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(54) Title: SOLUBILIZING AGENTS FOR UV FILTERS IN COSMETIC FORMULATIONS

(57) Abstract: Disclosed is the use of (A) an ester of levulinic acid with a fatty alcohol as solubilizing agent for oil soluble organic UV filters (B).



## Solubilizing agents for UV filters in cosmetic formulations

## Description

5 The present invention relates to the use of ester of levulinic acid with a fatty alcohol as solubilizing agents for dissolving organic UV filters and the use of these compounds in cosmetically acceptable products for improved protection against UV radiation as well as cosmetic formulations exhibiting enhanced UV protection performance.

10 It is well known that ultraviolet radiation (light) is harmful to human skin. Depending on the wavelength the UV radiation causes different types of skin damage. UV-B radiation (about 290 to about 320 nm) is responsible for sunburn and can cause skin cancer. UV-A radiation (about 320 to about 400 nm) while producing tanning of the skin, contributes also to sunburn and the induction of skin cancers. Moreover, the harmful effects of the UV-B radiation may  
15 be aggravated by UV-A radiation.

Therefore, an effective sunscreen formulation preferably comprises both at least one UV-A, UV-B filter and a broad band UV filter covering the full range of about 290 nm to about 400 nm to prevent the human skin from damaging by the sunlight.

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Very effective organic UV filters are the classes of benzophenone derivatives, hydroxyphenyl triazine derivatives and trianilino-s-triazine derivatives.

Unfortunately, these UV absorbers have a poor oil-solubility at a certain concentration and  
25 tend to crystallization. Consequently, the UV protection efficacy is significantly decreased.

Moreover, the oil soluble UV filters should be included in cosmetic sun care products, preferably emulsions, without any impact on the sensorial characteristic of the emulsion. For this reason, the optimal distribution of the UV absorber within the hydro-lipid film left on the  
30 skin after spreading should be guaranteed.

It is therefore an object of the present invention to find UV absorber formulations which have improved properties regarding the UV absorber.

35 Surprisingly it was found that certain esters of levulinic acid with a fatty alcohol guarantee optimal distribution of the organic UV absorber within the hydro-lipid film of the UV absorber formulation left on the skin after spreading and promotes the highest degree of solubilization of the organic UV absorber.

Therefore, the present invention relates to the use of (A) an ester of levulinic acid with a fatty alcohol as solubilizing agent for oil soluble organic UV filters (B).

Levulinic acid and derivatives of levulinic acid are described in Ullmann's Encyclopedia of Industrial Chemistry (online database, copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany) in the article on oxocarboxylic acids, chapter 4 "levulinic acid". It is reported that levulinic acid esters (also called levulinate) are used in the production of cosmetics. In this context reference is made to "Y. Hikotaro, JP 73 43 178, 1973" (reference no. 47). This reference seems to be a typographical error. Japanese patent 480 43 178 which issued in 1973 with Y. Hikotaro as inventor and which can be found in other databases as Japanese patent no. 73 043 178, according to an abstract retrieved (abstract of the Derwent World Patent Index), discloses adhesive compounds containing levulinic acid.

US2,008,720 discloses the synthesis of levulinic acid esters of alcohols having from 7 to 18 carbon atoms. The use of the levulinic acid esters as plasticizers for cellulose derivatives is also disclosed.

WO2005/044960 discloses the use of levulinate and in particular short chain levulinate (C4-C8 alkyl levulinate) as biofuel.

DE2311675A1 discloses levulinic acid esters having antimicrobial properties. Amongst other esters levulinic acid hexyl ester is disclosed. The use of said levulinic acid esters as antimicrobial agents in cosmetic applications and personal care applications is disclosed. It is disclosed that said levulinic acid esters may be applied in the form of solutions or creams which may contain anionic or nonionic surfactants.

JP2012131716A, according to its English abstract (abstract of the Derwent World Patent Index) discloses a deodorizing aerosol product containing levulinic acid and its derivatives.

Levulinic acid is accessible by fermentation and is therefore based on renewable raw materials. Fatty acid moieties are also accessible based on renewable raw materials, e. g. based on oils of plant origin.

According to the present invention, a fatty alcohol is an aliphatic alcohol having exactly one OH-group. This OH-group is a primary OH-group. The hydrocarbon moiety of the fatty alcohol has 6 to 22 carbon atoms. The hydrocarbon moiety of the fatty alcohol may be

saturated or unsaturated, it may be linear or branched, it may not be cyclic. Preferably, it is linear.

Preferably, the fatty alcohol has 8 to 22, preferably 8 to 18, C-atoms.

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The levulinic acid esters according to the present invention may be prepared according to the process disclosed in US2,008,720 which discloses the synthesis of levulinic acid esters of alcohols having from 7 to 18 carbon atoms.

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In one embodiment of the present invention the at least one ester of levulinic acid with a fatty alcohol comprises or is levulinic acid octyl ester.

In one embodiment of the present invention the at least one ester of levulinic acid with a fatty alcohol comprises or is levulinic acid decyl ester.

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In one embodiment of the present invention the at least one ester of levulinic acid with a fatty alcohol comprises or is levulinic acid dodecyl ester.

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In one embodiment of the present invention the at least one ester of levulinic acid with a fatty alcohol comprises or is levulinic acid tetradecyl ester.

In one embodiment of the present invention the at least one ester of levulinic acid with a fatty alcohol comprises or is a mixture of levulinic acid octyl ester and levulinic acid decyl ester in a weight ratio of 1:4 to 4:1.

25

In one embodiment of the present invention the at least one ester of levulinic acid with a fatty alcohol comprises or is a mixture of levulinic acid dodecyl ester and levulinic acid tetradecyl ester in a weight ratio of 1:4 to 4:1.

30

Preferably, the oil soluble organic UV filters (B) are selected from

(B<sub>1</sub>) benzophenone derivatives;

(B<sub>2</sub>) camphor derivatives;

(B<sub>3</sub>) triazine derivatives

(B<sub>4</sub>) dibenzoylmethane derivatives (BMBM);

35

(B<sub>5</sub>) cinnamic acid derivatives;

(B<sub>6</sub>) Benzyldenemalonates (BM);

(B<sub>7</sub>) diphenylacrylates;

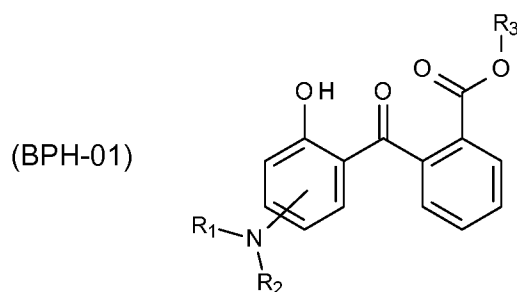
- (d<sub>8</sub>) polymeric UV absorbers;  
 (B<sub>9</sub>) Homosalates;  
 (B<sub>10</sub>) Salicylic acid derivatives; and  
 (B<sub>11</sub>) Merocyanine derivatives.

5

More preferably, the oil soluble organic UV filters (B) are selected from  
 (B1) benzophenone derivatives,  
 (B2) hydroxyphenyl triazine derivatives; and  
 (B3) trianilino-s-triazine derivatives.

10

Preferred benzophenone derivatives (B1) correspond to the formula

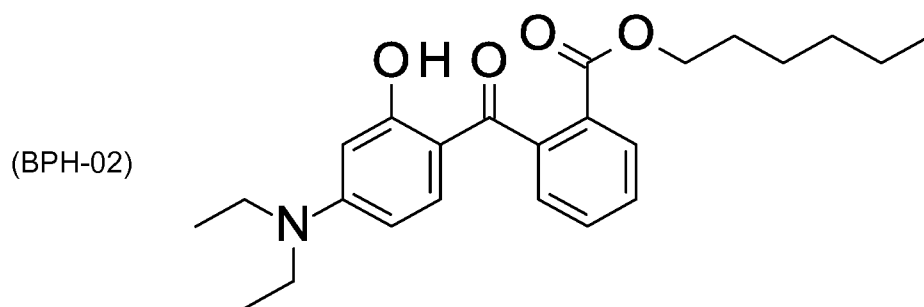


wherein

R<sub>1</sub> and R<sub>2</sub> independently from each other are hydrogen; C<sub>1</sub>-C<sub>20</sub>alkyl; C<sub>3</sub>-C<sub>10</sub>cycloalkyl; or C<sub>3</sub>-C<sub>10</sub>cycloalkenyl, wherein the radicals R<sub>1</sub> and R<sub>2</sub> together with the nitrogen atom, to which they are bonded may form a 5- or 6-membered ring; and  
 R<sub>3</sub> is C<sub>1</sub>-C<sub>20</sub>alkyl.

15

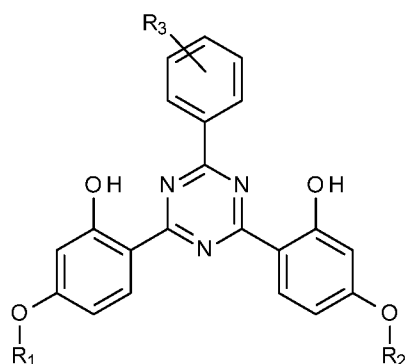
Most preferred benzophenone derivatives (B1) according to the present invention correspond to the formula



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Preferred hydroxyphenyl triazine derivatives (B2) according to the present invention correspond to formula

(HTP-01)



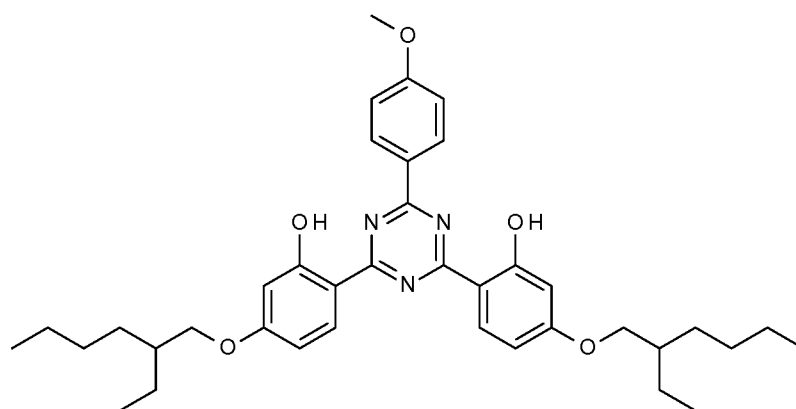
wherein

R<sub>1</sub> and R<sub>2</sub> independently from each other are C<sub>1</sub>-C<sub>18</sub>alkyl; and

R<sub>3</sub> is C<sub>1</sub>-C<sub>10</sub>alkoxy.

- 5 Most preferred hydroxyphenyl triazine derivatives (B2) according to the present invention correspond to formula

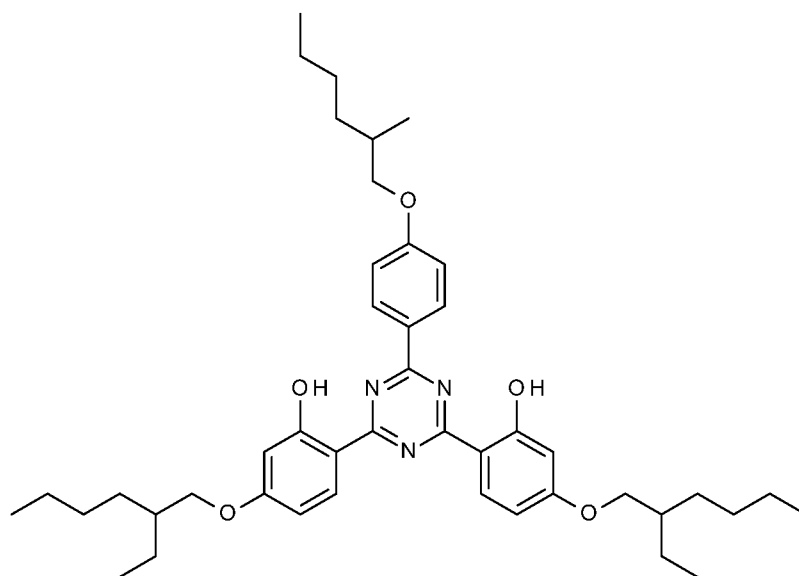
(HTP-02)



Further preferred hydroxyphenyl triazine derivatives (B2) according to the present invention correspond to formula

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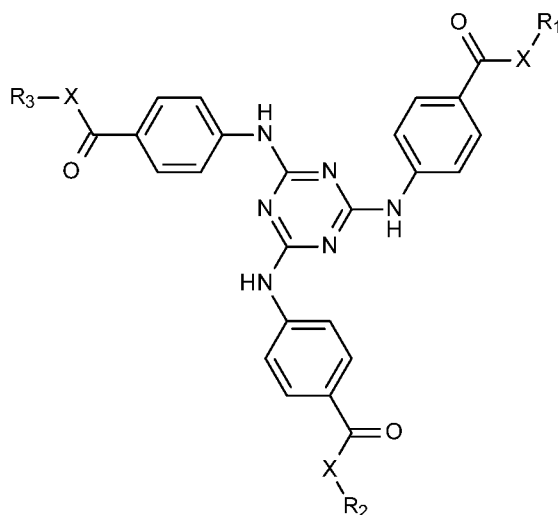
(HTP-03)



The hydroxyphenyl triazine derivatives (B2) as used in the present invention can be prepared by manners known per se, as described for example in EP 775698 B1.

