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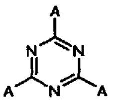
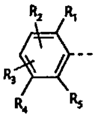
WO 2004/085412 A3

(54) **Title:** SYMMETRICAL TRIAZINE DERIVATIVES

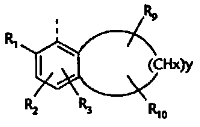
(1)



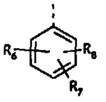
(1a)



(1b)



(1c)



(57) **Abstract:** Disclosed is the use of the compounds of formula wherein A is a radical of formula (1a) or (1b) R, R_1 and R_5 independently from each other are hydrogen; C_1-C_{18}alkyl; or C_6-C_{12}aryl; R_2, R_3 and R_4 independently from each other are hydrogen; or a radical of formula wherein at least one of the radicals R_2, R_3 and $R_4$are a radical of formula (1c); R_6, R_7, R_8, R_9 and R_{10} independently from each other are hydrogen; hydroxy; C_1-C_{18}alkyl; C_1-C_{18}alkoxy;C_6-C_{12}aryl; 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; M is an alkali metal ion; x is 1 or 2; and y is a number from 2 to 10; for the protection of human and animal hair and skin against the damaging effect of UV radiation. The compounds of formula (1) are high effective UV absorbers for cosmetic formulations aund can - depending on their physical properties - be used in micronized or soluble form.

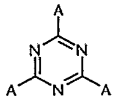
Symmetrical Triazine derivatives

The present invention relates to the use of specific symmetrical triazine derivatives for the protection of human and animal hair and skin against the damaging effect of UV radiation, cosmetic compositions comprising these triazine derivatives and process for preparation of these compounds.

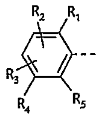
Triazines which are symmetrically substituted by biphenyl or naphthyl are known, for example from US-A-6,225,467. They are used as for electroluminescent devices.

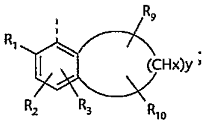
Surprisingly it has been found that these compounds can be used as highly effective UV absorbers for cosmetic applications.

Therefore, the present invention refers to the non-therapeutic use of the compounds of formula

(1) 

, wherein

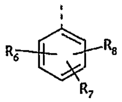
A is a radical of formula (1a) 

; or (1b) 

;

R_1 and R_5 independently from each other are hydrogen; C_1-C_{18}alkyl; or C_6-C_{12}aryl;

R_2, R_3 and R_4 independently from each other are hydrogen; or a radical of formula

(1c) 

, wherein at least one of the radicals R_2, R_3 and R_4 are a radical of formula (1c);

R_6, R_7, R_8, R_9 and R_{10} 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;

for the protection of human and animal hair and skin against the damaging effect of UV radiation.

C_1-C_{18}alkyl according to the definition for the radicals of the compound of formula (1) are straight-chain or branched alkyl radicals like methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.butyl, tert.butyl, amyl, isoamyl or tert.amyl, hexyl, 2-ethylhexyl, heptyl, octyl, isooctyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl.

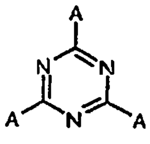
C_1-C_{18}alkyl according to the definition for the radicals of the compound of formula (1) may be substituted by methoxyethyl, ethoxypropyl, 2-ethylhexyl, hydroxyethyl, chloropropyl, N,N-diethylaminopropyl, cyanoethyl, phenethyl, benzyl, p-tert-butylphenethyl, p-tert-octylphenoxy-ethyl, 3-(2,4-di-tert-amylphenoxy)-propyl, ethoxycarbonylmethyl-2-(2-hydroxyethoxy)ethyl, or 2-furylethyl.

C_1-C_{18}alkyl according to the definition for the radicals of the compound of formula (1) are for example methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec.butoxy, tert.butoxy, amyloxy, isoamyloxy or tert.amyloxy, hexyloxy, heptyloxy, octyloxy, isooctyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy or octa-decyloxy.

C_6-C_{10}aryl according to the definition for the radicals of the compound of formula (1) is for example naphthyl und preferably phenyl.

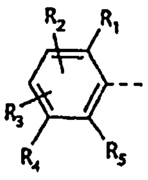
According to another aspect the present invention provides use of the compounds of formula

(1)



, wherein

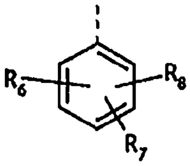
A is a radical of formula (1a)



;

R_1 and R_5 independently from each other are hydrogen; C_1-C_{18}alkyl; or C_6-C_{12}aryl; R_2, R_3 and R_4 independently from each other are hydrogen; or a radical of formula

(1c)



, wherein, in formula (1a), at least one of the radicals R_2, R_3 and R_4 are a radical of formula (1c);

R_6, R_7 and R_8 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; and

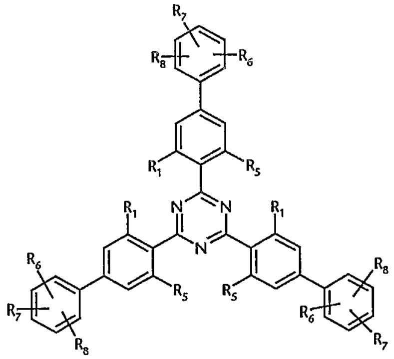
M is an alkali metal ion;

for the protection of human and animal hair and skin against the damaging effect of UV radiation.

In another form, the present invention provides a cosmetic preparation comprising at least one compound of formula (1) together with cosmetically tolerable carriers or adjuvants.

Preferably compounds of formula

(2)



are used, wherein

R_1, R_5, R_6, R_7 und R_8 are defined as in formula (1).

In formula (2) $R_1$and R_5 are preferably hydrogen.

Most preferably compounds of formula (1) or (2) are used wherein R_6 and R_8 are hydrogen.

Compounds of formula (1) of preferred interest are those, wherein

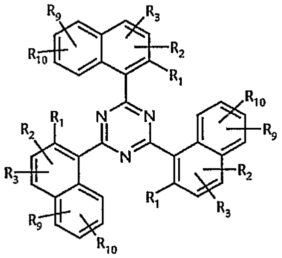
R_7 is hydrogen; hydroxy; C_1-C_5alkyl; C_1-C_5alkoxy; -COOM; -COOH; or $COOR_{10}$;

M is an alkali metal ion; and

R_{10} is C_1-C_5alkyl.

Furthermore compounds of formula

(3)



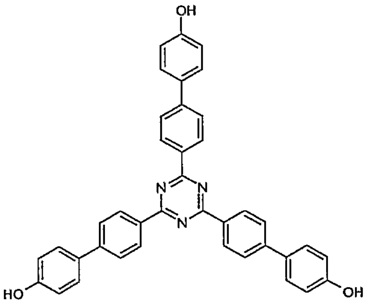
are preferably used, wherein

R_1, R_2, R_3, R_9 and R_{10} are defined as in formula (1).

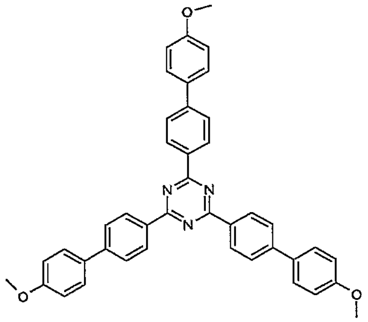
Preferably compounds of formula (3) are used, wherein
R_1, R_2, R_3, R_9 and R_{10} are hydrogen; or, independently from each other, C_1-C_{18}alkyl.

Examples of triazine derivatives, which are preferably used in the present invention, are the compounds of formula

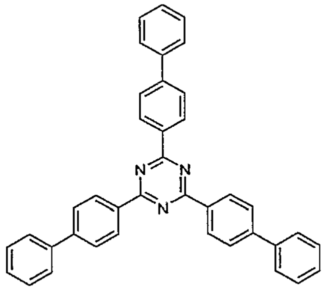
(4)



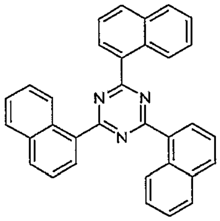
; (5)



(6)



; (7)



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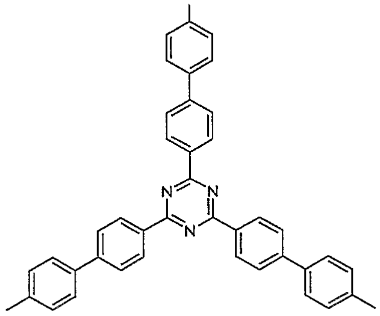
(8)



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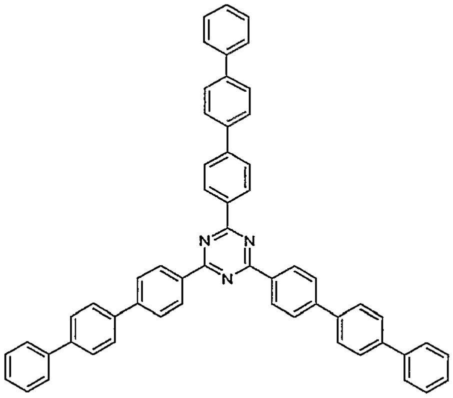
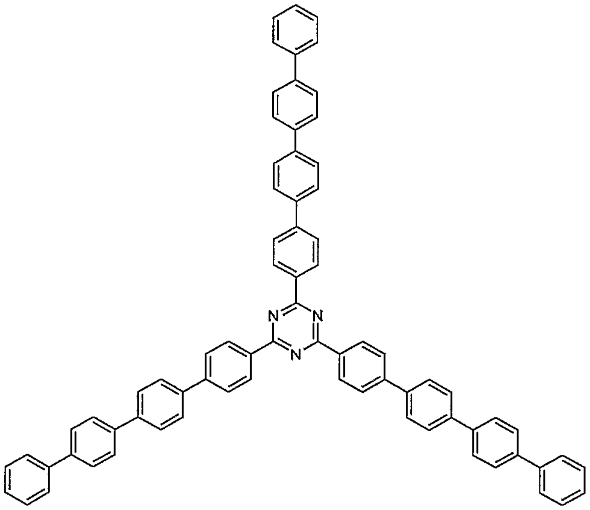
(9)



; or

(10)



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The compounds of the formula (1) according to the present invention are particularly suitable as UV filters, i.e. for protecting ultraviolet-sensitive organic materials, in particular the skin and hair of humans and animals, from the harmful effects of UV radiation. These compounds are therefore suitable as sunscreens in cosmetic, pharmaceutical and veterinary medical preparations. These compounds can be used both in dissolved form and in the micronized state.

The UV absorbers according to the present invention – depending on the substituents of the triazine aryl groups R_1, R_2 R_5, R_6, R_7 , R_8 , R_9 and R_{10} in formulae (1a), 1(b) or (1c) - can be used either in the dissolved state (soluble organic filters, solubelized organic filters) or in the micronised state (nanoscalar organic filters, particulate organic filters, UV-absorber pigments).

The triazine derivatives of formula (1) which have no alkyl substituents or only lower-alkyl substituents are characterized by a poor oil-solubility and a high melting point. They are therefore suitable in particular as UV absorbers in the micronized state.

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 the present invention can also be used as dry substrates in powder form.

The UV absorbers according to the present invention can also be used in specific carriers for cosmetics, for example in solid lipid nanoparticles (SLN) or in inert sol-gel microcapsules wherein the UV absorbers are encapsulated (Pharmazie, 2001 (56), p. 783-786).
Lipid nanoparticles (CLN, = Crystalline Lipid Nanoparticles) as described in Internat. J. Pharmaceutics, 2002, 242, P. 373-375 can be used as active carrier for UV filter according to the invention (for example the compound of formula 6).

