</sub> is a C<sub>4</sub>-C<sub>5</sub> radical,
  - n' = 0,

the (C=O)XR<sub>1</sub> group is in the para position with respect to the amino group,

Z = -CH<sub>2</sub>-,

W = H.

- 5 Preferably, the s-triazine compounds of the invention are represented by the following formulae (VIa), (VIb) and (VIc):



10

(VIc)

(D) - Si (R<sub>8</sub>)<sub>3</sub>

in which:

- 15 - (D) corresponds to the formula (VII) as defined above,
- R<sub>7</sub>, which are identical or different, are chosen from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl, phenyl, 3,3,3-trifluoropropyl and trimethylsilyloxy radicals or the
- 20 hydroxyl radical,
- R<sub>8</sub>, which are identical or different, are chosen from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl and alkenyl radicals, hydroxyl radicals or phenyl radicals,
- (B), which are identical or different, are chosen
- 25 from the R<sub>7</sub> radicals and the (D) radical,

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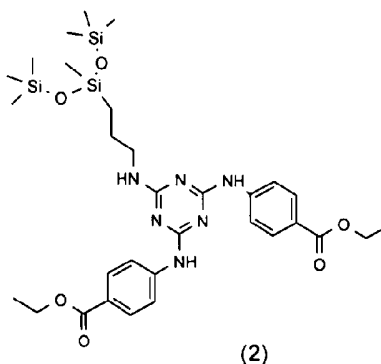
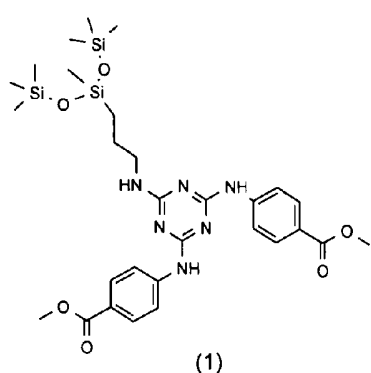
- r is an integer between 0 and 200 inclusive,
  - s is an integer ranging from 0 to 50 and, if s = 0, at least one of the two (B) symbols denotes (D),
  - u is an integer ranging from 1 to 10,
- 5 - t is an integer ranging from 0 to 10, it being understood that t + u is equal to or greater than 3, and their tautomeric forms.

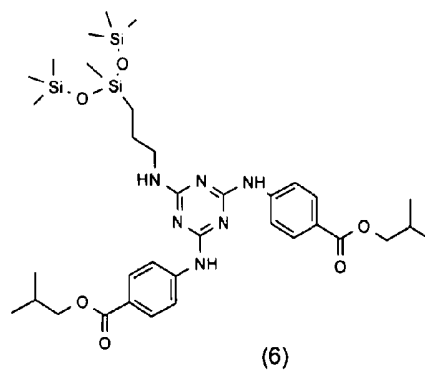
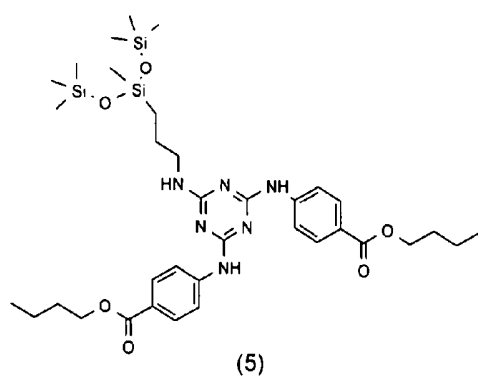
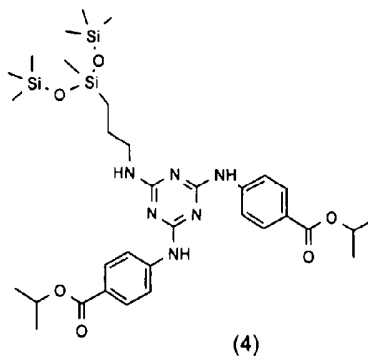
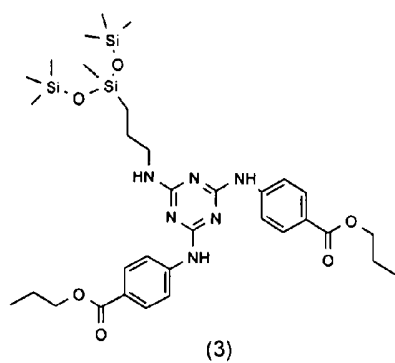
The linear diorganosiloxanes of formula (VIa) are particularly preferred.

- 10 The linear or cyclic diorganosiloxanes of formula (VIa) or (VIb) coming within the scope of the present invention are random oligomers or polymers preferably exhibiting at least one or more preferably still all of the following characteristics:

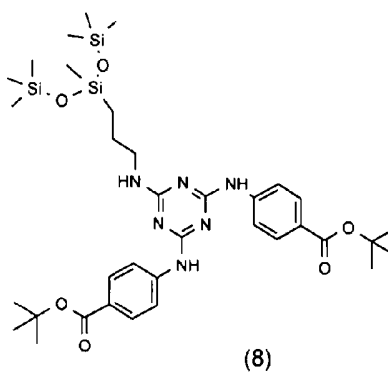
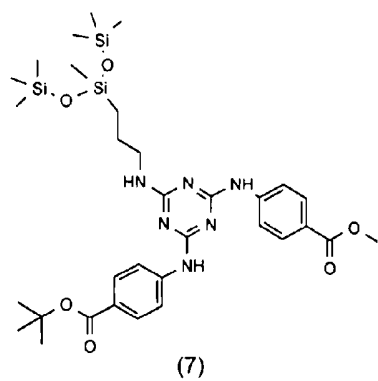
- 15 - R<sub>7</sub> is the methyl radical or the hydroxyl radical,  
 - B is preferably methyl (case of the linear compounds of formula (VIa)).

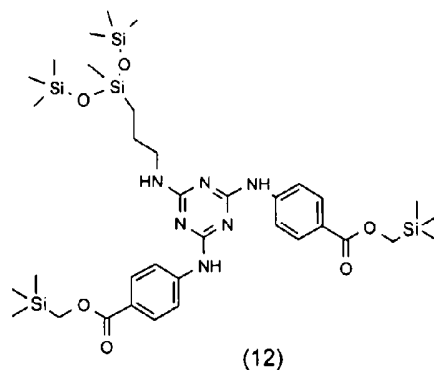
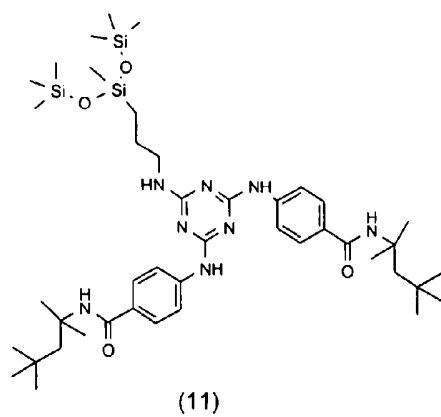
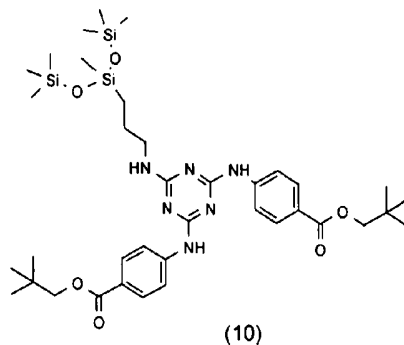
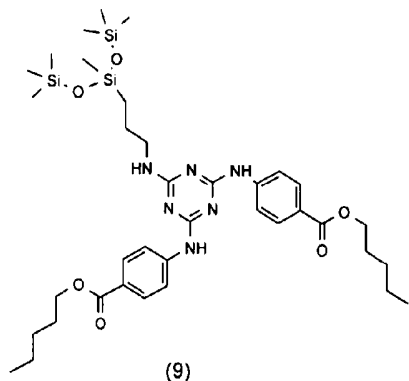
- Mention will be made, as examples of particularly preferred compounds of formula (VI), of the compounds  
 20 of following formulae (1) to (26) and their tautomeric forms:



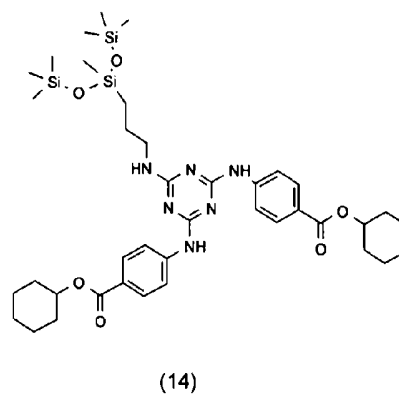
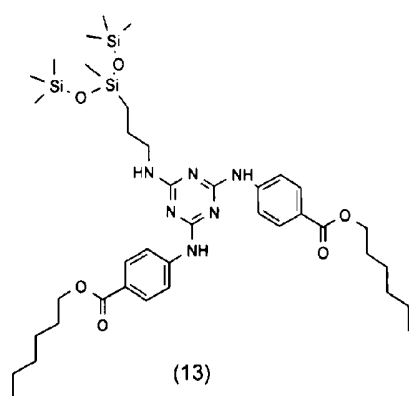