- 5 Preferred trianilino-s-triazine derivatives (B3) correspond to the formula

(TAT-01)



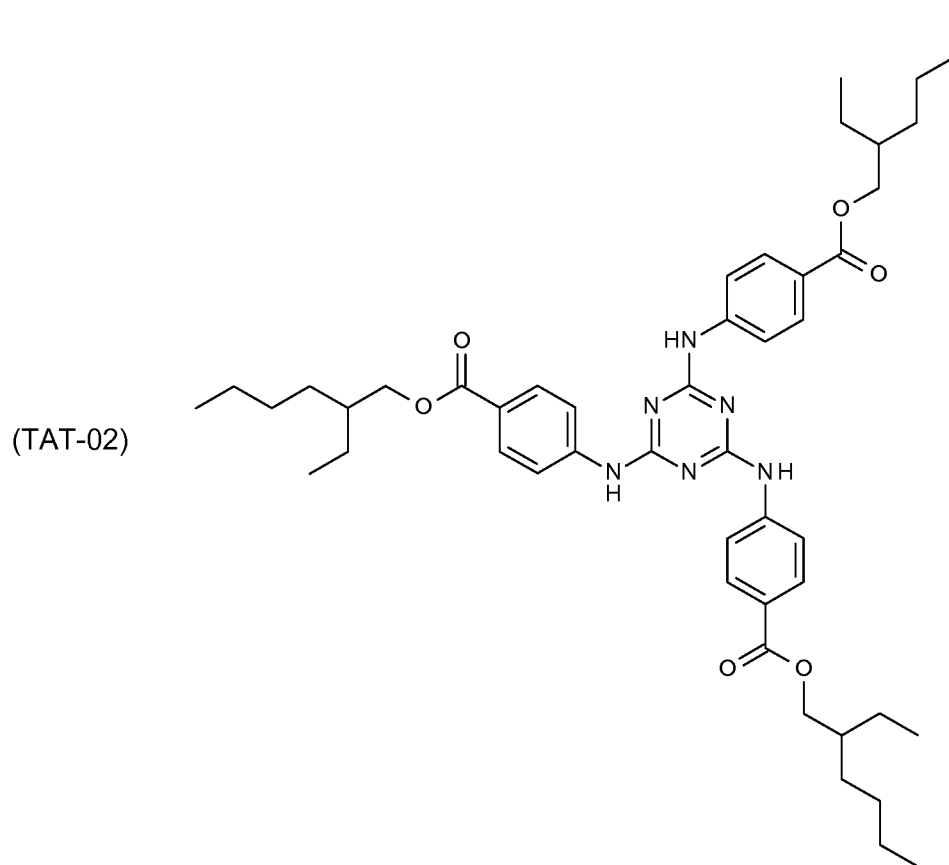
wherein

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> independently from each other are optionally substituted C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>6</sub>-C<sub>10</sub>aryl or C<sub>6</sub>-C<sub>10</sub>heteroaryl;

X is O; or NR<sub>4</sub>; and

- 10 R<sub>4</sub> is hydrogen; or optionally substituted C<sub>1</sub>-C<sub>20</sub>alkyl, aryl or heteroaryl.

Most preferred trianilino-s-triazine derivatives (B3) correspond to the formula



Preferably, the organic UV filters (B) according to the present invention are used as mixtures.

Preferably, mixtures of UV filters (BPH-02), (HTP-02) and (TAT-02) are used.

5

Further preferred mixtures of organic UV filters according to the present invention are:

- UV filters (BPH-02) and (HTP-02);
- UV filters (BPH-02) and (TAT-02); and
- UV filters (HTP-02) and (TAT-02)

10

Preferably, the organic UV filters (B) are used in admixtures of at least two different UV filters selected from (B1), (B2) and (B3).

Furthermore, the present invention relates to a cosmetic composition, which preferably comprises

15

(A) an ester of levulinic acid with a fatty alcohol; and

(B) oil soluble organic UV filters (B).

The cosmetic composition of the present invention preferably comprises



- (A) an ester of levulinic acid with a C<sub>8</sub>-C<sub>22</sub> fatty alcohol; and  
 (B) mixtures of UV filters (HTP-02), (BPH-02) and (TAT-02).

Furthermore, the cosmetic composition of the present invention preferably comprises

- 5 (A) an ester of levulinic acid with a C<sub>8</sub>-C<sub>22</sub> fatty alcohol; and  
 (B) mixtures of UV filters (BPH-02) and (HTP-02); or  
 (A) an ester of levulinic acid with a C<sub>8</sub>-C<sub>22</sub> fatty alcohol; and  
 (B) mixtures of UV filters (HTP-02) and (TAT-02); or  
 (A) an ester of levulinic acid with a C<sub>8</sub>-C<sub>22</sub> fatty alcohol; and  
 10 (B) mixtures of UV filters (BPH-02) and (TAT-02).

The cosmetic composition of the present invention preferably comprises

- 0.1 to 25% b.w. of a solubilizing agent (A);  
 0.1 to 20 % b.w. of at least one organic UV filter (B); and  
 15 10 to 90 % b.w. of a cosmetically acceptable carrier (C),  
 based on the total weight of the cosmetic end-product composition.

The cosmetic composition according to the present invention may comprise one or more  
 than one additional UV absorbers (component (D)) as described in the Tables 1 and 2.

20

Table 1: Suitable UV filter substances which can be additionally used with the organic UV absorbers (B) according to the present invention

p-aminobenzoic acid derivatives, for example 4-dimethylaminobenzoic acid 2-ethylhexyl ester;
salicylic acid derivatives, for example salicylic acid 2-ethylhexyl ester;
benzophenone derivatives, for example 2-hydroxy-4-methoxybenzophenone and its 5-sulfonic acid derivative;
diphenylacrylates, for example 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, and 3-(benzofuranyl) 2-cyanoacrylate;
3-imidazol-4-ylacrylic acid and esters;
benzofuran derivatives, especially 2-(p-aminophenyl)benzofuran derivatives, described in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
polymeric UV absorbers, for example the benzylidene malonate derivatives described in EP-A-709 080;
cinnamic acid derivatives, for example the 4-methoxycinnamic acid 2-ethylhexyl ester and isoamyl ester or cinnamic acid derivatives described in US-A-5 601 811 and WO 97/00851;
camphor derivatives, for example 3-(4'-methyl)benzylidene-bornan-2-one, 3-benzylidene-bornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidene-methyl]-benzyl]acrylamide polymer, 3-(4'-trimethylammonium)-benzylidene-bornan-2-one methyl sulfate, 3,3'-(1,4-phenylene-dimethine)-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methanesulfonic acid) and salts, 3-(4'-sulfo)benzylidene-bornan-2-one and salts; camphorbenzalkonium methosulfate;
phenyl-benzimidazole derivatives as disclosed in EP 1 167 358

Table 2. Suitable UV filter substances and adjuvants which can be additionally used with the UV absorbers (B) according to the present invention

No.	Chemical Name	CAS No.
1	(+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo[2.2.1]heptan-2-one; p-methyl benzylidene camphor	36861-47-9
2	1,7,7-trimethyl-3-(phenylmethylene)bicyclo[2.2.1]heptan-2-one; benzylidene camphor	15087-24-8
3	(2-Hydroxy-4-methoxyphenyl)(4-methylphenyl)methanone	1641-17-4
4	2,4-dihydroxybenzophenone	131-56-6
5	2,2',4,4'-tetrahydroxybenzophenone	131-55-5
6	2-Hydroxy-4-methoxy benzophenone;	131-57-7
7	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid	4065-45-6
8	2,2'-dihydroxy-4,4'-dimethoxybenzophenone	131-54-4
9	2,2'-Dihydroxy-4-methoxybenzophenone	131-53-3
10	Alpha-(2-oxoborn-3-ylidene)toluene-4-sulphonic acid and its salts; Mexoryl SL	56039-58-8
11	1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)propane-1,3-dione; Avobenzone	70356-09-1
12	Methyl N,N,N-trimethyl-4-[(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]anilinium sulphate; Mexoryl SO	52793-97-2
13	3,3,5-Trimethyl cyclohexyl-2-hydroxy benzoate; homosalate	118-56-9
14	Isopentyl p-methoxycinnamate; isoamyl methoxy cinnamate	71617-10-2
27	Menthyl-o-aminobenzoate	134-09-8
15	Menthyl salicylate	89-46-3
16	2-Ethylhexyl 2-cyano,3,3-diphenylacrylate; Octocrylene	6197-30-4
17	2- ethylhexyl 4- methoxycinnamate; Octyl Methoxy Cinnamate	5466-77-3
18	2- ethylhexyl salicylate	118-60-5
19	4- aminobenzoic acid	150-13-0
20	Benzoic acid, 4-amino-, ethyl ester, polymer with oxirane	113010-52-9
21	2- phenyl- 1H- benzimidazole- 5- sulphonic acid; phenylbenzimidazolsulfonic acid	27503-81-7
22	2-Propenamide, N-[[4-[(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phenyl]methyl]-, homopolymer	147897-12-9
23	Triethanolamine salicylate	2174-16-5
24	3, 3'-(1,4-phenylenedimethylene)bis[7, 7-dimethyl- 2-oxo-bicyclo[2.2.1]heptane-1 methanesulfonic acid]; Cibafast H	90457-82-2
25	Titanium dioxide	13463-67-7
26	Zinc oxide	1314-13-2
27	2,2'-Methylene-bis-[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethyl-	103597-45-1

Table 2. Suitable UV filter substances and adjuvants which can be additionally used with the UV absorbers (B) according to the present invention

No.	Chemical Name	CAS No.
	butyl)-phenol]; Tinosorb M	
28	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt	180898-37-7
29	Benzoic acid, 4,4'-[[6-[[4-[[[(1,1-dimethylethyl)amino]carbonyl]phenyl]amino]1,3,5-triazine-2,4-diyl]diimino]bis-, bis(2-ethylhexyl)ester; diethylhexyl butamido triazone; Uvasorb HEB	154702-15-5
30	Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]-; drometrizole trisiloxane; Mexoryl XL	155633-54-8
31	Dimethicodiethylbenzalmalonate; Polysilicone 15; Parsol SLX	207574-74-1
32	1-Dodecanaminium, N-[3-[[4-(dimethylamino)benzoyl]amino]propyl]-N,N-dimethyl-, salt with 4-methylbenzenesulfonic acid (1:1); Escalol HP610	156679-41-3
33	1-Propanaminium, N,N,N-trimethyl-3-[(1-oxo-3-phenyl-2-propenyl)-amino]-, chloride	177190-98-6
34	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-	170864-82-1
35	1-Propanaminium, 3-[[3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]amino]-N,N-diethyl-N-methyl-, methyl sulfate (salt)	340964-15-0
36	2-Propenoic acid, 3-(1H-imidazol-4-yl)-	104-98-3
37	Benzoic acid, 2-hydroxy-, [4-(1-methylethyl)phenyl]methyl ester	94134-93-7
38	1,2,3-Propanetriol, 1-(4-aminobenzoate); glyceryl PABA	136-44-7
39	Benzeneacetic acid, 3,4-dimethoxy-a-oxo-	4732-70-1
40	2-Propenoic acid, 2-cyano-3,3-diphenyl-, ethyl ester	5232-99-5
41	Anthralinic acid, p-menth-3-yl ester	134-09-8
42	2,2'-bis(1,4-phenylene)-1H-benzimidazole-4,6-disulphonic acid mono sodium salt or Disodium phenyl dibenzimidazole tetrasulfonate or Neo Heliopan AP	349580-12-7,
43	sterols (cholesterol, lanosterol, phytosterols), as described in WO0341675	
44	mycosporines and/or mycosporine-like amino acids as described in WO2002039974, e.g. Helioguard 365 from Milbelle AG, isolated mycosporine like amino acids from the red alga porphyra umbilicalis (INCI: Porphyra Umbilicalis) that are encapsulated into liposomes,)	
45	alpha-lipoic-acid as described in DE 10229995	
46	synthetic organic polymers as described in EP 1371358, [0033]-[0041]	
47	phyllosilicates as described in EP 1371357 [0034]-[0037]	
48	silica compounds as described in EP1371356, [0033]-[0041]	

Table 2. Suitable UV filter substances and adjuvants which can be additionally used with the UV absorbers (B) according to the present invention

No.	Chemical Name	CAS No.
49	inorganic particles as described in DE10138496 [0043]-[0055]	
50	latex particles as described in DE10138496 [0027]-[0040]	
51	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt ; Bisimidazylate; Neo Heliopan APC	180898-37-7
52	2,4,6-Tris(p-biphenyl)-s-triazine, Tinosorb A2B	31274-51-8
53	2,4,6-Tris-1,1',4',1''-terphenyl-4-yl-1,3,5-triazine	
54	Di-2-ethylhexyl-3,5-dimethoxy-4-hydroxy-benzalmalonate (Oxy-nex ST, EMD Chemicals, as described in US 20040247536)	
55	Benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt ; Tinogard HS	92484-48-5

The cosmetic composition according to the present invention can be prepared by physically mixing the UV filter(s) (B) with the adjuvant using customary methods, for example by simply stirring together the individual components, especially by making use of the dissolution properties of already known cosmetic UV filters, like octyl methoxy cinnamate, salicylic acid isooctyl ester, etc.. The UV filter (B) can be used, for example, without further treatment.

