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WO 2005/084630 A1 WO 1997/028785 A1
DE 019926671 A1

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Other: ONLINE: EPODOC, WPI, TXTE

(54) Abstract Title: **Micro-particulate organic UV absorber composition**

(57) A topically applicable water-in-oil (w/o) or water-in-silicone (w/Si) formulation comprises:
(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 2μm.; 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.

GB 2418141 A

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1995

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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;

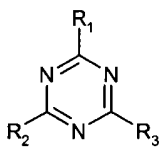
(c) an effective UV-photoprotecting composition comprising

(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.

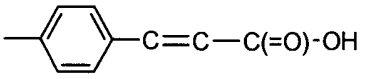
Suitable organic UV absorber (c_1) may be, e.g. a triazine, a benzotriazole, a benzophenone, a vinyl group-containing amide, a cinnamic acid amide or a sulfonated benzimidazole UV absorber.

A preferred class of triazine compounds is that having the formula

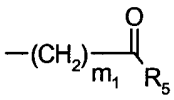
(1) 

, 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)

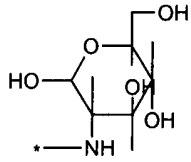


;

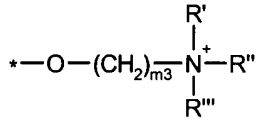
R_4 is C_1-C_5alkyl;

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

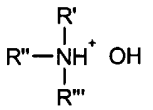
(1b)



; (1c)

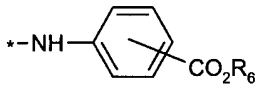


; (1d)



; 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 $-(CH_2)_{m_2}-O-T_1$;

M is a metal cation;

T_1 is hydrogen; or C_1-C_8alkyl;

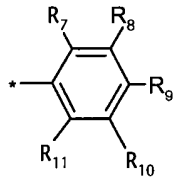
m is 0 or 1;

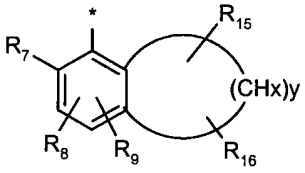
m_1 is from 1 to 5;

m_2 is from 1 to 4; and

m_3 is from 2 to 14.

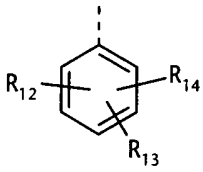
Preferred compounds of formula (1) are those, wherein

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);

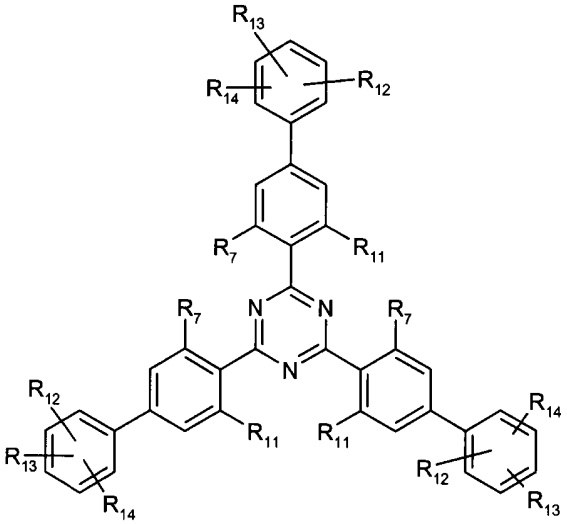
R_{12}, R_{13}, R_{14}, R_{15} and R_{16} independently from each other are hydrogen; hydroxy; halogen; C_1-C_{18}alkyl; C_1-C_{18}alkoxy; C_6-C_{12}aryl; biphenylyl; C_6-C_{12}aryloxy; C_1-C_{18}alkylthio; carboxy; -COOM; C_1-C_{18}-alkylcarboxyl; aminocarbonyl; or mono- or di-C_1-C_{18}alkylamino;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

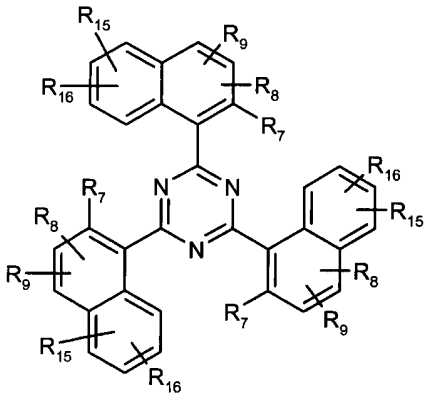
Most preferred triazine derivatives are compounds of formula

(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

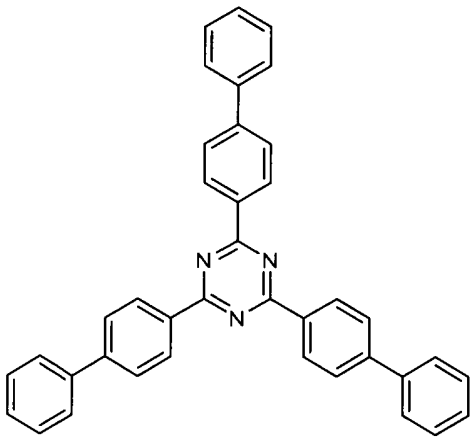
(3) 

are preferred, wherein

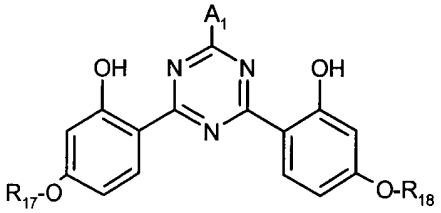
R_7, R_8, R_9, R_{15} and R_{16} are defined as in formula (1g), and most preferably compounds of formula (3), wherein

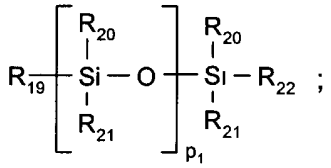
R_7, R_8, R_9, R_{15} and R_{16} are hydrogen; or, independently from each other, C_1-C_{18}alkyl.

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

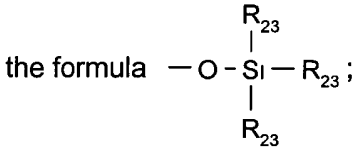
(4) 

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  ;

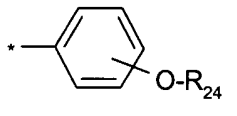
R_{23} is C_1-C_5alkyl;

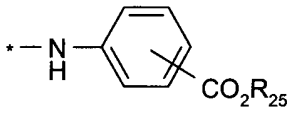
T_1 and T_2, independently from each other, are hydrogen; or C_1-C_8alkyl;

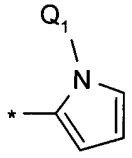
m_1, m_2 and m_3, independently of one another, are 1 to 4;

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 $-(CH_2)_{m_2}-O-T_1$;

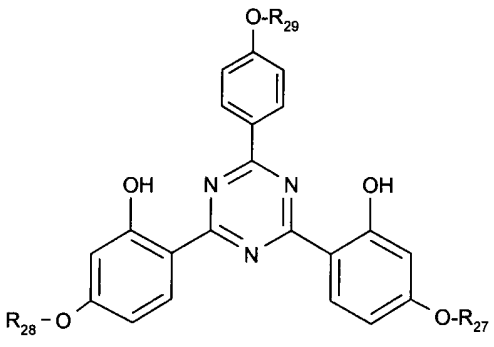
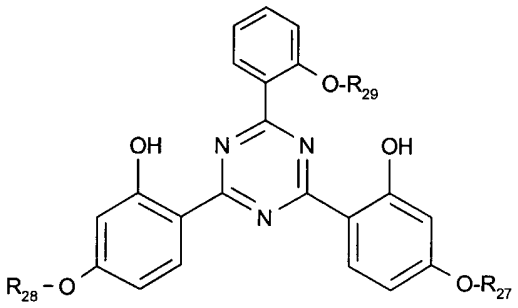
R_{26} is hydrogen; or methyl;

