(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 March 2006 (09.03.2006)

PCT

(10) International Publication Number
WO 2006/024633 A1

(51) International Patent Classification:
A61Q 17/04 (2006.01) *A61K 8/49* (2006.01)
A61K 8/34 (2006.01)

(21) International Application Number:
PCT/EP2005/054225

(22) International Filing Date: 29 August 2005 (29.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
04104185.6 1 September 2004 (01.09.2004) EP

(71) Applicant *(for all designated States except US)*: **CIBA SPECIALTY CHEMICALS HOLDING INC.** [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **DESHAYES, Cyrille** [FR/FR]; 52, rue de Village-Neuf, F-68128 Rosenau (FR). **MONGIAT, Sébastien** [FR/FR]; 9, rue des Fauvettes, F-68510 Sierentz (FR).

(74) Common Representative: **CIBA SPECIALTY CHEMICALS HOLDING INC.**; Patent Department, Klybeckstrasse 141, CH-4057 Basel (CH).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/024633 A1

(54) Title: MICRO-PARTICULATE ORGANIC UV ABSORBER COMPOSITION

(57) Abstract: Disclosed is a topically applicable water-in-oil (w/o) or water-in-silicone (w/Si) formulation comprising: (a) at least one aqueous phase; (b) at least one fatty phase; (c) an effective UV-photoprotecting composition comprising (c_1) 20% to 99% of at least one insoluble micronized organic UV-screening active with a mean particle size ranging from 0,01µm to 2 µm.; and (c_2) 0.5% to 80% of at least one primary C_6-C_{28} fatty alcohol. The combination of a micronized organic UV absorber and a specific fatty alcohol allows a maximum of miscibility of micronized organic particles within the continuous oil phase of w/o emulsion wherein the micronized particles are stabilized in the oil phase of the composition. Simultaneously the crystal growth of micronized organic UV absorbers within W/O emulsions is limited or even eliminated.

Micro-particulate organic UV absorber composition

The present invention relates to topically applicable water-in-oil (w/o) or water-in-silicone (w/Si) formulations, in particular, to new UV-protection formulations which comprise a micronised UV absorber, wherein the micronised UV absorber is combined with specific fatty acid alcohol.

It has long been known that prolonged exposure to UV radiation can lead to the formation of erythemas or light dermatoses, as well as to an increased incidence of skin cancers, or accelerated skin ageing.

Various sunscreen formulations have been proposed which include materials which are intended to counteract UV radiation, thereby inhibiting the said undesired effects on the skin.

A great number of compounds have been proposed for use as UV protectants in sunscreen formulations, especially soluble organic UV absorbers and insoluble micronised inorganic compounds, in particular zinc oxide and titanium dioxide.

With respect to the use in sunscreen formulations of soluble organic UV absorbers, they have the disadvantages that their effectiveness as UV protectants in terms of SPF (Sun Protection Factor) in a sunscreen formulation is often too low for commercial purposes; as a result of their solubility, they exhibit relatively high allergenic potential; and that as a result of intrinsic photochemical lability, the duration of the protective effect is often too low.

The high specific weight of insoluble inorganic compounds, such as titanium dioxide leads to a reduced stability of formulations containing them. Moreover, such inorganic compounds have been claimed to generate toxic radicals under the influence of light and water ("Redox Mechanisms in Heterogeneous Photocatalysis", Serpone *et al,* Electrochemistry in Colloids and Dispersions, Editors Mackay and Texter, VCH Publishers Inc., NewYork 1992).

In GB-A-2303549, there is described a method of producing micronised, insoluble organic UV absorbers, as well as a sunscreen composition comprising a micronised formulation of an insoluble organic UV absorber, produced according to the said method.

Micronised insoluble organic When the so obtained UV absorbers are used in sunscreen formulations theyprovide excellent UV protection and have an SPF rating which is at least as high as corresponding sunscreen formulations containing a known inorganic UV absorber. Unlike the latter UV absorbers micronised insoluble organic UV absorbers show no tendency for generating radicals which could damage or sensitise human skin under the influence of light.

In WO 99/66896 a micronised organic UV absorber sun screen composition is disclosed, wherein the micronised organic UV absorber is present in the oil phase of the formulation.

Surprisingly it was found that the combination of a micronized organic UV absorber and a specific fatty alcohol allows a maximum of miscibility of micronized organic particles within the continuous oil phase of w/o emulsions wherein the micronized particles are stabilized in the oil phase of the composition. Simultaneously the crystal growth of micronized organic UV absorbers within W/O emulsions is limited or even eliminated.

Therefore, the present invention relates to a topically applicable water-in-oil (w/o) or water-in-silicone (w/Si) formulation comprising:

(a) at least one aqueous phase;

(b) at least one fatty phase;

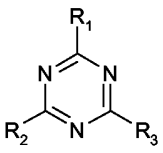
(c) an effective UV-photoprotecting composition comprising

(c_1) 20% to 99% of at least one insoluble micronized organic UV-screening active with a mean particle size ranging from 0,01µm to 2 µm; and

(c_2) 0.5% to 80% of at least one primary C_6-C_{28} fatty alcohol.

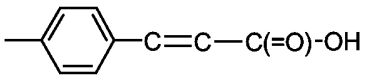
Suitable organic UV absorber (c_1) may be, e.g. a triazine, a benzotriazole, a benzophenone, a vinyl group-containing amide, a cinnamic acid amide or a sulfonated benzimidazole UV absorber.

A preferred class of triazine compounds is that having the formula

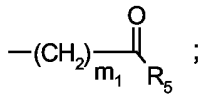
(1) 

, wherein

R_1, R_2 and R_3, independently from each other, are hydrogen; hydroxy; C_1-C_3alkoxy; NH_2; NHR_4; $N(R_4)_2$; OR_4; C_6-C_{12}aryl; phenoxy; anilino; pyrrolo; in which the respective phenyl, phenoxy, anilino or pyrrolo moieties are not substituted or substituted by one, two or three substitutents selected from OH, carboxy, CO-NH_2, C_1-C_{12}alkyl, C_1-C_{12}alkoxy, a methylidenecamphor group, a group -$(CH=CH)_mC(=O)$-OR_4, a group



or the corresponding alkali metal, ammonium, mono-, di- or tri-C_1-C_4alkylammonium, mono-, di- or tri-C_2-C_4alkanolammonium salts, or the C_1-C_3alkyl esters thereof or by a radical of formula (1a)

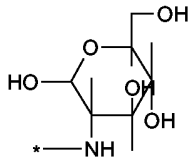


;

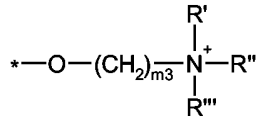
R_4 is C_1-C_5alkyl;

R_5 is hydroxy; C_1-C_5alkyl that is unsubstituted or substituted by one or more OH groups; C_1-C_5alkoxy; amino; mono- or di-C_1-C_5alkylamino; M; a radical of formula

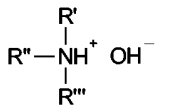
(1b)



; (1c)

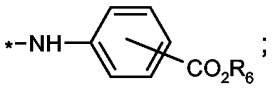


; (1d)



; or

(1e)



;

R', R" and R"' independently of the other are C_1-C_{14}alkyl that is unsubstituted or substituted by one or more OH groups;

R_6 is hydrogen; M; C_1-C_5alkyl; or a radical of the formula ;

M is a metal cation;

T_1 is hydrogen; or C_1-C_8alkyl;

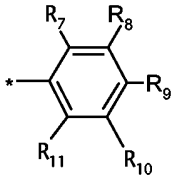
m is 0 or 1;

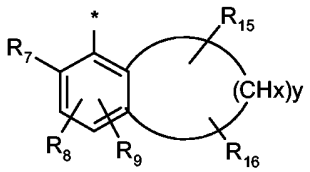
m_1 is from 1 to 5;

m_2 is from 1 to 4; and

m_3 is from 2 to 14.

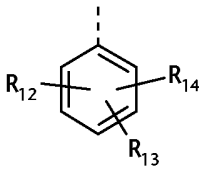
Preferred compounds of formula (1) are those, wherein

R_1, R_2 and R_3 independently from each other are a radical of formula (1f)  ; or

(1g) 

R_7 and R_{11} independently from each other are hydrogen; C_1-C_{18}alkyl; or C_6-C_{12}aryl;

R_8, R_9 and R_{10}, independently from each other, are hydrogen; or a radical of formula

(1h)  , wherein, in formula (1f), at least one of the radicals R_8, R_9 and R_{10} are a radical of formula (1h);

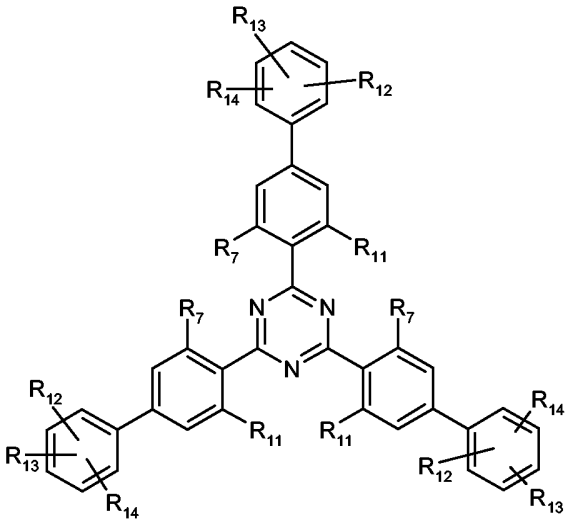
R_{12}, R_{13}, R_{14}, R_{15} and R_{16} independently from each other are hydrogen; hydroxy; halogen; C_1-C_{18}alkyl; C_1-C_{18}alkoxy; C_6-C_{12}aryl; biphenylyl; C_6-C_{12}aryloxy; C_1-C_{18}alkylthio; carboxy; -COOM; C_1-C_{18}-alkylcarboxyl; aminocarbonyl; or mono- or di-C_1-C_{18}alkylamino; C_1-C_{10}acylamino; -COOH;

M is an alkali metal ion;

x is 1 or 2; and

y is a number from 2 to 10.