The cosmetic or pharmaceutical compositions/preparations according to the invention may also contain one or one more additional compounds as described below.

#### Fatty alcohols

Guerbet alcohols based on fatty alcohols having from 6 to 18, preferably from 8 to 10 carbon atoms including cetyl alcohol, stearyl alcohol, cetearyl alcohol, oleyl alcohol, octyldodecanol, benzoate of C<sub>12</sub>-C<sub>15</sub> alcohols, acetylated lanolin alcohol, etc..

#### Esters of fatty acids

Esters of linear C<sub>6</sub>-C<sub>24</sub> fatty acids with linear C<sub>3</sub>-C<sub>24</sub> alcohols, esters of branched C<sub>6</sub>-C<sub>13</sub> carboxylic acids with linear C<sub>6</sub>-C<sub>24</sub> fatty alcohols, esters of linear C<sub>6</sub>-C<sub>24</sub> fatty acids with branched alcohols, especially 2-ethylhexanol, esters of hydroxycarboxylic acids with linear or branched C<sub>6</sub>-C<sub>22</sub> fatty alcohols, especially dioctyl malates, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or Guerbet alcohols, for example caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselinic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid and technical-grade

mixtures thereof (obtained, for example, in the pressure removal of natural fats and oils, in the reduction of aldehydes from Roelen's oxosynthesis or in the dimerisation of unsaturated fatty acids) with alcohols, for example, isopropyl alcohol, caproic alcohol, capryl alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linoyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachidyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and technical-grade mixtures thereof (obtained, for example, in the high-pressure hydrogenation of technical-grade methyl esters based on fats and oils or aldehydes from Roelen's oxosynthesis and as monomer fractions in the dimerisation of unsaturated fatty alcohols).

Examples of such ester oils are isopropylmyristate, isopropylpalmitate, isopropylstearate, isopropyl isostearate, isopropyloleate, n-butylstearate, n-hexyllaurate, n-decyloleate, isooctylstearate, iso-nonylstearate, isononyl isononanoate, 2-ethylhexylpalmitate, 2-hexyllaurate, 2-hexyldecylstearate, 2-octyldodecylpalmitate, oleyloleate, oleylerucate, erucyloleate, erucyl-erucate, cetearyl octanoate, cetyl palmitate, cetyl stearate, cetyl oleate, cetyl behenate, cetyl acetate, myristyl myristate, myristyl behenate, myristyl oleate, myristyl stearate, myristyl palmitate, myristyl lactate, propylene glycol dicaprylate/caprinate, stearyl heptanoate, diisostearyl malate, octyl hydroxystearate, etc..

#### Natural or synthetic triglycerides including glyceryl esters and derivatives

Di- or tri-glycerides, based on C<sub>6</sub>-C<sub>18</sub> fatty acids, modified by reaction with other alcohols (caprylic/capric triglyceride, wheat germ glycerides, etc.). Fatty acid esters of polyglycerin (polyglyceryl-n such as polyglyceryl-4 caprate, polyglyceryl-2 isostearate, etc. or castor oil, hydrogenated vegetable oil, sweet almond oil, wheat germ oil, sesame oil, hydrogenated cottonseed oil, coconut oil, avocado oil, corn oil, hydrogenated castor oil, shea butter, cocoa butter, soybean oil, mink oil, sunflower oil, safflower oil, macadamia nut oil, olive oil, hydrogenated tallow, apricot kernel oil, hazelnut oil, borago oil, etc.

Waxes including esters of long-chain acids and alcohols as well as compounds having wax-like properties, e.g., carnauba wax, beeswax (white or yellow), lanolin wax, candellila wax, ozokerite, japan wax, paraffin wax, microcrystalline wax, ceresin, cetearyl esters wax, synthetic beeswax, etc. Also, hydrophilic waxes as Cetearyl Alcohol or partial glycerides.

#### Pearlescent waxes:

Alkylene glycol esters, especially ethylene glycol distearate; fatty acid alkanolamides, especially coco fatty acid diethanolamide; partial glycerides, especially stearic acid

monoglyceride; esters of polyvalent, unsubstituted or hydroxy-substituted carboxylic acids with fatty alcohols having from 6 to 22 carbon atoms, especially long-chained esters of tartaric acid; fatty substances, for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates, which in total have at least 24 carbon atoms, especially laurone and distearyl ether; fatty acids, such as stearic acid, hydroxystearic acid or behenic acid, ring-opening products of olefin epoxides having from 12 to 22 carbon atoms with fatty alcohols having from 12 to 22 carbon atoms and/or polyols having from 2 to 15 carbon atoms and from 2 to 10 hydroxy groups, and mixtures thereof.

#### Hydrocarbon oils:

Mineral oil (light or heavy), petrolatum (yellow or white), microcrystalline wax, paraffinic and isoparaffinic compounds, hydrogenated isoparaffinic molecules as polydecenes and polybutene, hydrogenated polyisobutene, squalane, isohexadecane, isododecane and others from plant and animal kingdom.

#### Silicones or siloxanes (organosubstituted polysiloxanes)

Dimethylpolysiloxanes, methylphenylpolysiloxanes, cyclic silicones, and also amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine-, glycoside- and/or alkyl-modified silicone compounds, which at room temperature may be in either liquid or resinous form. Linear polysiloxanes, dimethicone (Dow Corning 200 fluid, Rhodia Mirasil DM), dimethiconol, cyclic silicone fluids, cyclopentasiloxanes volatiles (Dow Corning 345 fluid), phenyltrimethicone (Dow Corning 556 fluid). Also suitable are simethicones, which are mixtures of dimethicones having an average chain length of from 200 to 300 dimethylsiloxane units with hydrogenated silicates. A detailed survey by Todd *et al.* of suitable volatile silicones may in addition be found in Cosm. Toil. 91, 27 (1976).

#### Fluorinated or perfluorinated oils

Perfluorohexane, dimethylcyclohexane, ethylcyclopentane, polyperfluoromethylisopropyl ether.

#### Emulsifiers

Any conventionally usable emulsifier can be used for the compositions. Emulsifier systems may comprise for example: carboxylic acids and their salts: alkaline soap of sodium, potassium and ammonium, metallic soap of calcium or magnesium, organic basis soap such as Lauric, palmitic, stearic and oleic acid etc... Alkyl phosphates or phosphoric acid esters, acid phosphate, diethanolamine phosphate, potassium cetyl phosphate. Ethoxylated carboxylic acids or polyethyleneglycol esters, PEG-n acylates. Linear fatty alcohols having

from 8 to 22 carbon atoms, branched from 2 to 30 mol of ethylene oxide and/or from 0 to 5 mol propylene oxide with fatty acids having from 12 to 22 carbon atoms and with alkylphenols having from 8 to 15 carbon atoms in the alkyl group. Fatty alcohol polyglycol-ether such as laureth-n, cetareth-n, steareth-n, oleth-n. Fatty acid polyglycoether such as PEG-n stearate, PEG-n oleate, PEG-n cocoate. Monoglycerides and polyol esters. C12-C22 fatty acid mono- and di-esters of addition products of from 1 to 30 mol of ethylene oxide with polyols. Fatty acid and polyglycerol ester such as monostearate glycerol, diisostearyl polyglyceryl-3-diisostearates, polyglyceryl-3-diisostearates, triglyceryl diisostearates, polyglyceryl-2-sesquiisostearates or polyglyceryl dimerates. Mixtures of compounds from a plurality of those substance classes are also suitable. Fatty acid polyglycolesters such as monostearate diethylene glycol, fatty acid and polyethylene glycol esters, fatty acid and saccharose esters such as sucro esters, glycerol and saccharose esters such as sucro glycerides. Sorbitol and sorbitan, sorbitan mono- and di-esters of saturated and unsaturated fatty acids having from 6 to 22 carbon atoms and ethylene oxide addition products. Polysorbate-n series, sorbitan esters such as sesquiisostearate, sorbitan, PEG-(6)-isostearate sorbitan, PEG-(10)-sorbitan laurate, PEG-17- dioleate sorbitan. Glucose derivatives, C8-C22 alkyl-mono and oligo-glycosides and ethoxylated analogues with glucose being preferred as the sugar component. O/W emulsifiers such as methyl gluceth-20 sesquisteate, sorbitan stearate/sucrose cocoate, methyl glucose sesquisteate, cetearyl alcohol/cetearyl glucoside. W/O emulsifiers such as methyl glucose dioleate/ methyl glucose isostearate. Sulfates and sulfonated derivatives, dialkylsulfosuccinates, dioctyl succinate, alkyl lauryl sulfonate, linear sulfonated paraffins, sulfonated tetrapropylene sulfonate, sodium lauryl sulfates, ammonium and ethanolamine lauryl sulfates, lauryl ether sulfates, sodium laureth sulfates, sulfosuccinates, acetyl isothionates, alkanolamide sulfates, taurines, methyl taurines, imidazole sulfates. Amine derivatives, amine salts, ethoxylated amines, oxide amine with chains containing an heterocycle such as alkyl imidazolines, pyridine derivatives, isoquinoline, cetyl pyridinium chloride, cetyl pyridinium bromide, quaternary ammonium such as cetyltrimethylbromide ammonium bromide (CTBA), stearylalkonium. Amide derivatives, alkanolamides such as acylamide DEA, ethoxylated amides such as PEG-n acylamide, oxydeamide; polysiloxane/-polyalkyl/polyether copolymers and derivatives, dimethicone, copolyols, silicone polyethylene oxide copolymer, silicone glycol copolymer; propoxylated or POE-n ethers (Meropols); polaxamers or poly(oxyethylene)m-block-poly(oxypropylene)n-block(oxyethylene); zwitterionic surfactants that carry at least one quaternary ammonium group and at least one carboxylate and/or sulfonate group in the molecule. Zwitterionic surfactants that are especially suitable are betaines, such as N-alkyl-N,N-dimethylammonium glycinate, cocoalkyldimethylammonium glycinate, N-acylaminopropyl-N,N-dimethylammonium glycinate, cocoacylaminopropyldimethylammonium glycinate and 2-alkyl-3-carboxymethyl-3-hydroxyethyl-

imidazolines each having from 8 to 18 carbon atoms in the alkyl or acyl group and also coco-acylaminoethylhydroxyethylcarboxymethylglycinate, N-alkylbetaine, N-alkylaminobetaines, alkylimidazolines, alkylopeptides, lipoaminoacides, self emulsifying bases and the compounds as described in K.F.DePolo, A short textbook of cosmetology, Chapter 8, Table 8-7, p250-251.

Non ionic emulsifiers such as PEG-6 beeswax (and) PEG-6 stearate (and) polyglyceryl – 2-isostearate [Apifac], glyceryl stearate (and) PEG-100 stearate. [Arlacel 165], PEG-5 glyceryl stearate [Arlatone 983 S], sorbitan oleate (and) polyglyceryl-3 ricinoleate.[Arlacel 1689], sorbitan stearate and sucrose cocoate [Arlatone 2121], glyceryl stearate and laureth-23 [Cerasynth 945], cetearyl alcohol and ceteth-20 [Cetomacrogol Wax], cetearyl alcohol and colysorbate 60 and PEG-150 and stearate-20[Polawax GP 200, Polawax NF], cetearyl alcohol and cetearyl polyglucoside [Emulgade PL 1618], cetearyl alcohol and cetareth-20 [Emulgade 1000NI, Cosmowax], cetearyl alcohol and PEG-40 castor oil [Emulgade F Special], cetearyl alcohol and PEG-40 castor oil and sodium cetearyl sulfate [Emulgade F], stearyl alcohol and steareth-7 and steareth-10 [Emulgator E 2155], cetearyl alcohol and steareth-7 and steareth-10 [Emulsifying wax U.S.N.F.], glyceryl stearate and PEG-75 stearate [Gelot 64], propylene glycol ceteth-3 acetate .[Hetester PCS], propylene glycol isoceth-3 acetate [Hetester PHA], cetearyl alcohol and ceteth-12 and oleth-12 [Lanbritol Wax N 21], PEG –6 stearate and PEG-32 stearate [Tefose 1500], PEG-6 stearate and ceteth-20 and steareth-20 [Tefose 2000], PEG-6 stearate and ceteth-20 and glyceryl stearate and steareth-20 [Tefose 2561], glyceryl stearate and cetareth-20 [Teginacid H, C, X].