Q_1 C_1-C_{18}alkyl;

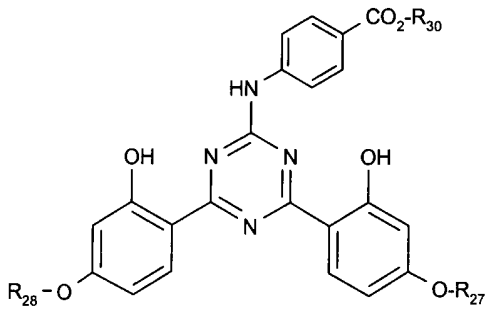
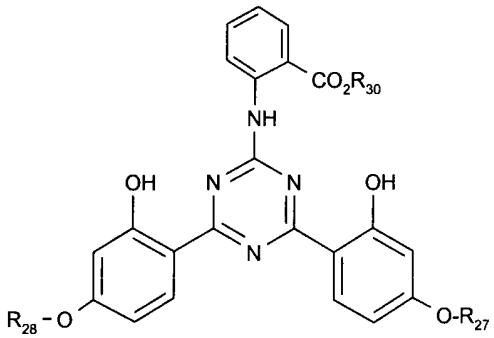
M is a metal cation; and

n_1 is 1-16.

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

(5e)  , (5f)  ,

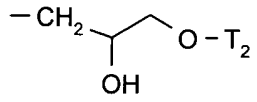
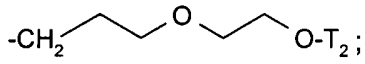
the formula

(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;

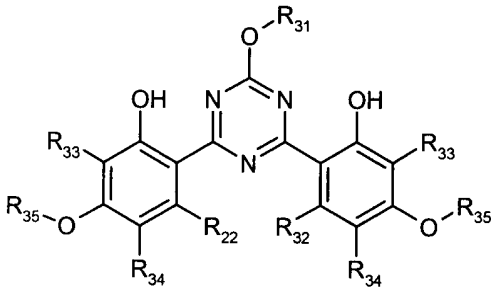
and compounds of the formulae (5g) and (5h), in which

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.

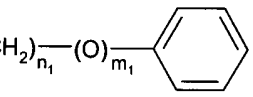
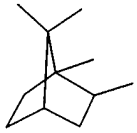
Very particularly preferred in this case are triazine compounds of the formula (5e) - (5h), in which R_{27} and R_{28} have the same meaning.

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)  ;

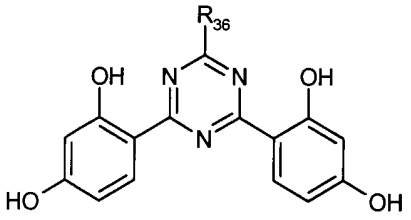
R_{32}, R_{33} and R_{34}, independently of one another, are hydrogen;, hydroxyl; C_1-C_{30}alkyl; or C_2-C_{30}alkenyl;

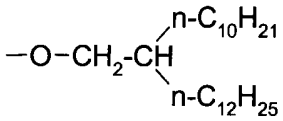
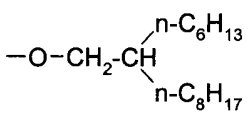
R_{35} is hydrogen; or C_1-C_5alkyl;

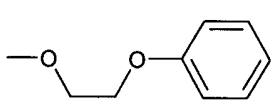
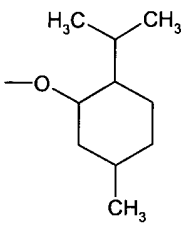
m_1 is 0 or 1; and

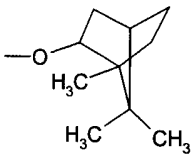
n_1 is 1 to 5.

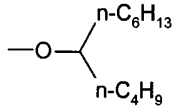
Preferred compounds correspond to the formula

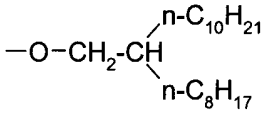
(7)  , wherein

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

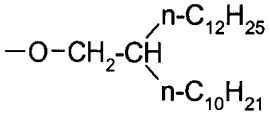
-O-2-ethylhexyl; -O-$(CH_2)_3$-$N(C_2H_5)_2$;;  ;  ,

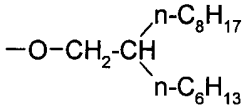


,


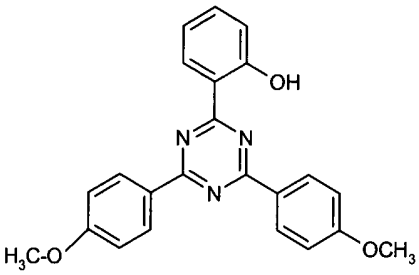
; -O-n-$C_{18}H_{37}$;


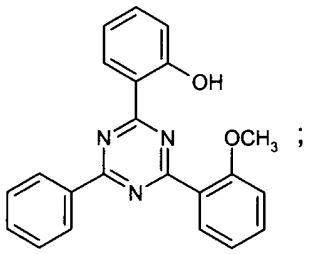
,



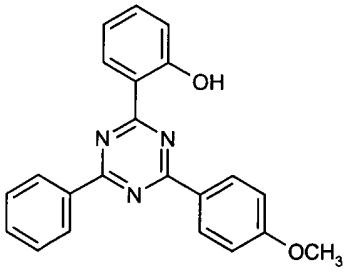
; or


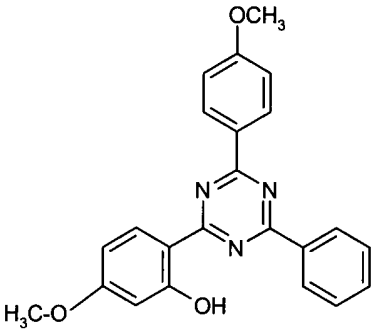
Further preferred triazine derivatives according to component (c_1) are those compounds having one of the formulae

(8)


; (9)


;

(10)


; (11)