The cosmetic formulations or pharmaceutical compositions according to the present invention may additionally contain one or more than one further UV filter as listed in tables 1-3.

The cosmetic or pharmaceutical preparations can be prepared by physically mixing the UV absorber(s) with the adjuvant using customary methods, for example by simply stirring together the individual components, especially by making use of the dissolution properties of already known cosmetic UV absorbers, like octyl methoxy cinnamate, salicylic acid isooctyl ester, etc. The UV absorber can be used, for example, without further treatment, or in the micronised state, or in the form of a powder.

Cosmetic or pharmaceutical preparations contain from 0.05-40% by weight, based on the total weight of the composition, of one UV absorber or UV absorber mixtures.

The UV absorbers of formula (1) according to the present invention or combinations of UV filters are useful to protect skin, hair and/or natural or artificial hair color.

Table 1. Suitable 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-(benzofuranyl) 2-cyanoacrylate;
3-imidazol-4-ylacrylic acid and esters;
benzofuran derivatives, especially 2-(p-aminophenyl)benzofuran derivatives, described in EP-A-582 189, US-A-5 338 539, US-A-5 518 713 and EP-A-613 893;
polymeric UV absorbers, for example the benzylidene malonate derivatives described in EP-A-709 080;
cinnamic acid derivatives, for example the 4-methoxycinnamic acid 2-ethylhexyl ester and isoamyl ester or cinnamic acid derivatives described in US-A-5 601 811 and WO 97/00851;
camphor derivatives, for example 3-(4'-methyl)benzylidene-bornan-2-one, 3-benzylidene-bornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidene-methyl)-benzyl]acrylamide polymer, 3-(4'-trimethylammonium)-benzylidene-bornan-2-one methyl sulfate, 3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methanesulfonic acid) and salts, 3-(4'-sulfo)benzylidene-bornan-2-one and salts; camphorbenzalkonium methosulfate;
hydroxyphenyltriazine compounds, for example 2-(4'-methoxyphenyl)-4,6-bis(2'-hydroxy-4'-n-octyloxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(2-ethyl-hexyloxy)-2-hydroxy]-phenyl}-6-[4-(2-methoxyethyl-carboxyl)-phenylamino]-1,3,5-triazine; 2,4-bis{[4-(tris(trimethylsilyloxy-silylpropyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(2"-methylpropenyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(1',1',1',3',5',5',5'-heptamethyltrisilyl-2"-methyl-propyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine; 2,4-bis{[4-(3-(2-propyloxy)-2-hydroxy-propyloxy)-2-hydroxy]-phenyl}-6-[4-ethylcarboxy)-phenylamino]-1,3,5-triazine;
benzotriazole compounds, for example 2,2'-methylene-bis(6-(2H-benzotriazol-2-yl)-4-

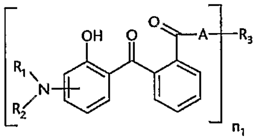
Table 1. Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention
(1,1,3,3-tetramethylbutyl)-phenol;
trianilino-s-triazine derivatives, for example 2,4,6-trianiline-(p-carbo-2'-ethyl-1'-oxy)-1,3,5-triazine and the UV absorbers disclosed in 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.

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

- UV-filter combinations (A) comprising

(a_1) at least one symmetrical triazine derivatives of formula (1) 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;

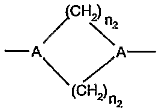
n_1 is a number from 1 to 4;

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,

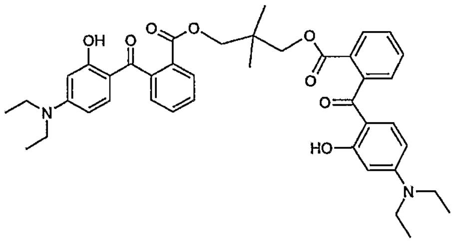
R_3 is an alkanetetrayl radical;

A is -O-; or –N(R_5)-; and

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

Most preferred are UV-filter combinations (A1) comprising

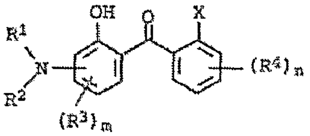
(a_3) at least one compound of formula (6) and/or (9); and

(a_4) the compound of formula 

- UV-filter combinations (B) comprising

(b_1) at least one symmetrical triazine derivatives of formula (1); 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, 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; $(Y\text{-}O)_q\text{-}Z$; 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;

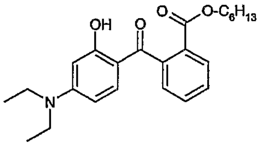
n is 0; 1; 2; 3; or 4; and

q is a number from 1 to 20.

Most preferred are UV-filter combinations (B1) comprising

(b_3) the compound of formula (6) and/or (9); and

(b_4) the compound of formula

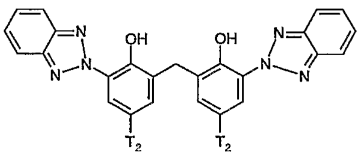


;

- UV-filter combinations (C) comprising

(c_1) at least one symmetrical triazine derivatives of formula (1); and

(c_2) at least one benzotriazole derivative of formula



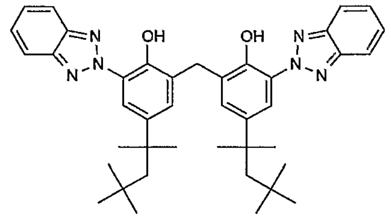
, wherein

T_2 is C_1-C_{10}alkyl or phenyl-substituted C_1-C_4alkyl;

Most preferred are UV-filter combinations (C1) comprising

(c_3) the compound of formula (6) and/or (9); and

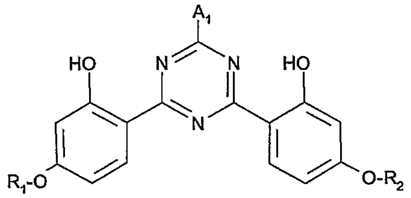
(c_4) the micronized compound of formula



- UV-filter combinations (D) comprising

(d_1) at least one symmetrical triazine derivatives of formula (1); and

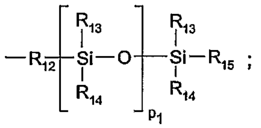
(d_2) at least one compound of formula



in which

R_1 and R_2, independently of one another, are C_3-C_{18}alkyl; C_2-C_{18}alkenyl; a radical of the formula $-CH_2-CH(-OH)-CH_2-O-T_1$; or

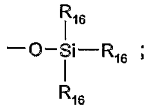
R_1 and R_2 are a radical of the formula (4a)



$$-R_{12}\left[\overset{R_{13}}{\underset{R_{14}}{Si}}-O\right]_{p_1}\overset{R_{13}}{\underset{R_{14}}{Si}}-R_{15} \;;$$

R_{12} 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_{13}, R_{14} and R_{15}, independently of one another, are C_1-C_{18}alkyl; C_1-C_{18}alkoxy or a radical of the formula



$$-O-\overset{\displaystyle R_{16}}{\underset{\displaystyle R_{16}}{Si}}-R_{16}$$;

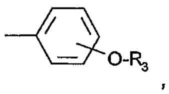
R_{16} is C_1-C_5alkyl;

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

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

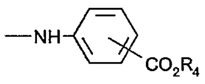
A_1 is a radical of the formula

(1b)



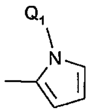
,

(1c)



or of the formula

(1d)



;

R_3 is hydrogen; C_1-C_{10}alkyl, $-(CH_2CHR_5\text{-}O)_{n_1}\text{-}R_4$; or a radical of the formula $-CH_2\text{-}CH(\text{-}OH)\text{-}CH_2\text{-}O\text{-}T_1$;

R_4 is hydrogen; M; C_1-C_5alkyl; or a radical of the formula $-(CH_2)_{m_2}\text{-}O\text{-}T_1$;

R_5 is hydrogen; or methyl;

T_1 is hydrogen; or C_1-C_8alkyl;

Q_1 C_1-C_{18}alkyl;

M is a metal cation;

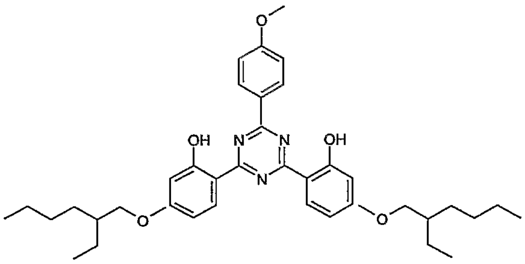
m_2 is 1 to 4; and

n_1 is 1-16.

Most preferred are UV-filter combinations (D1) comprising

(d_3) the compound of formula (6) and/or (9); and

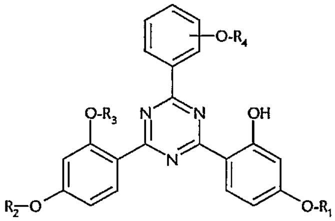
(d_4) the compound of

formula  ;

- UV-filter combinations (E) comprising

(e_1) at least one symmetrical triazine derivatives of formula (1) and

(e_2) at least one hydroxyphenyltriazine compound of formula

(1)  , wherein

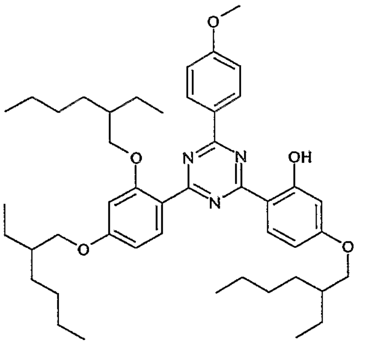
R_1, R_2 and R_3 are each independently of the others C_1-C_{18}alkyl; C_2-C_{10}alkenyl; or phenyl-C_1-C_4alkyl; and

R_4 is hydrogen; or C_1-C_5alkyl.

Most preferred are UV-filter combinations (E1) comprising

(e_3) the compound of formula (6) and/or (9); and

(e_4) the compound of formula

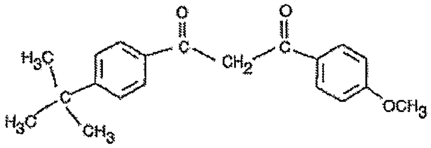


- UV-filter combinations (F) comprising

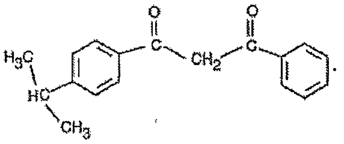
(f_1) at least one symmetrical triazine derivatives of formula (1); and

(f_2) at least one dibenzoylmethane derivative of

formula



or



Most preferred are UV-filter combinations (F1) comprising

(f_3) the compound of formula (6) and/or (9); and

(f_4) 1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)propane-1,3-dione (Avobenzone);

- UV-filter combinations (G) comprising

(g_1) at least one symmetrical triazine derivative of formula (1), preferably the compound of formula (6) and/or (9); and

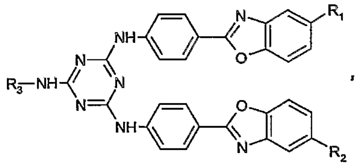
(g_2) disodium phenyl dibenzimidazole tetrasulfonate (Heliopan AP).

- UV-filter combinations (H) comprising

(h$_1$) at least one symmetrical triazine derivatives of formula (1); and

(h$_2$) benzoxazole-substituted triazines of formula

(h$_2$1)



, wherein

R$_1$, R$_2$ and R$_3$ independently from each other are branched or unbranched C$_1$-C$_{12}$alkyl.

Most preferred are UV-filter combinations comprising

(h$_3$) the compound of formula (6) and/or (9); and

(h$_4$) 1,3,5-triazine-2,4,6-triamine, N,N'-bis[4-[5-(1,1-dimethylpropyl)-2-benzoxazolyl]phenyl]-N"-(2-ethylhexyl); (CAS No. 288254-16-0).