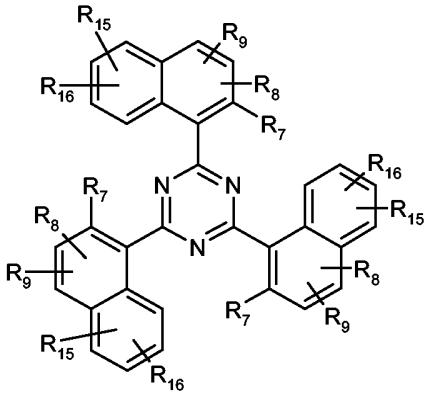
Most preferred triazine derivatives are compounds of formula

(2)  , wherein

R_7, R_{11}, R_{12}, R_{13} und R_{14} are defined as in formula (1f), (1g) or (1h), and most preferably compound of formula (2), wherein

$R_{7\ and}$ R_{11} are hydrogen.

Furthermore, triazinederivatives of formula

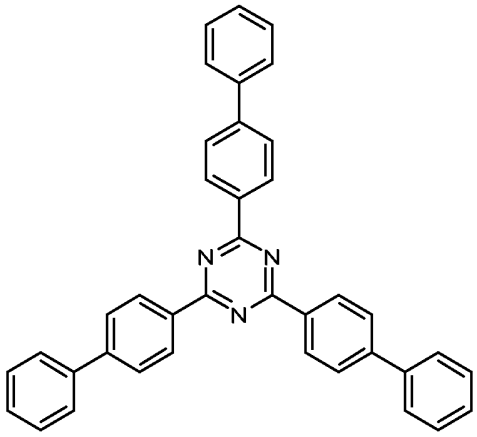
(3) 

are preferred, wherein

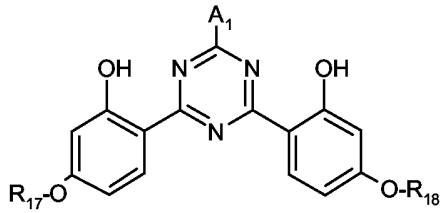
R_7, R_8, R_9, R_{15} and R_{16} are defined as in formula (1g), and most preferably compounds of formula (3), wherein

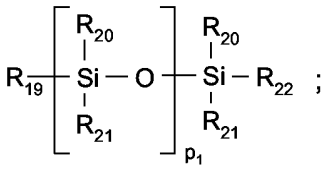
R_7, R_8, R_9, R_{15} and R_{16} are hydrogen; or, independently from each other, C_1-C_{18}alkyl.

Most preferred as component (c_1) are triazine derivatives of formula

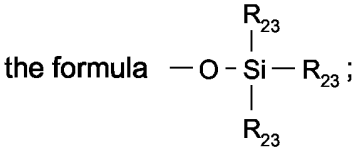
(4)  .

Further preferred triazine derivatives according to component (c_1) correspond to formula

(5)  , wherein

R_{17} and R_{18}, independently of one another, are C_1-C_{18}alkyl; C_2-C_{18}alkenyl; a radical of the formula $-CH_2-CH(-OH)-CH_2-O-T_1$; or a radical of the formula $-(CH_2)_{m_1}-O-(CH_2)_{m_2}-T_2$; a radical of the formula (5a)  ;

R_{19} is a direct bond; a straight-chain or branched C_1-C_4alkylene radical or a radical of the formula $-C_{m_1}H_{2m_1}-$ or $-C_{m_1}H_{2m_1}-O-$;

R_{20}, R_{21} and R_{22}, independently of one another, are C_1-C_{18}alkyl; C_1-C_{18}alkoxy or a radical of the formula  ;

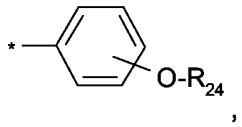
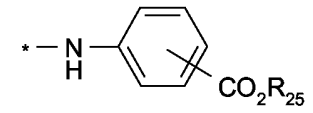
R_{23} is C_1-C_5alkyl;

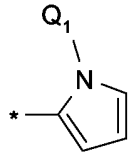
T_1 and T_2, independently from each other, are hydrogen; or C_1-C_8alkyl;

m_1, m_2 and m_3, independently of one another, are 1 to 4;

p_1 is 0; or a number from 1 to 5;

A_1 is a radical of the formula

(5b)  , (5c)  ; or of the formula

(5d) 

R_{24} is hydrogen; C_1-C_{10}alkyl, $-(CH_2CHR_{26}-O)_{n_1}-R_{25}$; a $-CH_2-CH(-OH)-CH_2-O-T_1$; or radical of the formula $-(CH_2)_{m_1}-O-(CH_2)_{m_2}-T_2$

R_{25} is hydrogen; M; C_1-C_5alkyl; or a radical of the formula $-(CH_2)_{m_2}-O-T_1$;

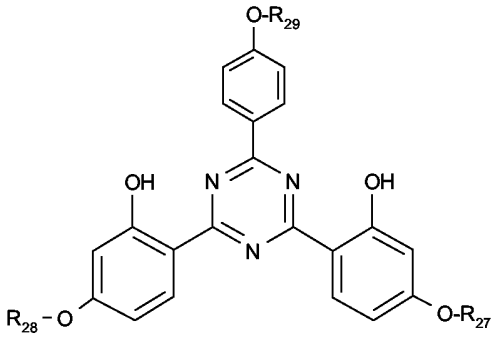
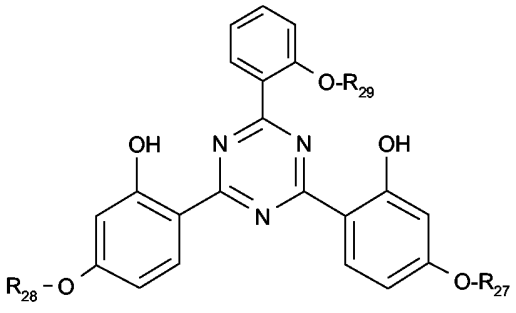
R_{26} is hydrogen; or methyl;

Q_1 C_1-C_{18}alkyl;

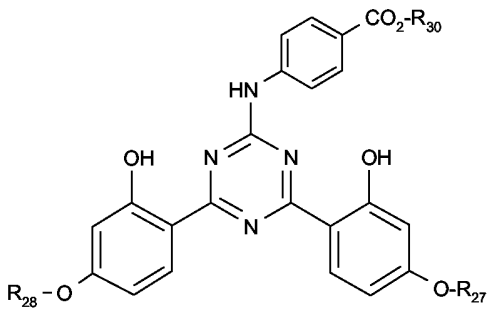
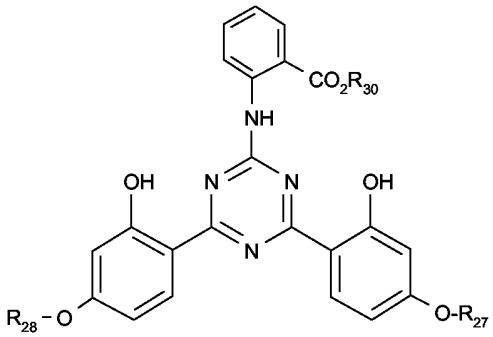
M is a metal cation; and

n_1 is 1-16.

Further preferred triazine derivatives according to component (c_1) are compounds of formulae

(5e)  , (5f)  ,

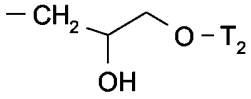
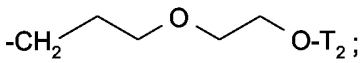
the formula

(5g)  ; (5h) 

in which

R_{27} and R_{28}, independently of one another, are C_3-C_{18}alkyl; or -CH_2-CH(-OH)-CH_2-O-T_1;

R_{30} is C_1-C_{10}alkyl or a radical of the formula

(5a$_1$)  or the formula (5a$_2$) ;

R_{30} is hydrogen; M; C_1-C_5alkyl; -NH-C_1-C_5alkyl, preferably -NH-tert.alkyl; or a radical of the formula -$(CH_2)_m$-O-T_2;

T_1 and T_2, independently of one another, are hydrogen; or C_1-C_5alkyl; and

m is 1 to 4.

Uppermost of interest are compounds of the formulae (5e) and (5f), in which

R_{27} and R_{28}, independently of one another, are C_3-C_{18}alkyl; or -CH_2-CH(-OH)-CH_2-O-T_1;

R_{29} is C_1-C_{10}alkyl;

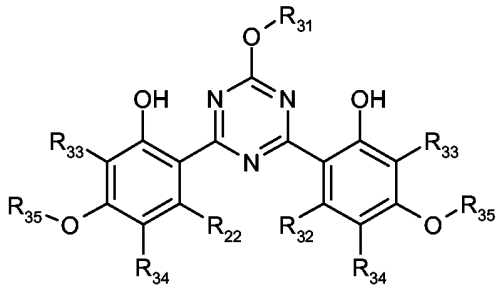
and compounds of the formulae (5g) and (5h), in which

R_{27} and R_{28}, independently of one another, are C_3-C_{18}alkyl or -CH_2-CH(-OH)-CH_2-O-T_1; and

T_1 is hydrogen; or C_1-C_5alkyl.

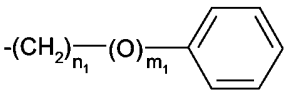
Very particularly preferred in this case are triazine compounds of the formula (5e) - (5h), in which R_{27} and R_{28} have the same meaning.