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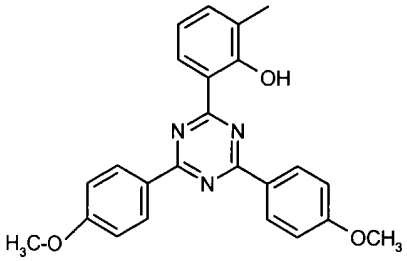
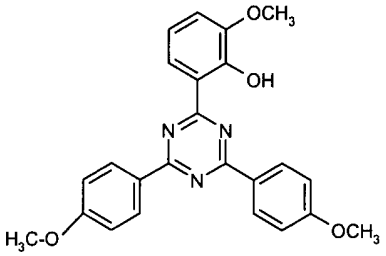
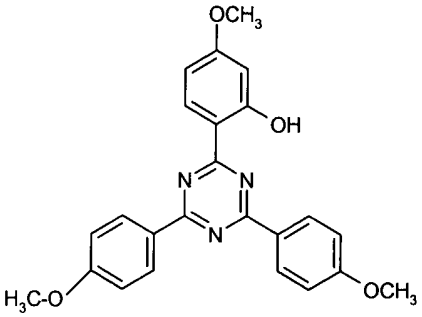
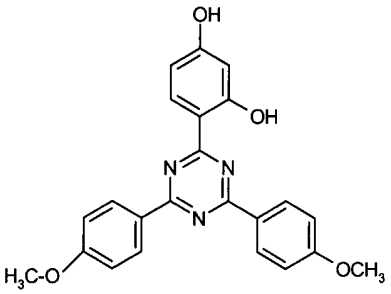
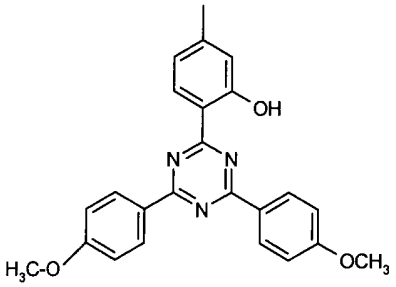
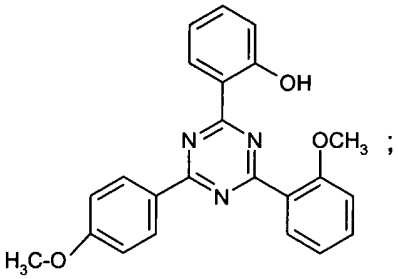
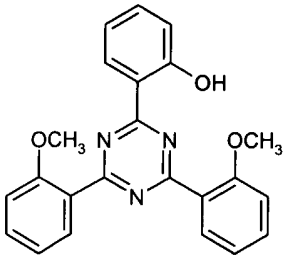
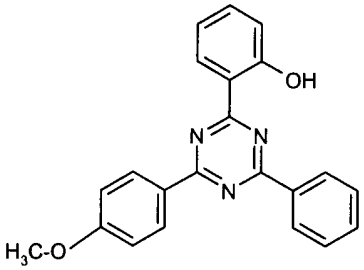
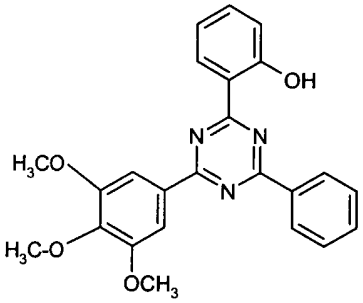
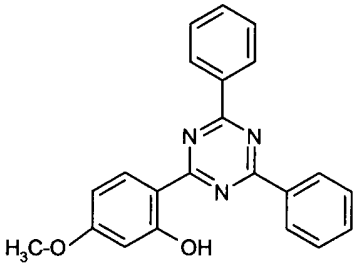
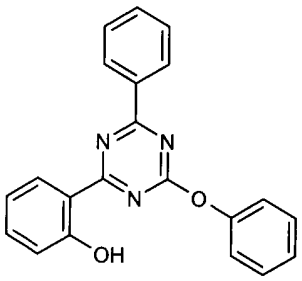
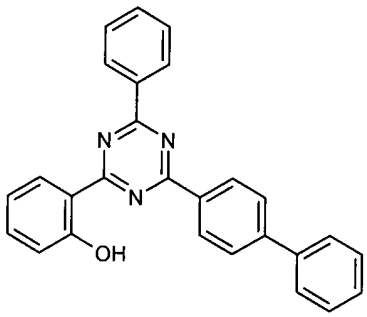
(12)  ; (13)  ;

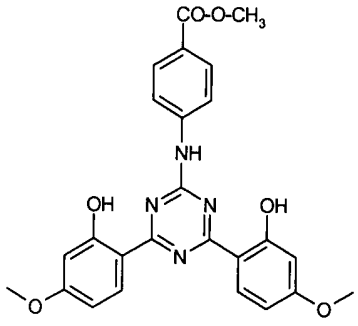
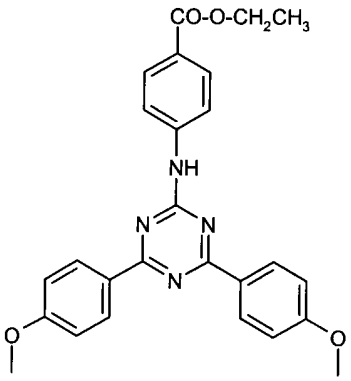
(14)  ; (15)  ;

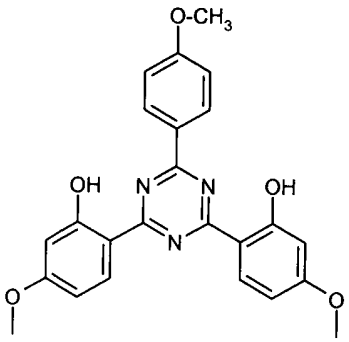
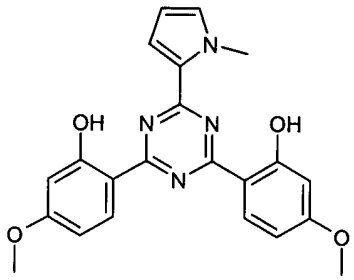
(16)  ; (17)  ;

(18)  ; (19)  ;

(20)  ; (21)  ;

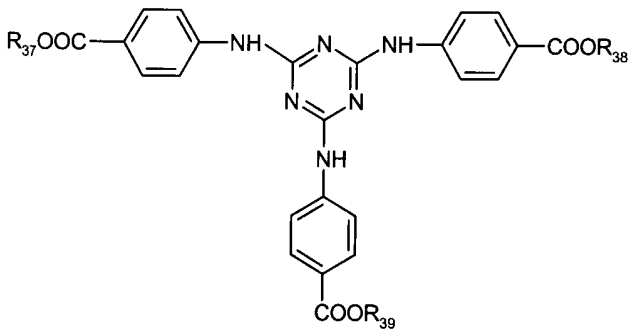
(22)  ; (23)  ;

(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:

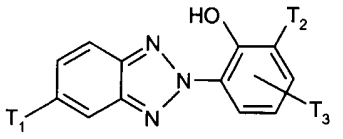
(28)  , wherein

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

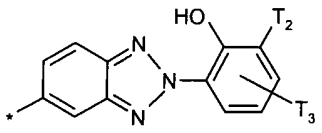
R_{40} is hydrogen; or an organic radical; C_1-C_3alkyl; or a polyoxyethylene radical which contains from 1 to 10 ethylene oxide units and the terminal OH group of which may be etherified by a C_1-C_3alcohol.

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

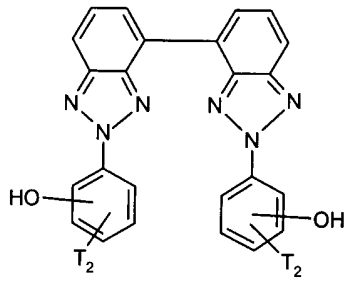
(29)  , wherein

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

(29a)  ; and

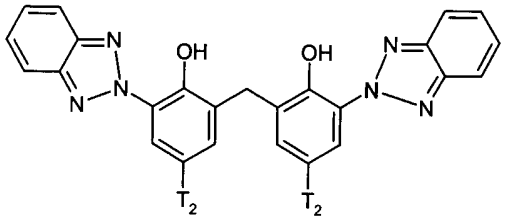
T_2 and T_3, independently from each other are C_1-C_{12}alkyl, preferably i-octyl; or C_1-C_4alkyl substituted by phenyl, preferably α,α-dimethylbenzyl.