Furthermore, UV filter combination (H2) comprising

(h$_5$) the compound of formula (6) or (9); and

(h$_6$) at least one of the compound of formula (h$_2$1), wherein

(h$_{61}$) R$_1$ and R$_2$ are tert.amyl; and R$_3$ is tert.butyl; or wherein

(h$_{62}$) R$_1$ and R$_2$ are tert.butyl and R$_3$ is tert.octyl; or wherein

(h$_{63}$) R$_1$ and R$_2$ are tert.butyl; and R$_3$ is 2-ethylhexyl; or wherein

(h$_{64}$) R$_1$ and R$_2$ are tert.amyl; and R$_3$ is 2-ethylhexyl;

are of preferred interest.

- UV-filter combinations (I) comprising

(i$_1$) at least one symmetrical triazine derivatives of formula (1), preferably the compound of formula (6) and/or (9); and

(i$_2$) 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 (K) comprising

(k$_1$) at least one symmetrical triazine derivatives of formula (1), preferably the compound of formula (6) and/or (9); and

(k$_2$) 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 (L) comprising

(l_1) at least one symmetrical triazine derivatives of formula (1), preferably the compound of formula (6) and/or (9); and

(l_2) (+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo[2.2.1]heptan-2-one; p-methyl benzylidene camphor;

- UV-filter combinations (M) comprising

(m_1) at least one symmetrical triazine derivatives of formula (1), preferably the compound of formula (6) and/or (9); and

(m_2) α-(2-oxoborn-3-ylidene)toluene-4-sulphonic acid and its salts (Mexoryl SL);

- UV-filter combinations (N) comprising

(n_1) at least one symmetrical triazine derivatives of formula (1), preferably the compound of formula (6) and/or (9); and

(n_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 (O) comprising

(o_1) at least one symmetrical triazine derivatives of formula (1), preferably the compound of formula (6) and/or (9); and

(o_2) 2-ethylhexyl 2-cyano,3,3-diphenylacrylate (Octocrylene);

- UV-filter combinations (P) comprising

(p_1) at least one symmetrical triazine derivatives of formula (1), preferably the micronized compound of formula (6) and/or (9); and

(p_2) 2- ethylhexyl 4-methoxycinnamate (octyl methoxy cinnamate);

- UV-filter combinations (Q) comprising

(q_1) at least one symmetrical triazine derivative of formula (1), preferably the compound of formula (6) and/or (9); and

(q_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 (R) comprising

(r_1) at least one symmetrical triazine derivative of formula (1), preferably the compound of formula (6) and/or (9); and

(r_2) 2-phenyl-1H- benzimidazole-5-sulphonic acid (Phenylbenzimidazolsulfonic Acid);

- UV-filter combinations (S) comprising

(s_1) at least one symmetrical triazine derivative of formula (1), preferably the compound of formula (6) and/or (9); and

(s_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).

In the compositions (A) – (S) the compound of formula (1), (6) and (9) respectively are preferably present in the composition in micronized form.

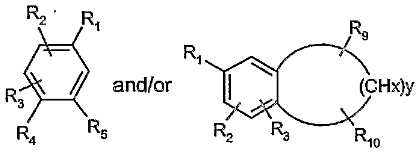
The compounds of formula (1) may also be used as as an anti-wrinkle perception modifier (see Example 29). This is a futher object of the present invention.

The compounds of formula (1) can be prepared according to known methods as described for example in US-A-6,225,467.

Furthermore, the compounds of formula (1) may be obtained in a Grignard reaction starting from the corresponding halogen aromatic compounds and a trihalogen triazine.

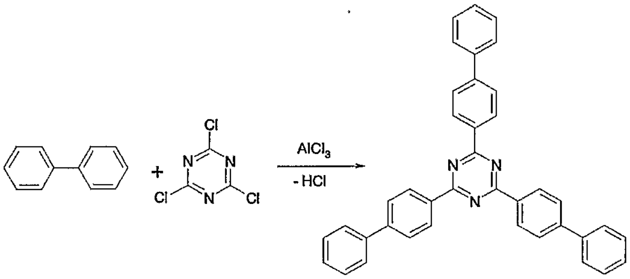
The cyclotrimerisation of aromatc nitrilic compounds is a further well method for the preparation of symmetrical triazine derivatives of formula (1) achieving minor yields.

Surprisingly a simple method for the preparation of the compounds of formula (1) was found. The reaction of trihalogen-1,3,5-triazines with aromatic compounds in a Friedel-Crafts-reaction delivers high yields of symmetrical triazine derivatives.
Suitable aromatic compounds are:



wherein R_1-R_{10} are defined as in formula (1).

According to this method the compound of formula (101) can be prepared according to the following reaction scheme:



Cyanuric chloride is preferably used as trihalogen-1,3,5-triazine.

The reaction temperature is from –10 to 250°C, preferably from 5-150°C, most preferably from 70-130°C.

Classes of compounds that can be used as catalyst are listed in the table below:

Acidic halides	$AlCl_3$, $AlBr_3$, $SnCl_4$, $SbCl_5$, $FeCl_3$
Metal alkyls and alkoxides	AlR_3, BR_3, ZnR_2, $Al(OPh)_3$
Proton acids	HCl, HCl – $AlCl_3$, H_2SO_4, HF, H_3PO_4
Acidic oxides and derivatives	zeolites, mixed oxides and solid superacids, clays, heteropolyacids, modified clays
Supported acids	H_3PO_4 – SiO_2, BF_3 – Al_2O_3
Cation-exchange resins	Permutit Q, Amberlite IR 112, Dowex 50, Nafion–silica, Deloxan
Other catalysts	Solid superacids, Heteropolyacids, Proton or Lewis acids on a support, Nafion and Nafion like composites

Preferred catalysts are (as single compounds or in combination: $AlCl_3$, $AlBr_3$, BF_3, BCl_3, BBr_3, $BeCl_2$, $CdCl_2$, $ZnCl_2$, $GaCl_3$, $GaBr_3$, $FeCl_3$, $SbCl_3$, $BiCl_3$, $TiCl_4$, $ZrCl_4$, $SnCl_4$, UCl_4 and $SbCl_5$.

Advantageously the compounds listed in the table above are used in stoichiometric amounts or in excess.

As co-catalysts are used: alcohols, water, HCl, HF, H_2SO_4, H_3PO_4, RCOOH (organic acids), sulfonic acids like for example p-toluene sulfonic acid.

The co-catalysts can also be used in stoichiometric amounts or in excess.

Preferably gaseus HCl is used as co-catalyst.

As catalysts, co-catalysts or promotors compounds or classes of compounds are used:

- Cations forming compounds: preferred are alkyl- and acyl-halogenides as well as compounds comprising oxygen-, sulfur-, or halogen-donor atoms.

- Adducts: $ZnCl_2$–$AlCl_3$, $SnCl_4$, $AlCl_3$–ketones, $AlCl_3$–Pyridine, $AlCl_3$-RNO_2, $AlBr_3$-RNO_2, $GaCl_3$-RNO_2, SbF_5, BF_3-OEt_2, BF_3-C_6H_5OH; $AlCl_3$-Sulfolane. (R-NO_2: nitroaliphatic and nitroaromatic compounds).

Suitable solvents are: aliphatic hydrocarbons, aromatic hydrocarbons, sulfur-hydrocarbons, halogenaromatic compounds, halogenaliphatic compounds, alyl-aryl ethers, alkyl-alkyl ethers, sulfolane, nitroaromatic compounds and nitroaliphatic compounds.

Mostly preferred are: chlorbenzene, 1,2-dichlorbenzene, 1,4-dichlorbenzene, nitrobenzene, nitromethane, tetrachlormethane.

Furthermore, the reaction can be carried out in ionic fluids like for example 1-butylpyridiniume chloride – aluminum(III) chloride and 1-butyl-3-methylimidazolium chloride – aluminum(III) chloride (s. 1-ethyl-3-methylimidazolium halogenoaluminate ionic liquids as solvents for Friedel-Crafts acylation reactions of ferrocene. Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry 1999 (1), 63).

Surprisingly it was found that the reaction can be carried out in absence of a solvent like 1,2-dichlorobenzene. The reaction runs particularly well when gaseous HCl is discharged into the reaction mixture.

This preparation process has specific significance since the use of halogenated aromatic solvents causes residues of solvents which are only difficult to remove in the end product. These kinds of solvents are inappropriate for cosmetic applications.

The cosmetic or pharmaceutical preparations may be, for example, creams, gels, lotions, alcoholic and aqueous/alcoholic solutions, emulsions, wax/fat compositions, stick preparations, powders or ointments. In addition to the above mentioned UV filters, the cosmetic or pharmaceutical preparations may contain further adjuvants as described below.

As water- and oil-containing emulsions (e.g. W/O, O/W, O/W/O and W/O/W 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 one or more UV absorbers, 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 cosmetic or pharmaceutical compositions/preparations according to the invention may also contain one or one more additional compounds like fatty alcohols esters of fatty acids, natural or synthetic triglycerides including glyceryl esters and derivatives, pearlescent waxes: hydrocarbon oils, silicones or siloxanes (organosubstituted polysiloxanes) fluorinated or perfluorinated oilsemulsifiers, super-fatting agents, surfactants, consistency regulators/thickeners and rheology modifiers, polymers, biogenic active ingredients, deodorising active ingredients anti-dandruff agents, antioxidants, hydrotropic agents, preservatives and bacteria-inhibiting agents, perfume oils, colourants, polymeric beads or hollow spheres as SPF enhancers.

Cosmetic or pharmaceutical formulations are contained in a wide variety of cosmetic preparations. There come into consideration, for example, especially the following preparations like skin-care preparations, bath preparations, cosmetic personal care preparations, foot-care preparations,; light-protective preparations, skin-tanning preparations, depigmenting preparations, insect-repellents, deodorants, antiperspirants, preparations for cleansing and caring for blemished skin,hair-removal preparations in chemical form (depilation), shaving preparations, fragrance preparations or cosmetic hair-treatment preparations.

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

- in the form of liquid preparations as a W/O, O/W, O/W/O, W/O/W or PIT emulsion and all kinds of microemulsions, in the form of a gel, an oil, a cream, milk or lotion, a powder, a lacquer, a tablet or make-up, a stick, a spray or an aerosol, a foam, or 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.

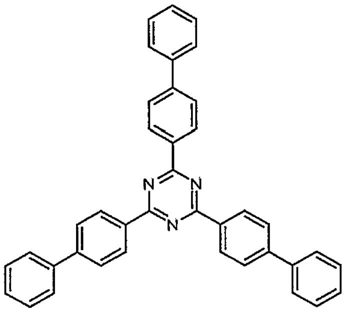
The cosmetic preparation according to the invention is distinguished by excellent protection of human skin against the damaging effect of sunlight.

Examples

Preparation of UV absorbers

Example 1: Preparation of the compound of formula (101)

(101)



Cyanuric chloride (36.9 g, 0.20 mol) is dissolved in 1,2-dichlorobenzene (500 ml). Aluminum chloride (96.0 g, 0.72 mol) is added and the reaction mixture is heated up to 140°C. Biphenyl (111.0 g, 0.72 mol), dissolved in 200 ml 1,2-dichlorobenzene, is added slowly dropwise and the temperature is maintained at 140-145°C for 1 to 4 hours.

The reaction mixture is cooled down to about 60°C and added to a mixture of 150ml conc. HCl and 350g ice. After phase separation at about 110°C the dichloro benzene phase is removed, stirred with Na_2CO_3 and filtered hot at 100 – 110°C. The desired compound recrystallizes from the filtrate.

For purification the compound is recrystallized from dichlorobenzene and dioxane.