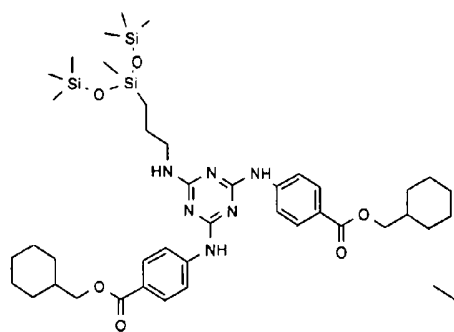
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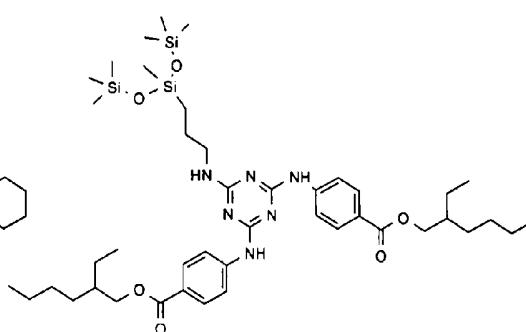


5

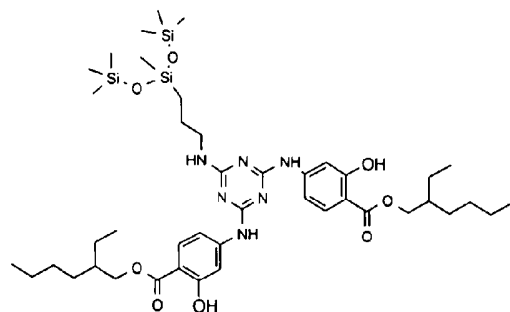




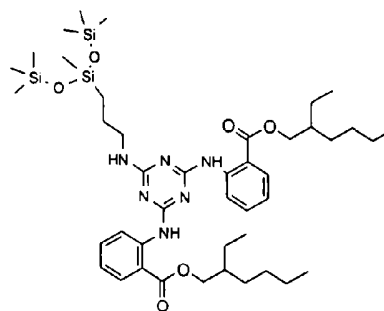
(15)



(16)

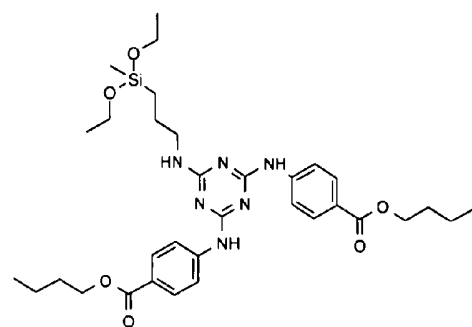


(17)

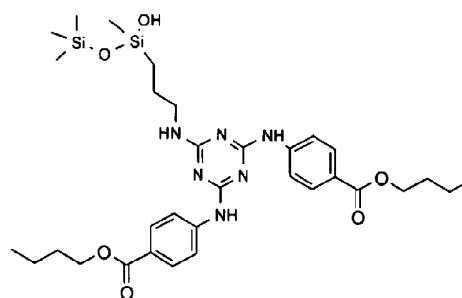


(18)

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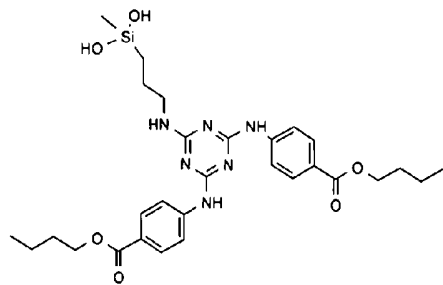


(19)

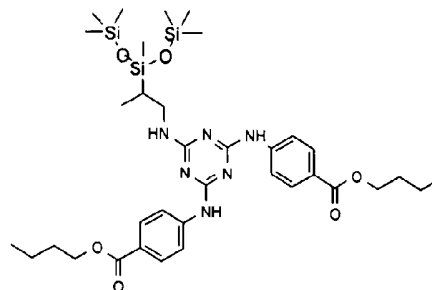


(20)



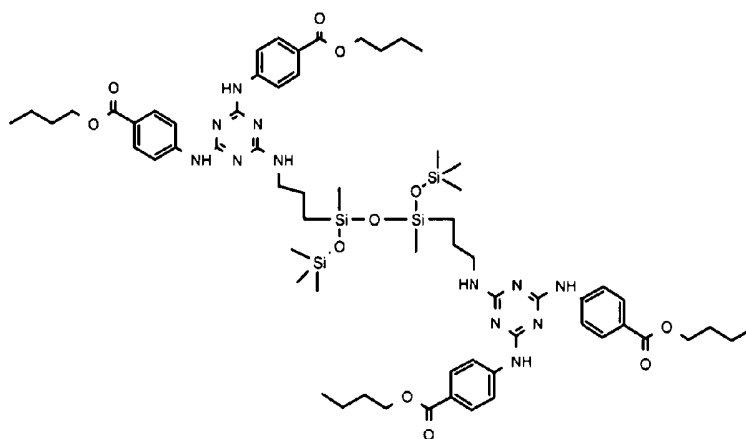


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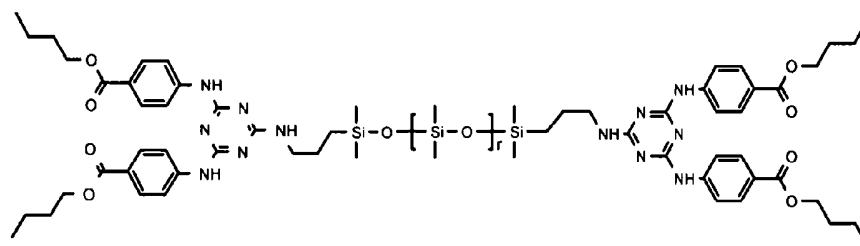


(22)

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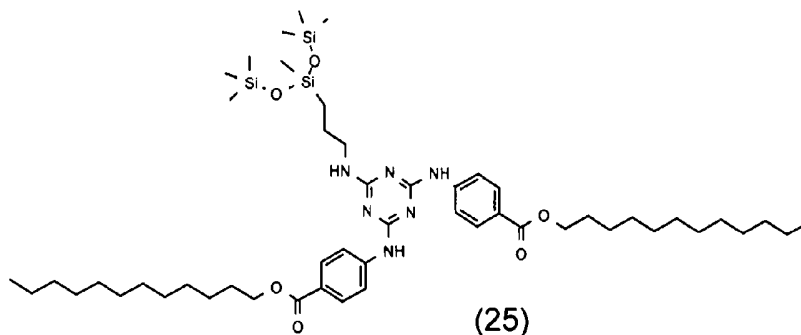


(23)



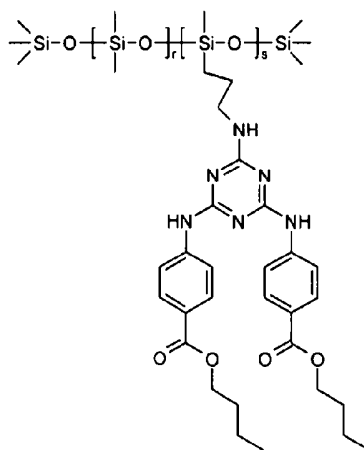
(24)

random r = 8.1



(25)

5

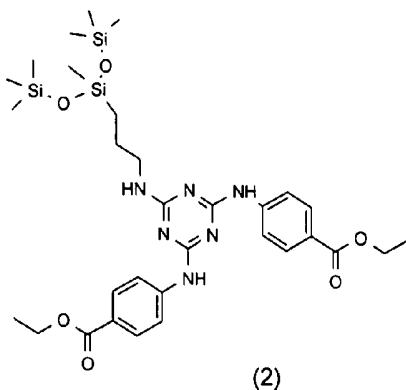


(26)

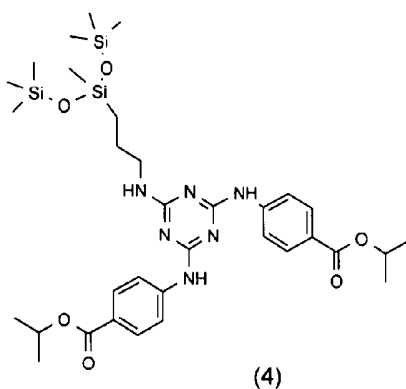
random r = 9 and random s = 1.8

Use will more particularly be made of the compounds chosen from:

- 5 - 2,4-bis(ethyl 4'-aminobenzoate)-6-[(3-{1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl}propyl)amino]-s-triazine of formula (2),

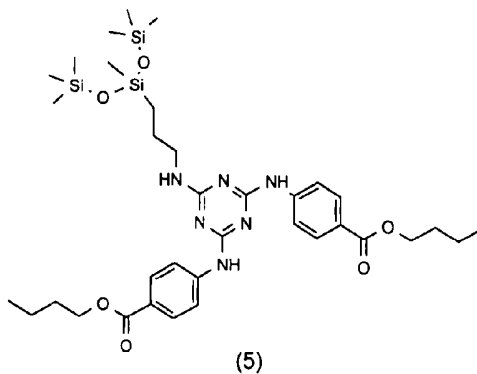


- 10 - 2,4-bis(isopropyl 4'-aminobenzoate)-6-[(3-{1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl}propyl)amino]-s-triazine of formula (4)

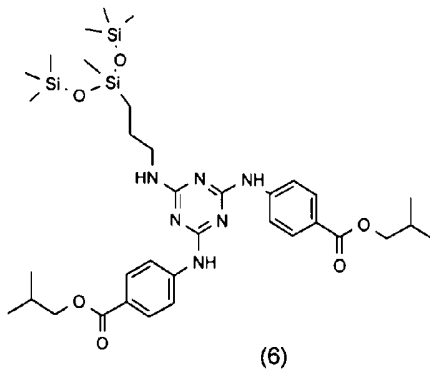


- 15 - 2,4-bis(n-butyl 4'-aminobenzoate)-6-[(3-{1,3,3,3-

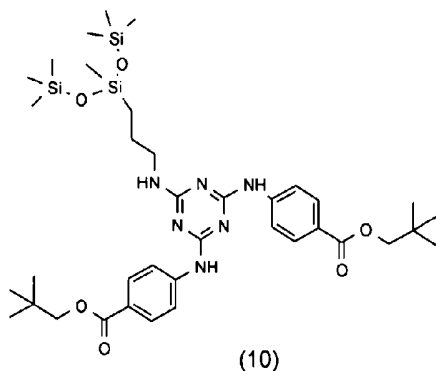
tetramethyl-1-[(trimethylsilyl)oxy]-  
disiloxanyl}propyl)amino]-s-triazine of formula (5)



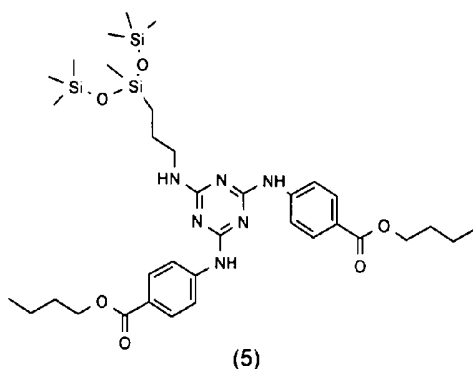
2,4-bis(isobutyl 4'-aminobenzoate)-6-[(3-{1,3,3,3-  
5 tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl}propyl)-  
amino]-s-triazine of formula (6)



10 - 2,4-bis(neopentyl 4'-aminobenzoate)-6-[(3-  
{1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]-  
disiloxanyl}propyl)amino]-s-triazine of formula (10)



Use will more particularly still be made of 2,4-  
 bis(n-butyl 4'-aminobenzoate)-6-[(3-{1,3,3,3-tetra-  
 5 methyl-1-[(trimethylsilyl)oxy]disiloxanyl}propyl)-  
 amino]-s-triazine of formula (5):



10 Some among the triazine compounds of formula (II)  
 and their tautomeric forms are known and have been  
 described in Patents EP 0 841 341 and FR 2 886 143.

The compositions according to the invention can  
 additionally comprise other additional organic UV  
 15 screening agents active in the UV-A and/or UV-B regions  
 which are water-soluble or fat-soluble or else  
 insoluble in the cosmetic solvents commonly used.

Of course, a person skilled in the art will take care to choose the optional additional screening agent or agents and/or their amounts so that the advantageous properties intrinsically attached to the compositions in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions, in particular the improvement in the photostability of the dibenzoylmethane derivative.

The additional organic screening agents are chosen in particular from anthranilates; cinnamic derivatives; salicylic derivatives; camphor derivatives; benzophenone derivatives;  $\beta,\beta$ -diphenylacrylate derivatives; triazine derivatives; benzotriazole derivatives; benzalmalonate derivatives, in particular those cited in Patent US 5 624 663; benzimidazole derivatives; imidazolines; bis-benzoazolyl derivatives, such as described in Patents EP 669 323 and US 2 463 264; p-aminobenzoic acid (PABA) derivatives;

methylenebis(hydroxyphenylbenzotriazole) derivatives, such as described in Applications US 5 237 071, US 5 166 355, GB 2 303 549, DE 197 26 184 and EP 893 119; benzoxazole derivatives, such as described in Patent Applications EP 0 832 642, EP 1 027 883, EP 1 300 137 and DE 10162844; screening polymers and screening silicones, such as those described in particular in Application WO 93/04665; dimers derived from  $\alpha$ -alkylstyrene, such as those described in Patent Application DE 19855649; 4,4-diarylbutadienes, such as described in Applications EP 0 967 200, DE 19746654, DE 19755649, EP-A-1 008 586, EP 1 133 980 and EP 133 981; merocyanine derivatives, such as those described in Applications WO04006878, WO05058269 and WO06032741; and their mixtures.

Mention may be made, as examples of additional organic photoprotective agents, of those denoted below under their INCI names:

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Cinnamic derivatives:

Ethylhexyl Methoxycinnamate, sold in particular under the trade name "Parsol MCX" by DSM Nutritional Products Inc.,

5 Isopropyl Methoxycinnamate,

Isoamyl Methoxycinnamate, sold under the trade name "Neo Heliopan E 1000" by Symrise,

DEA Methoxycinnamate,

Diisopropyl Methylcinnamate,

10 Glyceryl Ethylhexanoate Dimethoxycinnamate,

para-Aminobenzoic acid derivatives:

PABA,

Ethyl PABA,

15 Ethyl Dihydroxypropyl PABA,

Ethylhexyl Dimethyl PABA, sold in particular under the name "Escalol 507" by ISP,

Glyceryl PABA,

PEG-25 PABA, sold under the name "Uvinul P25" by BASF,

20

Salicylic derivatives:

Homosalate, sold under the name "Eusolex HMS" by Rona/EM Industries,

25 Ethylhexyl Salicylate, sold under the name "Neo Heliopan OS" by Symrise,

Dipropyleneglycol Salicylate, sold under the name "Dipsal" by Scher,

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TEA Salicylate, sold under the name "Neo Heliopan TS"  
by Symrise,

$\beta,\beta$ -Diphenylacrylate derivatives:

5 Octocrylene, sold in particular under the trade name  
"Uvinul N539" by BASF,

Etocrylene, sold in particular under the trade name  
"Uvinul N35" by BASF,

Benzophenone derivatives:

10 Benzophenone-1, sold under the trade name "Uvinul 400"  
by BASF,

Benzophenone-2, sold under the trade name "Uvinul D50"  
by BASF,

15 Benzophenone-3 or Oxybenzone, sold under the trade  
name "Uvinul M40" by BASF,

Benzophenone-4, sold under the trade name "Uvinul  
MS40" by BASF,

Benzophenone-5,

20 Benzophenone-6, sold under the trade name "Helisorb  
11" by Norquay,

Benzophenone-8, sold under the trade name "Spectra-  
Sorb UV-24" by American Cyanamid,

Benzophenone-9, sold under the trade name "Uvinul DS-  
49" by BASF,

25 Benzophenone-12,

n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate,  
sold under the trade name "Uvinul A+" by BASF,

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Benzylidenecamphor derivatives:

3-Benzylidene camphor, manufactured under the name  
"Mexoryl SD" by Chimex,

5 4-Methylbenzylidene camphor, sold under the name  
"Eusolex 6300" by Merck,

Benzylidene Camphor Sulfonic Acid, manufactured under  
the name "Mexoryl SL" by Chimex,

Camphor Benzalkonium Methosulfate, manufactured under  
the name "Mexoryl SO" by Chimex,

10 Terephthalylidene Dicumphor Sulfonic Acid,  
manufactured under the name "Mexoryl SX" by Chimex,

Polyacrylamidomethyl Benzylidene Camphor, manufactured  
under the name "Mexoryl SW" by Chimex,