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;

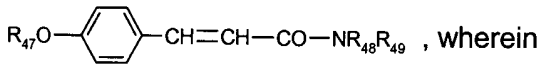
R_{42}, R_{43}, R_{44} and R_{45} are the same or different and each is C_1-C_3alkyl, preferably C_1-C_2alkyl; or hydrogen;

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

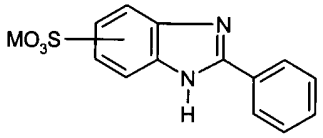
R_{47} is hydroxy or C_1-C_4alkoxy, preferably methoxy or ethoxy;

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:

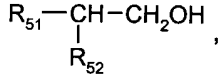
- p-aminobenzoic acid derivatives, typically 2-ethylhexyl-4-dimethylaminobenzoate
- salicylic acid derivatives, typically 2-ethylhexyl salicylate; homosalates; and isopropyl sylicylates;
- benzophenone derivatives, typically 2-hydroxy-4-methoxybenzophenone;
- dibenzoylmethane derivatives, typically 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;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

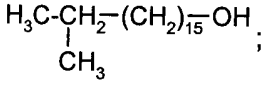
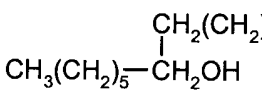
Preferably the fatty alcohol according to component (c_2) is a linear or linear branched C_8-C_{20}alcohol.

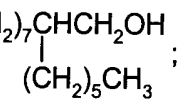
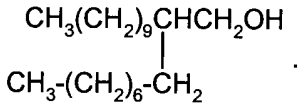
The fatty alcohols according to component (c_2) are preferably characterized by primary alcohols which correspond to the formula

(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

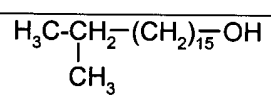
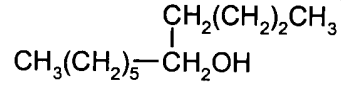
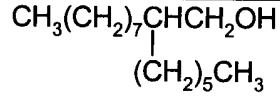
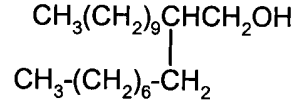
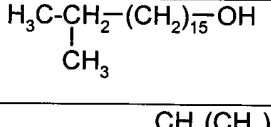
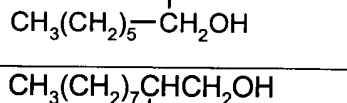
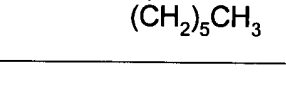
(35a)  ; (35b)  ;

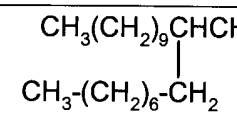
(35c)  ; and (35d)  .

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 (low viscous micronisation process for pumpable dispersions), with a hard grinding medium, for example zirconium silicate balls in a ball mill and a protective surfactant or a protective polymer in water or in a suitable organic solvent;
- wet-kneading (high viscous micronisation process non pump-able pastes) using a continuous or discontinuous (batch) kneader. For a wet-kneading process a solvent (water or cosmetically acceptable oils), a grinding-aid (surfactant, emulsifier) and a polymeric grinding aid may be used.
- spray-drying from a suitable solvent, for example aqueous suspensions or suspensions containing organic solvents, or true solutions in water, ethanol, dichloroethane, toluene or N-methylpyrrolidone etc..
- by the expansion according to the RESS process (Rapid Expansion of Supercritical Solutions) of supercritical fluids (e.g. CO_2) in which the UV filter or filters is/are dissolved, or the expansion of fluid carbon dioxide together with a solution of one or more UV filters in a suitable organic solvent;
- by reprecipitation from suitable solvents, including supercritical fluids (GASR process = Gas Anti-Solvent Recrystallisation / PCA process = Precipitation with Compressed Anti-solvents).

As milling apparatus for the preparation of the micronised organic UV absorbers there may be used, for example, a jet mill, ball mill, vibratory mill or hammer mill, preferably a high-speed mixing mill. Even more preferably used are modern ball mills; manufactures of these mill-types are for example Netzsch (LMZ-mill), Drais (DCP-viscoflow or cosmo), Bühler AG (centrifugal mills) or Bachhofer. The grinding is preferably carried out with a grinding aid. As kneading apparatus for the preparation of the micronized organic UV absorbers examples are typically sigma-hook batch kneaders but also serial batch kneaders (IKA-Werke) or continuous kneaders (Contiuna from Werner und Pfleiderer).

Useful low molecular weight grinding aids for all the above micronizing processes are surfactants and emulsifiers as disclosed below in the chapters "emulsifiers" and "surfactants.

Useful polymeric grinding aids for water dispersion are cosmetically acceptable water soluble polymers with Mn > 500 g/mol for example acrylates (Salcare types), modified or non-modified polysaccharides, polyglucosides or xanthan gum. Furthermore an alkylated vinylpyrrolidone polymer, a vinylpyrrolidone/vinyl acetate copolymer, an acyl glutamate, an alkyl polyglucoside, ceteareth-25 or a phospholipid may be used. Oil dispersions may contain cosmetically acceptable waxy polymers or natural waxes as polymeric grinding aid in order to adjust viscosity during and after processing. Examples of other useful polymeric grinding aids are dieclosed below in the chapter "polymers".

Useful solvents for the grinding process are water, brine, (poly-)ethylenglycol, glycerine or cosmetically acceptable oils. Other useful sovents are disclosed below in the chapters "esters of fatty acids", "natural and synthetic triglycerides including glyceryl esters and derivatives", "perlescent waxes", "hydrocarbon oils" and "silicones or siloxanes".

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. For that purpose the corresponding UV absorbers are subjected to known grinding methods, such as vacuum atomization, countercurrent spray-drying etc.. Such powders have a particle size from 0.1 micrometer to 2 micrometer. In order to eliminate the occurrence of agglomeration, the UV absorbers may be coated with a surface-active compound prior to the

pulverization process, for example with an anionic, non-ionic or amphoteric surfactant, e.g. a phospholipid or a known polymer, such as PVP, an acrylate etc..

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-

Table 1. Suitable non-micronized UV filter substances which can be additionally used with the UV absorbers according to the present invention
(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;
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

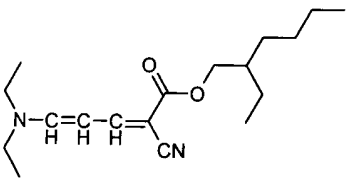
Table 2: Suitable specific non-micronized UV filter substances and adjuvants which can be additionally used with the UV absorbers according to the present invention

No.	Chemical Name	CAS No.
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
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

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.
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
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 mo-no 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	

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.
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 (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

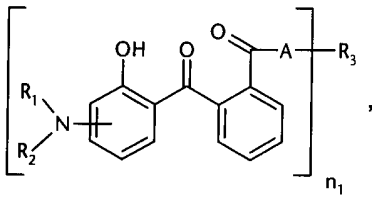
Preferably, the following UV filter combinations are of special interest:

- UV-filter combinations (A) comprising

(a_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol and

(a_2) at least one aminobenzophenone derivative of formula  ,

wherein

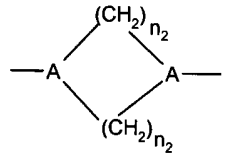
R_1 and R_2 independently from each other are; C_1-C_{20}alkyl; C_2-C_{20}alkenyl; C_3-C_{10}cycloalkyl; C_3-C_{10}cycloalkenyl; or R_1 and R_2 together with the linking nitrogen atom form a 5- or 6-membered heterocyclic ring;

n_1 is a number from 1 to 4;

when n_1 = 1,

R_3 is a saturated or unsaturated heterocyclic radical; hydroxy-C_1-C_5alkyl; cyclohexyl,M optionally substituted with one or more C_1-C_5alkyl; phenyl optionally substituted with a heterocyclic radical, aminocarbonyl or C_1-C_5alkylcarboxy;

when n_1 is 2,

R_3 is an alkylene-, cycloalkylene, alkenylene or phenylene radical which is optionally substituted by a carbonyl- or carboxy group; a radical of formula $*-CH_2-C\equiv C-CH_2-*$ or R_3 together with A forms a bivalent radical of the formula (1a)  ; wherein

n_2 is a number from 1 to 3;

when n_1 is 3,

R_3 is an alkanetriyl radical;

wenn n_1 is 4,

R_3 is an alkanetetrayl radical;

A is -O-; or $-N(R_5)-$; and

R_5 is hydrogen; C_1-C_5alkyl; or hydroxy-C_1-C_5alkyl.

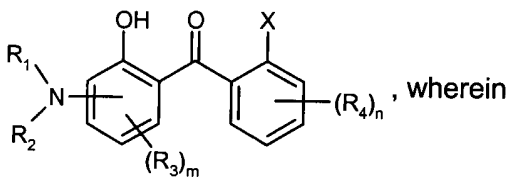
- UV-filter combinations (B) comprising

(b_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(b_2) at least one aminobenzophenone derivative of the formula

 , wherein

R_1 and R_2 independently from each other is hydrogen, C_1-C_{20}alkyl; C_2-C_{20}alkenyl; C_3-C_{10}cycloalkenyl; wherein R^1 and R^2 may form a five- or six-membered ring;

R_3 and R_4 independently from each other is C_1-C_{20}alkyl; C_2-C_{20}alkenyl; C_3-C_{10}cycloalkenyl, C_1-C_{20}alkoxy, C_1-C_{20}alkoxycarbonyl, C_1-C_{20}alkylamino, di(C_1-C_{20}alkyl)amino, optionally substituted aryl or Heteroaryl;

X is hydrogen; $COOR^5$; or $CONR^6R^{7,}$

R_5, R_6 and R_7 independently from each other are hydrogen, C_1-C_{20}alkyl; C_2-C_{20}alkenyl; C_3-C_{10}cycloalkyl; C_3-C_{10}cycloalkenyl; $(Y\text{-}O)_q$-Z; optionally substituted aryl;

Y is $-(CH_2)_2$-; $-(CH_2)_3$-; $-(CH_2)_4$-; $-CH(CH_3)-CH_2$-;

Z is $-CH_2-CH_3$; $-CH_2-CH_2-CH_3$; $-CH_2-CH_2-CH_2-CH_3$; $CH(CH_3)-CH_3$;

m is 0; 1; 2; or 3;

n is 0; 1; 2; 3; or 4; and

q is a number from 1 to 20.

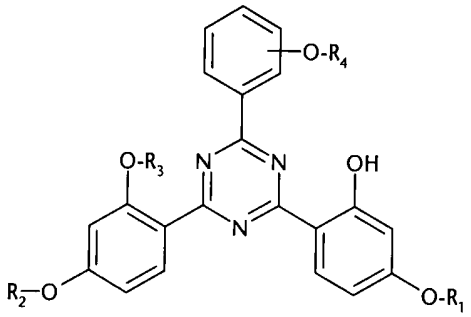
- UV-filter combinations (C) comprising

(c_1) an effective UV-photoprotecting composition comprising

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

0.5% to 80% of at least a primary C_6-C_{28} fatty alcohol and

(c_2) at least one hydroxyphenyltriazine compound of formula

(C1) 

, wherein

R_1, R_2 and R_3 are each independently of the others hydrogen; C_1-C_{18}alkyl; C_2-C_{10}alkenyl; or phenyl-C_1-C_4alkyl; and

R_4 is hydrogen; or C_1-C_5alkyl.

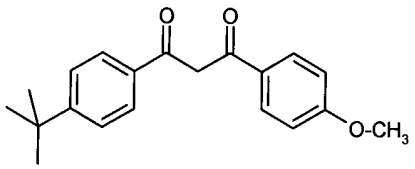
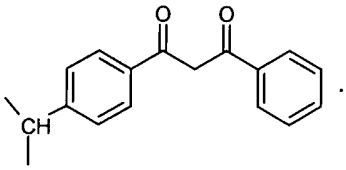
- UV-filter combinations (D) comprising

(d_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol and

(d_2) at least one dibenzoylmethane derivative of formula

(D1)  or (D2)  .

- UV-filter combinations (e) comprising

(f_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(f_2) disodium phenyl dibenzimidazole tetrasulfonate (Heliopan AP).

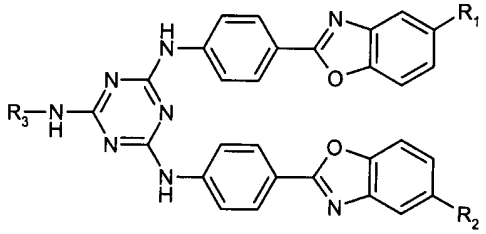
- UV-filter combinations (F) comprising

(f_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol and and

(f_2) benzoxazole-substituted triazines of formula

(F1)  , wherein

R_1, R_2 and R_3 independently from each other are branched or unbranched C_1-C_{12}alkyl.

- UV-filter combinations (G) comprising

(g_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(g_2) 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]-; (CAS-No. 155633-54-8; Drometrizole Trisiloxane; Mexoryl XL);

- UV-filter combinations (h) comprising

(h_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(h_2) siloxanes and silicones, di-Me, 1-[[4-[3-ethoxy-2-(ethoxycarbonyl)-3-oxo-1-propenyl]phenoxy]methyl]ethenyl Me, 3-[4-[3-ethoxy-2-(ethoxycarbonyl)-3-oxo-1-propenyl]-phenoxy]-1-propenyl Me, Me hydrogen (Dimethicodiethylbenzalmalonate ; CAS-No. 207574-74-1);

- UV-filter combinations (I) comprising

(i_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(i_2) (+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo[2.2.1]heptan-2-one; p-methyl benzylidene camphor;

- UV-filter combinations (K) comprising

(k_1) an effective UV-photoprotecting composition comprising

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

0.5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(k_2) α-(2-oxoborn-3-ylidene)toluene-4-sulphonic acid and its salts (Mexoryl SL);

- UV-filter combinations (L) comprising

(l_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(l_2) methyl N,N,N-trimethyl-4-[(4,7,7-trimethyl-3-oxobicyclo[2,2,1]hept-2-ylidene)methyl]-anilinium sulphate (Mexoryl SO);

- UV-filter combinations (M) comprising

(m_1)an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(m_2)2-ethylhexyl 2-cyano,3,3-diphenylacrylate (Octocrylene);

- UV-filter combinations (N) comprising

(n_1) an effective UV-photoprotecting composition comprising

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

0.5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(n_2) 2- ethylhexyl 4-methoxycinnamate (octyl methoxy cinnamate);

- UV-filter combinations (O) comprising

(o_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(o_2) 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);

- UV-filter combinations (P) comprising

(p_1) an effective UV-photoprotecting composition comprising

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

0.5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(p_2) 2-phenyl-1H- benzimidazole-5-sulphonic acid (Phenylbenzimidazolsulfonic Acid);

- UV-filter combinations (Q) comprising

(q_1) an effective UV-photoprotecting composition comprising

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

0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol; and

(q_2) 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).