^{13}C NMR (90 MHz, $CDCl_3$, TMS):

Peak	δ (ppm)	%Int.	Peak Nr.	δ (ppm)	%Int.
1	171.8	15.6	6	129.3	98.6
2	145.6	21.6	7	128.4	32.5
3	140.8	18.3	8	127.8	62.9
4	135.6	26.4	9	127.7	100.0
5	129.9	62.2			

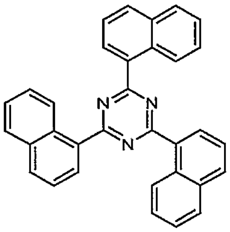
Example 2:

Biphenyl (200.0 g, 1.28 mol) is submitted and melted at 70-75°C. Cyanuric chloride (9.2 g, 0.05 mol) is added and hydrogen chloride is discharged for 10 minutes. Aluminum chloride (20.0 g, 0.15 mol) is added within 40 minutes in 5 equal portions, whereby hydrogen chloride is discharged again after the first two additions. After termination of the reaction 95 per cent ethanol (200 ml) is added dropwise slowly. The reaction mixture is heated up for 1h under reflux. Finally, acetone (400 ml) is added and agitated for 1h, cooled down to room temperature and the failed product is filterd under suction.

Yield of tris(biphenyl)-1,3,5-triazin (formula 101): approx. 65%

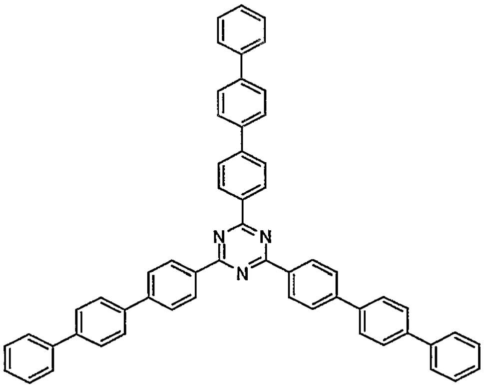
Example 3: Preparation of the compound of formula (102)

(102)

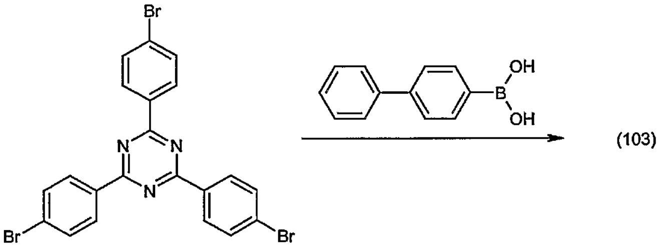


According to the procedure described in Example 1 the compound of formula (102) is obtained, if naphthalene is used instead of biphenyl.

Example 4: Preparation of the compound of formula (103)



Reaction Scheme:



Example 4a:

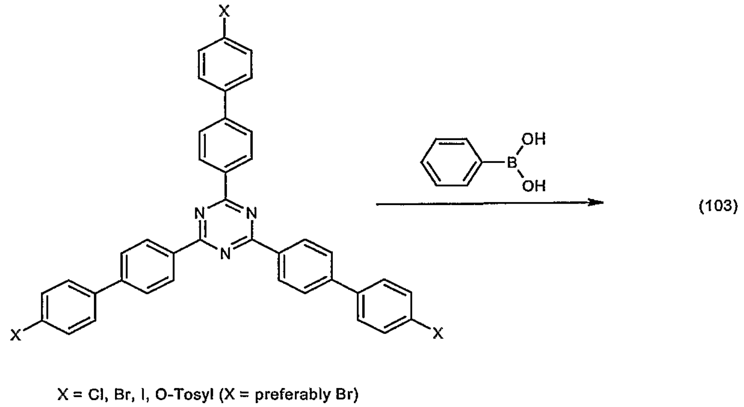
0.5g 2,4,6-Tris-(4-Bromophenyl)-1,3,5-triazin (CAS Nr. 30363-03-2) and 0.816g of 4-biphenylboronic acid are added to 10ml of toluene under argon. 2.238g of Cesium carbonate are dissolved in 3.5ml water and added to the reaction mixture. After the addition of 0.03 equivalents of a palladium(II) catalyst, the reaction mixture is heated under reflux for 4h. The reaction mixture is cooled down to room temperature and then filtered. The filter cake is dissolved in hot DMF, filtered and under cooling the desired product crystallized out. The white fine needles have a melting point of 360°C and the ^{1}H-NM confirmed the structure.

NMR-Data: 1H-NMR (340 MHz, CDCl3): δ= 8.83 (d, 6H), 7.82 (d, 6H), 7.75 (d, 6H), 7.67 (d, 6H), 7.62-7.60 (m, 6H), 7.44-7.40 (m, 6H), 7.34-7.30 ppm (m, 3H).

Instead of the bromide, also the chloride, iodide or tosylate might be used as starting material. Bromide is preferred.

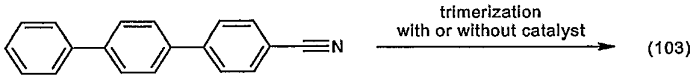
Example 4b:

The compound of formula (103) can be synthesized alternatively via the following pathway:



Example 4c:

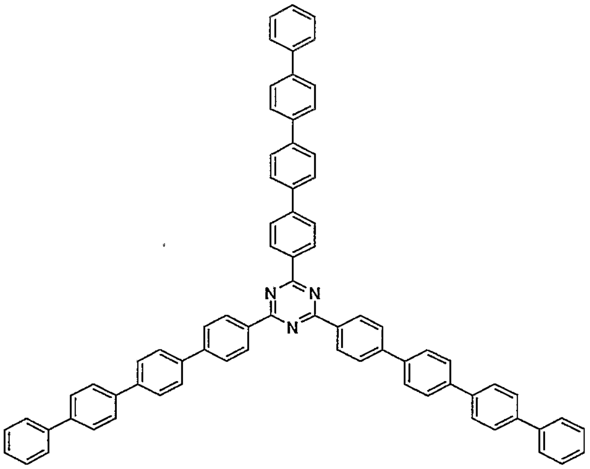
Another pathway for the preparation of the compound of formula (103) is as follows:



Example 4d:

According to the procedure described in Example 1 the compound of formula (103) is obtained, if p-terphenyl is used instead of biphenyl.

Example 5: Preparation of the compound of formula (104)



According to the procedure described in Example 1 the compound of formula (104) is obtained, if p,p-quarterphenyl is used instead of biphenyl as starting compound.

Example 6: Preparation of a micronized UV absorber

100 parts of the compound of formula (101), (102), (103) or (104) respectively are milled together with zirconium silicate bells (diameter: 0,1 to 4 mm) as grinding aids, a dispersing agent (15 parts of C_8-C_{16}polyglucoside) and water (85 parts) in a ball mill to a mean particle size of d_{50} = 130nm.

With this method a micropigment dispersion of a UV absorber is obtained.

Example 7: Preparation of a micronized UV absorber

100 parts of the compound of formula (101), (102), (103) or (104) respectively are milled together with zirconium silicate bells (diameter: 0,1 to 4 mm) as grinding aids, a dispersing agent (15 parts C_{12}gyceride-PEG10) and water (85 parts) in a ball mill to a mean particle size of d_{50} = 130nm.

With this method a micropigment dispersion of a UV absorber is obtained.

Application Examples

Example 8a: UV-A/UV-B Daily Care UV Protection Lotion							
	INCI-Name	% w/w (as supplied)					
		8a	8b	8c	8d	8e	8f
Part A	Oleth-3 Phosphate	0.60	0.60	0.60	0.60	0.60	0.60
	Steareth-21	2.50	2.50	2.50	2.50	2.50	2.50
	Steareth-2	1.00	1.00	1.00	1.00	1.00	1.00
	Cetyl Alcohol	0.80	0.80	0.80	0.80	0.80	0.80
	Stearyl Alcohol	1.50	1.50	1.50	1.50	1.50	1.50
	Tribehenin	0.80	0.80	0.80	0.80	0.80	0.80
	Isohexadecane	8.00	8.00	8.00	8.00	8.00	8.00
	Ethylhexyl Methoxycinnamate	3.00	3.00	3.00	3.00	3.00	3.00
	Compound of the formula (a_4)	2.00					
	Compound of the formula (d_4) as described in claim 18		1.30				
	Compound of the formula (h_2,1) as described in claim 21			1.50			
	Compound of the formula (i_2) (Mexoryl DTS)				2.00		
	Compound of the formula (I2) as described in claim 26					1.50	
	Compound of the formula (b_4)						2.00
Part B	Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
	Glycerin	2.00	2.00	2.00	2.00	2.00	2.00
	UV-absorber dispersion as described in example 6; compound of formula (101)	3.00	3.00	3.00	3.00	3.00	3.00
	Phenylbenzimidazolsulfonic acid (Eusolex 232)				2.00		
	Disodium EDTA	0.10	0.10	0.10	0.10	0.10	0.10
Part C	Water	20.00	20.00	20.00	20.00	20.00	20.00
	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15	0.15	0.15	0.15	0.15	0.15
	Propylene Glycol	4.00	4.00	4.00	4.00	4.00	4.00
Part D	Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6	1.50	1.50	1.50	1.50	1.50	1.50

Example 8a: UV-A/UV-B Daily Care UV Protection Lotion							
	INCI-Name	% w/w (as supplied)					
		8a	8b	8c	8d	8e	8f
	Cyclopentasiloxane	4.00	4.00	4.00	4.00	4.00	4.00
	PEG-12 Dimethicone	2.00	2.00	2.00	2.00	2.00	2.00
	Tocopheryl Acetate	0.45	0.45	0.45	0.45	0.45	0.45
	Water (and) Citric Acid	Qs	Qs	Qs	Qs	Qs	Qs
Part E	Fragrance	Qs	Qs	Qs	Qs	Qs	Qs

Example 8b: UV-A/UV-B Daily Care UV Protection Lotion							
	INCI-Name	% w/w (as supplied)					
		8a	8b	8c	8d	8e	8f
Part A	Oleth-3 Phosphate	0.60	0.60	0.60	0.60	0.60	0.60
	Steareth-21	2.50	2.50	2.50	2.50	2.50	2.50
	Steareth-2	1.00	1.00	1.00	1.00	1.00	1.00
	Cetyl Alcohol	0.80	0.80	0.80	0.80	0.80	0.80
	Stearyl Alcohol	1.50	1.50	1.50	1.50	1.50	1.50
	Tribehenin	0.80	0.80	0.80	0.80	0.80	0.80
	Isohexadecane	8.00	8.00	8.00	8.00	8.00	8.00
	Ethylhexyl Methoxycinnamate	3.00	3.00	3.00	3.00	3.00	3.00
	Compound of the formula (a_4)	2.00					
	Compound of the formula (d_4) as described in claim 18		1.30				
	Compound of the formula (h_2,1) as described in claim 21			1.50			
	Compound of the formula (i_2) (Mexoryl DTS)				2.00		
	Compound of the formula (I2) as described in claim 26					1.50	
	Compound of the formula (b_4)						2.00
Part B	Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
	Glycerin	2.00	2.00	2.00	2.00	2.00	2.00
	UV-absorber dispersion as described in example 6; compound of formula (103)	3.00	3.00	3.00	3.00	3.00	3.00