15 Phenylbenzimidazole derivatives:

Phenylbenzimidazole Sulfonic Acid, sold in particular  
under the trade name "Eusolex 232" by Merck,

Disodium Phenyl Dibenzimidazole Tetrasulfonate, sold  
under the trade name "Neo Heliopan AP" by Symrise,

20

Phenylbenzotriazole derivatives:

Drometrizole Trisiloxane, sold under the name  
"Silatrizole" by Rhodia Chimie,

25 Methylene Bis-Benzotriazolyl Tetramethylbutylphenol,  
sold in the solid form under the trade name "Mixxim  
BB/100" by Fairmount Chemical or in the micronized  
form in aqueous dispersion under the trade name  
"Tinosorb M" by Ciba Specialty Chemicals,

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Triazine derivatives:

Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, sold under the trade name "Tinosorb S" by Ciba-Geigy,

5 Ethylhexyl Triazone, sold in particular under the trade name "Uvinul T150" by BASF,

Diethylhexyl Butamido Triazone, sold under the trade name "Uvasorb HEB" by Sigma 3V,

2,4,6-Tris(dineopentyl 4'-aminobenzalmalonate)-s-triazine,

10 2,4,6-Tris(diisobutyl 4'-aminobenzalmalonate)-s-triazine,

2,4-Bis(dineopentyl 4'-aminobenzalmalonate)-6-(n-butyl 4'-aminobenzoate)-s-triazine,

15 The symmetrical triazine screening agents described in Patent US 6 225 467, Application WO 2004/085412 (see compounds 6 and 9) or the document "Symmetrical Triazine Derivatives", IP.COM Journal, IP.COM INC, WEST HENRIETTA, NY, US (20 September 2004), in particular the 2,4,6-tris(biphenyl)-1,3,5-triazines  
20 (especially 2,4,6-tris(biphenyl-4-yl)-1,3,5-triazine) and 2,4,6-tris(terphenyl)-1,3,5-triazine, which are taken up again in Patent Applications WO 06/035000, WO 06/034982, WO 06/034991, WO 06/035007, WO 2006/034992 and WO 2006/034985.

25

Anthranilic derivatives:

Menthyl anthranilate, sold under the trade name "Neo Heliopan MA" by Symrise,

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Imidazoline derivatives:

Ethylhexyl Dimethoxybenzylidene Dioxoimidazoline  
Propionate,

Benzalmalonate derivatives:

- 5 Polyorganosiloxane comprising benzalmalonate  
functional groups, such as Polysilicone-15, sold under  
the trade name "Parsol SLX" by DSM Nutritional  
Products Inc.,

10 4,4-Diarylbutadiene derivatives:

1,1-Dicarboxy(2,2'-dimethylpropyl)-4,4-  
diphenylbutadiene,

Benzoxazole derivatives:

- 15 2,4-bis[5-1(dimethylpropyl)benzoxazol-2-yl-(4-  
phenyl)imino]-6-(2-ethylhexyl)imino-1,3,5-triazine,  
sold under the name of Uvasorb K2A by Sigma 3V,

Merocyanine derivatives:

- 20 Octyl 5-N,N-diethylamino-2-phenylsulphonyl-2,4-  
pentadienoate,  
  
and their mixtures.

- 25 The preferred organic screening agents are chosen  
from:

Ethylhexyl Methoxycinnamate,

Ethylhexyl Salicylate,

Homosalate,

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- Octocrylene,  
Phenylbenzimidazole Sulfonic Acid,  
Benzophenone-3,  
Benzophenone-4,  
5 Benzophenone-5,  
n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate,  
4-Methylbenzylidene Camphor,  
Terephthalylidene Dicumyl Sulfonic Acid,  
Disodium Phenyl Dibenzimidazole Tetrasulfonate,  
10 Methylene Bis-Benzotriazolyl Tetramethylbutylphenol,  
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine,  
Ethylhexyl Triazone,  
Diethylhexyl Butamido Triazone,  
2,4,6-Tris(dineopentyl 4'-aminobenzalmalonate)-s-  
15 triazine,  
2,4,6-Tris(diisobutyl 4'-aminobenzalmalonate)-s-  
triazine,  
2,4-Bis(n-butyl 4'-aminobenzoate)-6-(aminopropyltri-  
siloxane)-s-triazine,  
20 2,4-Bis(dineopentyl 4'-aminobenzalmalonate)-6-(n-butyl  
4'-aminobenzoate)-s-triazine,  
2,4,6-Tris(biphenyl-4-yl)-1,3,5-triazine,  
2,4,6-Tris(terphenyl)-1,3,5-triazine,  
Drometrizole Trisiloxane,  
25 Polysilicone-15,

1,1-Dicarboxy(2,2'-dimethylpropyl)-4,4-diphenylbutadiene,

2,4-Bis[5-1(dimethylpropyl)benzoxazol-2-yl-(4-phenyl)imino]-6-(2-ethylhexyl)imino-1,3,5-triazine,

5 Octyl 5-N,N-diethylamino-2-phenylsulphonyl-2,4-pentadienoate,

and their mixtures.

The additional organic screening agents in accordance with the invention generally represent from  
10 0.1 to 30%, preferably from 1 to 25%, of the total weight of the composition.

Of course, a person skilled in the art will take care to choose the optional additional screening agent or agents and/or their amounts so that the advantageous  
15 properties intrinsically attached to the compositions in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions.

The compositions according to the invention can also comprise agents for the artificial tanning and/or  
20 browning of the skin (self-tanning agents) and more particularly dihydroxyacetone (DHA). They are preferably present in amounts ranging from 0.1 to 10% by weight, with respect to the total weight of the  
25 composition.

The aqueous compositions in accordance with the present invention can additionally comprise conventional cosmetic adjuvants chosen in particular from fatty substances, organic solvents, ionic or  
30 nonionic and hydrophilic or lipophilic thickeners, softening agents, humectants, opacifiers, stabilizing agents, emollients, silicones, antifoaming agents, fragrances, preservatives, anionic, cationic, nonionic, zwitterionic or amphoteric surfactants, active

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principles, fillers, polymers, propellants, basifying or acidifying agents or any other ingredient commonly used in the cosmetics and/or dermatological field.

Of course, a person skilled in the art will take  
5 care to choose the optional additive or additives  
and/or their amounts so that the advantageous  
properties intrinsically attached to the compositions  
in accordance with the invention are not, or not  
substantially, detrimentally affected by the envisaged  
10 addition or additions.

The fatty substances can be composed of an oil or  
a wax, other than the nonpolar waxes as defined above,  
or their mixtures. The term "oil" is understood to  
mean a compound which is liquid at ambient  
15 temperature. The term "wax" is understood to mean a  
compound which is solid or substantially solid at  
ambient temperature and which has a melting point  
generally of greater than 35°C.

Mention may be made, as oils, of mineral oils  
20 (liquid paraffin); vegetable oils (sweet almond,  
macadamia, blackcurrant seed or jojoba oil); synthetic  
oils, such as perhydrosqualene, fatty alcohols, fatty  
amides (such as isopropyl lauroyl sarcosinate, sold  
under the name of "Eldew SL-205" by Ajinomoto), fatty  
25 acids or esters (such as C<sub>12</sub>-C<sub>15</sub> alkyl benzoate, sold  
under the trade name "Finsolv TN" or "Witconol TN" by  
Witco, 2-ethylphenyl benzoate, such as the commercial  
product sold under the name X-Tend 226® by ISP, octyl  
palmitate, isopropyl lanolate, triglycerides,  
30 including those of capric/caprylic acids, or  
dicaprylyl carbonate, sold under the name "Cetiol CC"  
by Cognis), or oxyethylenated or oxypropylenated fatty  
esters and ethers; silicone oils (cyclomethicone,  
polydimethylsiloxanes or PDMSs); fluorinated oils; or  
35 polyalkylenes.

Mention may be made, as waxy compounds, of carnauba wax, beeswax, hydrogenated castor oil, polyethylene waxes and polymethylene waxes, such as that sold under the name Cirebelle 303 by Sasol.

5           Mention may be made, among organic solvents, of lower alcohols and polyols. The latter can be chosen from glycols and glycol ethers, such as ethylene glycol, propylene glycol, butylene glycol, dipropylene glycol or diethylene glycol.