Anionic emulsifiers such as PEG-2 stearate SE, glyceryl stearate SE [Monelgine, Cutina KD], propylene glycol stearate [Tegin P], cetearyl Alcohol and Sodium cetearyl sulfate [Lanette N, Cutina LE, Crodacol GP], cetearyl alcohol and sodium lauryl sulfate [Lanette W], trilaneth-4 phopshate and glycol stearate and PEG-2 stearate [Sedefos 75], glyceryl stearate and sodium lauryl Sulfate [Teginacid Special]. Cationic acid bases such as cetearyl alcohol and cetrimonium bromide.

The emulsifiers may be used in an amount of, for example, from 1 to 30 % by weight, especially from 4 to 20 % by weight and preferably from 5 to 10 % by weight, based on the total weight of the composition.

When formulated in O/W emulsions, the preferably amount of such emulsifier system could represent 5% to 20% of the oil phase.



### Adjuvants and additives

The cosmetic / pharmaceutical preparations, for example creams, gels, lotions, alcoholic and aqueous/alcoholic solutions, emulsions, wax/fat compositions, stick preparations, powders or ointments, may in addition contain, as further adjuvants and additives, mild surfactants, super-fatting agents, consistency regulators, thickeners, polymers, stabilisers, biogenic active ingredients, deodorising active ingredients, anti-dandruff agents, film formers, swelling agents, further UV light-protective factors, antioxidants, hydrotropic agents, preservatives, insect repellents, self-tanning agents, solubilisers, perfume oils, colourants, bacteria-inhibiting agents and the like.

### Super-fatting agents

Substances suitable for use as super-fatting agents are, for example, lanolin and lecithin and also polyethoxylated or acrylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, the latter simultaneously acting as foam stabilisers.

### Surfactants

Examples of suitable mild surfactants, that is to say surfactants especially well tolerated by the skin, include fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, mono- and/or di-alkyl sulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, fatty acid glutamates,  $\alpha$ -olefin sulfonates, ethercarboxylic acids, alkyl oligoglucosides, fatty acid glucamides, alkylamidobetaines and/or protein fatty acid condensation products, the latter preferably being based on wheat proteins.

### Consistency regulators/thickeners and rheology modifiers

Silicium dioxide, magnesium silicates, aluminium silicates, polysaccharides or derivatives thereof for example hyaluronic acid, xanthan gum, guar-guar, agar-agar, alginates, carrageenan, gellan, pectines, or modified cellulose such as hydroxycellulose, hydroxypropyl-methylcellulose. In addition polyacrylates or homopolymer of reticulated acrylic acids and polyacrylamides, carbomer (carbopol types 980, 981, 1382, ETD 2001, ETD2020, Ultrez 10) or Salcare range such as Salcare SC80(steareth-10 allyl ether/acrylates copolymer), Salcare SC81(acrylates copolymer), Salcare SC91 and Salcare AST(sodium acrylates copolymer/PPG-1 trideceth-6), sepigel 305(polyacrylamide/laureth-7), Simulgel NS and Simulgel EG (hydroxyethyl acrylate / sodium acryloyldimethyl taurate copolymer), Stablen 30 (acrylates / vinyl isodecanoate crosspolymer), Pemulen TR-1(acrylates / C10-30 alkyl acry-

late crosspolymer), Luvigel EM (sodium acrylates copolymer), Aculyn 28 (acrylates/- beheneth-25 methacrylate copolymer), etc..

### Polymers

5 Suitable cationic polymers are, for example, cationic cellulose derivatives, for example a quaternised hydroxymethyl cellulose obtainable under the name Polymer JR 400 from Amerchol, cationic starches, copolymers of diallylammonium salts and acrylamides, quaternised vinylpyrrolidone/vinyl imidazole polymers, for example Luviquat® (BASF), condensation products of polyglycols and amines, quaternised collagen polypeptides, for example lauryldimonium  
10 hydroxypropyl hydrolyzed collagen (Lamequat® L/Grünau), quaternised wheat polypeptides, polyethyleneimine, cationic silicone polymers, for example amidomethicones, copolymers of adipic acid and dimethylaminohydroxypropyldiethylenetriamine (Cartaretin/Sandoz), copolymers of acrylic acid with dimethyldiallylammonium chloride (Merquat 550 / Chemviron), polyaminopolyamides, as described, for example, in FR-A-2 252 840, and the crosslinked water-  
15 soluble polymers thereof, cationic chitin derivatives, for example of quaternised chitosan, optionally distributed as microcrystals; condensation products of dihaloalkyls, for example dibromobutane, with bisdialkylamines, for example bisdimethylamino-1,3-propane, cationic guar gum, for example Jaguar C-17, Jaguar C-16 from Celanese, quaternised ammonium salt polymers, for example Mirapol A-15, Mirapol AD-1, Mirapol AZ-1 from Miranol. As an-  
20 ionic, zwitterionic, amphoteric and non-ionic polymers there come into consideration, for example, vinyl acetate / crotonic acid copolymers, vinylpyrrolidone / vinyl acrylate copolymers, vinyl acetate / butyl maleate / isobornyl acrylate copolymers, methyl vinyl ether / maleic anhydride copolymers and esters thereof, uncrosslinked polyacrylic acids and polyacrylic acids crosslinked with polyols, acrylamidopropyl-trimethylammonium chloride /acrylate  
25 copolymers, octyl acrylamide/methyl methacrylate/tert-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers, polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers, vinylpyrrolidone/dimethylaminoethyl methacrylate/vinyl caprolactam terpolymers and also optionally derivatized cellulose ethers and silicones. Furthermore the polymers as described in EP 1093796 (pages 3-8, paragraphs 17-68) may be used.

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### Biogenic active ingredients

Biogenic active ingredients are to be understood as meaning, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, deoxyribonucleic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides,  
35 essential oils, plant extracts and vitamin complexes.

### Deodorising active ingredients

As deodorising active ingredients there come into consideration, for example, antiperspirants, for example aluminium chlorohydrates (see J. Soc. Cosm. Chem. 24, 281 (1973)). Under the trade mark Locron® of Hoechst AG, Frankfurt (FRG), there is available commercially, for example, an aluminium chlorohydrate corresponding to formula  $Al_2(OH)_5Cl \times 2.5 H_2O$ , the use of which is especially preferred (see J. Pharm. Pharmacol. 26, 531 (1975)). Besides the chlorohydrates, it is also possible to use aluminium hydroxyacetates and acidic aluminium/zirconium salts. Esterase inhibitors may be added as further deodorising active ingredients. Such inhibitors are preferably trialkyl citrates, such as trimethyl citrate, tripropyl citrate, triisopropyl citrate, tributyl citrate and especially triethyl citrate (Hydagen CAT, Henkel), which inhibit enzyme activity and hence reduce odour formation. Further substances that come into consideration as esterase inhibitors are sterol sulfates or phosphates, for example lanosterol, cholesterol, campesterol, stigmasterol and sitosterol sulfate or phosphate, dicarboxylic acids and esters thereof, for example glutaric acid, glutaric acid monoethyl ester, glutaric acid diethyl ester, adipic acid, adipic acid monoethyl ester, adipic acid diethyl ester, malonic acid and malonic acid diethyl ester and hydroxycarboxylic acids and esters thereof, for example citric acid, malic acid, tartaric acid or tartaric acid diethyl ester. Antibacterial active ingredients that influence the germ flora and kill or inhibit the growth of sweat-decomposing bacteria can likewise be present in the preparations (especially in stick preparations). Examples include chitosan, phenoxyethanol and chlorhexidine gluconate. 5-chloro-2-(2,4-dichlorophenoxy)-phenol (Triclosan, Irgasan, Ciba Specialty Chemicals Inc.) has also proved especially effective.

### Anti-dandruff agents

As anti-dandruff agents there may be used, for example, climbazole, octopirox and zinc pyrithione. Customary film formers include, for example, chitosan, microcrystalline chitosan, quaternised chitosan, polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers, polymers of quaternary cellulose derivatives containing a high proportion of acrylic acid, collagen, hyaluronic acid and salts thereof and similar compounds.

### Antioxidants

In addition to the primary light-protective substances it is also possible to use secondary light-protective substances of the antioxidant kind that interrupt the photochemical reaction chain triggered when UV radiation penetrates the skin or hair. Typical examples of such antioxidants are amino acids (e.g. glycine, histidine, tyrosine, tryptophan) and derivatives thereof, imidazoles (e.g. urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (e.g. anserine), carotinoids, carotenes,

lycopene and derivatives thereof, chlorogenic acid and derivatives thereof, lipoic acid and derivatives thereof (e.g. dihydrolipoic acid), aurothioglycose, propylthiouracil and other thiols (e.g. thioredoxin, glutathione, cysteine, cystine, cystamine and the glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl, lauryl, palmitoyl, oleyl, linoleyl, cholesteryl and glyceryl esters thereof) and also salts thereof, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and also sulfoximine compounds (e.g. buthionine sulfoximines, homocysteine sulfoximine, buthionine sulfones, penta-, hexa-, hepta-thionine sulfoximine), also (metal) chelating agents (e.g. hydroxy fatty acids, palmitic acid phytic acid, lactoferrin), hydroxy acids (e.g. citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EDDS, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (e.g. linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives (e.g. ascorbyl palmitate, magnesium ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (e.g. vitamin E acetate), vitamin A and derivatives (e.g. vitamin A palmitate) and also coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, glycosylrutin, ferulic acid, furfurylidene glucitol, carnosine, butyl hydroxytoluene, butyl hydroxyanisole, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and derivatives thereof, mannose and derivatives thereof, superoxide dismutase, N-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl]sulfanilic acid (and salts thereof, for example the disodium salts), zinc and derivatives thereof (e.g. ZnO, ZnSO<sub>4</sub>), selenium and derivatives thereof (e.g. selenium methionine), stilbene and derivatives thereof (e.g. stilbene oxide, trans-stilbene oxide) and the derivatives suitable according to the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids) of those mentioned active ingredients. HALS ("Hindered Amine Light Stabilizers") compounds may also be mentioned.

Further synthetic and natural antioxidants are listed e.g. in patent WO 0025731:

Structures 1-3 (page 2), structure 4 (page 6), structures 5-6 (page 7) and compounds 7-33 (page 8-14).

### Hydrotropic agents

To improve the flow behaviour it is also possible to employ hydrotropic agents, for example ethoxylated or non ethoxylated mono-alcohols, diols or polyols with a low number of carbon atoms or their ethers (e.g. ethanol, isopropanol, 1,2-dipropanediol, propyleneglycol, glycerin, ethylene glycol, ethylene glycol monoethylether, ethylene glycol monobutylether, propylene glycol monomethylether, propylene glycol monoethylether, propylene glycol monobutylether, diethylene glycol monomethylether; diethylene glycol monoethylether, diethylene glycol mo-

nobutylether and similar products). The polyols that come into consideration for that purpose have preferably from 2 to 15 carbon atoms and at least two hydroxy groups. The polyols may also contain further functional groups, especially amino groups, and/or may be modified with nitrogen. Typical examples are as follows: glycerol, alkylene glycols, for example ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and also poly-  
5 ethylene glycols having an average molecular weight of from 100 to 1000 Dalton; technical oligoglycerol mixtures having an intrinsic degree of condensation of from 1.5 to 10, for example technical diglycerol mixtures having a diglycerol content of from 40 to 50 % by weight; methylol compounds, such as, especially, trimethylolethane, trimethylolpropane,  
10 trimethylolbutane, pentaerythritol and dipentaerythritol; lower alkyl-glucosides, especially those having from 1 to 8 carbon atoms in the alkyl radical, for example methyl and butyl glucoside; sugar alcohols having from 5 to 12 carbon atoms, for example sorbitol or mannitol; sugars having from 5 to 12 carbon atoms, for example glucose or saccharose; amino sugars, for example glucamine; dialcohol amines, such as diethanolamine or 2-amino-1,3-propane-  
15 diol.