Example 8b: UV-A/UV-B Daily Care UV Protection Lotion							
	INCI-Name	% w/w (as supplied)					
		8a	8b	8c	8d	8e	8f
	Phenylbenzimidazolsulfonic acid (Eusolex 232)	2.00					
	Disodium EDTA	0.10	0.10	0.10	0.10	0.10	0.10
Part C	Water	20.0 0	20.0 0	20.0 0	20.0 0	20.0 0	20.0 0
	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15	0.15	0.15	0.15	0.15	0.15
	Propylene Glycol	4.00	4.00	4.00	4.00	4.00	4.00
Part D	Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6	1.50	1.50	1.50	1.50	1.50	1.50
	Cyclopentasiloxane	4.00	4.00	4.00	4.00	4.00	4.00
	PEG-12 Dimethicone	2.00	2.00	2.00	2.00	2.00	2.00
	Tocopheryl Acetate	0.45	0.45	0.45	0.45	0.45	0.45
	Water (and) Citric Acid	Qs	Qs	Qs	Qs	Qs	Qs
Part E	Fragrance	Qs	Qs	Qs	Qs	Qs	Qs

Example 8c: UV-A/UV-B Daily Care UV Protection Lotion							
	INCI-Name	% w/w (as supplied)					
		8a	8b	8c	8d	8e	8f
Part A	Oleth-3 Phosphate	0.60	0.60	0.60	0.60	0.60	0.60
	Steareth-21	2.50	2.50	2.50	2.50	2.50	2.50
	Steareth-2	1.00	1.00	1.00	1.00	1.00	1.00
	Cetyl Alcohol	0.80	0.80	0.80	0.80	0.80	0.80
	Stearyl Alcohol	1.50	1.50	1.50	1.50	1.50	1.50
	Tribehenin	0.80	0.80	0.80	0.80	0.80	0.80
	Isohexadecane	8.00	8.00	8.00	8.00	8.00	8.00
	Ethylhexyl Methoxycinnamate	3.00	3.00	3.00	3.00	3.00	3.00
Part B	Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
	Glycerin	2.00	2.00	2.00	2.00	2.00	2.00

Example 8c: UV-A/UV-B Daily Care UV Protection Lotion							
	INCI-Name	% w/w (as supplied)					
		8a	8b	8c	8d	8e	8f
	UV-absorber dispersion as described in example 6; compound of formula (101)	3.00	3.00	3.00	3.00	3.00	3.00
	Compound of the formula (m_2) (Mexoryl SL)	2.00					
	Compound of the formula (n2) (Mexoryl SO)		1.50				
	Ubiquinone			0.01			
	Micronized compound of the formula (c_4)				2.00		
	Phenylbenzimidazolsulfonic acid (Eusolex 232)						2.00
	Disodium EDTA	0.10	0.10	0.10	0.10	0.10	0.10
Part C	Water	20.00	20.00	20.00	20.00	20.00	20.00
	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15	0.15	0.15	0.15	0.15	0.15
	Propylene Glycol	4.00	4.00	4.00	4.00	4.00	4.00
Part D	Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6	1.50	1.50	1.50	1.50	1.50	1.50
	Cyclopentasiloxane	4.00	4.00	4.00	4.00	4.00	4.00
	PEG-12 Dimethicone	2.00	2.00	2.00	2.00	2.00	2.00
	Tocopheryl Acetate	0.45	0.45	0.45	0.45	0.45	0.45
	Water (and) Citric Acid	Qs	Qs	Qs	Qs	Qs	Qs
Part E	Fragrance	Qs	Qs	Qs	Qs	Qs	Qs

Example 8d: UV-A/UV-B Daily Care UV Protection Lotion							
	INCI-Name	% w/w (as supplied)					
		8a	8b	8c	8d	8e	8f
Part A	Oleth-3 Phosphate	0.60	0.60	0.60	0.60	0.60	0.60
	Steareth-21	2.50	2.50	2.50	2.50	2.50	2.50
	Steareth-2	1.00	1.00	1.00	1.00	1.00	1.00
	Cetyl Alcohol	0.80	0.80	0.80	0.80	0.80	0.80

Example 8d: UV-A/UV-B Daily Care UV Protection Lotion							
	INCI-Name	% w/w (as supplied)					
		8a	8b	8c	8d	8e	8f
	Stearyl Alcohol	1.50	1.50	1.50	1.50	1.50	1.50
	Tribehenin	0.80	0.80	0.80	0.80	0.80	0.80
	Isohexadecane	8.00	8.00	8.00	8.00	8.00	8.00
	Ethylhexyl Methoxycinnamate	3.00	3.00	3.00	3.00	3.00	3.00
Part B	Water	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100	qs to 100
	Glycerin	2.00	2.00	2.00	2.00	2.00	2.00
	UV-absorber dispersion as described in example 6; compound of formula (103)	3.00	3.00	3.00	3.00	3.00	3.00
	Compound of the formula (m$_2$) (Mexoryl SL)	2.00					
	Compound of the formula (n2) (Mexoryl SO)		1.50				
	Ubiquinone			0.01			
	Micronized compound of the formula (c$_4$)				2.00		
	Phenylbenzimidazolsulfonic acid (Eusolex 232)						2.00
	Disodium EDTA	0.10	0.10	0.10	0.10	0.10	0.10
Part C	Water	20.00	20.00	20.00	20.00	20.00	20.00
	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15	0.15	0.15	0.15	0.15	0.15
	Propylene Glycol	4.00	4.00	4.00	4.00	4.00	4.00
Part D	Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6	1.50	1.50	1.50	1.50	1.50	1.50
	Cyclopentasiloxane	4.00	4.00	4.00	4.00	4.00	4.00
	PEG-12 Dimethicone	2.00	2.00	2.00	2.00	2.00	2.00
	Tocopheryl Acetate	0.45	0.45	0.45	0.45	0.45	0.45
	Water (and) Citric Acid	Qs	Qs	Qs	Qs	Qs	Qs
Part E	Fragrance	Qs	Qs	Qs	Qs	Qs	Qs

Manufacturing instruction for Examples 8a-8d:

Part A and part B are heated separately to 75°C. Part A is poured into part B under continuous stirring. Immediately after the emulsification, cyclopentasiloxane and PEG-12 Dimethicone from part D are incorporated into the mixture. Afterwards the mixture is homogenized with an Ultra Turrax at 11 000 rpm for 30 sec. After cooling down to 65°C Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6 are incorporated. Part C is added at a temperature < 50°C. At a temperature ≤ 35°C Tocopheryl Acetate is incorporated and subsequently the pH is adjusted with Water (and) Citric Acid. At room temperature part E is added.

Example 9: UV Day Lotion

	INCI-Name	% w/w (as supplied)
Part A	Cetyl Phosphate	1.75
	C12-C15 Alkyl Benzoate	4.00
	Cetearyl Alcohol/ PEG-20 Stearate	2.00
	Ethoxydiglycol Oleate	2.00
	Stearic Acid	1.50
	Ethylhexyl Methoxycinnamate	3.00
	Isononyl Isononanoate	2.00
	Bis-ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S)	1.00
Part B	Aqua	qs to 100
	Xanthan Gum	0.35
	UV-absorber dispersion as described in example 6	5.00
	Disodium EDTA	0.20
	Propylene Glycol	2.00
	Diazolidinyl Urea (and) Methylparaben (and) Propylparaben (and) Propylene Glycol	0.70
	Glycerin	1.50
Part C	Cyclopentasiloxane (and) Dimethiconol	1.00
	Ethoxydiglycol	3.00
	Dimethicone	2.00
Part D	Triethanolamine	qs

Manufacturing instruction:

Part A by is prepared by incorporating all ingredients, then stirred under moderate speed and heated to 75°C. Part B s prepared and heated to 75°C. At this temperature part B is poured into part A under progressive stirring speed. Then the mixture is homogenized (30sec., 15000 rpm). At a temperature < 55°C the ingredients of part C are incorporated. The mixture is cooled down under moderate stirring, then the pH is checked and adjusted with triethanolamine.

Example 10: Sun Protection Emulsion

	INCI-Name	% w/w (as supplied)
Part A	Cetearyl Alcohol (and) Dicetyl Phosphate (and) Ceteth-10 Phosphate	4.00
	C12-15 Alkyl Benzoate	2.00
	Dicaprylyl Ether	3.00
	Ethoxydiglycol Oleate	2.00
	Stearic Acid	1.00
	Ethylhexyl Methoxycinnamate	3.00
	Sodium Acrylates Copolymer (and) Glycine Soja (and) PPG-1 Trideceth-6	0.30
	Squalane	3.50
Part B	Aqua	qs to 100
	UV-absorber dispersion as described in example 6	5.00
Part C	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
	Propylene Glycol	2.50
	Aqua	10.00
Part D	Cyclopentasiloxane, Dimethiconol	2.00
	Ethoxydiglycol	5.00
	Cyclopentasiloxane (and) Dimethicone/Vinyl-dimethicone Crosspolymer	2.00
Part E	Sodium Hydroxide	0.10

Manufacturing instruction:

Part A is prepared by incorporating all ingredients, then stirred under moderate speed and heated to 75°C. Part B is prepared and heated to 75°C. At this temperature, part B is poured into part A under progressive stirring speed. Below 65°C the ingredients of part D are added separately. After cooling down under moderate stirring to 55°C part C is added. The pH is then checked and adjusted with sodium hydroxide. The mixture is homogenized for 30 sec at 16000rpm.

Example 11: Every Day Lotion

	INCI-Name	% w/w (as supplied)
Part A	Stearyl Phosphate	5.00
	Tricontanyl PVP	1.00
	Ethoxydiglycol Oleate	3.00
	Squalane	5.00
	C12-15 Alkyl Benzoate	5.00
	Ethylhexyl Methoxycinnamate	3.00
	Glyceryl Stearate	2.00
	Cetyl Alcohol	2.00
	Butyl methoxydibenzoylmethane (Parsol 1789)	1.50
Part B	Aqua	20.00
	UV-absorber dispersion as described in example 5	3.00
	Methylene bis-benzotriazolyl tetramethylbutylphenol (TinosorbM)	2.00
Part C	Aqua	qs to 100
	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50
	Glycerin	2.50
	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
	Sodium Lauroyl Glutamate	0.70
Part D	Cyclopentasiloxane (and) Dimethiconol	1.50
	Triethanolamine	1.85

Manufacturing instruction:

Part A is prepared by incorporating all ingredients, then stirred under moderate speed and heated to 75°C. Part C is prepared and heated to 75°C. Part C is poured into the part A under moderate stirring. Immediately after the emulsification part B is added, then neutralized with a part of the triethanolamine. The mixture is homogenized for 30 sec. After cooling down under moderate stirring Cyclopentasiloxane (and) Dimethiconol are added. Below 35°C the pH is checked and adjusted with triethanolamine.

Example 12: Sprayable Sunscreen Emulsion

	INCI-Name	% w/w (as supplied)
Part A	Ceteareth-15 (and) Glyceryl Stearate	3.00
	Stearyl Alcohol	1.00
	Cetyl Ricinoleate	0.80
	Dicaprylyl Ether	3.00
	C12-15 Alkyl Benzoate	3.00
	Isohexadecane	2.50
	Stearyl Dimethicone	1.00
	Ethylhexyl Methoxycinnamate	4.00
	Cetyl Alcohol	0.80
	Di-C12-13 Alkyl Tartrate	3.00
Part B	Aqua	qs to 100
	Steareth-10 Allyl Ether/Acrylates Copolymer	0.45
	PEG-7 Glyceryl Cocoate	2.50
	Glycerin	2.00
	Propylene Glycol	3.00
Part C	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
	Aqua	20.00
	UV-absorber dispersion as described in example 6	12.00
	Titanium Dioxide (and) Silica (and) Sodium Polyacrylate	8.00
Part D	Cyclopentasiloxane (and) Dimethiconol	0.85
Part E	Sodium Hydroxide (and) Water	qs to pH 6.50 –7.00
Part F	Fragrance	qs

Manufacturing instruction

Part A and part B are heated up to 80°C. Part A is blended into part B under stirring and homogenized with an UltraTurrax at 11 000 rpm for 30 sec. Part C is heated to 60°C and added slowly to the emulsion. After cooling down to 40°C part D is incorporated at room temperature and part E is added.