Furthermore, interesting triazines correspond to the formula

(6) 

in which

R_{31} is C_1-C_{30}alkyl; C_2-C_{30}alkenyl; unsubstituted or C_1-C_5alkyl-mono- or polysubstituted C_5-C_{12}cycloalkyl, C_1-C_5alkoxy-C_1-C_{12}alkyl; amino- C_1-C_{12}alkyl; C_1-C_5monoalkylamino-C_1-C_{12}alkyl; C_1-C_5dialkylamino-C_1-C_{12}alkyl; a radical of the formula

(6a)  ; or (6b)  ;

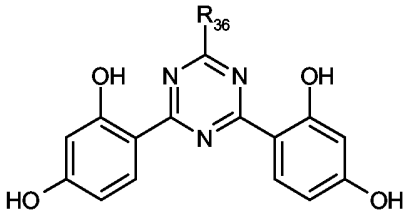
R_{32}, R_{33} and R_{34}, independently of one another, are hydrogen;, hydroxyl; C_1-C_{30}alkyl; or C_2-C_{30}alkenyl;

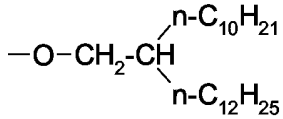
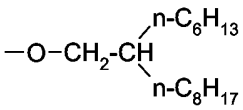
R_{35} is hydrogen; or C_1-C_5alkyl;

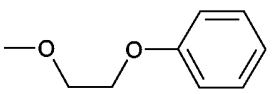
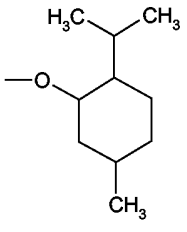
m_1 is 0 or 1; and

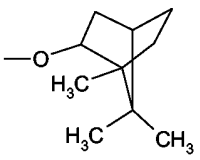
n_1 is 1 to 5.

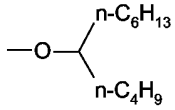
Preferred compounds correspond to the formula

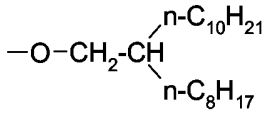
(7)  , wherein

R_{36} is  ;-O-iso-$C_{18}H_{38}$;  -O-n-$C_{18}H_{37}$; or

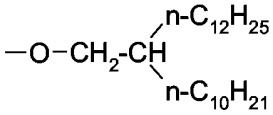
-O-2-ethylhexyl; -O-$(CH_2)_3$-$N(C_2H_5)_2$;;  ;  ;

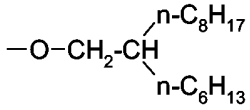


; 

; -O-n-$C_{18}H_{37}$; 

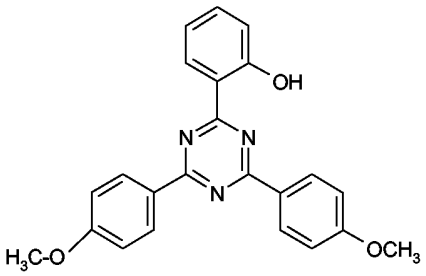
;

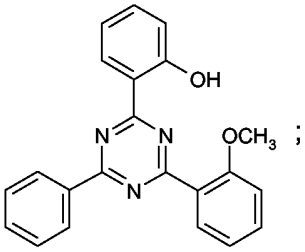


; or 

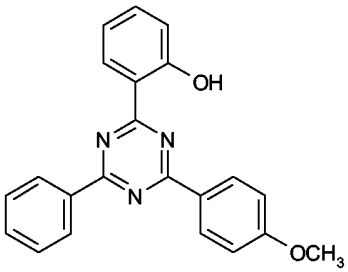
.

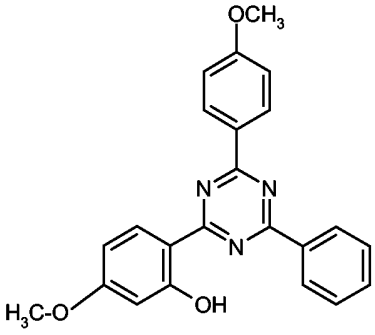
5 Further preferred triazine derivatives according to component (c_1) are those compounds having one of the formulae

(8) 

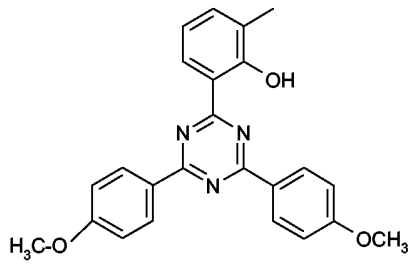
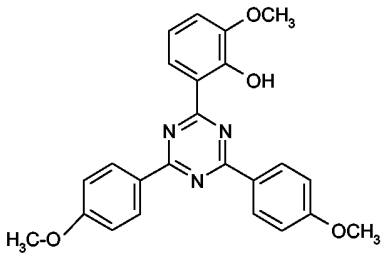
; (9) 

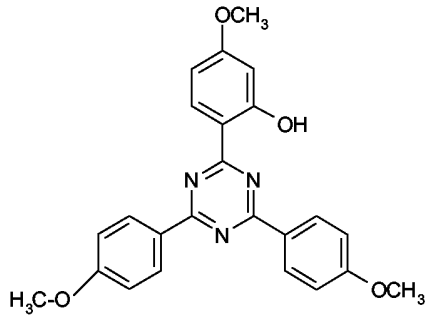
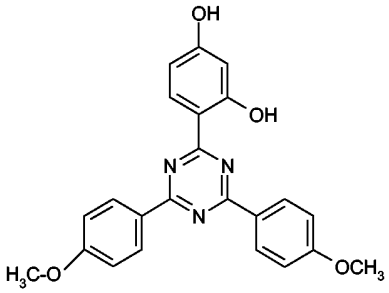
;

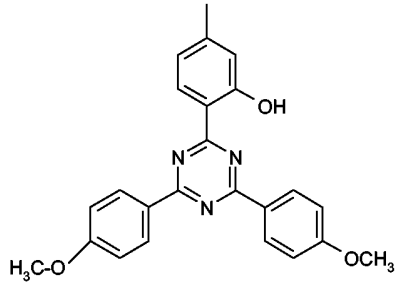
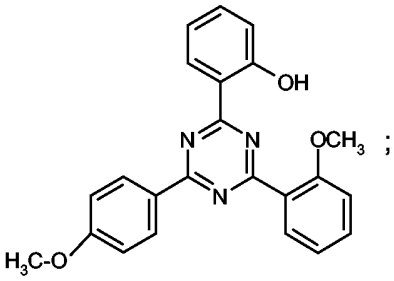
(10) 

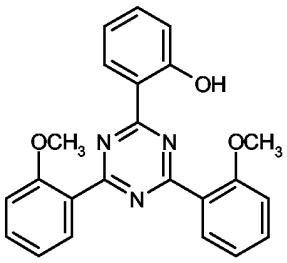
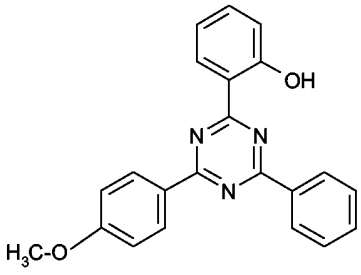
; (11) 

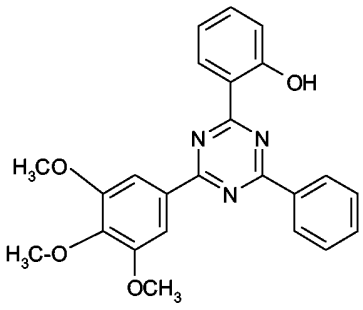
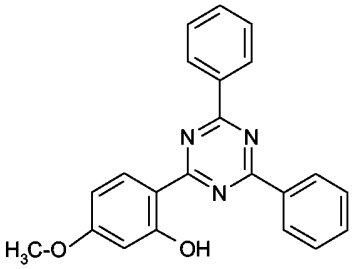
;

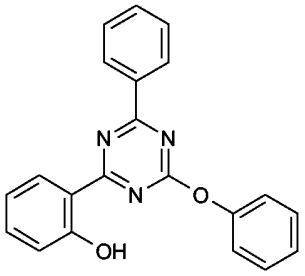
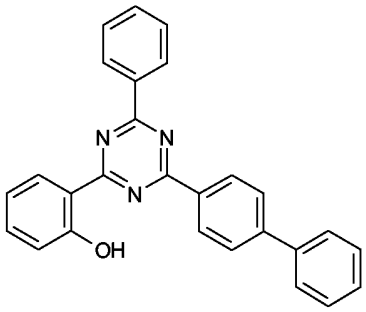
(12)  ; (13)  ;

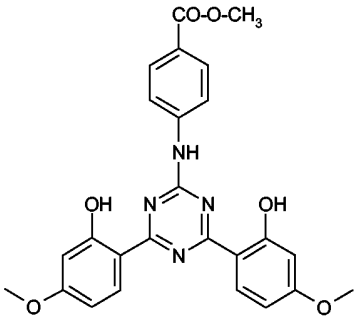
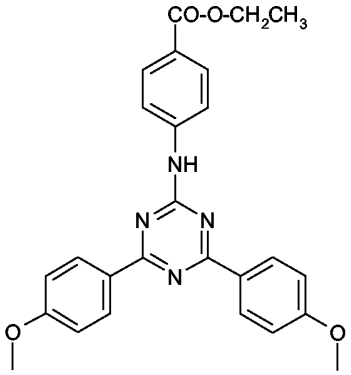
(14)  ; (15)  ;