#### Preservatives and Bacteria-inhibiting agents

Suitable preservatives include, for example, Methyl-, Ethyl-, Propyl-, Butyl- parabens, Benzalkonium chloride, 2-Bromo-2-nitro-propane-1,3-diol, Dehydroacetic acid, Diazolidinyl Urea, 2-  
20 Dichloro-benzyl alcohol, DMDM hydantoin, Formaldehyde solution, Methyltribromoglutaritrile, Phenoxyethanol, Sodium Hydroxymethylglycinate, Imidazolidinyl Urea, Triclosan and further substance classes listed in the following reference: K.F.DePolo – A short textbook of cosmetology, Chapter 7, Table 7-2, 7-3, 7-4 and 7-5, p210-219.

25 Typical examples of bacteria-inhibiting agents are preservatives that have a specific action against gram-positive bacteria, such as 2,4,4'-trichloro-2'-hydroxydiphenyl ether, chlorhexidine (1,6-di(4-chlorophenyl-biguanido)hexane) or TCC (3,4,4'-trichlorocarbanilide). A large number of aromatic substances and ethereal oils also have antimicrobial properties. Typical examples are the active ingredients eugenol, menthol and thymol in clove oil, mint oil and  
30 thyme oil. A natural deodorising agent of interest is the terpene alcohol farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol), which is present in lime blossom oil. Glycerol monolaurate has also proved to be a bacteriostatic agent. The amount of the additional bacteria-inhibiting agents present is usually from 0.1 to 2 % by weight, based on the solids content of the preparations.

### Perfume oils

There may be mentioned as perfume oils mixtures of natural and/or synthetic aromatic substances. Natural aromatic substances are, for example, extracts from blossom (lilies, lavender, roses, jasmine, neroli, ylang-ylang), from stems and leaves (geranium, patchouli, petit-grain), from fruit (aniseed, coriander, carraway, juniper), from fruit peel (bergamot, lemons, oranges), from roots (mace, angelica, celery, cardamom, costus, iris, calmus), from wood (pinewood, sandalwood, guaiacum wood, cedarwood, rosewood), from herbs and grasses (tarragon, lemon grass, sage, thyme), from needles and twigs (spruce, pine, Scots pine, mountain pine), from resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax). Animal raw materials also come into consideration, for example civet and castoreum. Typical synthetic aromatic substances are, for example, products of the ester, ether, aldehyde, ketone, alcohol or hydrocarbon type. Aromatic substance compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butylcyclohexyl acetate, linalyl acetate, dimethylbenzylcarbonyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styryl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals having from 8 to 18 hydrocarbon atoms, citral, citronellal, citronellyl oxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilyal and bourgeonal; the ketones include, for example, the ionones, isomethylionone and methyl cedryl ketone; the alcohols include, for example, anethol, citronellol, eugenol, isoeugenol, geraniol, linalool, phenyl ethyl alcohol and terpinol; and the hydrocarbons include mainly the terpenes and balsams. It is preferable, however, to use mixtures of various aromatic substances that together produce an attractive scent. Ethereal oils of relatively low volatility, which are chiefly used as aroma components, are also suitable as perfume oils, e.g. sage oil, camomile oil, clove oil, melissa oil, oil of cinnamon leaves, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, labolanum oil and lavandin oil. Preference is given to the use of bergamot oil, dihydromyrcenol, lilyal, lylal, citronellol, phenyl ethyl alcohol, hexyl cinnamaldehyde, geraniol, benzyl acetone, cyclamen aldehyde, linalool, boisambrene forte, ambroxan, indole, hedione, sandelice, lemon oil, tangerine oil, orange oil, allyl amyl glycolate, cyclovertal, lavandin oil, muscatel sage oil, damascone, bourbon geranium oil, cyclohexyl salicylate, vertofix coeur, iso-E-Super, Fixolide NP, evernyl, ionaldein gamma, phenylacetic acid, geranyl acetate, benzyl acetate, rose oxide, romillat, irotyl and floramat alone or in admixture with one another.

### Colourants

There may be used as colourants the substances that are suitable and permitted for cosmetic purposes, as compiled, for example, in the publication "Kosmetische Färbemittel" of the Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Wein-

heim, 1984, pages 81 to 106. The colourants are usually used in concentrations of from 0.001 to 0.1 % by weight, based on the total mixture.

#### Other adjuvants

- 5 It is furthermore possible for the cosmetic preparations to contain, as adjuvants, anti-foams, such as silicones, structurants, such as maleic acid, solubilisers, such as ethylene glycol, propylene glycol, glycerol or diethylene glycol, opacifiers, such as latex, styrene/PVP or styrene/acrylamide copolymers, complexing agents, such as EDTA, NTA, alaninediacetic acid or phosphonic acids, propellants, such as propane/butane mixtures, N<sub>2</sub>O, dimethyl ether,
- 10 CO<sub>2</sub>, N<sub>2</sub> or air, so-called coupler and developer components as oxidation dye precursors, reducing agents, such as thioglycolic acid and derivatives thereof, thiolactic acid, cysteamine, thiomalic acid or mercaptoethanesulfonic acid, or oxidising agents, such as hydrogen peroxide, potassium bromate or sodium bromate.
- 15 Suitable insect repellents are, for example, N,N-diethyl-m-toluamide, 1,2-pentanediol or insect repellent 3535; suitable self-tanning agents are, for example, dihydroxyacetone and/or erythrulose or dihydroxy acetone and/or dihydroxy acetone precursors as described in WO 01/85124 and/or erythrulose.

#### Polymeric beads or hollow spheres as SPF enhancers

- The combination of the UV-absorbers and UV-absorber combinations, listed above, with SPF enhancers, such as non-active ingredients like Styrene/acrylates copolymer, silica beads, spheroidal magnesium silicate, crosslinked Polymethylmethacrylates (PMMA ; Micopearl M305 Seppic), can maximize better the UV protection of the sun products. Holosphere addi-
- 25 tives (Sunspheres® ISP, Silica Shells Kobo.) deflect radiation and the effective path length of the photon is therefore increased ( EP0893119). Some beads, as mentioned previously, provide a soft feel during spreading. Moreover, the optical activity of such beads, e.g. Micropearl M305, cans modulate skin shine by eliminating reflection phenomena and indirectly may scatter the UV light.

30

#### Cosmetic or pharmaceutical preparations

Cosmetic or pharmaceutical formulations are contained in a wide variety of cosmetic preparations. There come into consideration, for example, especially the following preparations:

35

- skin-care preparations, e.g. skin-washing and cleansing preparations in the form of tablet-form or liquid soaps, soapless detergents or washing pastes,

- bath preparations, e.g. liquid (foam baths, milks, shower preparations) or solid bath preparations, e.g. bath cubes and bath salts;
- skin-care preparations, e.g. skin emulsions, multi-emulsions or skin oils;
- cosmetic personal care preparations, e.g. facial make-up in the form of day creams or powder creams, face powder (loose or pressed), rouge or cream make-up, eye-care preparations, e.g. eye shadow preparations, mascara, eyeliner, eye creams or eye-fix creams; lip-care preparations, e.g. lipsticks, lip gloss, lip contour pencils, nail-care preparations, such as nail varnish, nail varnish removers, nail hardeners or cuticle removers;
- foot-care preparations, e.g. foot baths, foot powders, foot creams or foot balsams, special deodorants and antiperspirants or callus-removing preparations;
- light-protective preparations, such as sun milks, lotions, creams or oils, sunblocks or tropicals, pre-tanning preparations or after-sun preparations;
- skin-tanning preparations, e.g. self-tanning creams;
- depigmenting preparations, e.g. preparations for bleaching the skin or skin-lightening preparations;
- insect-repellents, e.g. insect-repellent oils, lotions, sprays or sticks;
- deodorants, such as deodorant sprays, pump-action sprays, deodorant gels, sticks or roll-ons;
- antiperspirants, e.g. antiperspirant sticks, creams or roll-ons;
- preparations for cleansing and caring for blemished skin, e.g. synthetic detergents (solid or liquid), peeling or scrub preparations or peeling masks;
- hair-removal preparations in chemical form (depilation), e.g. hair-removing powders, liquid hair-removing preparations, cream- or paste-form hair-removing preparations, hair-removing preparations in gel form or aerosol foams;
- shaving preparations, e.g. shaving soap, foaming shaving creams, non-foaming shaving creams, foams and gels, pre shave preparations for dry shaving, aftershaves or aftershave lotions;
- fragrance preparations, e.g. fragrances (eau de Cologne, eau de toilette, eau de parfum, parfum de toilette, parfume), parfume oils or parfume creams;
- cosmetic hair-treatment preparations, e.g. hair-washing preparations in the form of shampoos and conditioners, hair-care preparations, e.g. pre-treatments preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-structuring preparations, e.g. hair-waving preparations for permanent waves (hot wave, mild wave, cold wave), hair-straightening preparations, liquid hair-setting preparations, hair foams, hairsprays, bleaching preparations, e.g. hydrogen peroxide solutions, lightening shampoos, bleaching creams, bleaching



powders, bleaching pastes or oils, temporary, semi-permanent or permanent hair colourants, preparations containing self-oxidising dyes, or natural hair colourants, such as henna or camomile.

5 Presentation forms

The final formulations listed may exist in a wide variety of presentation forms, for example:

- in the form of liquid preparations as a W/O, O/W, O/W/O, W/O/W or PIT emulsion and all kinds of microemulsions,
- 10 - in the form of a gel,
- in the form of an oil, a cream, milk or lotion,
- in the form of a powder, a lacquer, a tablet or make-up,
- in the form of a stick,
- in the form of a spray (spray with propellant gas or pump-action spray) or an aerosol,
- 15 - in the form of a foam, or
- in the form of a paste.

Of special importance as cosmetic preparations for the skin are light-protective preparations, such as sun milks, lotions, creams, oils, sunblocks or tropicals, pretanning preparations or  
20 after-sun preparations, also skin-tanning preparations, for example self-tanning creams. Of particular interest are sun protection creams, sun protection lotions, sun protection milks and sun protection preparations in the form of a spray.

Of special importance as cosmetic preparations for the hair are the above-mentioned prepa-  
25 rations for hair treatment, especially hair-washing preparations in the form of shampoos, hair conditioners, hair-care preparations, e.g. pre-treatment preparations, hair tonics, styling creams, styling gels, pomades, hair rinses, treatment packs, intensive hair treatments, hair-straightening preparations, liquid hair-setting preparations, hair foams and hairsprays. Of special interest are hair-washing preparations in the form of shampoos.

30

A shampoo has, for example, the following composition: from 0.01 to 5 % by weight of a UV absorber according to the invention, 12.0 % by weight of sodium laureth-2-sulfate, 4.0 % by weight of cocamidopropyl betaine, 3.0 % by weight of sodium chloride, and water ad 100%.

35 For example, especially the following hair-cosmetic formulations may be used:

- a<sub>1</sub>) spontaneously emulsifying stock formulation, consisting of the UV absorber according to the invention, PEG-6-C<sub>10</sub>oxoalcohol and sorbitan sesquioleate, to which water and any desired quaternary ammonium compound, for example 4 % minkamidopropyl dimethyl-2-hydroxyethylammonium chloride or Quaternium 80 is added;
- 5 a<sub>2</sub>) spontaneously emulsifying stock formulation consisting of the UV absorber according to the invention, tributyl citrate and PEG-20-sorbitan monooleate, to which water and any desired quaternary ammonium compound, for example 4 % minkamidopropyl dimethyl-2-hydroxyethylammonium chloride or Quaternium 80 is added;
- b) quat-doped solutions of the UV absorber according to the invention in butyl triglycol and
- 10 tributyl citrate;
- c) mixtures or solutions of the UV absorber according to the invention with n-alkylpyrrolidone.

The cosmetic preparation according to the invention is characterized by excellent protection

15 of human skin against the damaging effect of sunlight.