10           Mention may be made, as hydrophilic thickeners, of carboxyvinyl polymers, such as the Carbopols (Carbomers) and the Pemulens (acrylate/C<sub>10</sub>-C<sub>30</sub>-alkyl acrylate copolymer); polyacrylamides, such as, for example, the crosslinked copolymers sold under the  
15 names Sepigel 305 (CTFA name: polyacrylamide/C13-14 isoparaffin/Laureth 7) or Simulgel 600 (CTFA name: acrylamide/sodium acryloyldimethyltaurate copolymer/ isohexadecane/polysorbate 80) by Seppic; optionally crosslinked and/or neutralized polymers and copolymers  
20 of 2-acrylamido-2-methylpropanesulphonic acid, such as the poly(2-acrylamido-2-methylpropanesulphonic acid) sold by Hoechst under the trade name "Hostacerin AMPS" (CTFA name: ammonium polyacryloyldimethyl taurate) or Simulgel 800, sold by Seppic (CTFA name: sodium  
25 polyacryloyldimethyl taurate/polysorbate 80/sorbitan oleate); copolymers of 2-acrylamido-2-methylpropanesulphonic acid and of hydroxyethyl acrylate, such as Simulgel NS and Sepinov EMT 10, sold by Seppic; cellulose derivatives, such as  
30 hydroxyethylcellulose; polysaccharides and in particular gums, such as xanthan gum; and their mixtures.

Mention may be made, as lipophilic thickeners, of synthetic polymers, such as the poly(C<sub>10</sub>-C<sub>30</sub> alkyl  
35 acrylates) sold under the names "Intelimer IPA 13-1" and "Intelimer IPA 13-6" by Landec, or of modified

clays, such as hectorite and its derivatives, such as the products sold under the Bentone names.

Mention may be made, among active principles, of:

- 5 - vitamins (C, K, PP, and the like) and their derivatives or precursors, alone or as mixtures;
- agents for combating pollution and/or agents for combating free radicals;
- depigmenting agents and/or propigmenting agents;
- antiglycation agents;
- 10 - soothing agents;
- NO-synthase inhibitors;
- agents which stimulate the synthesis of dermal or epidermal macromolecules and/or which prevent their decomposition;
- 15 - agents which stimulate the proliferation of fibroblasts;
- agents which stimulate the proliferation of keratinocytes;
- muscle-relaxing agents;
- 20 - tightening agents;
- matifying agents;
- keratolytic agents;
- desquamating agents;
- moisturizing agents;
- 25 - antiinflammatory agents;
- agents which act on the energy metabolism of the cells;



- insect repellents;
- substance P or substance CRGP antagonists;
- agents for combating hair loss and/or for the regrowth of the hair;
- 5 - antiwrinkle agents.

The compositions according to the invention can be prepared according to techniques well known to a person skilled in the art. They can in particular be provided in the form of a simple or complex (O/W, W/O, 10 O/W/O or W/O/W) emulsion, such as a cream or a milk, or of a cream gel; in the form of an aqueous gel; in the form of a lotion. They can optionally be packaged as an aerosol and be provided in the foam or spray form.

15 Preferably, the compositions according to the invention are provided in the form of an oil-in-water or water-in-oil emulsion.

The emulsions generally comprise at least one emulsifier chosen from amphoteric, anionic, cationic 20 or nonionic emulsifiers, used alone or as a mixture. The emulsifiers are appropriately chosen according to the emulsion to be obtained (W/O or O/W emulsion). The emulsions can also comprise other types of stabilizing agents, such as, for example, fillers or gelling or 25 thickening polymers.

Mention may be made, as emulsifying surfactants which can be used for the preparation of the W/O emulsions, for example, of sorbitan, glycerol or sugar alkyl esters or ethers; silicone surfactants, such as 30 dimethicone copolyols, for example the mixture of cyclomethicone and of dimethicone copolyol sold under the name "DC 5225 C" by Dow Corning, and alkyl dimethicone copolyols, such as lauryl methicone copolyol, sold under the name "Dow Corning 5200

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Formulation Aid" by Dow Corning; cetyl dimethicone copolyol, such as the product sold under the name Abil EM 90R by Goldschmidt, and the mixture of cetyl dimethicone copolyol, of polyglycerol (4 mol) isostearate and of hexyl laurate sold under the name Abil WE 09 by Goldschmidt. It is also possible to add thereto one or more coemulsifiers which, advantageously, can be chosen from the group consisting of polyol alkyl esters.

10           Mention may in particular be made, as polyol alkyl esters, of polyethylene glycol esters, such as PEG-30 dipolyhydroxystearate, such as the product sold under the name Arlancel P135 by ICI.

15           Mention may be made, as esters of glycerol and/or of sorbitan, for example, of polyglycerol isostearate, such as the product sold under the name Isolan GI 34 by Goldschmidt; sorbitan isostearate, such as the product sold under the name Arlancel 987 by ICI; glycerol sorbitan isostearate, such as the product sold under the name Arlancel 986 by ICI, and their mixtures.

20           Mention may be made, for the O/W emulsions, for example, as emulsifiers, of nonionic emulsifiers, such as oxyalkylenated (more particularly polyoxyethylenated) esters of fatty acids and of glycerol; oxyalkylenated esters of fatty acids and of sorbitan; oxyalkylenated (oxyethylenated and/or oxypropylenated) fatty acid esters, such as the PEG-100 stearate/glyceryl stearate mixture sold, for example, by ICI under the name Arlancel 165; oxyalkylenated (oxyethylenated and/or oxypropylenated) fatty alcohol ethers; sugar esters, such as sucrose stearate; ethers of fatty alcohol and of sugar, in particular alkyl polyglucosides (APG), such as decyl glucoside and lauryl glucoside, for example sold by 35 Henkel under the respective names Plantaren 2000 and

Plantaren 1200, cetearyl glucoside, optionally as a mixture with cetearyl alcohol, for example sold under the name Montanov 68 by Seppic, under the name Tegocare CG90 by Goldschmidt and under the name

5 Emulgade KE3302 by Henkel, and arachidyl glucoside, for example in the form of the mixture of arachidyl and behenyl alcohols and of arachidyl glucoside sold under the name Montanov 202 by Seppic. According to a specific embodiment of the invention, the mixture of

10 the alkyl polyglucoside as defined above with the corresponding fatty alcohol can be in the form of a self-emulsifying composition, for example as disclosed in the document WO-A-92/06778.

Use will more particularly be made, among other emulsion stabilizers, of polymers of isophthalic acid or sulphoisophthalic acid and in particular the phthalate/sulphoisophthalate/glycol copolymers, for example the diethyleneglycol/

phthalate/isophthalate/1,4-cyclohexanedimethanol

20 copolymer (INCI name: Polyester-5) sold under the names "Eastman AQ polymer" (AQ35S, AQ38S, AQ55S, AQ48 Ultra) by Eastman Chemical.

When an emulsion is involved, the aqueous phase of the latter can comprise a nonionic vesicular

25 dispersion prepared according to known methods (Bangham, Standish and Watkins, J. Mol. Biol., 13, 238 (1965), FR 2 315 991 and FR 2 416 008).

The compositions according to the invention have applications in a large number of treatments, in

30 particular cosmetic treatments, of the skin, lips and hair, including the scalp, in particular for protecting and/or caring for the skin, lips and/or hair and/or for making up the skin and/or lips.

Another subject-matter of the present invention

35 is composed of the use of the compositions according

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to the invention as defined above in the manufacture  
of products for the cosmetic treatment of the skin,  
lips, nails, hair, eyelashes, eyebrows and/or scalp,  
in particular of care products, sun protection  
5 products and makeup products.

The cosmetic compositions according to the  
invention can, for example, be used as makeup product.

The cosmetic compositions according to the  
invention can, for example, be used as care product  
10 and/or sun protection product for the face and/or body  
with a liquid to semi-liquid consistency, such as  
milks, relatively smooth creams, cream gels or pastes.  
They can optionally be packaged in an aerosol and be  
provided in the foam or spray form.

15 The compositions according to the invention in  
the form of vaporizable fluid lotions in accordance  
with the invention are applied to the skin or hair in  
the form of fine particles by means of pressurizing  
devices. The devices in accordance with the invention  
20 are well known to a person skilled in the art and  
comprise non-aerosol pumps or "atomizers", aerosol  
containers comprising a propellant and aerosol pumps  
using compressed air as propellant. The latter are  
disclosed in Patents US 4 077 441 and US 4 850 517  
25 (forming an integral part of the content of the  
description).

The compositions packaged as an aerosol in  
accordance with the invention generally comprise  
conventional propellants, such as, for example,  
30 hydrofluorinated compounds, dichlorodifluoromethane,  
difluoroethane, dimethyl ether, isobutane, n-butane,  
propane or trichlorofluoromethane. They are preferably  
present in amounts ranging from 15 to 50% by weight,  
with respect to the total weight of the composition.

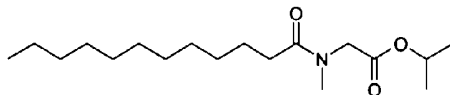
The following examples serve to illustrate the invention. In these examples, the amounts of the ingredients in the compositions are given as % by weight, with respect to the total weight of the composition.