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..

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 with 2 to 30 mol of ethylene oxide and/or from 0 to 5 mol propylene oxide with 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 polyglycolether such as laureth-n, ceteareth-n, steareth-n, oleth-n. Fatty acid polyglycolether 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, diisostearoyl 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, C_8-C_{22} alkyl-mono and oligo-glycosides and ethoxylated analogues with glucose being preferred as the sugar component;
- W/O emulsifiers such as methyl glucose dioleate/ methyl glucose isostearate;
- Sulfates and sulfonated derivatives, dialkylsulfosuccinates, dioctyl succinate, alkyl lauryl sulfonate, linear sulfonated parafins, sulfonated tetraproplyne sulfonate, sodium lauryl sulfates, amonium and ethanolamine lauryl sulfates, lauyl ether sulfates, sodium laureth sulfates, sulfosuccinates, aceyl 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, isoquinoteines, cetyl pyridinium chlorure, cetyl pyridinium bromide, quaternary ammonium such as cetyltrimethylbroide amonium broide (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 (Meroxapols);
- 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; especially suitable are betaines, such as N-alkyl-N,N-dimethylammonium glycinates, cocoalkyldimethylammonium glycinate, N-acylaminopropyl-N,N-dimethylammonium glycinates, cocoacylaminopropyl-dimethylammonium glycinate and 2-alkyl-3-carboxymethyl-3-hydroxyethylimidazolines each having from 8 to 18 carbon atoms in the alkyl or acyl group and also cocoacyl-aminoethylhydroxyethylcarboxymethylglycinate, 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 ceteareth-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 szeareth-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 ceteareth-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 0.1 to 30 % by weight, especially from 0.2 to 20 % by weight and preferably from 0.5 to 10 % by weight, based on the total weight of the composition.

The emulsifier in these formulations may be replaced by an associative polymer (0.1 to 10 % 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.

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%.

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

a_1) spontaneously emulsifying stock formulation, consisting of the UV absorber according to the invention, PEG-6-C_{10}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;

a_2) 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 tributyl citrate;

c) mixtures or solutions of the UV absorber according to the invention with n-alkylpyrrolidone.

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 described below.

Esters of fatty acids

Esters of linear C_6-C_{24} fatty acids with linear C_3-C_{24} alcohols, esters of branched C_6-C_{13}carboxylic acids with linear C_6-C_{24} fatty alcohols, esters of linear C_6-C_{24} fatty acids with branched alcohols, especially 2-ethylhexanol, esters of hydroxycarboxylic acids with linear or branched C_6-C_{22} 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, erucylerucate, 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/caprate, stearyl heptanoate, diisostearyl malate, octyl hydroxystearate, etc..

Natural or synthetic triglycerides including glyceryl esters and derivatives

Di- or tri-glycerides, based on C_6-C_{18} 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:

Ikylene 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

Perfluorhexane, dimethylcyclohexane, ethylcyclopentane, polyperfluoromethylisopropyl ether.

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, α-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, carraghenan, gellan, pectines, or modified cellulose such as hydroxycellulose, hydroxypropylmethylcellulose. 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), Stabilen 30 (acrylates / vinyl isodecanoate crosspolymer), Pemulen TR-1(acrylates / C10-30 alkyl acrylate crosspolymer), Luvigel EM (sodium acrylates copolymer), Aculyn 28 (acrylates/beheneth-25 methacrylate copolymer), etc.

Polymers

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, quarternised vinylpyrrolidone/vinyl imidazole polymers, for example Luviquat® (BASF), condensation products of polyglycols and amines, quaternised collagen polypeptides, for example lauryldimonium 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-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 anionic, 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 copolymers, octyl acrylamide/methyl methacrylatetert-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers, polyvinylpyrrolidone, vinylpyrrolidone/-vinyl acetate copolymers, vinylpyrrolidone/dimethylaminoethyl methacrylate/vinyl caprolactam terpolymers and also optionally derivatised cellulose ethers and silicones. Furthermore the polymers as described in EP 1093796 (pages 3-8, paragraphs 17-68) may be used.

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, 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, $ZnSO_4$), 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).

The amount of antioxidants present is usually from 0.001 to 30 % by weight, preferably from 0.01 to 3 % by weight, based on the weight of the UV absorber of formula (1).

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, glyerin, 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 monobutylether 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 polyethylene 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, 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-propanediol.

Preservatives and Bacteria-inhibiting agents

Suitable preservatives include, for example, methyl-, ethyl-, propyl-, butyl- parabenes, benzalkonium chloride, 2-bromo-2-nitro-propane-1,3-diol, dehydroacetic acid, diazolidinyl urea, 2-dichloro-benzyl alcohol, dmdm hydantoin, formaldehyde solution, methyldibromoglutanitrile, 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.

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 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, petitgrain), 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, dimethylbenzylcarbinyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethylmethylphenyl glycinate, allylcyclohexyl propionate, styrallyl 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, lilial 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, lilial, lyral, 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, iraldein 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, Weinheim, 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.

Insect repellents

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 ; Micropearl M305 Seppic), can maximize better the UV protection of the sun products. Holosphere additives (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, can modulate skin shine by eliminating reflection phenomena and indirectly may scatter the UV light.

Other adjuvants

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_2O, dimethyl ether, CO_2, N_2 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.

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:

- 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. eyeshadow 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, preshave 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, perfume), perfume oils or perfume creams;
- cosmetic hair-treatment preparations, e.g. hair-washing preparations in the form of shampoos and conditioners, hair-care preparations, e.g. pretreatment 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.

Examples of cosmetic and pharmaceutical preparations (X = preferred combinations)

W/O systems					
Ingredients	1	2	3	4	5
Emulsifiers	X	X	X	X	X
Polyglyceryl-2 Dipolyhydroxystearate 2%-4%	X	X	X	X	X
PEG-30 Dipolyhydroxystearate 2%-4%		X			
Rapeseed Oil Sorbitol Esters 1%-5%			X		
PEG-45/Dodecyl Glycol Copolymer 1%-5%				X	
Sorbitan Oleate / Polycerol-3 ricinoleate 1%-5%					X
Lipophilic emollient/dispersant oil 10% - 20%	X	X	X	X	X
Fatty Alcohols and/or Waxes 10% - 15%	X	X	X	X	X
Electrolytes (NaCl, $MgSO_4$) 0.5% - 1%	X	X	X	X	X
Polyol phase (Propylene glycol, glycerin) 1% - 8%	X	X	X	X	X
Preservatives 0.3% - 0.8%	X	X	X	X	X
Perfume oils 0.1% - 0.4%	X	X	X	X	X
Chelating agents (such as EDTA) 0% - 0.2%	X	X	X	X	X
Antioxidants 0.05% - 0.2%	X	X	X	X	X
Water deionized Qs 100%	X	X	X	X	X
effective UV-photoprotecting composition comprising 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 0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol 0,1% - 20%.	X	X	X	X	X
UV-absorber as described in Table 1 and 2 3 0% - 30%.	X	X	X	X	X