Examples A1 – A 21: Cosmetic sunscreen preparations:

Example		A1	A2	A3	A4	A5	A6	A7	A8	A9
	INCI-Name	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)	% (w/w)
Part A	PEG-30 Dipolyhydroxystearate	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50
	Cetyl PEG/PPG-10/1 Dimethicone	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Disobutyl Adipate		5.00	5.00		5.00	5.00		5.00	5.00
	C12-15 Alkyl Benzoate	5.00		5.00	5.00		5.00	5.00		5.00
	Isohexadecane	3.00	3.00		3.00	3.00		3.00	3.00	
	Magnesium Stearate	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
	Ethylhexyl Methoxycinnamate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
	Diethylamino Hydroxybenzoyl Hexyl Benzoate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
	Ethylhexyl Triazone	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	2.20	2.20	2.20	2.20	2.20	2.20	2.20	2.20	2.20
	C <sub>8</sub> levylinate	5.00								
	C <sub>8</sub> levylinate		5.00							
	C <sub>8</sub> levylinate			3.00						
	C <sub>9</sub> levylinate				5.00					
	C <sub>9</sub> levylinate					5.00				
	C <sub>9</sub> levylinate						3.00			
	C <sub>14</sub> levylinate							5.00		
	C <sub>14</sub> levylinate								5.00	
	C <sub>14</sub> levylinate									3.00
Part B	Aqua	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100
	SPF	50.93	50.93	50.93	50.93	50.93	50.93	50.93	50.93	50.93
	Glycerin	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
	Magnesium Sulfate	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Part C	Cyclopentasiloxane, Cyclohexasiloxane	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
	Phenoxyethanol	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Manufacturing Instruction		Heat up phase A and B to 80°C. Add phase B slowly into phase A under increased stirring speed. Homogenize for a short time. Cool down under gentle stirring. Below 40°C add phase C. Finally homogenize for a short time again.								
Specifications		Viscosity: 700 - 900 mPas (Brookfield; DV-III+; spindle LV2; 20 rpm; 20°C)								
Performance		SPF in vivo: 50.9								

la Boite de Pandore Sun Care Cream SPF 30												
Composition	A10	A11	A12	A13	A14	A15	A16	A17	A18	A19	A20	A21
INCI-Name	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w
Part A	Sodium Stearoyl Glutamate	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
	Stearyl Alcohol	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Phenoxyethyl Caprylate		8.00	8.00	8.00		8.00	8.00		8.00	8.00	8.00

la Boite de Pandore Sun Care Cream SPF 30													
Composition		A10	A11	A12	A13	A14	A15	A16	A17	A18	A19	A20	A21
INCI-Name		% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w
	Dibutyl Adipate	5.00		5.00	5.00	5.00		5.00	5.00	5.00		5.00	5.00
	Ethylhexyl Benzoate	5.00	5.00		5.00	5.00	5.00		5.00	5.00	5.00		5.00
	Lauryl Lactate	3.00	3.00	3.00		3.00	3.00	3.00		3.00	3.00	3.00	
	Diethylamino Hydroxybenzoyl Hexyl Benzoate	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
	Ethylhexyl Triazone	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
	C <sub>8</sub> levulinate	8.00	5.00	5.00	3.00								
	C <sub>10</sub> -levulynate					8.00	5.00	5.00	3.00				
	C <sub>8/10</sub> -levulynate									8.00	5.00	5.00	3.00
Part B	Aqua	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100	Qs to 100
		58.52	58.52	58.52	58.52	58.52	58.52	58.52	58.52	58.52	58.52	58.52	58.52
	Glycerin	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
	Sodium Polyacrylate	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
	Xanthan Gum	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
	Disodium EDTA	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Part C	Polyamide-5	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
	Phenoxyethanol	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
pH value		6.00 - 6.40											
Viscosity		28 000 - 32 000 mPas											
Manufacturing Instruction		Heat phase A and B to 80°C. Add phase A into B, homogenize. Cool to room temperature then add phase C under stirring. Continue stirring for a while.											
Specifications		pH value: 6.00 - 6.40 Viscosity: 28 000 - 32 000 mPas											
Performance		UVA-PF in vitro: 30											

## Examples A22 – A33

The values for SPF (in silico) and UVA-PF (in silico) given in the following examples are calculated according to the method described in Pure Appl. Chem. 87 (2015), 937–951.

5

Example A22		
Trade Name	INCI-Name	% (w/w) as supplied
Eumulgin® SG	Sodium Stearoyl Glutamate	2.00
Lanette® 18	Stearyl Alcohol	1.00
Levulynate	C <sub>8</sub> or C <sub>10</sub> or C <sub>8/10</sub> Levulynate	14.00
Cetiol® AB	C12-15 Alkyl Benzoate	5.00
Finsolv EB	Ethylhexyl Benzoate	3.00

Example A22		
Trade Name	INCI-Name	% (w/w) as supplied
Euxyl PE9010	Phenoxyethanol (and) Ethylhexylglycerin	1.00
Uvinul® T150	Ethylhexyl Triazone	3.00
Uvinul® A Plus	Diethylamino Hydroxybenzoyl Hexyl Benzoate	10.00
Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	3.00
Water, demin.	Aqua	Qs. 100
Glycerin	Glycerol	3.00
Cosmedia SP	Sodium Polyacrylate	0.60
Keltrol CG-RD	Xanthan Gum	0.50
EDTA BD	Disodium EDTA	0.20
SPF (in silico)		30.1
UVA-PF (in silico)		26.7
The formulation is prepared using a standard sunscreen emulsion as shown in the Table by heating phase A and B to 80°C then adding phase A into B to homogenize then cooling to room temperature and continued stirring for a while. pH value 6.00-6.40.		

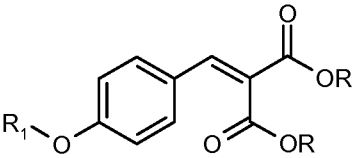




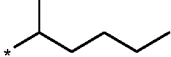
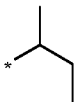
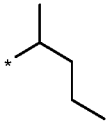
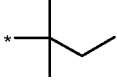
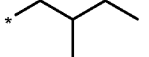



Example A23		
Trade Name	INCI-Name	% (w/w) as supplied
Phase A		
Cetiol® B	Dibutyl Adipate	15.00
Levulynate	C <sub>8</sub> or C <sub>10</sub> or C <sub>8/10</sub> Levulynate	14.00
Lanette® O	Cetearyl Alcohol	1.50
Lanette® 18	Stearyl Alcohol	1.00
Euxyl PE9010	Phenoxyethanol (and) Ethylhexylglycerin	1.00
Uvinul® T150	Ethylhexyl Triazone	2.10
BMDBM	Butyl Methoxydibenzoylmethane	2.50
Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	1.30
Phase B		
Water, demin.	Aqua	Qs. 100
Glycerin	Glycerol	3.00
Amphisol K	Potassium Cetyl Phosphate	2.50
Keltrol CG-RD	Xanthan Gum	0.25
Edeta® BD	Disodium EDTA	0.20
Phase C		
Tinosorb M	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (nano) (and) Aqua (and) Decyl Glucoside (and) Propylene Glycol (and) Xanthan Gum	4.00
Tinosorb A2B	Tris-Biphenyl Triazine (nano) (and) Aqua (and) Decyl Glucoside (and) Butylene Glycol (and) Disodium Phosphate (and) Xanthan Gum	5.00
SPF (in silico)		33.4
UVA-PF (in silico)		12.4
The formulation is prepared using a standard sunscreen emulsion as shown in Table 2 by heating phase A to 75°C under stirring followed by heating up phase B without Amphisol K to 75°C under stirring. At 75°C added Amphisol K into phase B, continue stirring. Add phase A into phase B under stirring to homogenize. Cool down to 40°C under stirring. Add the ingredients of phase C and D under stirring. Cool down to room temperature under stirring. pH value 6.0.		

Example A24		
<u>Trade Name</u>	<u>INCI-Name</u>	<u>% (w/w) as supplied</u>
Phase A		
Eumulgin B2	Ceteareth-20	2.00
Eldew SL-205	Isopropyl Lauryl Sarcosinate	10.00
Levulynate	C <sub>8</sub> or C <sub>10</sub> or C <sub>8/10</sub> Levulynate	30.00
Euxyl PE9010	Phenoxyethanol (and) Ethylhexylglycerin	2.00
Uvinul® T150	Ethylhexyl Triazone	1.50
Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	1.70
Phase B		
Water, demin.	Aqua	qs. to 100
1,3-Butandiol	Butylene Glycol	2.00
Tinovis GTC	Acrylates/Beheneth-25 Methacrylate copolymer	2.00
EDTA® BD	Disodium EDTA	0.20
Phase C		
Tinosorb® M	Tris-Biphenyl Triazine	6.00
Tinsorb® A2B	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol	6.00
SPF (in silico)		33.7
UVA-PF (in silico)		11.2
The formulation is prepared using a standard sunscreen emulsion as shown in Table 3 described below, by heating up phase A and phase B (first phase B without Tinovis GTC, add under stirring) to 75°C under stirring. (to solve all crystalline ingredients). Add phase A into B under homogenizer. (Ultra Turrax at speed 9500 rpm, time 90sec). Cool down to room temperature under continuous stirring. (stirring with helice paddle). Meanwhile, in case of order, mix phase C, at RT add phase C and adjust the pH approx at 6,5. Finally adjust the pH at 6.5-7.0.		

Example A25		
<u>Trade Name</u>	<u>INCI-Name</u>	<u>% (w/w) as supplied</u>
Phase A		
Cetiol® OE	Dicaprylyl Ether	6.00
Isopropyl Palmitate	Isopropyl Palmitate	5.00
Levulynate	C <sub>8</sub> or C <sub>10</sub> or C <sub>8/10</sub> Levulynate	4.00
Antaron V-220	VP/Eicosene Copolymer	4.00
Lanette® 22	Behenyl Alcohol	2.50
Uvinul® MC 80	Ethylhexyl Methoxycinnamate	7.00
Uvinul® T150	Ethylhexyl Triazone	
Uvinul® A Plus	Diethylamino Hydroxybenzoyl Hexyl Benzoate	4.00
Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	
Phase B		
Water, demin.	Aqua	Qs. 100
Amphisol K	Potassium Cetyl Phosphate	2.50
Edeta® BD	Disodium EDTA	0.20

Example A25		
<u>Trade Name</u>	<u>INCI-Name</u>	<u>% (w/w) as supplied</u>
Keltrol CG-RD	Xantham Gum	0.15
Phase C		
Xiameter PMX-200 Silicone Fluid 1CS	Dimethicone	5.00
Tinosorb®S Aqua	Aqua, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Polymethyl Methacrylate, Sodium Laureth Sulfate, Aminomethyl Propanol	5.00
Preservative		qs
SPF (in silico)		23.4
UVA-PF (in silico)		9.9
The formulation is prepared using a standard sunscreen emulsion as shown in the Table described below, by heating up phase A to 75°C under stirring followed by heating up phase B without Amphisol K to 75°C under stirring. At 75°C add Amphisol K into Phase B, continue stirring. Add phase A into phase B under stirring, homogenize. Cool down to RT, add the ingredients of phase C. pH value 6.1-6.5.		

Example A26		
<u>Trade Name</u>	<u>INCI-Name</u>	<u>% (w/w) as supplied</u>
Phase A		
Dehymuls PGPH	Polyglyceryl-2-Dipolyhydroxystearate	4.00
Levulynate	C <sub>8/10</sub> Levulynate	10.00
Cetion AB	C12-15 Alkyl Benzoate	5.00
Lanette O	Cetearyl Alcohol	2.50
Benzylidene Malonate*	MBM-01 or MBM-02 or MBM-03 or MBM-04 or MBM-05 or MBM-06 or MBM-07 or MBM-08 or MBM-09 or MBM-10 or MBM-11 or MBM-12	9.50
Uvinul® T150	Ethylhexyl Triazone	2.50
Uvinul® A Plus	Diethylamino Hydroxybenzoyl Hexyl Benzoate	10.00
Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	1.00
Phase B		
Water, demin.	Aqua	Qs. 100
Glycerin	Glycerin	3.00
Plantapon® LGC SORB	Sodium Lauryl Glucose Carboxylate (and) Lauryl Glucoside	1.50
Cosmedia® SP	Sodium Polyacrylate	0.80
Edeta® BD	Disodium EDTA	0.20
Keltrol CG-RD	Xantham Gum	0.15
Phase C		
Tinosorb®M	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol	4.00
Preservative		qs
SPF (in silico)		50.9
UVA-PF (in silico)		21.2
The formulation is prepared using a standard sunscreen emulsion as shown in Table 5 described below, by heating phase A to 75°C under stirring followed by heating phase B to 75°C under stirring. Add phase A to B under stirring, homogenize. Cool down under stirring, below 40°C add phase C. Continue stirring. pH value 5.6-6.5		

		
	$R_1$	$R$
MBM-01	methyl	
MBM-02	methyl	
MBM-03	methyl	
MBM-04	methyl	
MBM-05	methyl	
MBM-06	methyl	
MBM-07	methyl	
MBM-08	methyl	
MBM-09	methyl	
MBM-10	ethyl	
MBM-11	propyl	
MBM-12	n-butyl	

Example A27		
<u>Trade Name</u>	<u>INCI-Name</u>	<u>% (w/w) as supplied</u>
Phase A		
Dehymuls LE	PEG-30 Dipolyhydroxystearate	4.00
Cetiol CC	Dicaprylyl Carbonate	12.00
Levulynate	C <sub>8</sub> or C <sub>10</sub> or C <sub>8/10</sub> Levulynate	6.00
Uvinul® MC 80	Ethylhexyl Methoxycinnamate	7.50
Uvinul® A Plus	Diethylamino Hydroxybenzoyl Hexyl Benzoate	7.00
Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	2.50
Phase B		



Example A27		
<u>Trade Name</u>	<u>INCI-Name</u>	<u>% (w/w) as supplied</u>
Water, demin.	Aqua	Qs. 100
Butylene Glycol	Butylene Glycol	3.00
Sodium Chloride	Sodium Chloride	1.00
Edeta BD	Disodium EDTA	0.10
Phase C		
Tinosorb®A2B	Tris-Biphenyl Triazine	10.0
Phase D		
Xiameter PMX-200 Silicone Fluid 1CS	Dimethicone	22.00
Ethanol	Alcohol	8.00
Orasol 2002 D NAT COS	Nylon-12	2.00
Preservative		qs.
SPF (in silico)		51.1
UVA-PF (in silico)		18.4
The formulation is prepared using a standard sunscreen emulsion as shown in Table 6 described below, by heating up phases A and B to 75°C. At 75°C add phase B into A under quick stirring. Under 40°C add phase C. Cool down to RT, then add phase D in the given order.		