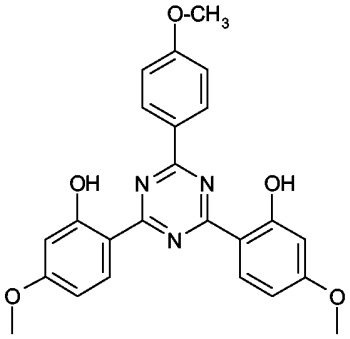
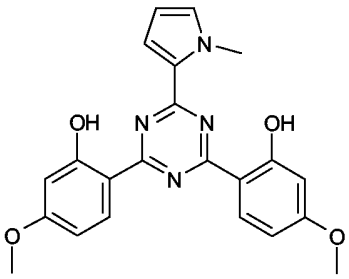
(16)  ; (17)  ;

(18)  ; (19)  ;

(20)  ; (21)  ;

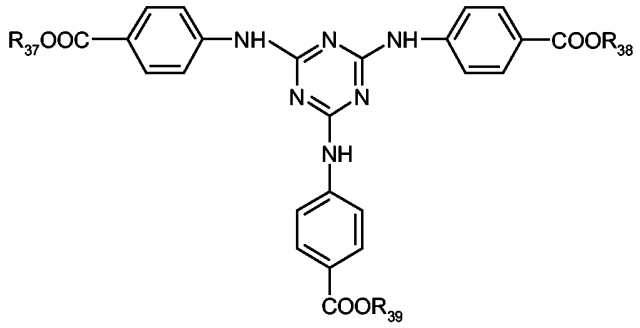
(22)  ; (23)  ;

(24)  ; (25)  ;

(26)  ; and (27)  ;

as well as 2,4,6-tris(diisobutyl-4'-aminobenzalmalonate)-s-triazine and 2,4-bis(diisobutyl-4-aminobenzalmalonate)-6-(4'-aminobenzylidenecamphor)-s-triazine.

Particularly preferred compounds of formula (1) are those having the formula:

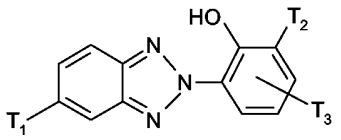
(28)  , wherein

R_{37}, R_{38} and R_{39}, independently from each other are hydrogen; an alkali metal; or an ammonium group $N^+(R_{40})_4$;

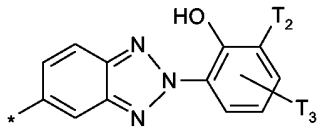
R_{40} is hydrogen; or an organic radical; C_1-C_3alkyl; or a polyoxyethylene radical which contains from 1 to 10 ethylene oxide units and the terminal OH group of which may be etherified by a C_1-C_3alcohol.

In relation to the compounds of formula (28), when R_{37}, R_{38} and R_{39} is an alkali metal it is preferably potassium or, especially sodium; when R_{37}, R_{38} and R_{39} is a group $N(R_{40})_4$ in which R_{30} has its previous significance, it is preferably a mono-, di- or tri-C_1-C_4alkylammonium salt, a mono-, di- or tri-C_2-C_4alkanolammonium salt or a C_1-C_3alkyl ester thereof; when R_{40} is a C_1-C_3alkyl group, it is preferably a C_1-C_2alkyl group, more preferably a methyl group; and when R_{30} is polyoxyethylene group, this preferably contains from 2-6 ethylene oxide units.

One preferred class of triazole micronised organic UV absorbers is that having the formula

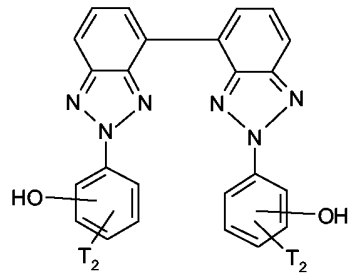
(29)  , wherein

T_1 is C_1-C_3alkyl or, preferably, hydrogen; or a radical of formula

(29a)  ; and

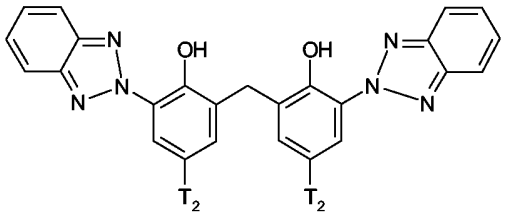
T_2 and T_3, independently from each other are C_1-C_{12}alkyl, preferably i-octyl; or C_1-C_4alkyl substituted by phenyl, preferably α,α-dimethylbenzyl.

A further preferred class of triazole micronised organic UV absorbers corresponds to the formula

(30)  , wherein

T_2 has its previous significance.

A still further preferred class of triazole micronised organic UV absorbers corresponds to the formula

(31)  , wherein

T_2 is hydrogen; C_1-C_{12}alkyl, preferably iso-octyl, or C_1-C_4alkyl substituted by phenyl, preferably α,α-dimethylbenzyl.

A preferred class of vinyl group-containing amide micronised organic UV absorbers corresponds to the formula:

(32) R_{41}-$(Y)_m$-CO-$C(R_{42})$=$C(R_{43})$-$N(R_{44})(R_{45})$, wherein

R_{41} is C_1-C_3alkyl, preferably C_1-C_2alkyl, or phenyl optionally substituted by one, two or three substituents selected from OH, C_1-C_3alkyl, C_1-C_3alkoxy or CO-OR_{46},

R_{46} C_1-C_3alkyl;

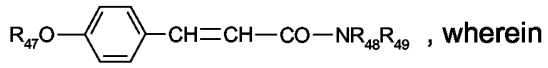
R_{42}, R_{43}, R_{44} and R_{45} are the same or different and each is C_1-C_3alkyl, preferably C_1-C_2alkyl; or hydrogen;

Y is -NH- ; or -O-; and

m is 0; or 1.

Preferred compounds of formula (32) are 4-methyl-3-penten-2-one, ethyl-3-methylamino-2-butenoate, 3-methylamino-1-phenyl-2-buten-1-one and 3-methylamino-1-phenyl-2-buten-1-one.

A preferred class of cinnamic acid amide micronised organic UV absorbers corresponds to the formula:

(33)  , wherein

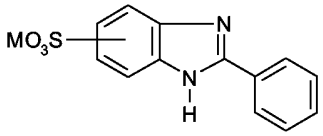
R_{47} is hydroxy or C_1-C_4alkoxy, preferably methoxy or ethoxy;

R_{48} is hydrogen or C_1-C_4alkyl, preferably methyl or ethyl; and

R_{49} is -$(CONH)_m$-phenyl in which m is 0 or 1 and the phenyl group is optionally substituted by one, two or three substituents selected from OH, C_1-C_3alkyl, C_1-C_3alkoxy or CO-OR_{50}; and

R_{50} is C_1-C_4alkyl.

A preferred class of sulfonated benzimidazole micronised organic UV absorbers corresponds to the formula

(34)  , in which

M is hydrogen; or an alkali metal, preferably sodium, an alkaline earth metal, such as magnesium or calcium, or zinc.

Further preferred classes of micronised or micronisable UV absorbers used for the present invention are:

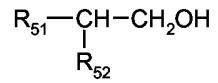
- p-aminobenzoic acid derivatives, typically 2-ethylhexyl-4-dimethylaminobenzoate
- salicylic acid derivatives, typically 2-ethylhexyl salicylate; homosalates; and isopropyl sylicylates;
- benzophenone derivatives, typically 2-hydroxy-4-methoxybenzophenone;
- dibenzoylmethane derivatives, typically 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;
- diphenylacrylates, typically 2-ethylhexyl-2-cyano-3,3-diphenylacrylate and 3-(benzo-furanyl)-2-cyanoacrylate;

- 3-imidazol-4-yl-acrylic acid and 3-imidazol-4-yl-acrylate;
- benzofurane derivatives, preferably 2-(p-aminophenyl)benzofuran derivatives, disclosed in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
- polymeric UV absorbers, such as the benzylidenemalonate derivatives described, inter alia in EPA-709 080;
- cinnamic acid derivatives, typically the 2-ethylhexyl-4-methoxycinnamate or isoamylate or cinnamic acid derivatives disclosed, inter alia, in US-A-5 601 811 and WO 97/00851;
- camphor derivatives, typically 3-(4'-methyl)benzylidenebornan-2-one, 3-benzylidenebornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidenemethyl)benzyl]acrylamide polymer, 3-(4'-trimethylammonium)benzylidenebornan-2-one methylsulfate, 3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxobicyclo-[2.2.1]heptane-1-methanesulfonic acid) and the salts thereof, 3-(4'-sulfo)benzylidenebornan-2-one and the salts thereof;
- 2-phenylbenzimidazole-5-sulfonic acids and the salts thereof; and
- menthyl-o-aminobenzoate.

Fatty alcohols are generally understood as saturated or unsaturated primary alcohols (1-alkanols) having 6 to 22 carbon atoms. They are obtained by reduction of triglycerides, fatty acids or fatty acid methyl esters.

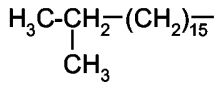
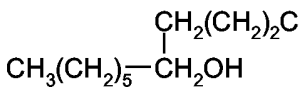
Preferably the fatty alcohol according to component (c_2) is a linear or linear branched C_8-C_{20}alcohol.

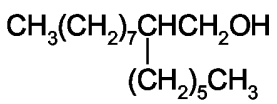
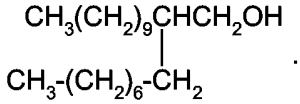
The fatty alcohols according to component (c_2) are preferably characterized by primary alcohols which correspond to the formula

(35) , wherein

R_{51} and R_{52}, independently from each other, are a linear C_1-C_{18}alkyl, wherein the sum of carbon atoms in R_{51} and R_{52} is ≤ 18.