Example 13: Daily Care Lotion

	INCI-Name	% w/w (as supplied)
Part A	Polyglyceryl Methyl Glucose Distearate	2.50
	Cetearyl Alcohol	2.00
	Octyl Stearate	3.00
	Caprylic/Capric Triglyceride	4.00
	Isohexadecane	4.00
	Ethylhexyl Methoxycinnamate	2.70
Part B	Aqua	64.80
	Glycerin	5.00
	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.50
	UV-absorber dispersion as described in example 6	8.00
Part C	Cyclomethicone (and) Dimethicone	3.00
Part D	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50

Manufacturing instruction

Part A and B are heated to 75°C. Part A is added into part B under continuous stirring and homogenized with 11000 rpm for 1 minute. After cooling down to 50°C part C is added under continuous stirring. After cooling further down to 30°C part D is added. Afterwards the pH is adjusted between 6.00 - 6.50.

Example 14: Daily Care with UV Protection

	INCI-Name	% w/w (as supplied)
Part A	Glyceryl Stearate SE	3.00
	Glyceryl Stearate and PEG-100 Stearate	3.50
	Cetyl Alcohol	1.50
	Myristyl Myristate	2.00
	Isopropyl Palmitate	2.50
	Paraffinum Perliquidum	5.00
	Octyl Dimethyl PABA	3.00
Part B	Aqua	qs to 100

	INCI-Name	% w/w (as supplied)
	Propylene Glycol	7.50
	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	1.00
Part C	Aqua	30.00
	UV-absorber dispersion as described in example 6	10.00
Part D	Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6	2.00
Part E	Citric Acid	0.30

Manufacturing instruction:

Part A and B are heated separately to 75°C. After adding part B into part A the mixture is homogenized with Ultra Turrax for one minute at 11000 rpm. After cooling down to 50°C part C is added. Afterwards the mixture is homogenized for one minute at 16000 rpm. At a temperature < 40°C part D is added. At room temperature the pH-value is adjusted with part E between 6.00 and 6.50.

Example 15: O/W Every Day UV Protection Lotion

	INCI-Name	% w/w (as supplied)
Part A	Glyceryl Stearate (and) PEG-100 Stearate	5.00
	Stearyl Alcohol	1.00
	Tripalmitin	0.70
	Dimethicone	2.00
	C12-15 Alkyl Benzoate	5.00
	Isopropyl Palmitate	5.00
	Ethylhexyl Methoxycinnamate	3.00
Part B	Water	qs to 100
	Polysorbate 60	0.50
	Glycerin	3.00
Part C	Water	10.00

	INCI-Name	% w/w (as supplied)
	UV-absorber dispersion as described in example 6	8.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
	Steareth-10 Allyl Ether/Acrylates Copolymer	1.50
Part E	Water (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

Manufacturing instruction:

Part A and B are heated separately up to 75°C, part C is heated to 60°C. Afterwards part B is poured into part A under stirring. The mixture is homogenized with an Ultra Turrax for 30 sec. at 11 000 rpm and part C is incorporated. After cooling down to 40°C part D is added. At room temperature the pH-value is adjusted with Sodium Hydroxide between 6.30 and 6.70 and part F is added.

Example 16: O/W Every Day UV Protection

	INCI-Name	% w/w (as supplied)
Part A	Glyceryl Stearate (and) PEG-100 Stearate	5.00
	Stearyl Alcohol	1.00
	Tripalmitin	0.70
	Dimethicone	2.00
	C12-15 Alkyl Benzoate	4.00
	Isopropyl Palmitate	4.00
	Ethylhexyl Methoxycinnamate	3.00
	Benzophenone-3	1.00
	Benzophenone-4	1.00
Part B	Water	qs to 100
	Polysorbate 60	0.50

	INCI-Name	% w/w (as supplied)
	Glycerin	3.00
Part C	Water	10.00
	UV-absorber dispersion as described in example 6	8.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
	Steareth-10 Allyl Ether/Acrylates Copolymer	1.50
Part E	Water (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

Manufacturing instruction:

Part A and B are heated separately up to 75°C, part C is heated to 60°C. Afterwards part B is poured into part A under stirring. The mixture is homogenized with an Ultra Turrax for 30 sec. at 11 000 rpm and part C is incorporated. After cooling down to 40°C part D is added. At room temperature the pH-value is adjusted with Sodium Hydroxide between 6.30 and 6.70 and part F is added.

Example 17: Sunscreen Cream

	INCI-Name	% w/w (as supplied)
Part A	Cetearyl Alcohol (and) Dicetyl Phosphate (and) Ceteth-10 Phosphate	4.50
	C12-15 Alkyl Benzoate	6.00
	Caprylic/Capric Triglyceride	7.00
	Pentaerythritol Tetraisostearate	2.00
	Ethylhexyl Methoxycinnamate	3.00
	Isoamyl p-Methoxycinnamate	2.00
Part B	Aqua	qs to 100
	Glycerin	2.00

	INCI-Name	% w/w (as supplied)
	Propylene Glycol	1.50
	Magnesium Aluminium Silicate	1.20
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50
	UV-absorber dispersion as described in example 5	12.00
Part D	Phenyl Trimethicone	1.50
	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.70
Part E	Sodium Hydroxide	0.90

Manufacturing instruction:

Part A and part B are heated separately to 75°C. Part B is added into part A under continuous stirring and afterwards homogenized with Ultra Turrax for 30sec at 11000 rpm . After cooling down to 60°C part C is added. At 40°C part C is added and homogenized for 15sec at 11000 rpm. At room temperature the pH-value is adjusted with part E.

Example 18: UVA/UVB Daily Care Lotion, type O/W

	INCI-Name	% w/w (as supplied)
Part A	Glyceryl Stearate (and) PEG-100 Stearate	5.00
	Stearyl Alcohol	1.00
	Tripalmitin	0.70
	Mineral Oil	15.00
Part B	Water	qs to 100
	Polysorbate 60	0.50
	Glycerin	3.00
Part C	Water	10.00
	UV-absorber dispersion as described in example 6	8.00

	INCI-Name	% w/w (as supplied)
Part D	Steareth-10 Allyl Ether/Acrylates Copolymer	1.50
	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
Part E	Water (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

Manufacturing instruction:

Part A and B are heated separately to 75°C; part C to 60°C. Part B is poured into part A under stirring. After one-minute of homogenization at 11000 rpm part C is added to the mixture of A/B. After cooling down to 40°C part D is incorporated. At room temperature the pH value is adjusted with part E between 6.3 and 7.0. Finally part F is added.

Example 19: UVA/UVB Daily Care Lotion, type O/W

	INCI-Name	% w/w (as supplied)
Part A	Oleth-3 Phosphate	0.60
	Steareth-21	2.50
	Steareth-2	1.00
	Cetyl Alcohol	0.80
	Stearyl Alcohol	1.50
	Tribehenin	0.80
	Isohexadecane	8.00
Part B	Water	qs to 100
	Glycerin	2.00
	Disodium EDTA	0.10
Part C	Cyclopentasiloxane	4.50
	PEG-12 Dimethicone	2.00

	INCI-Name	% w/w (as supplied)
Part D	Sodium Acrylates Copolymer (and) Mineral Oil (and) PPG-1 Trideceth-6	1.50
Part E	UV-absorber dispersion as described in example 6	10.00
Part F	Tocopheryl Acetate	0.45
	DMDM Hydantoin (and) Iodopropynyl Butylcarbamate (and) Aqua (and) Butylene Glycol	0.85
Part G	Water (and) Citric Acid	qs
	Fragrance	qs

Manufacturing instruction:

Part A and part B are heated separately to 75°C. Part A is poured into part B under stirring. Immediately after the emulsification, part C is added to the mixture and homogenized with an Ultra Turrax at 11000 rpm for 30 sec. After cooling down to 65°C Sodium Acrylates Copolymer (and) Mineral Oil (and) PPG-1 Trideceth-6 At 50°C is added slowly to the UV absorber dispersion. At about 35-30°C part F is incorporated. The pH is adjusted with part G between 5.5 and 6.5.

Example 20: UV-A/UV-B Every Day Protection Lotion O/W

	INCI-Name	% w/w (as supplied)
Part A	Glyceryl Dilaurate	2.00
	Ethylhexyl Palmitate	6.00
	Cetyl Alcohol	1.00
	Glyceryl Stearate	2.00
	Laureth-23	1.00
	Isopropyl Palmitate	2.00
	Tribehenin	0.80
	Beeswax	1.50
	Lanolin Oil	1.00

	INCI-Name	% w/w (as supplied)
Part B	Water	qs to 100
	Propylene Glycol	4.00
	Water (and) Titanium Dioxide (and) Alumina (and) Sodium Metaphosphate (and) Phenoxyethanol (and) Sodium Methylparaben	4.00
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	1.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	1.00
	UV-absorber dispersion as described in example 6	8.00
Part E	Water (and) Sodium Hydroxide	qs

Manufacturing instruction:

Part A and part B are heated separately up to 80°C. Part A is poured into part B while stirring and homogenized with an Ultra Turrax by 11000 rpm for 30 sec. After cooling down to 60°C part C is incorporated. At 40°C part D is added slowly under continuous stirring. The pH is adjusted with part E between 6.50 - 7.00.

Example 21: Sprayable Sunscreen Lotion

	INCI-Name	% w/w (as supplied)
Part A	Potassium Cetyl Phosphate	0.20
	Isohexadecane	7.00
	VP/Eicosene Copolymer	1.50
	Di-C12-13 Alkyl Tartrate	6.00
	Ethylhexyl Triazone	2.50
	C12-15 Alkyl Benzoate	4.50
Part B	Water	qs to 100
	Sorbeth-30	2.00
	Sorbitan Stearate (and) Sucrose Cocoate	4.00

	INCI-Name	% w/w (as supplied)
	Titanium Dioxide (and) Alumina (and) Silica (and) Sodium Polyacrylate	2.50
Part C	Water	30.00
	UV-absorber dispersion as described in example 6	12.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
Part E	Water (and) Citric Acid	qs

Manufacturing instruction:

Part A and part B are heated separately up to 80°C, part C is heated to 50°C. Part B is poured into part A and homogenized with an Ultra Turrax for 1 minute at 11000 rpm. After cooling down to 50°C part C is added under continuous stirring. At 40°C part D is incorporated and homogenized again for 10 sec. at 11000 rpm. The pH is adjusted with part E.

Example 22: O/W Every Day UV Protection Lotion

	INCI-Name	% w/w (as supplied)
Part A	Glyceryl Stearate (and) PEG-100 Stearate	5.00
	Stearyl Alcohol	1.00
	Tripalmitin	0.70
	Dimethicone	2.00
	Caprylic/Capric Triglyceride	5.00
	Isopropyl Palmitate	5.00
	Ethylhexyl Methoxycinnamate	3.00
Part B	Water	qs to 100
	Polysorbate 60	0.50
	Glycerin	3.00
Part C	Water	10.00

	INCI-Name	% w/w (as supplied)
	UV-absorber dispersion as described in example 6	8.00
	ZnO (Nanox Zinc Oxide)	3.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
	Steareth-10 Allyl Ether/Acrylates Copolymer	1.50
Part E	Water (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

Manufacturing instruction:

Part A and part B are heated separately up to 75°C, part C is heated to 60°C. Afterwards part B is poured into part A under stirring. The mixture is homogenized with an Ultra Turrax for 30 sec. at 11 000 rpm and part C is incorporated. After cooling down to 40°C part D is added. At room temperature the pH-value is adjusted with Sodium Hydroxide between 6.30 and 6.70 and part F is added.