Example A28 – A33 are prepared using standard sunscreen emulsions as shown in Tables described below.

	<u>Example A28</u>	<u>Example A29</u>
INCI	% w/w	% w/w
Ceateryl Glucoside (nad) Cetearyl Alcohol	4.00	4.00
Disodium Cetearyl Sulfosuccinate	1.00	1.00
C <sub>8</sub> or C <sub>10</sub> or C <sub>8/10</sub> Levulynate	10.00	10.00
C12-15 Alkyl Benzoate	8.00	8.00
Dibutyl Adipate	8.00	8.00
Coco-Caprylate	4.00	4.00
Pentaerythrityl Distearate	1.00	1.00
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	2.00	2.00
Aqua	Qs. 100	Qs. 100
Glycerin	3.00	3.00
Di Na EDTA	0.20	0.20
Xanthan Gum	0.40	0.40
Phenoxyethanol	1.00	1.00
Carbomer	0.15	0.15
Methylene Bis-Benzotriazolyl Tetramethylbutylphenol	4.00	4.00
Aqua, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Polymethyl Methacrylate, Sodium Laureth Sulfate, Aminomethyl Propanol	5.00	5.00
1,1'-(1,4-piperazinediyl)bis[1-[2-[4-(diethylamino)- 2-hydroxybenzoyl]phenyl]-methanone		8.00
Silica	1.00	1.00
Polyamide-5	2.00	2.00

Tetrahydroxypropyl Ethylenediamine	0.80	1.00
SPF in silico	11.0	14.2
UVA-PF (in silico)	10.2	11.4

	Example A30	Example A31
INCI	% w/w	% w/w
Ceatearyl Glucoside (and) Cetearyl Alcohol	4.00	4.00
Disodium Cetearyl Sulfosuccinate	1.50	1.50
C <sub>8</sub> or C <sub>10</sub> or C <sub>8/10</sub> Levulynate	8.00	8.00
Dibutyl Adipate	8.00	8.00
Diisopropyl Sebacate	5.00	5.00
Coco-Caprylate	4.00	4.00
Pentaerythrityl Distearate	1.00	1.00
Diethylamino Hydroxybenzoyl Hexyl Benzoate	3.00	3.00
Ethylhexyl Triazone	2.00	2.00
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	2.00	2.00
Aqua	Qs. 100	Qs. 100
Glycerin	3.00	3.00
Di Na EDTA	0.20	0.20
Xanthan Gum	0.40	0.40
Phenoxyethanol	1.00	1.00
Carbomer	0.15	0.15
Aqua, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Polymethyl Methacrylate, Sodium Laureth Sulfate, Aminomethyl Propanol	7.50	7.50
1,1'-(1,4-piperazinediyl)bis[1-[2-[4-(diethylamino)-2-hydroxybenzoyl]phenyl]-methanone		20.00
Silica	1.00	1.00
Polyamide-5	2.00	2.00
Tetrahydroxypropyl Ethylenediamine	0.80	0.80
SPF in silico	22.7	32.9
UVA-PF (in silico)	13.7	35.6

	Example A32	Example A33
INCI	% w/w	% w/w
Ceteareth-20	1.50	1.50
Disodium Cetearyl Sulfosuccinate	2.50	2.50
Dibutyl Adipate	11.00	11.00
C <sub>8</sub> or C <sub>10</sub> or C <sub>8/10</sub> Levulynate	7.00	7.00
Diethylamino Hydroxybenzoyl Hexyl Benzoate	8.00	8.00
Ethylhexyl Triazone	3.00	3.00
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	2.00	2.00
Aqua	Qs. 100	Qs. 100
Di Na EDTA	0.20	0.20
Xanthan Gum	0.50	0.50
Phenoxyethanol	1.00	1.00
Phenylbenzimidazole Sulfonic Acid	1.00	1.00
Aqua		
Tetrahydroxypropyl Ethylenediamine	2.90	2.90
Methylene Bis-Benzotriazolyl Tetramethylbutylphenol	6.00	6.00
Aqua, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine,	10.00	10.00

	<u>Example A32</u>	<u>Example A33</u>
<u>INCI</u>	<u>% w/w</u>	<u>% w/w</u>
Polymethyl Methacrylate, Sodium Laureth Sulfate, Aminomethyl Propanol		
1,1'-(1,4-piperazinediyl)bis[1-[2-[4-(diethylamino)-2-hydroxybenzoyl]phenyl]-methanone		20.00
Polymethyl Methacrylate	2.00	2.00
SPF in silico	51.7	61.2
UVA-PF (in silico)	37.7	64.0

It is understood that while the invention has been described in conjunction with the detailed description thereof, that the foregoing description is intended to illustrate and not limit the scope of the invention.

5

Example B: Determination of the solubility of

- Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine
- Diethylamino Hydroxybenzoyl Hexyl Benzoate and
- Ethylhexyl Triazone

10

Material

(suggested brand names/suppliers in parentheses. Equivalents can be used)

- a) Water bath: 25°C ± 1°C + magnetic stirrer + magnet bars
- b) Snap cap vials (VWR 548-0623, 20 mL)
- 15 c) Laboratory balance (Mettler Toledo AE 100)
- d) Micropipettor (2000µl) and tips (Eppendorf Research 2000)
- f) Lab centrifuge and tubes (VWR Galaxy 16 DH)
- g) Volumetric flasks (5-250ml)
- h) Beakers (e.g. 10ml)
- 20 h) Syringe filter units 0.2µm (Membrex 25 PET)
- i) Syringes 10 ml (Norm Ject by Henke Sass Wolf)
- e) UV-Spectrophotometer (Perkin Elmer Lambda 20) and Quarz cuvettes (Hellma QS 1cm)

Experimental

- 25 2 ml of the solvent are filled into a 20 ml vial with cap. Afterwards 0.02 g (1%) of the respective substance are weighed and added to the solvent. The vial is placed into a thermostated waterbath, where the suspension/solution is stirred during seven days at 25°C. If the amount of substance put into the solvent is fully soluble, additional substance is added until precipitation can be observed. After seven days, the sample is centrifuged for 30 minutes at 13000
- 30 rpm. The supernatant is transferred into a small beaker. In case the sample is still turbid, it is

filtered through a 0.2 µm non-steril Membrex 25 PET filter. Clear solutions must not be filtered. When a clear solution is obtained, the concentration of the substance is determined with UV/Vis-spectrometry. For this purpose the sample may be diluted with a suitable solvent or, in case of lower concentrations, may be measured as is.

- 5 Dilutions: If the test solvent is water, further dilution is done with water. If the test solvent is volatile, the same solvent is taken for dilution. If the test solvent is a cosmetic emollient, dioxane is used for further dilution. In order to evaluate the concentration from the UV-spectroscopic results, the extinction coefficient is needed, which is determined independently with a solvent of similar polarity like that one used for dilution of the saturated solutions.

10

#### Interpretation

The solubility can be calculated using the equation of the Lambert-Beer-Law:

$$c = \frac{E * f}{\epsilon * d}$$

$c$  = concentration (mol/l)

- 15  $E$  = extinction measured at  $\lambda$  max.

$f$  = dilution factor

$\epsilon$  = extinction coefficient at  $\lambda_{\max}$  [l/(mol\*cm)]

$d$  = optical pathlength [cm]

- 20 Exception

Due to spectra overlapping the solubility of some crystalline UV filters in liquid UV filters cannot be determined exactly by UV spectroscopy. In this case solubilities are determined via HPLC with reversed phase C-18 columns and UV-detectors.

- 25 Levulynates used as solvents:

<u>Product</u>	<u>Solubility [w/%]</u>		
	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	Ethylhexyl Triazone	Diethylamino Hydroxybenzoyl Hexyl Benzoate
C <sub>8</sub> -levulynate	10.4	25.1	42.6
C <sub>9</sub> -levulynate	9.7	22.7	/
C <sub>10</sub> -levulynate	9.1	21.0	31.0
C <sub>8/10</sub> -levulynate	9.0	23.3	35.3
C <sub>12</sub> -Levulynate	3.0	11.7	29.1
2-Ethylhexyl-levulynate	6.5	22.7	33.4

## Claims

1. Use of (A) an ester of levulinic acid with a fatty alcohol as solubilizing agent for oil soluble organic UV filters (B).

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2. Use according to claim 1, wherein the fatty alcohol has 8 to 22, preferably 8 to 18, C-atoms.

3. Use according to claim 1 or 2, wherein the oil soluble organic UV filters (B) are selected from

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(B<sub>1</sub>) benzophenone derivatives;

(B<sub>2</sub>) camphor derivatives;

(B<sub>3</sub>) triazine derivatives

(B<sub>4</sub>) dibenzoylmethane derivatives (BMBM);

15

(B<sub>5</sub>) cinnamic acid derivatives;

(B<sub>6</sub>) Benzylidenemalonates (BM);

(B<sub>7</sub>) diphenylacrylates;

(B<sub>8</sub>) polymeric UV absorbers;

(B<sub>9</sub>) Homosalates;

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(B<sub>10</sub>) Salicylic acid derivatives; and

(B<sub>11</sub>) Merocyanine derivatives.

4. Use according to any of claims 1 to 3, wherein the oil soluble organic UV filters (B) are

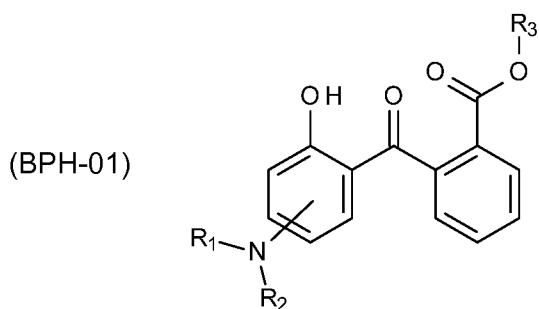
(B<sub>1</sub>) benzophenone derivatives,

25

(B<sub>2</sub>) hydroxyphenyl triazine derivatives; and

(B<sub>3</sub>) trianilino-s-triazine derivatives.

5. Use according to any of claims 1 to 4, wherein the benzophenone derivatives (B<sub>1</sub>) correspond to the formula



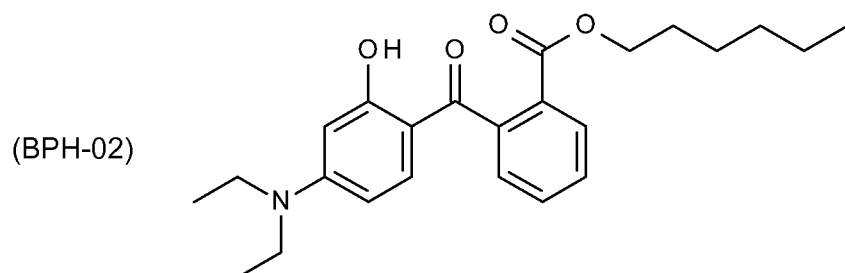
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wherein

R<sub>1</sub> and R<sub>2</sub> independently from each other are hydrogen; C<sub>1</sub>-C<sub>20</sub>alkyl; C<sub>3</sub>-C<sub>10</sub>cycloalkyl; or C<sub>3</sub>-C<sub>10</sub>cycloalkenyl, wherein the radicals R<sub>1</sub> and R<sub>2</sub> together with the nitrogen atom, to which they are bonded may form a 5- or 6-membered ring; and  
R<sub>3</sub> is C<sub>1</sub>-C<sub>20</sub>alkyl.