Examples of fatty alcohols according to component (c_2) correspond to the formula

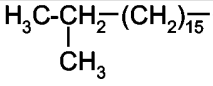
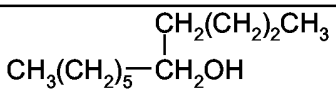
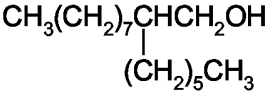
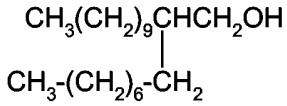
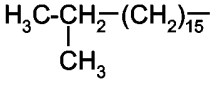
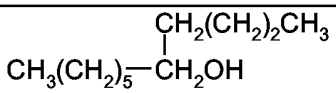
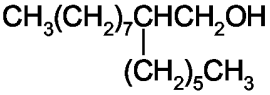
(35a)  ; (35b)  ;

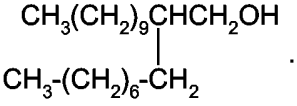
(35c)  ; and (35d)  .

The fatty alcohols according to component (c_2) in the composition of the present invention may be used as single compounds or as mixtures of 2 or more than 2 single compounds.

Preferably, mixtures of linear octanol and linear decanol are used as component (c_2).

Preferred combinations of insoluble micronized organic UV-screening actives (component (c_1) and primary C_6-C_{28} fatty alcohols (component (c_2)) are:

insoluble micronized organic UV-screening active (c_1)	primary C_6-C_{28} fatty alcohol (=c_2)
Compound of formula (31), wherein T_2 is isooctyl	(35a) 
Compound of formula (31), wherein T_2 is isooctyl	(35b) 
Compound of formula (31), wherein T_2 is isooctyl	(35c) 
Compound of formula (31), wherein T_2 is isooctyl	(35d) 
Compound of formula (31), wherein T_2 is isooctyl	mixture of linear octanol and linear decanol
Compound of formula (4)	(35a) 
Compound of formula (4)	(35b) 
Compound of formula (4)	(35c) 

insoluble micronized organic UV-screening active (c_1)	primary C_6-C_{28} fatty alcohol (=c_2)
Compound of formula (4)	(35d) 
Compound of formula (4)	mixture of linear octanol and linear decanol

The micronised organic UV absorber, component (c_1), is preferably produced by the method described in GB-A-2303549, namely by a process which comprises grinding the corresponding organic UV absorber, in coarse particle form, in a grinding apparatus, in the presence of 1 to 50%, preferably 5 to 40% by weight, based on the micronised organic UV absorber, of an alkyl polyglucoside having the formula $C_nH_{2n+1}O(C_6H_{10}O_5)_xH$, in which n is an integer ranging from 8 to 16 and x is the mean polymerisation level of the glucoside moiety ($C_6H_{10}O_5$) and ranges from 1.4 to 1.6, or an ester thereof.

Any known process suitable for the preparation of microparticles can be used for the preparation of the micronised UV absorbers, for example wet-milling, wet-kneading, spray-drying from a suitable solvent, by the expansion according to the RESS process (Rapid Expansion of Supercritical Solutions), by reprecipitation from suitable solvents, including supercritical fluids (GASR process = Gas Anti-Solvent Recrystallisation / PCA process = Precipitation with Compressed Anti-solvents).

The micronised UV absorbers so obtained usually have an average particle size from 0.02 to 2, preferably from 0.03 to 1.5, and more especially from 0.05 to 1.0 micrometer.

The UV absorbers according to component (c_1) can also be used as dry substrates in powder form

The topically applicable water-in-oil (w/o) or water-in-silicone (w/Si) formulation according to the present invention may additionally contain one or more than one further non-micronized UV filter as listed in Tables 1 and 2.

The UV absorbers as described in Tables 1 and 2 below may be added to the topically applicable water-in-oil (w/o) or water-in-silicone (w/Si) formulations according to the present

invention in a amounts from 0.1 to 20 % b.w. Mixtures of these UV absorbers can be used, *inter alia*, to improve the solubility or to increase UV absorption.

Table 1. Suitable non-micronized UV filter substances which can be additionally used with the UV absorbers 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;
dibenzoylmethane derivatives, for example 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;
diphenylacrylates, for example 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, and 3-(benzo-furanyl) 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-phenylenedimethine)-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;
hydroxyphenyltriazine compounds, for example 2-(4'-methoxyphenyl)-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(2-ethyl-hexyloxy)-2-hydroxy]-phenyl}-6-[4-(2-methoxyethyl-carboxyl)-phenylamino]-1,3,5-triazine; 2,4-bis{[4-(tris(trimethylsilyloxy-silylpropyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(2"-methylpropenyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(1',1',1',3',5',5',5'-heptamethyltrisilyl-2"-methyl-propyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl}-6-[4-ethylcarboxy)-phenylamino]-1,3,5-triazine;
benzotriazole compounds, for example 2,2'-methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol;
trianilino-s-triazine derivatives, for example 2,4,6-trianiline-(p-carbo-2'-ethyl-1'-oxy)-1,3,5-triazine and the UV absorbers disclosed in US-A-5 332 568, EP-A-517 104, EP-A-507 691, WO 93/17002 and EP-A-570 838;
2-phenylbenzimidazole-5-sulfonic acid and salts thereof;

Table 1. Suitable non-micronized UV filter substances which can be additionally used with the UV absorbers according to the present invention
menthyl o-aminobenzoates;
physical sunscreens coated or not as titanium dioxide, zinc oxide, iron oxides, mica, MnO, Fe_2O_3, Ce_2O_3, Al_2O_3, ZrO_2. (surface coatings: polymethylmethacrylate, methicone (methylhydrogenpolysiloxane as described in CAS 9004-73-3), dimethicone, isopropyl titanium triisostearate (as described in CAS 61417-49-0), metal soaps as magnesium stearate (as described in CAS 4086-70-8), perfluoroalcohol phosphate as C9-15 fluoroalcohol phosphate (as described in CAS 74499-44-8; JP 5-86984 , JP 4-330007)). The primary particle size is an average of 15nm–35nm and the particle size in dispersion is in the range of 100nm – 300nm.
aminohydroxy-benzophenone derivatives disclosed in DE 10011317, EP 1133980 and EP 1046391
phenyl-benzimidazole derivatives as disclosed in EP 1167358
the UV absorbers described in "Sunscreens", Eds. N.J. Lowe, N.A.Shaath, Marcel Dekker, Inc. , New York and Basle or in Cosmetics & Toiletries (107), 50ff (1992) also can be used as additional UV protective substances.

Table 2: Suitable specific non-micronized UV filter substances and adjuvants which can be additionally used with the UV absorbers 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
22	3,3,5-Trimethyl cyclohexyl-2-hydroxy benzoate; homosalate	118-56-9

Table 2: Suitable specific non-micronized UV filter substances and adjuvants which can be additionally used with the UV absorbers according to the present invention

No.	Chemical Name	CAS No.
23	Isopentyl p-methoxycinnamate; isoamyl methoxy cinnamate	71617-10-2
27	Menthyl-o-aminobenzoate	134-09-8
28	Menthyl salicylate	89-46-3
29	2-Ethylhexyl 2-cyano,3,3-diphenylacrylate; octocrylene	6197-30-4
30	2- ethylhexyl 4- (dimethylamino)benzoate	21245-02-3
31	2- ethylhexyl 4- methoxycinnamate; octyl methoxy cinnamate	5466-77-3
32	2- ethylhexyl salicylate	118-60-5
33	Benzoic acid, 4, 4', 4''- (1, 3, 5- triazine- 2, 4, 6- triyltriimino)tris-, tris(2-ethylhexyl)ester; 2,4,6-Trianilino-(p-carbo-2'-ethylhexyl-1'-oxi)-1,3,5-triazine; octyl triazone	88122-99-0
34	4- aminobenzoic acid	150-13-0
35	Benzoic acid, 4-amino-, ethyl ester, polymer with oxirane	113010-52-9
38	2- phenyl- 1H- benzimidazole- 5- sulphonic acid; phenylbenzimidazolsulfonic acid	27503-81-7
39	2-Propenamide, N-[[4-[(4,7,7-trimethyl-3-oxobicyclo[2.2.1]hept-2-ylidene)methyl]phenyl]methyl]-, homopolymer	147897-12-9
40	Triethanolamine salicylate	2174-16-5
41	3, 3'-(1,4-phenylenedimethylene)bis[7, 7-dimethyl- 2-oxo-bicyclo[2.2.1]heptane-1 methanesulfonic acid]; Cibafast H	90457-82-2
42	Titanium dioxide	13463-67-7
44	Zinc oxide	1314-13-2
45	2,4-bis{[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-(1,3,5)-triazine; Tinosorb S	187393-00-6
46	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt	180898-37-7
47	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
48	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
49	Dimethicodiethylbenzalmalonate; Polysilicone 15; Parsol SLX	207574-74-1
50	Benzenesulfonic acid, 3-(2H-benzotriazol-2-yl)-4-hydroxy-5-(1-methylpropyl)-, monosodium salt ; Tinogard HS	92484-48-5

Table 2: Suitable specific non-micronized UV filter substances and adjuvants which can be additionally used with the UV absorbers according to the present invention