Example 23: Water resistant Sunscreen Emulsion

	INCI-Name	% w/w (as supplied)
Part A	Polyglyceryl-10 Pentastearate (and) Behenyl Alcohol (and) Sodium Stearoyl Lactylate	2.50
	VP/Eicosene Copolymer	1.50
	Stearyl Alcohol	1.50
	Squalane	4.00
	C12-15 Alkyl Benzoate	5.50
	Octocrylene	1.50
	4-Methylbenzylidene Camphor	3.00
	Ethylhexyl Methoxycinnamate	2.00
	Ethyl hexyl salicylate (Neoheliopan OS)	2.00

	INCI-Name	% w/w (as supplied)
Part B	Water	qs to 100
	Glycerin	1.80
	Steareth-10 Allyl Ether/Acrylates Copolymer	0.80
Part C	UV-absorber dispersion as described in example 6	9.00
Part D	VP/Hexadecene Copolymer	2.70
	Cyclomethicone	1.50
	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.70
Part E	Aqua (and) Tocopheryl Acetate (and) Caprylic/Capric Triglyceride (and) Polysorbate 80 (and) Lecithin	3.50
Part F	Fragrance	qs
	Water (and) Sodium Hydroxide	qs

Manufacturing instruction:

Part A and part B are heated separately to 80°C. Part A is poured into part B under continuous stirring. Afterwards the mixture is homogenized with an Ultra Turrax at 11 000 rpm for 1 min. After cooling down to 60°C part C is incorporated. At 40°C part D is added and the mixture homogenized for a short time again. At 35°C part E is added and at room temperature Fragrance is added. Finally the pH is adjusted with Sodium Hydroxide.

Example 24: UVA/UVB Sun Protection Lotion, O/W type

	INCI-Name	% w/w (as supplied)
Part A	Potassium Cetyl Phosphate	2.00
	Tricontanyl PVP	1.00
	Caprylic/Capric Triglyceride	5.00
	C12-15 Alkyl Benzoate	5.00
	Cetearyl Isononanoate	5.00
	Glyceryl Stearate	3.00

	INCI-Name	% w/w (as supplied)
	Cetyl Alcohol	1.00
	Dimethicone	0.10
	Ethylhexyl Methoxycinnamate	5.00
Part B	Water	qs to 100
	Glycerin	3.00
	2,2'-bis(1,4-phenylene)-1H-benzimidazole-4,6-disulphonic acid mono sodium salt (Neoheliopan AP)	2.00
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50
Part D	UV-absorber dispersion as described in example 6	8.00
Part E	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	1.00
Part F	Water (and) Sodium Hydroxide	qs to pH 7.00
Part G	Fragrance	qs

Manufacturing instruction:

Part A and part B are heated separately up to 80°C. Part B is poured into part A under moderate stirring. The mixture is homogenized with an Ultra Turrax at 11000 rpm for 1 minute. After cooling down to 70°C part C is added under stirring. After cooling further down to 50°C part D is incorporated very slowly. At 40°C part E is added. At room temperature the pH adjusted with part F to 7.00 and part G is added.

Example 25: UVA/UVB Sun Protection Lotion, O/W type

	INCI-Name	% w/w (as supplied)
Part A	Potassium Cetyl Phosphate	2.00
	Tricontanyl PVP	1.00
	Caprylic/Capric Triglyceride	5.00
	C12-15 Alkyl Benzoate	5.00

	INCI-Name	% w/w (as supplied)
	Cetearyl Isononanoate	5.00
	Glyceryl Stearate	3.00
	Cetyl Alcohol	1.00
	Dimethicone	0.10
	Ethylhexyl Methoxycinnamate	4.00
	Diethylhexyl butamido triazone (UVASORB HEB)	1.00
Part B	Water	qs to 100
	Glycerin	3.00
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50
Part D	UV-absorber dispersion as described in example 6	20.00
Part E	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	1.00
Part F	Water (and) Sodium Hydroxide	qs to pH 7.00
Part G	Fragrance	qs

Manufacturing instruction:

Part A and part B are heated separately up to 80°C. Part B is poured into part A under moderate stirring. The mixture is homogenized with an Ultra Turrax at 11000 rpm for 1 minute. After cooling down to 70°C add part C is added under stirring. After cooling further down to 50°C part D is incorporated very slowly. At 40°C part E is added. At room temperature the pH is adjusted with part F to 7.00 and part G is added.

Example 26: Sunscreen Lotion

	INCI-Name	% w/w (as supplied)
Part A	Cetearyl Alcohol (and) Dicetyl Phosphate (and) Ceteth-10 Phosphate	4.00
	C12-15 Alkyl Benzoate	2.00
	Dicaprylyl Ether	3.00

	INCI-Name	% w/w (as supplied)
	Ethoxydiglycol Oleate	2.00
	Stearic Acid	1.00
	Ethylhexyl Methoxycinnamate	2.00
	Sodium Acrylates Copolymer (and) Glycine Soja (and) PPG-1 Trideceth-6	0.30
	Squalane	3.50
	VP/Eicosene Copolymer	2.00
	Benzylidene malonate polysiloxane (Parsol SLX)	2.00
Part B	Water	qs to 100
	UV-absorber dispersion as described in example 6	5.00
Part C	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
	Propylene Glycol	2.50
	Water	10.00
Part D	Cyclopentasiloxane (and) Dimethiconol	2.00
	Ethoxydiglycol	5.00
	Cyclopentasiloxane (and) Dimethicone/Vinyl Dimethicone Crosspolymer	2.00
Part E	Aqua (and) Sodium Hydroxide	qs
Part F	Fragrance	qs

Manufacturing instruction

Part A and part B are heated separately up to 75°C. Part B is poured into part A under progressive stirring speed. At a temperature < 65°C the ingredients of part D are added separately. After cooling down to 55°C under moderate stirring part C is added. At a temperature < 35°C the pH is checked and adjusted with Sodium Hydroxide and homogenized with an Ultra Turrax for 30 sec. at 11 000 rpm. At room temperature part F is added.

Example 27: W/O Sunscreen Lotion

	INCI-Name	% w/w (as supplied)
Part A	PEG-7 Hydrogenated Castor Oil	3.00
	Polyglyceryl-3 Diisostearate	4.00
	Microcrystalline Wax	1.00
	Magnesium Stearate	1.50
	Propylparaben	0.10
	Mineral Oil	15.00
	Octyldodecanol	8.00
	Ethylhexyl Triazone	1.00
	Ethylhexyl Methoxycinnamate	2.00
	Diethylamino Hydroxybenzoyl Hexyl Benzoate (Uvinul A+)	1.50
Part B	Water	qs to 100
	Water (and) Citric Acid	0.05
	Methylparaben	0.15
	Magnesium Sulfate	0.50
Part C	UV-absorber dispersion as described in example 6	9.00
	Fragrance	qs

Manufacturing instruction:

Part A is heated to 80°C whilst stirring. Part B is added into part A and homogenized with an Ultra Turrax at 11 000 rpm for one minute. After cooling down to 30°C part C is incorporated.

Example 28: Skin Protection Sunscreen Lotion W/O

	INCI-Name	% w/w (as supplied)
Part A	Polyglyceryl-2 Dipolyhydroxystearate	3.00

	INCI-Name	% w/w (as supplied)
	Glyceryl Oleate	3.00
	Cetearyl Isononanoate	7.00
	Hexyl Laurate	6.00
	Dicaprylyl Ether	6.00
	Propylparaben	0.10
	Hexyldecanol	3.00
	Magnesium Stearate	1.00
	Beeswax	1.00
	Ethylhexyl Methoxycinnamate	4.00
Part B	Water	qs to 100
	Methylparaben	0.15
	Magnesium Sulfate	1.00
Part C	UV-absorber dispersion as described in example 6	6.00

Manufacturing instruction:

Part A is heated separately to 80°C under gentle stirring. Part B is added to part A and homogenized for one minute at 11000 rpm. After cooling down to 30°C part C is added under continuous stirring.

Example 29: Sunscreen

	INCI-Name	% w/w (as supplied)
Part A	Hexyldecanol	2.70
	Polyoxyethylen-2-stearylalkohol	2.20
	PEG-30 Dipolyhydroxystearate	1.10
Disp.	UV-absorber as described in example 6; pH= 7 adjusted with citric acid	6
Part B	Cetyl Ethylhexanoate	4.00

	Isohexadecane	4.00
	Ethxlhexyl methoxy cinnamate	0.00
	Bis-ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S)	0.00
	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.60
Part C	Water	Qs. 100
	Glycerin	3.00
Part D	Sodium Acrylates Copolymer (and) Mineral Oil (and) PPG-1 Trideceth-6	2.00
Part E	Cyclopentasiloxane	2.00

This Sunscreen may also be used as an anti-wrinkle perception modifier.

Manufacturing instruction

Mix part A and heat up to 60°C to 65 °C and add Disp. Slowly under fast stirring.

Add part B under moderate stirring at 60 °C.

Add part B into part A under stirring at 60 °C-75 °C.

Add part C under stirring until homogenization (emulsification at fast stirring, may be with ultra turrax).

Add part D under moderate stirring (60 °C).

Finally add part E under stirring (60 °C) and cool down under moderate stirring.

Example 30: PEG-free sunscreen

	INCI-Name	w/w (as supplied %)
Part A	Hexyldecanol	2.30
	Polyglyceryl-3 Methylglucose Distearate	1.40
	Polyglyceryl polyhydroxy stearate	1.40
Disp.	UV-absorber as described in example 6; pH= 7 adjusted with citric acid	5.00
Part B	Cetyl Ethylhexanoate	3.00
	Isohexadecane	3.00

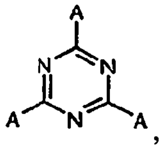
	Ethylhexyl methoxy cinnamate	3.00
	Bis-ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb S)	2.00
	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben	0.60
Part C	Water	Qs 100
	Glycerin	3.00
Part D	Sodium Acrylates Copolymer (and) Mineral Oil (and) PPG-1 Trideceth-6	1.50
Part E	Cyclopentasiloxane	1.50

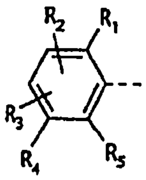
Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

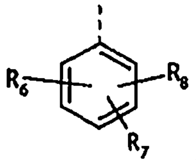
The claims defining the invention are as follows:

1. Use of the compounds of formula

(1) , wherein

A is a radical of formula (1a)  ;

R_1 and R_5 independently from each other are hydrogen; C_1-C_{18}alkyl; or C_6-C_{12}aryl; R_2, R_3 and R_4 independently from each other are hydrogen; or a radical of formula

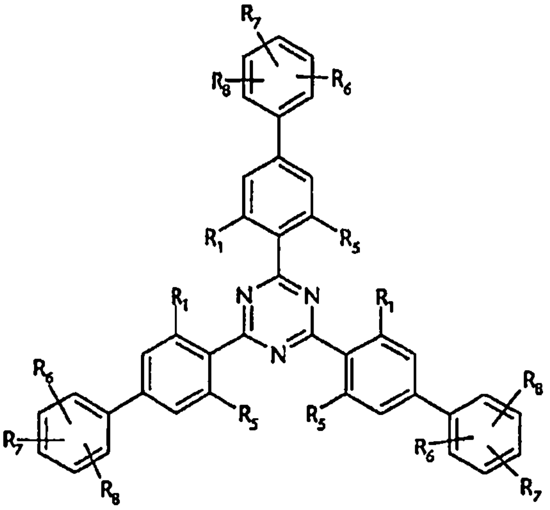
(1c) , wherein, in formula (1a), at least one of the radicals R_2, R_3 and R_4 are a radical of formula (1c);

R_6, R_7, and R_8 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; and

M is an alkali metal ion;

for the protection of human and animal hair and skin against the damaging effect of UV radiation.