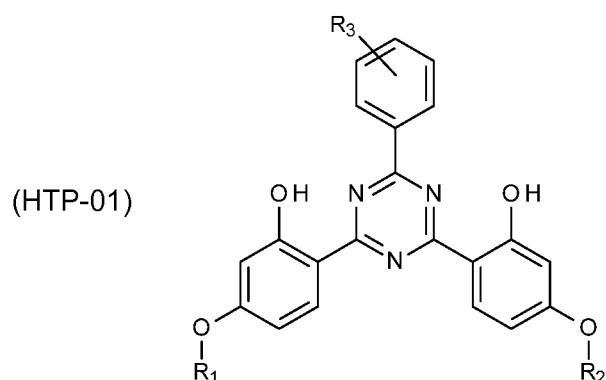
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6. Use according to any of claims 1 to 5, wherein the benzophenone derivatives (B1) correspond to the formula



7. Use according to any of claims 1 to 3, wherein the hydroxyphenyl triazine derivatives (B2) correspond to the formula

10



wherein

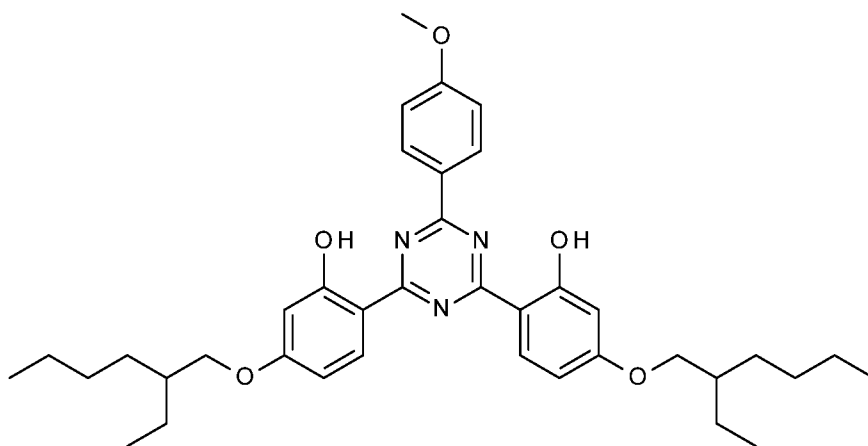
R<sub>1</sub> and R<sub>2</sub> independently from each other are C<sub>1</sub>-C<sub>18</sub>alkyl; and  
R<sub>3</sub> is C<sub>1</sub>-C<sub>10</sub>alkoxy.

15

8. Use according to claim 7, wherein the hydroxyphenyl triazine derivatives (B2) correspond to formula

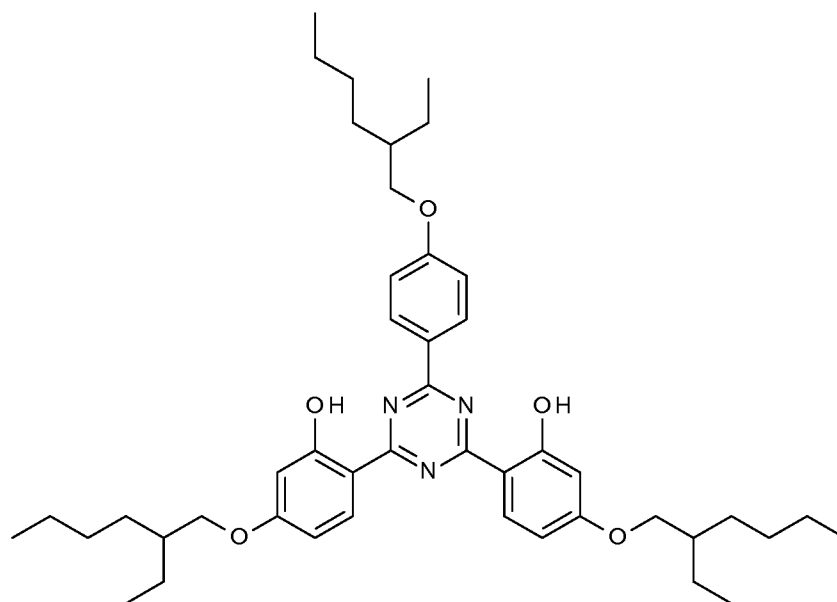
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(HTP-02)



9. Use according to claim 8, wherein the hydroxyphenyl triazine derivatives (B2) correspond to formula

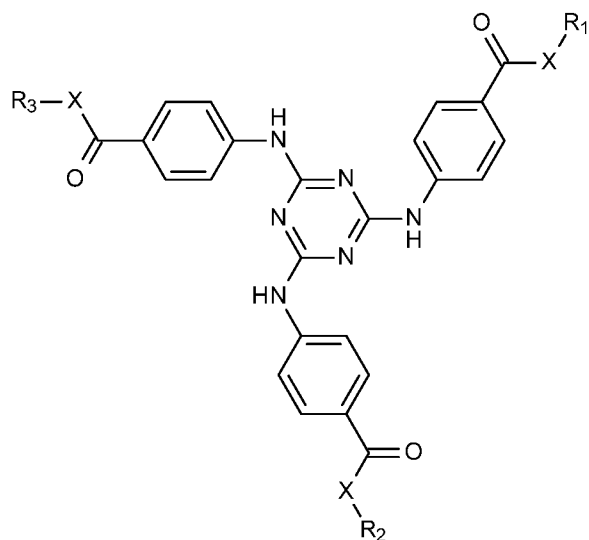
(HTP-03)



5 10. Use according to any of claims 1 to 3, wherein the trianilino-s-triazine derivatives (B3) correspond to the formula

39

(TAT-01)



wherein

$R_1$ ,  $R_2$  and  $R_3$  independently from each other are  $C_1$ - $C_{20}$ alkyl,  $C_6$ - $C_{10}$ aryl or  $C_6$ - $C_{10}$ eteroaryl;

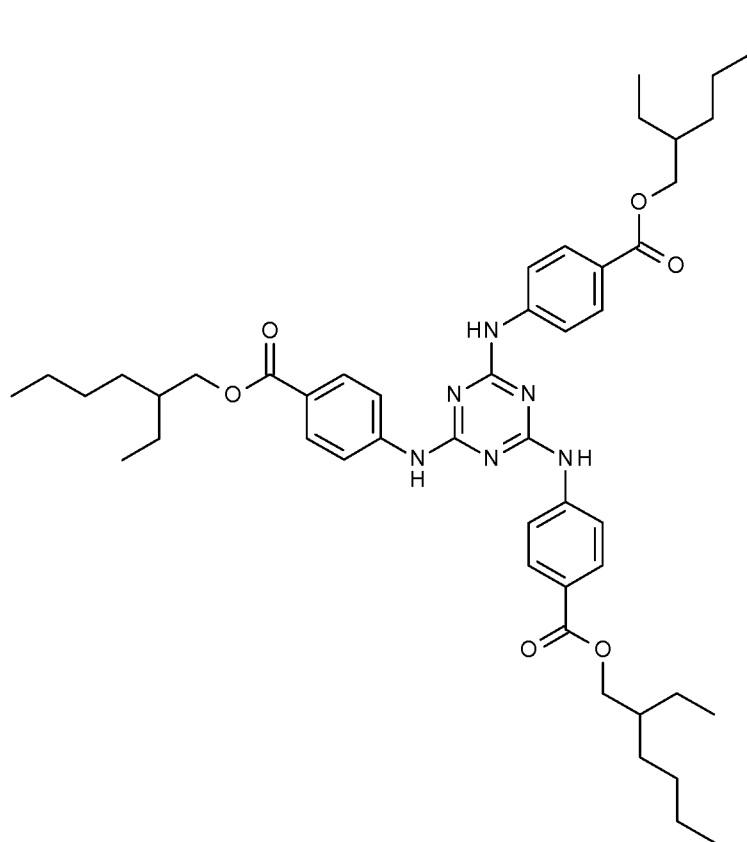
X is O; or  $NR_4$ ; and

$R_4$  is hydrogen; or  $C_1$ - $C_{20}$ alkyl, aryl or heteroaryl.

5

11. Use according to any of claims 10, wherein the trianilino-s-triazine derivatives (B3) correspond to the formula

(TAT-02)





12. Use according to any of claims 1 to 11, wherein mixtures of UV filters (BPH-02) as claimed in claim 6, (HTP-02) as claimed in claim 8 and (TAT-02) as claimed in claim 11 are used.

5 13. Use according to any of claims 1 to 12, wherein mixtures of UV filters (BPH-02) as claimed in claim 6 and (HTP-02) as claimed in claim 8 are used.

14. Use according to any of claims 1 to 12, wherein mixtures of UV filters (BPH-02) as claimed in claim 6 and (TAT-02) as claimed in claim 11 are used.

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15. Use according to any of claims 1 to 12, wherein mixtures of UV filters (HTP-02) as claimed in claim 8 and (TAT-02) as claimed in claim 11 are used.

15

16. Use according to any of claims 1 to 15, wherein the organic UV filters (B) are used in admixtures of at least two different UV filters selected from (B1), (B2) and (B3).

17. Cosmetic composition comprising  
(A) an ester of levulinic acid with a fatty alcohol; and  
(B) oil soluble organic UV filters (B).

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18. Composition according to claim 17, comprising  
(A) an ester of levulinic acid with a C<sub>8</sub>-C<sub>22</sub> fatty alcohol; and  
(B) mixtures of UV filters (HTP-02), (BPH-02) and (TAT-02).

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19. Composition according to claim 17, comprising  
(A) an ester of levulinic acid with a C<sub>8</sub>-C<sub>22</sub> fatty alcohol; and  
(B) mixtures of UV filters (BPH-02) and (HTP-02).

30

20. Composition according to claim 17, comprising  
(A) an ester of levulinic acid with a C<sub>8</sub>-C<sub>22</sub> fatty alcohol; and  
(B) mixtures of UV filters (HTP-02) and (TAT-02).

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21. Composition according to claim 17, comprising  
(A) an ester of levulinic acid with a C<sub>8</sub>-C<sub>22</sub> fatty alcohol; and  
(B) mixtures of UV filters (BPH-02) and (TAT-02).

22. Cosmetic composition according to any of claims 17 to 21 comprising

0.1 to 25% b.w. of a solubilizing agent (A);  
0.1 to 20 % b.w. of at least one organic UV filter (B); and  
10 to 90 % b.w. of a cosmetically acceptable carrier (C),  
based on the total weight of the cosmetic end-product composition.

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/067062

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. A61K8/35 A61K8/37 A61K8/49 A61Q17/04 ADD.											
According to International Patent Classification (IPC) or to both national classification and IPC											
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) A61K A61Q Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data											
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>WO 2016/091930 A1 (BASF SE [DE]) 16 June 2016 (2016-06-16) claims; examples page 1, line 5 - page 2, line 4 -----</td> <td>1-22</td> </tr> <tr> <td>Y</td> <td>"New solubilizers for organic UV filters in Personal Care An IP.com Prior Art Database Technical Disclosure", 4 October 2007 (2007-10-04), XP055135499, Retrieved from the Internet: URL:http://ip.com/pdf/ipcompad/IPCOM000158 883D.pdf [retrieved on 2014-08-20] tables 1, 2 ----- -/-</td> <td>1-22</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	WO 2016/091930 A1 (BASF SE [DE]) 16 June 2016 (2016-06-16) claims; examples page 1, line 5 - page 2, line 4 -----	1-22	Y	"New solubilizers for organic UV filters in Personal Care An IP.com Prior Art Database Technical Disclosure", 4 October 2007 (2007-10-04), XP055135499, Retrieved from the Internet: URL:http://ip.com/pdf/ipcompad/IPCOM000158 883D.pdf [retrieved on 2014-08-20] tables 1, 2 ----- -/-	1-22
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
Y	WO 2016/091930 A1 (BASF SE [DE]) 16 June 2016 (2016-06-16) claims; examples page 1, line 5 - page 2, line 4 -----	1-22									
Y	"New solubilizers for organic UV filters in Personal Care An IP.com Prior Art Database Technical Disclosure", 4 October 2007 (2007-10-04), XP055135499, Retrieved from the Internet: URL:http://ip.com/pdf/ipcompad/IPCOM000158 883D.pdf [retrieved on 2014-08-20] tables 1, 2 ----- -/-	1-22									
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.											
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Date of the actual completion of the international search		Date of mailing of the international search report									
2 August 2017		11/08/2017									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer  Perrone Dunet, S									

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/067062

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2015/091091 A1 (BASF SE [DE]) 25 June 2015 (2015-06-25) claims 1-4 table 2  -----	1-22

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/067062

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WO 2016091930	A1	16-06-2016	NONE
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			EP 3082742 A1 26-10-2016
			JP 2016540816 A 28-12-2016
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			US 2016310381 A1 27-10-2016
			WO 2015091091 A1 25-06-2015
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