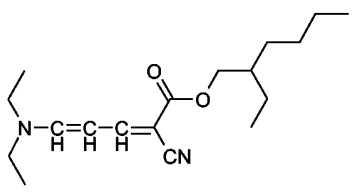
No.	Chemical Name	CAS No.
51	Benzoic acid, 2-[4-(diethylamino)-2-hydroxybenzoyl]-, hexyl ester; Uvinul a plus	302776-68-7
52	1-Dodecanaminium, N-[3-[[4-(dimethylamino)benzoyl]amino]propyl]-N,N-dimethyl-, salt with 4-methylbenzenesulfonic acid (1:1); Escalol HP610	156679-41-3
53	1-Propanaminium, N,N,N-trimethyl-3-[(1-oxo-3-phenyl-2-propenyl)-amino]-, chloride	177190-98-6
54	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-	170864-82-1
55	1,3,5-Triazine, 2,4,6-tris(4-methoxyphenyl)-	7753-12-0
56	1,3,5-Triazine, 2,4,6-tris[4-[(2-ethylhexyl)oxy]phenyl]-	208114-14-1
57	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
58	2-Propenoic acid, 3-(1H-imidazol-4-yl)-	104-98-3
59	Benzoic acid, 2-hydroxy-, [4-(1-methylethyl)phenyl]methyl ester	94134-93-7
60	1,2,3-Propanetriol, 1-(4-aminobenzoate); glyceryl PABA	136-44-7
61	Benzeneacetic acid, 3,4-dimethoxy-a-oxo-	4732-70-1
62	2-Propenoic acid, 2-cyano-3,3-diphenyl-, ethyl ester	5232-99-5
63	Anthralinic acid, p-menth-3-yl ester	134-09-8
64	2,2'-bis(1,4-phenylene)-1H-benzimidazole-4,6-disulphonic acid mono sodium salt or Disodium phenyl dibenzimidazole tetrasulfonate or Neoheliopan AP	349580-12-7,
65	1,3,5-Triazine-2,4,6-triamine, N,N'-bis[4-[5-(1,1-dimethylpropyl)-2-benzoxazolyl]phenyl]-N''-(2-ethylhexyl)- or Uvasorb K2A	288254-16-0
66	Merocyanine derivatives as described in WO 2004006878 and in IPCOM000022279D	
67		
68	sterols (cholesterol, lanosterol, phytosterols), as described in WO0341675	
69	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	

Table 2: Suitable specific non-micronized UV filter substances and adjuvants which can be additionally used with the UV absorbers according to the present invention		
No.	Chemical Name	CAS No.
	(INCI: Porphyra Umbilicalis) that are encapsulated into liposomes,)	
70	alpha-lipoic-acid as described in DE 10229995	
71	synthetic organic polymers as described in EP 1371358, [0033]-[0041]	
72	phyllosilicates as described in EP 1371357 [0034]-[0037]	
73	silica compounds as described in EP1371356, [0033]-[0041]	
74	inorganic particles as described in DE10138496 [0043]-[0055]	
75	latex particles as described in DE10138496 [0027]-[0040]	
76	1H-Benzimidazole-4,6-disulfonic acid, 2,2'-(1,4-phenylene)bis-, disodium salt ; Bisimidazylate; Neo Heliopan APC	180898-37-7

The topically applicable formulations of the present invention comprise at least a water phase and an oil-phase.

They are preferably formulated as water-in-oil (w/o) or water-in-silicone (w/Si) emulsions or microemulsions.

They may contain low molecular weight emulsifiers selected from non-ionic, cationic, amphoteric and anionic emulsifiers from 0.1 to 20 % bw..

The UV-photoprotecting composition (c) is prepared by incorporating the primary C_6-C_{28} fatty alcohol (componente (c_2)) into the UV absorber dispersion which contains the micronized UV absorber by simply mixing the 2 components.

The so obtained UV-photoprotecting composition (c) is preferably incorporated into the oil phase of the W/O emulsion.

The simple adding of such UV-photoprotecting composition helps to stabilize or even eliminate the crystal growth of the selected micronized organic UV-screening agent within the oil phase of the W/O or W/Si emulsion, or int the Si-phase of the w/Si emulsion respectively.

The final W/O or W/Si formulations according to the present invention 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,
- in the form of a gel,
- in the form of an oil, a cream, milk or lotion,
- in the form of a stick,
- in the form of a spray (spray with propellent gas or pump-action spray) or an aerosol,
- 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 after-sun preparations, also skin-tanning preparations, for example self-tanning creams. Of particular interest are sun protection creams, sun protection lotions, sun protection milk and sun protection preparations in the form of a spray.

Of special importance as cosmetic preparations for the hair are the above-mentioned preparations for hair treatment, especially hair-washing preparations in the form of shampoos, hair conditioners, hair-care preparations, e.g. pretreatment 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.

As water- and oil-containing emulsions or microemulsions the preparations contain, for example,

from 0.1 to 30 % by weight, preferably from 0.1 to 15 % by weight and especially from 0.5 to 10 % by weight, based on the total weight of the composition, of an effective UV-photoprotecting composition (= component (c));

from 1 to 60 % by weight, especially from 5 to 50 % by weight and preferably from 10 to 35 % by weight, based on the total weight of the composition, of at least one oil component,

from 0 to 30 % by weight, especially from 1 to 30 % by weight und preferably from 4 to 20 % by weight, based on the total weight of the composition, of at least one emulsifier,

from 10 to 90 % by weight, especially from 30 to 90 % by weight, based on the total weight of the composition, of water, and

from 0 to 88.9 % by weight, especially from 1 to 50 % by weight, of further cosmetically acceptable adjuvants.

The topically applicable water-in-oil (w/o) or water-in-silicone (w/si) formulation may also contain one or one more additional compounds as esters of fatty acids,natural or synthetic triglycerides including glyceryl esters and derivatives, pearlescent waxes, hydrocarbon oils, silicones or siloxanes (organosubstituted polysiloxanes), fluorinated or perfluorinated oils, super-fatting agents, surfactants, consistency regulators/thickeners and rheology modifiers, polymers, biogenic active ingredients, deodorising active ingredients, anti-dandruff agents, antioxidants, hydrotropic agents, preservatives and bacteria-inhibiting agents, perfume oils, colourants, insect repellents or polymeric beads or hollow spheres as spf enhancers.

Cosmetic or pharmaceutical formulations are contained in a wide variety of cosmetic preparations like skin-care preparations, bath preparations, cosmetic personal care preparations, foot-care preparations, light-protective preparations, skin-tanning preparations, depigmenting preparations, insect-repellents, deodorants 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), -shaving preparations, fragrance preparations, cosmetic hair-treatment preparations,

The cosmetic preparation according to the invention is distinguished by excellent protection of human skin against the damaging effect of sunlight.

Examples

Example 1: W/O SunscreenContaining TINOSORB®M & Tinosorb®OMC

Composition		Ex. 1a	Ex. 1b
	INCI-Name	% w/w (as supplied)	% w/w (as supplied)
Part A	Glyceryl Oleate	4.50	4.50
	PEG-7 Hydrogenated Castor Oil	1.50	1.50

	Hydrogenated Castor Oil	0.50	0.50
	Microcrystalline Wax	2.00	2.00
	Ethylhexyl Methoxycinnamate	5,00	5,00
	Beeswax	1.50	1.50
	C12-15 Alkyl Benzoate	8.00	8.00
	Isopropyl Isostearate	5.00	5.00
	Mineral Oil	5.00	5.00
Part B	Aqua	qs to 100	qs to 100
	Magnesium Sulfate	0.50	0.50
	Citric Acid	0.05	0.05
Part C	Methylene Bis-Benzotriazolyl Tetramethylbutyl-phenol (and) Aqua (and) Propylene Glycol (and) Decyl Glucoside (and) Xanthan Gum	3,75 a.i.	3,75 a.i.
	Butyloctanol	1.40	-
	Blend of Octanol and Decanol	-	0.90

Manufacturing instruction: Heat separately part A to 80°C and B to 80°C. Slowly add part B to part A under high stirring. Decrease the speed till moderate stirring 500 rpm. Let cool down to 35°C and add part C.

Example 2:W/O-Sunscreen

Composition		Ex. 2a	Ex. 2b
	INCI-Name	% w/w (as supplied)	% w/w (as supplied)
Part A	PEG-30 Dipolyhydroxystearate	2.00	2.00
	Cetearyl Isononanoate	5.00	5.00
	Hydrogenated Polydecene	3.50	3.50
	Ethylhexyl Methoxycinnamate	5.00	5.00
	C12-15 Alkyl Benzoate	4.00	4.00
	Cyclomethicone	3.00	3.00
Part B	Aqua	qs to 100	qs to 100
	Sorbeth-30	3.00	3.00
	Magnesium Sulfate	0.70	0.70
Part C	Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben	0.30	0.30

	Methylene Bis-Benzotriazolyl Tetramethyl-butylphenol (and) Aqua (and) Propylene Glycol (and) Decyl Glucoside (and) Xanthan Gum	3,75 a.i.	3,75 a.i.
	Butyloctanol	2.80	-
	Blend of Octanol and Decanol	-	1.40

Manufacturing instruction:Heat part A and part B separately to 80C under stirring. Add part B to part A with continuous stirring. Homogenize for 30 sec with Ultra Turrax at 11000 rpm. Let cool down to 40°C and add part C. Cool down to room temperature under continuous stirring.