Microemulsions										
Ingredients	1	2	3	4	5	6	7	8	9	10
PEG-8 Caprylic/Capric Glycerides 10%-25%	X			X	X			X	X	
PPG-5-ceteth-20 10%-25%		X	X			X	X			X
Polyglyceryl-6 Isostearate 5%-15%	X		X							
Polyglyceryl-3 Diisostearate 5%-15%		X		X						
Polyglyceryl-6 Dioleate 5%-15%					X		X			
PPG-10 Cetyl Ether 5%-15%						X		X		
Ethoxydiglycol 5%-15%									X	X
Oil phase 10%-80%	X	X	X	X	X	X	X	X	X	X
Isostearyl Benzoate	X	X	X	X	X	X	X	X	X	X
Isostearyl Isostearate	X	X	X	X	X	X	X	X	X	X
PEG-7 Glyceryl Cocoate	X	X	X	X	X	X	X	X	X	X
Cyclomethicone	X	X	X	X	X	X	X	X	X	X
Polyalcohols/Humectants 1%-10%	X	X	X	X	X	X	X	X	X	X
Preservatives 0.3 -0.8%	X	X	X	X	X	X	X	X	X	X
Perfume oils 0.1%-0.4%	X	X	X	X	X	X	X	X	X	X
Water Deioniz. qs 100%	X	X	X	X	X	X	X	X	X	X
effective UV-photoprotecting composition comprising 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 0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol 0,1%-20%	X	X	X	X	X	X	X	X	X	X
UV-absorber as described in Table 1 and 2 0%-30%	X	X	X	X	X	X	X	X	X	X

Oleogels										
Ingredients	1	2	3	4	5	6	7	8	9	10
Hydrogenated Lecithin 1%-10%	X									X
Silica Dimethyl Silylate 1%-10%		X							X	
Silica 1%-5%			X					X		
C_{24-28} Alkyl Dimethicone 1%-5%				X			X			
Aluminium or Magnesium Stearate 1%-5%					X	X				

Oleogels										
Ingredients	1	2	3	4	5	6	7	8	9	10
Polyols – Humectants 5%-70%	X	X	X	X	X	X	X	X	X	X
Oil phase 20% - 90%										
Dicaprylyl Ether	X					X		X		
Phenyl Trimethicone		X					X			
Hydrogenated Polyisobutene			X							
Isopropyl Isostearate				X					X	
Oleogel basis (Mineral oil and hydrogenated Butylene/Ethylene or Ethylene/Propylene Styrene Copolymer)					X					X
Silicone wax 1%-10%	X	X	X	X	X	X	X	X	X	X
Dimethiconol Behenate	X	X	X	X	X	X	X	X	X	X
Dimethiconol Stearate	X	X	X	X	X	X	X	X	X	X
Perfume oils 0.1%-0.5%	X	X	X	X	X	X	X	X	X	X
Antioxidants 0.05%-0.2%	X	X	X	X	X	X	X	X	X	X
effective UV-photoprotecting composition comprising 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 0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol 0,1%-20%	X	X	X	X	X	X	X	X	X	X
UV-absorber as described Table 1 and 2 0%-30%	X	X	X	X	X	X	X	X	X	X

Light/dry cosmetic oils				
Ingredients	1	2	3	4
Hydrocarbon oils 30%-70%	X			X
Fatty acid esters branched or not 10%-50%		X	X	
Silicones/Siloxanes 0% - 10%	X		X	
Perfluorinated oils and Perfluoroethers 0%-10%		X		X
Viscosifying agents 0%-10%	X	X	X	X
Esters of long chain acids and alcohols 0% - 2%	X	X	X	X
Antioxidants 0.1%-1%	X	X	X	X
Solubilisants/dispersing agents 0%-5%	X	X	X	X
Perfume oils 0.1%-0.5%	X	X	X	X

Light/dry cosmetic oils				
Ingredients	1	2	3	4
effective UV-photoprotecting composition comprising 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 0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol 0,1%-20%.	X	X	X	X
UV-absorber as described in Table 1 and 2 0%-30%	X	X	X	X

Foaming/mousse products	
Ingredients	1
SD Alcohol 40 0%-8%	X
Propellant 8%-15%	X
Nonionic Emulsifier/Surfactant 0.5% - 3%	X
Corrosion Inhibitor 0% - 1%	X
Perfume oils 0.1% - 0.5%	X
Preservatives 0.1%-1%	X
Miscellaneous 0%-1%	X
effective UV-photoprotecting composition comprising 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 0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol 0,1%-20%.	X
UV-absorber as described in Table 1 and 2 0%-30%	X

Stick products	
Ingredients	1
Waxes 15%-30%	X
Natural and silicone oils 20%-75%	X
Lanoline derivatives 5%->50%	X
Esters of lanolin	x
Acetylated lanolin	x
Lanolin oil	x
Colorants and pigments 10% - 15%	X
Antioxidants 0.1% - 0.8%	X
Perfume oils 0.1% - 2%	X
Preservatives 0.1%-0.7%	X

Stick products	
Ingredients	1
effective UV-photoprotecting composition comprising 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 0,5% to 80% of at least a primary C_6-C_{28} fatty alcohol 0,1%-20%	X
UV-absorber as described in Table 1 and 2 0%-30%	X

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

5 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

Composition		Ex. 4a	Ex. 4b
	INCI-Name	% w/w (as supplied)	% w/w (as supplied)
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

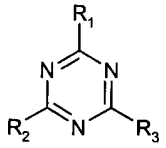
(c_1) 20% to 99% of at least one insoluble micronized organic UV-screening active with a mean particle size ranging from 0,01µm to 2 µm; and

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

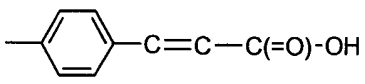
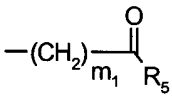
2. Formulation according to claim 1, wherein

(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

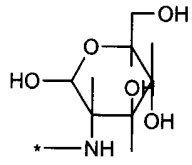
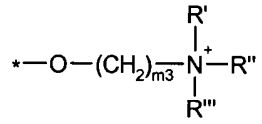
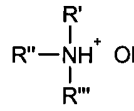
(1)  , wherein

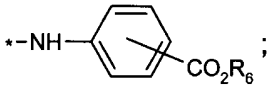
R_1, R_2 and R_3, independently from each other, are hydrogen; hydroxy; C_1-C_3alkoxy; NH_2; NHR_4; $N(R_4)_2$; OR_4; C_6-C_{12}aryl; phenoxy; anilino; pyrrolo; in which the respective phenyl, phenoxy, anilino or pyrrolo moieties are not substituted or substituted by one, two or three substitutents selected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

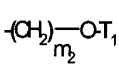
R_4 is C_1-C_5alkyl;

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;

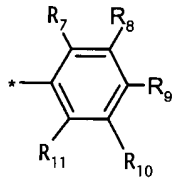
m is 0 or 1;

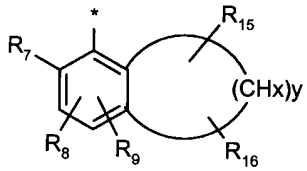
m_1 is from 1 to 5;

m_2 is from 1 to 4; and

m_3 is from 2 to 14.