#### EXAMPLES 1 to 4

##### 1. Photostability of the dibenzoylmethane

The photostabilizing effect of the 2-pyrrolidinone-4-carboxy ester compounds of formula (I) in accordance with the invention was evaluated with respect to the dibenzoylmethane derivative: Butyl Methoxy Dibenzoylmethane (avobenzene), provided for sale under the trade name "Parsol 1789" by Roche Vitamins (Examples 1, 2, 3 and 4).

The photostabilizing effect of these 2-pyrrolidinone-4-carboxy ester derivatives was also compared with that of Isopropyl Lauroyl Sarcosinate (Example A) of formula:



RN=230309-38-3  
Eldew SL-205

Example B comprises neither pyrrolidone-4-carboxy ester compound nor isopropyl lauroyl sarcosinate.

Phase	Ingredients	A	B	1	2	3	4
Fatty	C <sub>12</sub> -C <sub>15</sub> Alkyl benzoate	10.0	10.0	10.0	10.0	10.0	10.0

	Cetearyl alcohol and cetearyl glucoside	7.5	7.5	7.5	7.5	7.5	7.5
	Butyl Methoxy Dibenzoylmethane	1.0	1.0	1.0	1.0	1.0	1.0
	Isopropyl Lauroyl Sarcosinate	10.0	-	-	-	-	-
	Compound j	-	-	10.0	-	-	-
	Compound l	-	-	-	10.0	-	-
	Compound m	-	-	-	-	10.0	-
	Compound n	5.0	5.0	5.0	5.0	5.0	10.0
Aqueous	Water	q.s. for 100	q.s. for 100	q.s. for 100	q.s. for 100	q.s. for 100	q.s. for 100

**PRINCIPLE OF THE METHOD:**

The percentage of loss of dibenzoylmethane derivative brought about by the exposure to a solar simulator of a formulation spread as films with a thickness of approximately 20  $\mu\text{m}$  is measured. Evaluation is carried out by HPLC analysis of the screening agent in solution, after extraction of the films, by comparing irradiated and nonirradiated samples.

**EQUIPMENT AND METHOD:**

Solar simulator: Oriel 1000W device equipped with a 4-inch outlet, having an 81017 filter and a dichroic mirror. The samples are exposed in a horizontal

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position. The UV-meter used is the Osram Centra device equipped with 2 reading heads, one for UV-A radiation and the other for UV-B radiation. The simulator/UV-meter assembly is calibrated annually by  
5 spectroradiometry. The irradiance measurements are carried out at the beginning and at the end of exposure by placing the reading heads at the position of the sample. The irradiances are:

- 0.35 - 0.45 mW/cm<sup>2</sup> in UV-B radiation
- 10 16 - 18 mW/cm<sup>2</sup> in UV-A radiation.

The residual Butyl Methoxy Dibenzoylmethane is measured by chromatography: HPLC line with diode array detector. The 2-pyrrolidinone-4-carboxy ester derivatives are introduced into the common vehicle  
15 defined above at a concentration of 10% in the presence of 1% of Butyl Methoxy Dibenzoylmethane with the composition: The loss of Butyl Methoxy Dibenzoylmethane (avobenzone) after irradiation in the  
20 same vehicle not comprising compound of formula (I) (Composition B) is also measured.

**IMPLEMENTATION OF THE PHOTOSTABILITY TESTS**

Approximately 20 mg of each formulation tested are spread over a surface area of 10 cm<sup>2</sup> on a ground  
25 face of a fused silica disc. The exact amount is determined by weighing. 3 films are exposed to the solar simulator and 3 others act as a control. The samples are exposed 3 by 3 to the light of the solar simulator for a time sufficient to deliver a UV-A dose  
30 equal to 12J corrected for the sensitivity of the UV-meter, corresponding to the decomposition of approximately 50% of the Butyl Methoxy Dibenzoylmethane (avobenzone) in the absence of photoprotective agent. At the end of the exposure,  
35 each support disc is introduced into a 600 ml

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container with 10 ml of an appropriate solvent (generally EtOH); the assembly is placed in an ultrasonic bath for 5 minutes. The solution is subsequently transferred into flasks suitable for the vehicle compatible with the HPLC analytical device used. The analytical conditions can be adjusted according to the active principle tested. The residual levels are calculated from the means obtained with regard to the irradiated and nonirradiated samples, as described below:

TABLE I

Examples	Amidated compound	Residual % level of avobenzene
Example A	Eldew SL-205	64.2 ± 0.45
Example B	none	19.8 ± 0.8
Example 1	Compound (j)	72.8 ± 2.0
Example 2	Compound (l)	74.5 ± 2.7
Example 3	Compound (m)	78.5 ± 1.4
Example 4	Compound (n)	70.9 ± 1.3

The 2-pyrrolidinone-4-carboxy ester compounds of formulae (j), (l), (m) and (n) of Examples 1 to 4 according to the invention have a photostabilizing effect with regard to the dibenzoylmethane derivative which is better than that obtained with Isopropyl Lauroyl Sarcosinate.

**2. Formulation stability of the compositions:**

The thermal stabilities of Examples 1, 2, 3 and 4 corresponding to the derivatives of the invention are compared with formulation C, which is identical to

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formulation A but which comprises, in place of Isopropyl Lauroyl Sarcosinate, the amidated compound ethyl N-butyl-N-acetylaminopropionate (R3535, Merck). The appearance of each formulation after storing in an oven at 45°C for 2 months is observed with the naked eye (macroscopic appearance).

<b>Compositions</b>	<b>Macroscopic and microscopic appearance at a time of 2 months at 45°C</b>
Formulation 1 comprising compound (j)	The emulsion remains stable and homogeneous
Formulation 2 comprising compound (l)	The emulsion remains stable and homogeneous
Formulation 3 comprising compound (m)	The emulsion remains stable and homogeneous
Formulation 4 comprising compound (n)	The emulsion remains stable and homogeneous
Formulation C comprising ethyl N-butyl-N-acetylaminopropionate (R3535)	Phase separation is observed

It is clearly observed that, compared with ethyl N-butyl-N-acetylaminopropionate (R3535) as described in EP 717 982, compounds (j), (l), (m) and (n) of formula (I) according to the invention make it possible to obtain a good stable dispersion of the oil in the composition and, at the end, good formulation stability.

It is to be understood that, if any prior art publication is referred to herein, such reference does

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not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

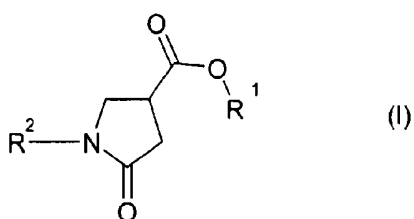
5 In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of  
10 the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

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## THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Composition comprising, in a cosmetically acceptable vehicle, at least one UV screening system, characterized in that it comprises:

- 5 (a) at least one dibenzoylmethane derivative and  
 (b) at least one 2-pyrrolidinone-4-carboxy ester compound of following formula (I):



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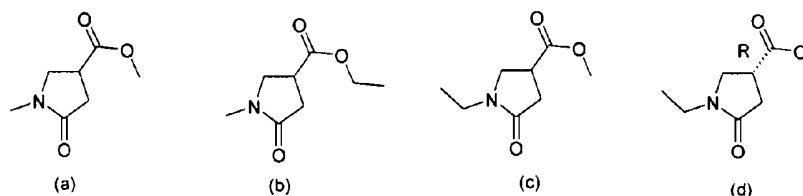
in which:

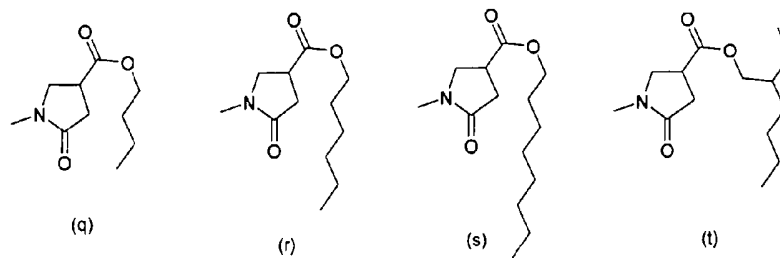
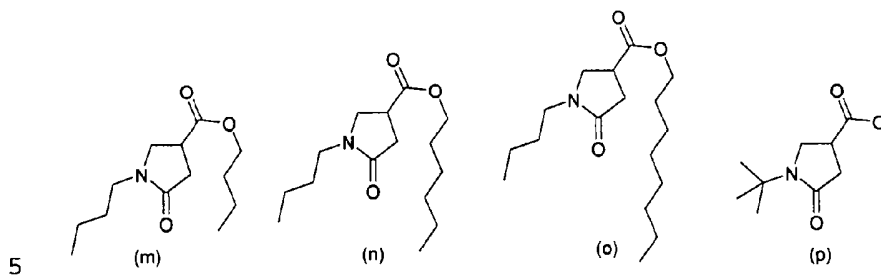
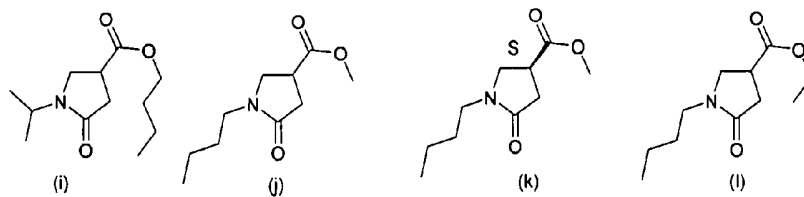
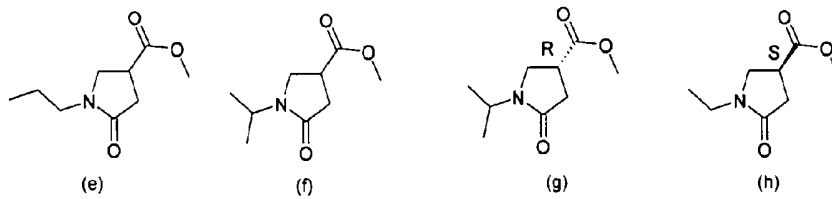
$R^1$  denotes a linear or branched  $C_1$ - $C_{20}$  alkyl radical,

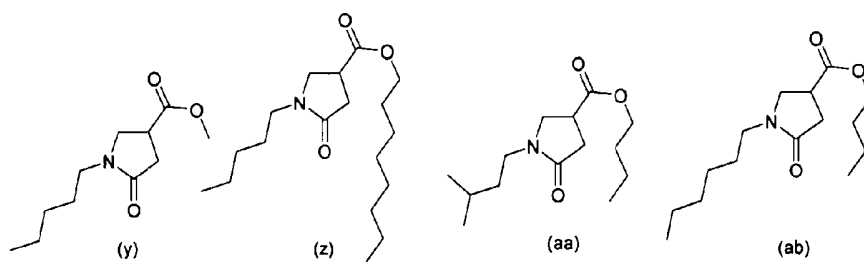
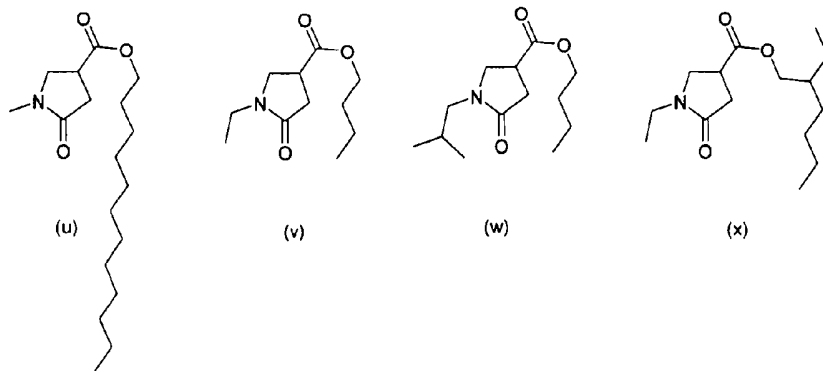
$R^2$  denotes a linear or branched  $C_1$ - $C_{20}$  alkyl radical which can comprise a  $C_5$ - $C_6$  ring, the phenyl radical, the  
 15 benzyl radical or the phenethyl radical.

2. Composition according to Claim 1, where the compound of formula (I) is chosen from the following compounds (a) to (oo):

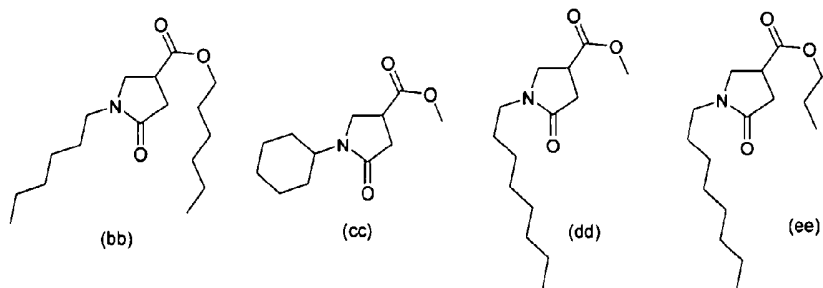
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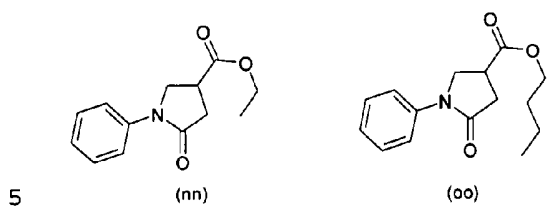
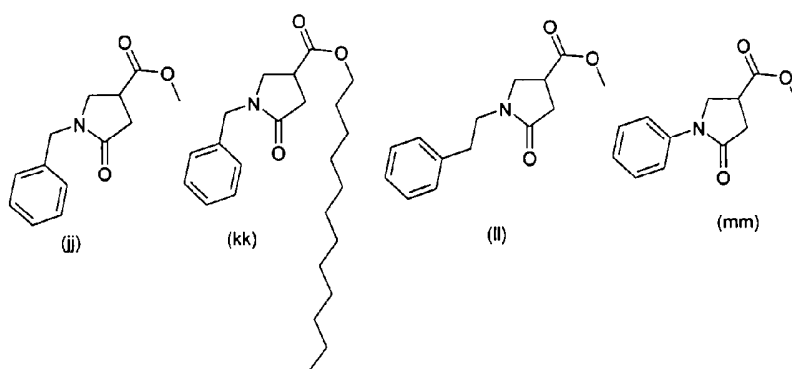
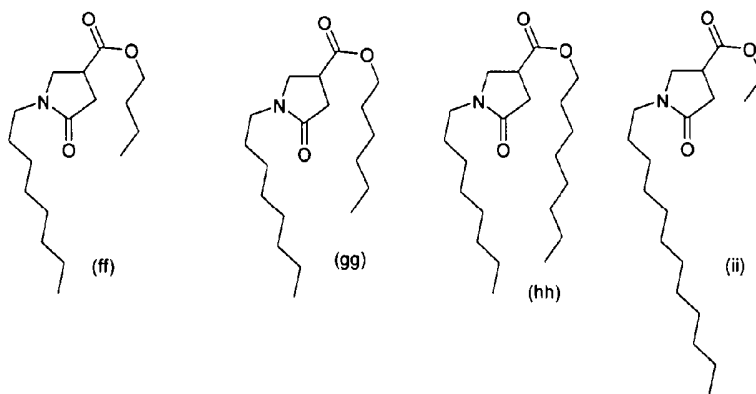




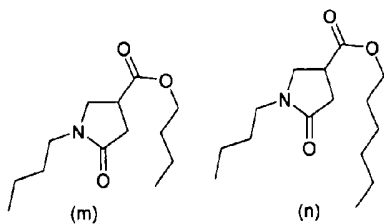
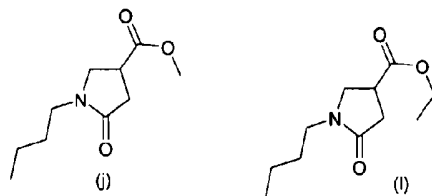


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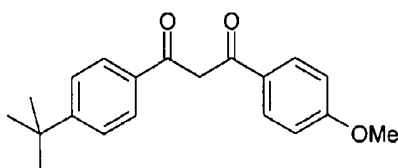




3. Composition according to Claim 2, where the compound of formula (I) is chosen from the compounds:

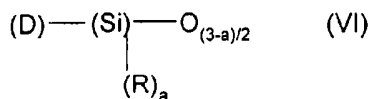


- 5 4. Composition according to any one of Claims 1 to 3, where the dibenzoylmethane derivative is 4-(tert-butyl)-4'-methoxydibenzoylmethane or butyl methoxy dibenzoylmethane of following formula:



10

5. Composition according to any one of Claims 1 to 3, characterized in that it additionally comprises a silicated s-triazine compound substituted by two aminobenzoate or aminobenzamide groups of following general formula (VI) or one of its tautomeric forms:



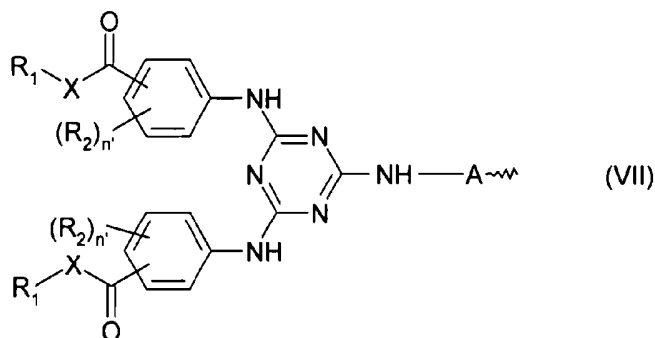
in which:

- R, which are identical or different, represent a linear or branched C<sub>1</sub>-C<sub>30</sub> alkyl radical which is optionally halogenated or unsaturated, a C<sub>6</sub>-C<sub>12</sub> aryl radical, a C<sub>1</sub>-C<sub>10</sub> alkoxy radical, a hydroxyl radical or the trimethylsilyloxy group;

a = 0 to 3; in addition to the units of formula -A-(Si)(R)<sub>a</sub>(O)<sub>(3-a)/2</sub>, the organosiloxane can comprise units of formula: (R)<sub>b</sub>-(Si)(O)<sub>(4-b)/2</sub>, in which:

- R has the same meaning as in the formula (II) and b = 1, 2 or 3;

- the group (D) denotes an s-triazine compound of following formula (VII):



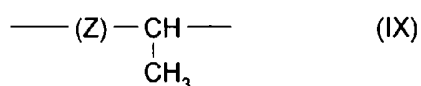
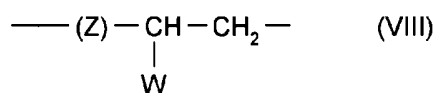
15

where

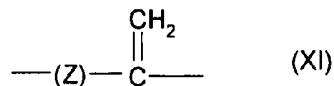
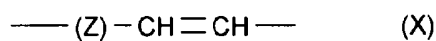
- X represents -O- or -NR<sub>3</sub>-, with R<sub>3</sub> representing hydrogen or a C<sub>1</sub>-C<sub>5</sub> alkyl radical,
- R<sub>1</sub> represents a linear or branched C<sub>1</sub>-C<sub>30</sub> alkyl radical which is optionally unsaturated and which can comprise a silicon atom, a C<sub>5</sub>-C<sub>20</sub> cycloalkyl group, optionally substituted by 1 to 3 linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl radicals, the -(CH<sub>2</sub>CHR<sub>4</sub>-O)<sub>m</sub>R<sub>5</sub> group or the -CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-O-R<sub>6</sub> group,



- R<sub>4</sub> represents hydrogen or methyl; it being possible for the (C=O)XR<sub>1</sub> group to be in the ortho, meta or para position with respect to the amino group,
- R<sub>5</sub> represents hydrogen or a C<sub>1</sub>-C<sub>8</sub> alkyl group,
- 5 - R<sub>6</sub> represents hydrogen or a C<sub>4</sub>-C<sub>8</sub> alkyl group,
- m is an integer ranging from 2 to 20,
- n' = 0 to 2,
- R<sub>2</sub>, which are identical or different, represent a hydroxyl radical, a linear or branched C<sub>1</sub>-C<sub>8</sub> alkyl radical or a C<sub>1</sub>-C<sub>8</sub> alkoxy radical, it being possible for  
10 two adjacent R<sub>2</sub> groups on the same aromatic nucleus to together form an alkylidenedioxy group in which the alkylidene group comprises 1 or 2 carbon atoms,
- A is a divalent radical chosen from methylene,  
15 -[CH(Si(CH<sub>3</sub>)<sub>3</sub>)]-, ethylene or a group corresponding to one of the following formulae (VIII), (IX), (X) or (XI):



20



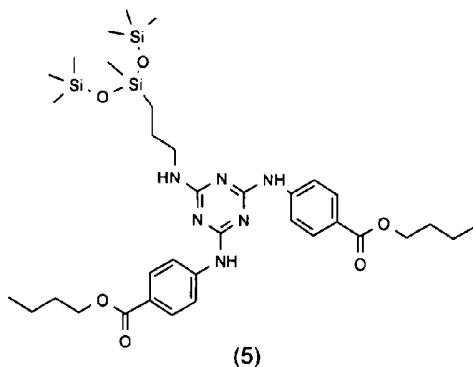
in which:

- 25 - Z is a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>10</sub> alkylene diradical which is optionally

substituted by a hydroxyl radical or oxygen atoms and which can optionally comprise an amino group,

- W represents a hydrogen atom, a hydroxyl radical or a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>8</sub> alkyl radical.

6. Composition according to Claim 5, where the compound of formula (VI) is 2,4-bis(n-butyl 4'-aminobenzoate)-6-[(3-{1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl}propyl)amino]-s-triazine of formula (5):



7. Composition according to any one of Claims 1 to 6, characterized in that it additionally comprises other organic or inorganic screening agents active in the UV-A and/or UV-B regions which are water-soluble or fat-soluble or else insoluble in the cosmetic solvents commonly used.

8. Composition according to Claim 7, where the additional organic screening agents are chosen from anthranilates; cinnamic derivatives; salicylic derivatives; camphor derivatives; benzophenone

derivatives;  $\beta,\beta$ -diphenylacrylate derivatives; triazine derivatives; benzotriazole derivatives; benzalmalonate derivatives; benzimidazole derivatives; imidazolines; bis-benzoazolyl derivatives; p-aminobenzoic acid (PABA) derivatives; methylenebis(hydroxyphenylbenzotriazole) derivatives; benzoxazole derivatives; screening polymers and screening silicones; dimers derived from  $\alpha$ -alkylstyrene; 4,4-diarylbutadienes; merocyanine derivatives and their mixtures.

10

9. Composition according to Claim 8, characterized in that the organic UV screening agent or agents are chosen from the following compounds:

Ethylhexyl Methoxycinnamate,

15 Ethylhexyl Salicylate,

Homosalate,

Octocrylene,

Phenylbenzimidazole Sulfonic Acid,

Benzophenone-3,

20 Benzophenone-4,

Benzophenone-5,

n-Hexyl 2-(4-diethylamino-2-hydroxybenzoyl)benzoate,

4-Methylbenzylidene Camphor,

Terephthalylidene Dicumyl Sulfonic Acid,

25 Disodium Phenyl Dibenzimidazole Tetrasulfonate,

Methylene Bis-Benzotriazolyl Tetramethylbutylphenol,

Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine,

Ethylhexyl Triazone,

- Diethylhexyl Butamido Triazone,  
2,4,6-Tris(dineopentyl 4'-aminobenzalmalonate)-s-triazine,  
2,4,6-Tris(diisobutyl 4'-aminobenzalmalonate)-s-triazine,  
5  
2,4-Bis(dineopentyl 4'-aminobenzalmalonate)-6-(n-butyl 4'-aminobenzoate)-s-triazine,  
2,4,6-Tris(biphenyl-4-yl)-1,3,5-triazine,  
2,4,6-Tris(terphenyl)-1,3,5-triazine,  
10 Drometrizole Trisiloxane,  
Polysilicone-15,  
1,1-Dicarboxy(2,2'-dimethylpropyl)-4,4-diphenylbutadiene,  
2,4-Bis[5-1(dimethylpropyl)benzoxazol-2-yl-(4-phenyl)imino]-6-(2-ethylhexyl)imino-1,3,5-triazine,  
15  
Octyl 5-N,N-diethylamino-2-phenylsulphonyl-2,4-pentadienoate,  
and their mixtures.
- 20 10. Composition according to Claim 7, characterized in that the additional inorganic screening agents are coated or uncoated metal oxide pigments.
- 25 11. Composition according to Claim 10, where the coated or uncoated metal oxide pigments have a mean primary particle size of between 5 nm and 100 nm or between 10 nm and 50 nm.
12. Composition according to Claim 10 or 11, where the

coated or uncoated metal oxide pigments are chosen from pigments formed of titanium oxide (amorphous or crystallized in the rutile and/or anatase form), iron oxide, zinc oxide, zirconium oxide or cerium oxide or their mixtures.

13. Composition according to any one of Claims 1 to 12, characterized in that it is provided in the form of an oil-in-water or water-in-oil emulsion.

14. Method for improving the chemical stability with regard to UV radiation of at least one dibenzoylmethane derivative as defined in any one of the preceding claims, characterized in that the said dibenzoylmethane derivative is combined with an effective amount of at least one 2-pyrrolidinone-4-carboxy ester compound of formula (I) as defined in any one of the preceding claims.

15. Use of at least one 2-pyrrolidinone-4-carboxy ester compound of formula (I) as defined in any one of the preceding claims in a composition comprising, in a cosmetically acceptable vehicle, at least one dibenzoylmethane derivative as defined in any one of the preceding claims with the aim of improving the effectiveness of the said composition with regard to UV-A rays.

16. Compositions or methods or uses involving the compositions, substantially as herein described with reference to the examples.