Example 3: W/O Sunscreen

Composition		Ex. 3a	Ex. 3b
	INCI-Name	% w/w (as supplied)	% w/w (as supplied)
Part A	PEG-30 Dipolyhydroxystearate		5.00
	Cetearyl Isononanoate		2.50
	Hydrogenated Polydecene		6,50
	Ethylhexyl Methoxycinnamate		4,00
	C12-15 Alkyl Benzoate		0.50
Part B	Aqua		Qs to 100
	Sorbeth-30		1.00
Part C	Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben		3,75 a.i.
	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (and) Aqua (and) Propylene Glycol (and) Decyl Glucoside (and) Xanthan Gum		0.30
	Butyloctanol	1.15	-
	Blend of Octanol and Decanol	-	1.15

Appearance: white viscous emulsion

Viscosity (Brookfield DVIII+LV/T-C/50rpm): 80000-100000 mPas

Manufacturing instruction: Heat part A to70°C under continuous stirring. Add part B to part A and homogenize for a minute by 11000 rpm. Let cool down to room temperature and add part C under gentle stirring

Example 4: W/O Sun Emulsion

Composition		Ex. 4a	Ex. 4b
	INCI-Name	% w/w (as supplied)	% w/w (as supplied)
Part A	Sorbitan Isostearate	5.00	5.00
	Lanolin Alcohol	1.00	1.00
	PEG-7 Hydrogenated Castor Oil	1.50	1.50
	Microcrystalline Wax	1.50	1.50
	Vaseline	3.00	3.00
	Caprylic/Capric Triglyceride	1,50	1,50
	Ethylhexyl Methoxycinnamate	5.00	5.00
	Paraffinium Subliquidum	5.00	5.00
Part B	Aqua	qs to 100	qs to 100
	Magnesium Sulfate	0.70	0.70
Part C	Methylene Bis-Benzotriazolyl Tetramethyl-butylphenol (and) Aqua (and) Propylene Glycol (and) Decyl Glucoside (and) Xanthan Gum	3,75 a.i.	3,75 a.i.
	Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben	0.30	0.30
	Butyloctanol	0.80	
	Blend of Octanol and Decanol		0.80

* measurement made on Labsphere UV Transmittance Analyzer 1.2µl/cm² on PMMA

Manufacturing instruction: Heat phase A to 75°C. Add part B to part A and homogenize for 30 sec. at 11000rpm. Let cool down to 50°C and add part C. Continuous stirring until room temperature.

Claims:

1. A topically applicable water-in-oil (w/o) or water-in-silicone (w/Si) formulation comprising:

(a) at least one aqueous phase;

(b) at least one fatty phase;

(c) an effective UV-photoprotecting composition comprising

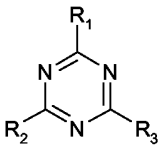
(c_1) 20% to 99% of at least one insoluble micronized organic UV-screening active with a mean particle size ranging from 0,01µm to 2 µm; and

(c_2) 0.5% to 80% of at least a primary C_6-C_{28} fatty alcohol.

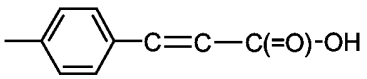
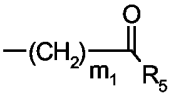
2. Formulation according to claim 1, wherein

(c_1) is selected from a triazine, a benzotriazole, a benzophenone, a vinyl group-containing amide, a cinnamic acid amide and a sulfonated benzimidazole UV absorber.

3. Formulation according to claim 1 or 2, wherein the triazine UV absorber corresponds to the formula

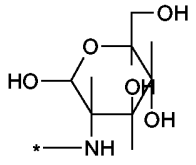
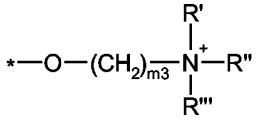
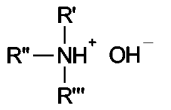
(1)  , wherein

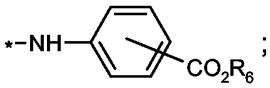
R_1, R_2 and R_3, independently from each other, are hydrogen; hydroxy; C_1-C_3alkoxy; NH_2; NHR_4; $N(R_4)_2$; OR_4; C_6-C_{12}aryl; phenoxy; anilino; pyrrolo; in which the respective phenyl, phenoxy, anilino or pyrrolo moieties are not substituted or substituted by one, two or three substitutents selected from OH, carboxy, CO-NH_2, C_1-C_{12}alkyl, C_1-C_{12}alkoxy, a methylidenecamphor group, a group -$(CH=CH)_mC(=O)$-OR_4, a group

 or the corresponding alkali metal, ammonium, mono-, di- or tri-C_1-C_4alkylammonium, mono-, di- or tri-C_2-C_4alkanolammonium salts, or the C_1-C_3alkyl esters thereof or by a radical of formula (1a)  ;

R_4 is C_1-C_5alkyl;

R_5 is hydroxy; C_1-C_5alkyl that is unsubstituted or substituted by one or more OH groups; C_1-C_5alkoxy; amino; mono- or di-C_1-C_5alkylamino; M; a radical of formula

(1b)  ; (1c)  ; (1d)  ; or

(1e)  ;

R', R" and R"' independently of the other are C_1-C_{14}alkyl that is unsubstituted or substituted by one or more OH groups;

R_6 is hydrogen; M; C_1-C_5alkyl; or a radical of the formula ;

M is a metal cation;

T_1 is hydrogen; or C_1-C_8alkyl;

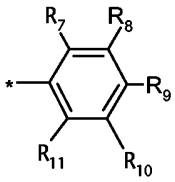
m is 0 or 1;

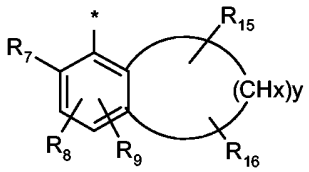
m_1 is from 1 to 5;

m_2 is from 1 to 4; and

m_3 is from 2 to 14.

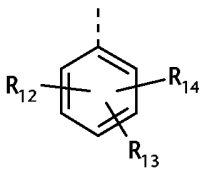
4. Formulation according to claim 2, wherein

R_1, R_2 and R_3 independently from each other are a radical of formula (1f)  ; or

(1g) 

R_7 and R_{11} independently from each other are hydrogen; C_1-C_{18}alkyl; or C_6-C_{12}aryl;

R_8, R_9 and R_{10}, independently from each other, are hydrogen; or a radical of formula

(1h)  , wherein, in formula (1f), at least one of the radicals R_8, R_9 and R_{10} are a radical of formula (1h);

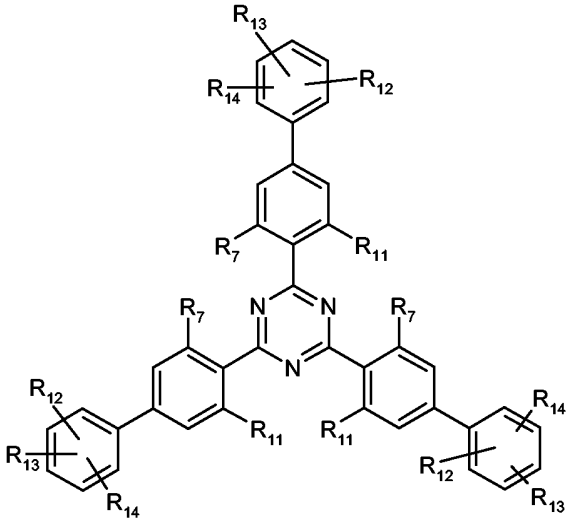
R_{12}, R_{13}, R_{14}, R_{15} and R_{16} independently from each other are hydrogen; hydroxy; halogen; C_1-C_{18}alkyl; C_1-C_{18}alkoxy; C_6-C_{12}aryl; biphenylyl; C_6-C_{12}aryloxy; C_1-C_{18}alkylthio; carboxy; -COOM; C_1-C_{18}-alkylcarboxyl; aminocarbonyl; mono- or di-C_1-C_{18}alkylamino; C_1-C_{10}acylamino; or -COOH;

M is an alkali metal ion;

x is 1 or 2; and

y is a number from 2 to 10.

5. Fromulation according to claim 4, wherein the triazines correspond to formula

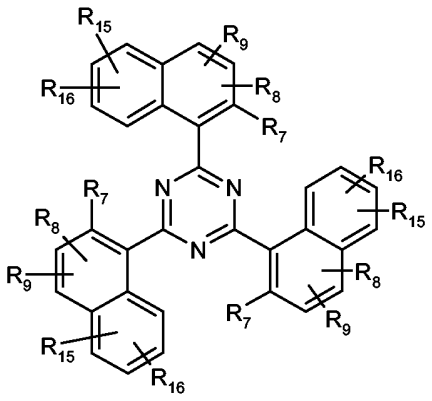
(2)  , wherein

R_7, R_{11}, R_{12}, R_{13} und R_{14} are defined as in claim 4.

6. Formulation according to claim 5, wherein

R_7 and R_{11} are hydrogen.

7. Formulation according to claim 4, wherin component (c_1) relates to compounds of formula

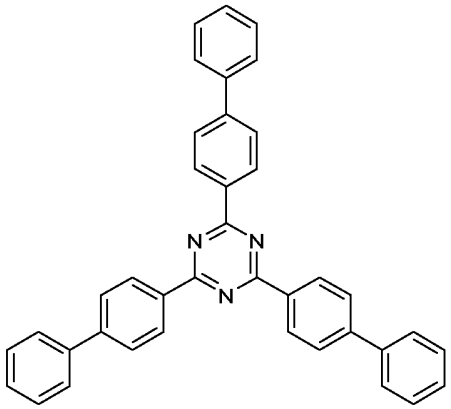
(3)  , wherein

R_7, R_8, R_9, R_{15} and R_{16} are defined as in claim 4.

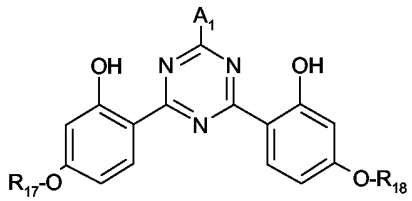
8. Formulation according to claim 7, wherein

R_7, R_8, R_9, R_{15} and R_{16} are hydrogen; or, independently from each other, C_1-C_{18}alkyl.

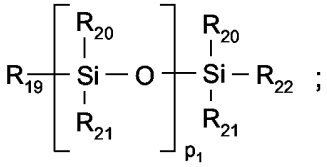
9. Formulation according to claim 5, wherein component (c_1) corresponds to the formula

(4)  .