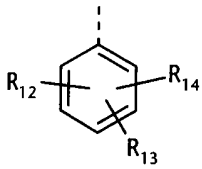
4. Formulation according to claim 2, wherein

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);

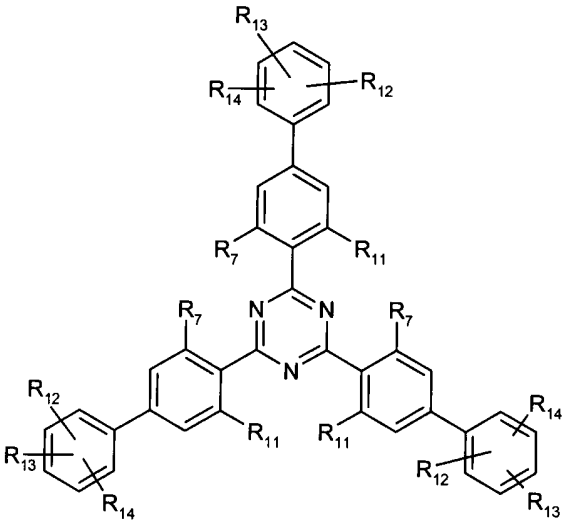
R_{12}, R_{13}, R_{14}, R_{15} and R_{16} independently from each other are hydrogen; hydroxy; halogen; C_1-C_{18}alkyl; C_1-C_{18}alkoxy; C_6-C_{12}aryl; biphenylyl; C_6-C_{12}aryloxy; C_1-C_{18}alkylthio; carboxy; -COOM; C_1-C_{18}-alkylcarboxyl; aminocarbonyl; mono- or di-C_1-C_{18}alkylamino; C_1-C_{10}acylamino;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

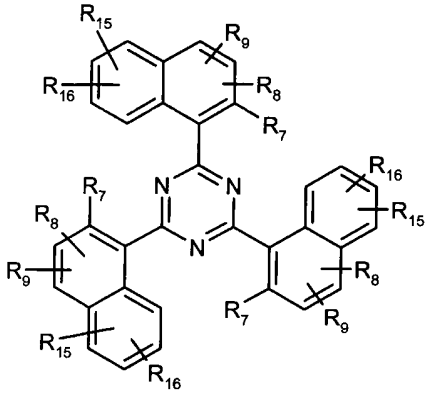
(2)  , wherein

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

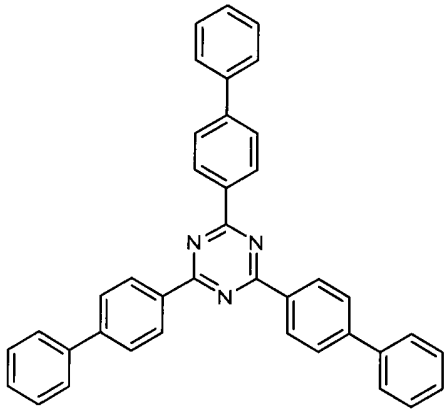
(3)  , wherein

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

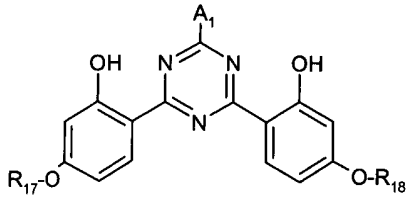
8. Formulation according to claim 7, wherein

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

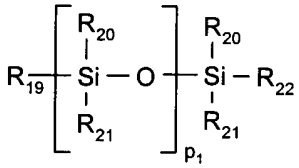
9. Formulation according to claim 5, wherein component (c_1) corresponds to the formula

(4) 

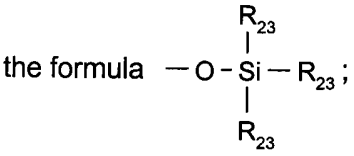
10. Formulation according to any of claims 1 to 3, wherein the triazine UV absorber has the formula

(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  ;

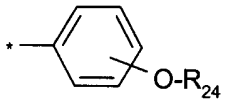
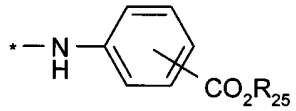
R_{23} is C_1-C_5alkyl;

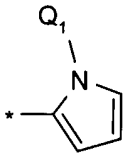
T_1 and T_2, independently from each other, are hydrogen; or C_1-C_8alkyl;

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 $-(CH_2)_{m_1}-O-(CH_2)_{m_2}-T_2$

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

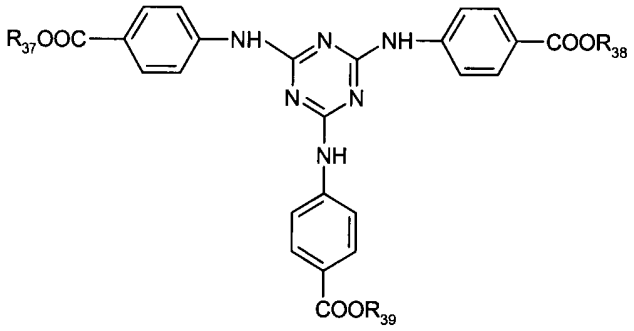
R_{26} is hydrogen; or methyl;

Q_1 C_1-C_{18}alkyl;

M is a metal cation; and

n_1 is 1-16.

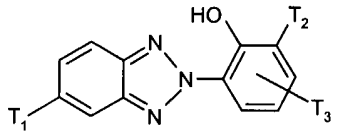
11. A sun screen formulation according to claim 1 or 2 wherein the triazine compound according to component (c_1) corresponds to formula

(28)  , wherein

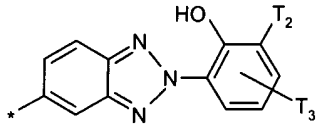
R_{37}, R_{38} and R_{39}, independently from each other are hydrogen; an alkali metal; an ammonium group $N^+(R_{40})_4$;

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

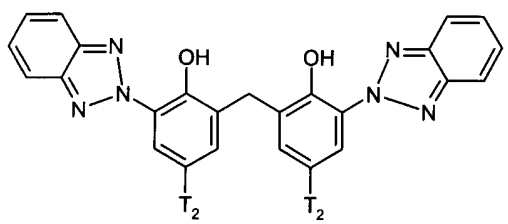
(29)  , wherein

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

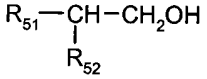
T_2 is iso-octyl.

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

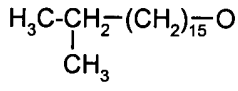
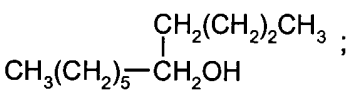
(c_2) is a linear or linear branched C_8-C_{20}alcohol.

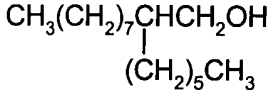
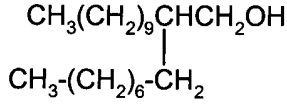
16. Formulation according to claim 15, wherein

(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 $\leq$ 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.

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Application No:	GB0517593.0	**Examiner:**	Vaughan Thomas
Claims searched:	1-19	**Date of search:**	10 January 2006

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1,2 at least	WO 97/28785 A1 (PROCTER & GAMBLE) see p.2 l.23 - p.3 l.3, p.4 l.17 - p.6 l.21 and Examples
X	1,2 at least	DE 19926671 A1 (WELLA AG) see p.2 ll.53-60, p.3 ll.28-37, Example 13 and WPI abstract Acc. No. 2001-092688 [11]
A,E	1	WO 2005/084630 A1 (SHELL OIL) see p.3 ll.9-31, p.6 ll.15-21, p.20 l.15 - p.21 l.28, p.23 ll.12-25 and p.26 ll.16-33

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

A61K; A61Q

The following online and other databases have been used in the preparation of this search report

Online: EPODOC, WPI, TXTE

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