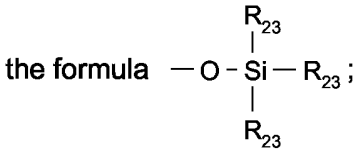
10. Formulation according to any of claims 1 to 3, wherein the triazine UV absorber has the formula

(5)  , wherein

R_{17} and R_{18}, independently of one another, are C_1-C_{18}alkyl; C_2-C_{18}alkenyl; a radical of the formula $-CH_2-CH(-OH)-CH_2-O-T_1$; or a radical of the formula $-(CH_2)_{m_1}-O-(CH_2)_{m_2}-T_2$; a

radical of the formula (5a)  ;

R_{19} is a direct bond; a straight-chain or branched C_1-C_4alkylene radical or a radical of the formula $-C_{m_1}H_{2m_1}-$ or $-C_{m_1}H_{2m_1}-O-$;

R_{20}, R_{21} and R_{22}, independently of one another, are C_1-C_{18}alkyl; C_1-C_{18}alkoxy or a radical of the formula ;

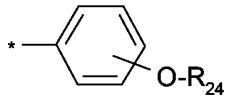
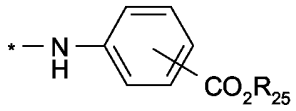
R_{23} is C_1-C_5alkyl;

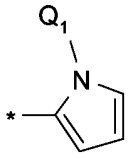
T_1 and T_2, independently from each other, are hydrogen; or C_1-C_8alkyl;

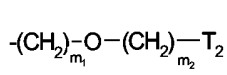
m_1, m_2 and m_3, independently of one another, are 1 to 4;

p_1 is 0; or a number from 1 to 5;

A_1 is a radical of the formula

(5b) , (5c) ; or of the formula

(5d) 

R_{24} is hydrogen; C_1-C_{10}alkyl, $-(CH_2CHR_{26}-O)_{n_1}-R_{25}$; a $-CH_2-CH(-OH)-CH_2-O-T_1$; or radical of the formula 

R_{25} is hydrogen; M; C_1-C_5alkyl; or a radical of the formula $-(CH_2)_{m_2}-O-T_1$;

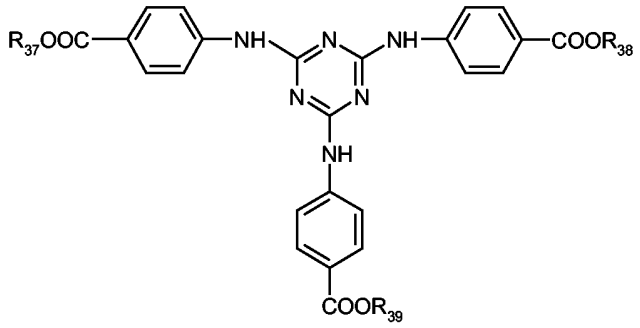
R_{26} is hydrogen; or methyl;

Q_1 C_1-C_{18}alkyl;

M is a metal cation; and

n_1 is 1-16.

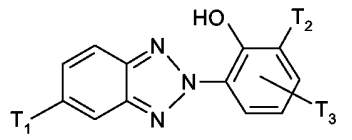
11. A sun screen formulation according to claim 1 or 2 wherein the triazine compound according to component (c_1) corresponds to formula

(28)  , wherein

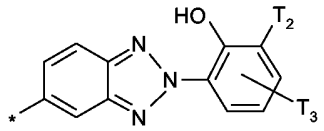
R_{37}, R_{38} and R_{39}, independently from each other are hydrogen; an alkali metal; an ammonium group $N^+(R_{40})_4$;

R_{40} is hydrogen; or an organic radical; C_1-C_3alkyl; or a polyoxyethylene radical which contains from 1 to 10 ethylene oxide units and the terminal OH group of which may be etherified by a C_1-C_3alcohol.

12. Formulation according to claim 1 or 2 in which the triazole organic UV absorber has the formula

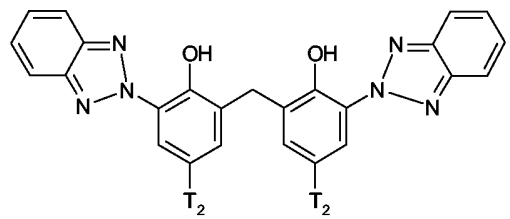
(29)  , wherein

T_1 is C_1-C_3alkyl or, preferably, hydrogen; or a radical of formula

(29a)  ; and

T_2 and T_3, independently fro each other are C_1-C_{12}alkyl, preferably i-octyl; or C_1-C_4alkyl substituted by phenyl, preferably α,α-dimethylbenzyl.

13. Formulation according to claim 2 in which the benzotriazole organic UV absorber corresponds to the formula

(31)  , wherein

T_2 is hydrogen; C_1-C_{12}alkyl; or C_1-C_4alkyl substituted by phenyl.

14. Formulation as according to claim 13 wherein

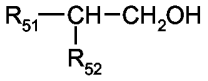
T_2 is iso-octyl.

15. Formulation according to any of claims 1 to 14, wherein

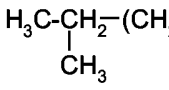
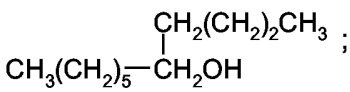
(c_2) is a linear or linear branched C_8-C_{20}alcohol.

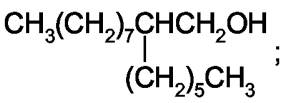
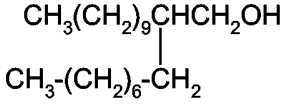
16. Formulation according to claim 15, wherein

(c_2) is a compound of the formula

(35) , wherein

R_{51} and R_{52}, independently fromch other, are a linear C_1-C_{18}alkyl, wherein the sum of carbon atoms in R_{51} and R_{52} is ≤ 18.

17. Formulation according to claim 15 or 16, wherein the fatty alcohol is selected from the compounds of formulae (35a) ; (35b) ;

(35c) ; and (35d) .

18. Formulation according to claim 15 wherein

(c_2) is a mixture of linear octanol and linear decanol.

19. Formulation according to any of the preceding claims wherein the sun screen formulation additionally comprises an oil-soluble organic UV absorber selected from a p-aminobenzoic acid derivative; a salicylic acid derivative; a benzophenone derivative; a dibenzoylmethane derivative; a diphenylacrylate derivative; a benzofuran derivative; a polymeric UV absorber containing one or more silico-organic residues; a cinnamate ester; a camphor derivative; a trianilino-s-triazine derivative; phenylbenzimidazole sulfonic acid or one of its salts; urocanic acid (3-imidazol-4-yl-acrylic acid) or its ethyl ester; menthyl anthranilate; a benzotriazole; a hydroxyphenyltriazine derivative; and a bis-resorcinol-dialkylaminotriazine.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/054225

A. CLASSIFICATION OF SUBJECT MATTER
A61Q17/04 A61K8/34 A61K8/49

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 521 217 B1 (H. LUTHER ET AL.) 18 February 2003 (2003-02-18) claim 1; examples 5,6	1-19
X	EP 1 068 866 A (CIBA SPECIALTY CHEM. HOLD. INC.) 17 January 2001 (2001-01-17) claims 1-32; examples 30,35-39	1-19
X	US 6 746 666 B1 (H. LUTHER) 8 June 2004 (2004-06-08) claims 1-26; examples 30,35-39	1-19
X	WO 03/063814 A (CIBA SPECIALTY CHEM. HOLD. INC.) 7 August 2003 (2003-08-07) page 29; claims 1-9	1-19

-/--

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

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 December 2005	13/12/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Glikman, J-F

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/054225

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE CHEMABS CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; XP002322968 retrieved from STN Database accession no. 140: 275 747 abstract & JP 2004 091374 A (SHISEIDO CO., LTD) 25 March 2004 (2004-03-25) -----	1
A	WO 03/070202 A (BEIERSDORF AG) 28 August 2003 (2003-08-28) example 1.3 -----	1
A	EP 1 285 648 A (BEIERSDORF AG) 26 February 2003 (2003-02-26) example 3.3 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2005/054225

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6521217 B1	18-02-2003	AU 757342 B2	20-02-2003
		AU 4510999 A	10-01-2000
		BR 9911414 A	20-03-2001
		CN 1306417 A	01-08-2001
		DE 69907454 D1	05-06-2003
		DE 69907454 T2	18-03-2004
		WO 9966896 A1	29-12-1999
		ES 2196816 T3	16-12-2003
		ID 26827 A	15-02-2001
		JP 2002518428 T	25-06-2002
EP 1068866 A	17-01-2001	AU 774383 B2	24-06-2004
		AU 4507000 A	18-01-2001
		CN 1281695 A	31-01-2001
		ID 26540 A	18-01-2001
		JP 2001048764 A	20-02-2001
US 6746666 B1	08-06-2004	AU 778175 B2	18-11-2004
		AU 6262600 A	09-01-2001
		BR 0011766 A	05-03-2002
		CN 1355686 A	26-06-2002
		WO 0078277 A1	28-12-2000
		JP 2003502354 T	21-01-2003
		MX PA01013101 A	04-06-2002
WO 03063814 A	07-08-2003	CN 1625386 A	08-06-2005
		JP 2005522421 T	28-07-2005
		US 2005196360 A1	08-09-2005
JP 2004091374 A	25-03-2004	NONE	
WO 03070202 A	28-08-2003	DE 10206796 A1	28-08-2003
		EP 1478325 A1	24-11-2004
EP 1285648 A	26-02-2003	DE 10140546 A1	06-03-2003