2. Use according to claim 1, which relates to compounds of formula



(2) wherein

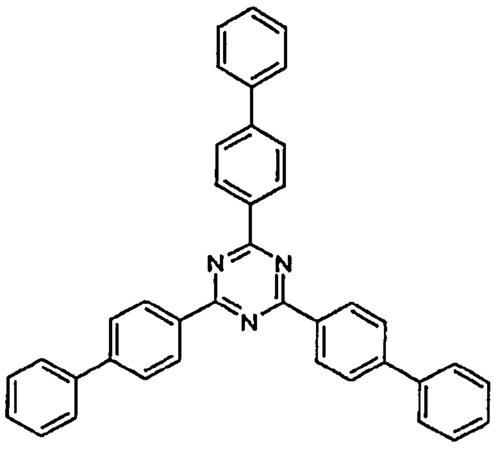
R_1, R_5, R_6, R_7 and R_8 are defined as in claim 1.

3. Use according to claim 1 or 2, wherein R_1 and R_5 are hydrogen.

4. Use according to any one of claims 1 to 3, wherein R_6 and R_8 are hydrogen.

5. Use according to any one of claims 1 to 4, wherein
R_7 is hydrogen; hydroxy; C_1-C_5alkyl; C_1-C_5alkoxy; -COOM;-COOH; or $COOR_{10}$;
M is an alkali metal ion; and
R_{10} is C_1-C_5alkyl.

6. Use according to any one of claims 1 to 5, wherein the compound of formula



(6)

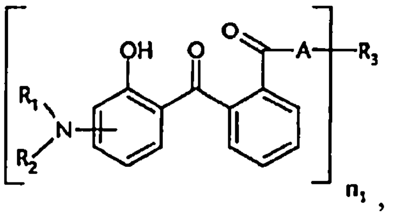
is used.

7. A cosmetic preparation comprising at least one compound of formula (1) according to claim 1 together with cosmetically tolerable carriers or adjuvants.

8. Cosmetic preparation according to claim 7 comprising the UV filter combination (A) comprising

(a_1) at least one symmetrical triazine derivative of formula (1) 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;

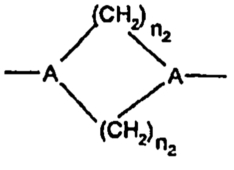
when n_1 =1,

R_3 is a saturated or unsaturated heterocyclic radical; hydroxy-C_1-C_5alkyl; cyclohexyl 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;

when n_1 is 4,

R_3 is an alkanetetrayl radical;

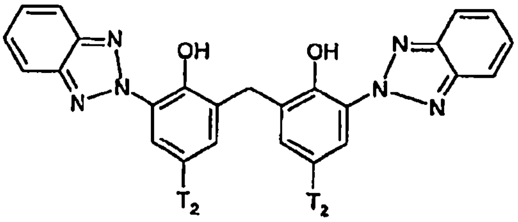
A is -O-; or -N(R_5)-; and

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

9. Cosmetic preparation according to claim 7 comprising the UV filter combination (C) comprising

(c_1) at least one symmetrical triazine derivative of formula (1); and

(c_2) at least one benzotriazole derivative of formula

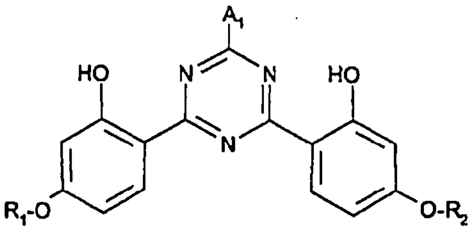


, wherein

T_2 is C_1-C_{10}alkyl, or phenyl-substituted C_1-C_4alkyl.

10. Cosmetic preparation according to claim 7 comprising the UV filter combination (D) comprising

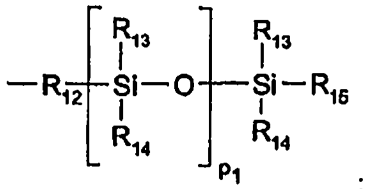
(d_1) at least one symmetrical triazine derivative of formula (1); and

(d_2) at least one compound of formula 

in which

R_1 and R_2, independently of one another, are C_3-C_{18}alkyl; C_2-C_{18}alkenyl; a radical of the formula -CH_2-CH(-OH)-CH_2-O-T_1; or

R_1 and R_2 are a radical of the formula (4a)

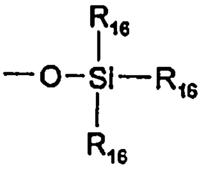


$$-R_{12}\left[\begin{matrix} R_{13} \\ | \\ -Si-O- \\ | \\ R_{14} \end{matrix}\right]_{p_1}\begin{matrix} R_{13} \\ | \\ -Si-R_{15} \\ | \\ R_{14} \end{matrix}$$

;

R_{12} is a direct bond; a straight-chain or branched C_1-C_4alkylene radical or a radical of the formula $-C_{m1}H_{2m1}-$ or $-C_{m1}H_{2m1}-O-$;

R_{13}, R_{14} and R_{15}, independently of one another, are C_1-C_{18}alkyl; C_1-C_{18}alkoxy or a radical of the formula



$$-O-\begin{matrix} R_{16} \\ | \\ Si \\ | \\ R_{16} \end{matrix}-R_{16}$$

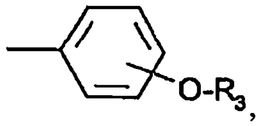
R_{16} is C_1-C_5alkyl;

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

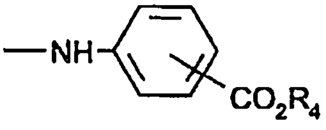
p_1 is 0 or a number from 1 to 5;

A_1 is a radical of the formula

(1b)

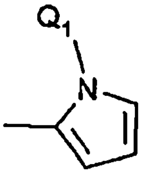


, (1c)



or of the formula

(1d)



;

R^3 is hydrogen; C_1-C_{10}alkyl, $-(CH_2CHR_5-O)_{n1}-R_4$; or a radical of the formula $-CH_2-CH(-OH)-CH_2-O-T_1$;

R_4 is hydrogen; M; C_1-C_5alkyl; or a radical of the formula $-(CH_2)_{m2}-O-T_1$;

R_5 is hydrogen; or methyl;

T_1 is hydrogen; or C_1-C_8alkyl;

Q_1 C_1-C_{18}alkyl;

M is a metal cation;

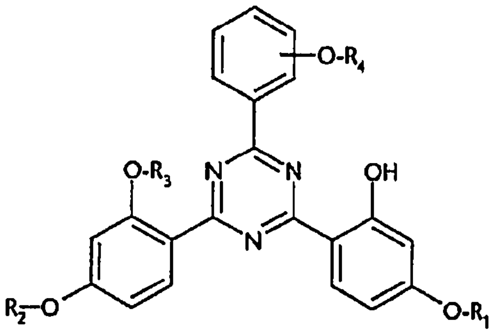
m_2 is 1 to 4; and

n_1 is 1-16.

11. Cosmetic preparation according to claim 7 comprising the UV filter combination (E) comprising

(e_1) at least one symmetrical triazine derivative of formula (1); and

(e_2) at least one hydroxyphenyltriazine compound of formula



(1) , wherein

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

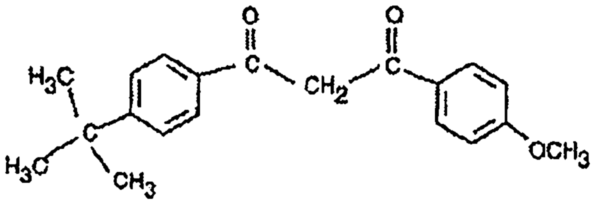
R_4 is hydrogen; or C_1-C_5alkyl.

12. Cosmetic preparation according to claim 7 comprising the UV filter combination (F) comprising

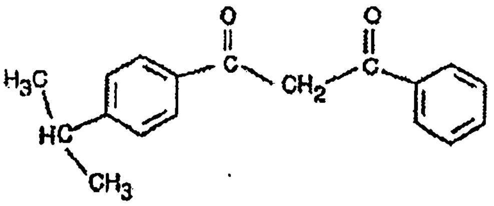
(f_1) at least one symmetrical triazine derivative of formula (1); and

(f_2) at least one dibenzoylmethane derivative of

formula



or



.

13. Cosmetic preparation according to claim 7 comprising the UV filter combination

(G) comprising

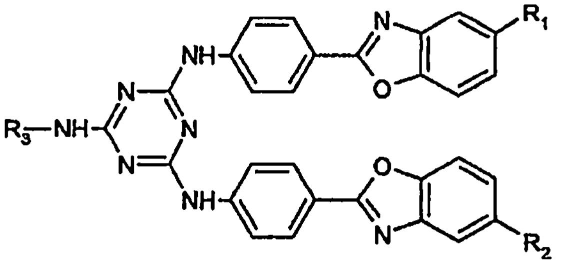
(g_1) at least one symmetrical triazine derivative of formula (1); and

(g_2) disodium phenyl dibenzimidazole tetrasulfonate.

14. Cosmetic preparation according to claim 7 comprising the UV filter combination (H) comprising

(h_1) at least one symmetrical triazine derivative of formula (1); and

(h_2) at least one benzoxazole-substituted triazine of the formula



($h_2$1)

wherein

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

15. Cosmetic preparation according to claim 7 comprising the UV filter combination (I) comprising

(i_1) at least one symmetrical triazine derivatives of formula (1); and

(i_2) 2-(2*H*-Benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]phenol.

16. Cosmetic preparation according to claim 7 comprising the UV filter combination (K) comprising

(k_1) at least one symmetrical triazine derivative of formula (1); and

(k_2) siloxane 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, wherein

Me is hydrogen.

17. Cosmetic preparation according to claim 7 comprising the UV filter combination (L) comprising

(l_1) at least one symmetrical triazine derivatives of formula (1); and

(l_2) (+/-)-1,7,7-trimethyl-3-[(4-methylphenyl)methylene]bicyclo[2.2.1]heptan-2-one.

18. Cosmetic preparation according to claim 7 comprising the UV filter combination (M)

(m_1) at least one symmetrical triazine derivatives of formula (1); and

(m_2) α-(2-oxoborn-3-ylidene)toluene4-sulphonic acid and its salts.

19. Cosmetic preparation according to claim 7 comprising the UV filter combination (N) comprising

(n_1) at least one symmetrical triazine derivatives of formula (1); and

(n_2) methyl N,N,N-trimethyl-4-[(4,7,7-trimethyl-3-oxobicyclo[2,2,1]hept-2-ylidene)methyl]-anilinium sulphate.

20. Cosmetic preparation according to claim 7 comprising the UV filter combination (O) comprising

(o_1) at least one symmetrical triazine derivatives of formula (1); and

(o_2) 2-ethylhexyl 2-cyano,3,3-diphenylacrylate.

21. Cosmetic preparation according to claim 7 comprising the UV filter combination (P) comprising

(p_1) at least one symmetrical triazine derivatives of formula (1); and

(p_2) 2-ethylhexyl 4-methoxycinnamate.

22. Cosmetic preparation according to claim 7 comprising the UV filter combination (Q) comprising

(q_1) at least one symmetrical triazine derivatives of formula (1); and

(q_2) benzoic acid, 4,4',4''-(1,3,5-triazine-2,4,6-triyltriimino)tris-,tris(2-ethylhexyl)ester.

23. Cosmetic preparation according to claim 7 comprising the UV filter combination (R) comprising

(r_1) at least one symmetrical triazine derivatives of formula (1); and

(r_2) 2-phenyl-1H-benzimidazole-5-sulphonic acid.

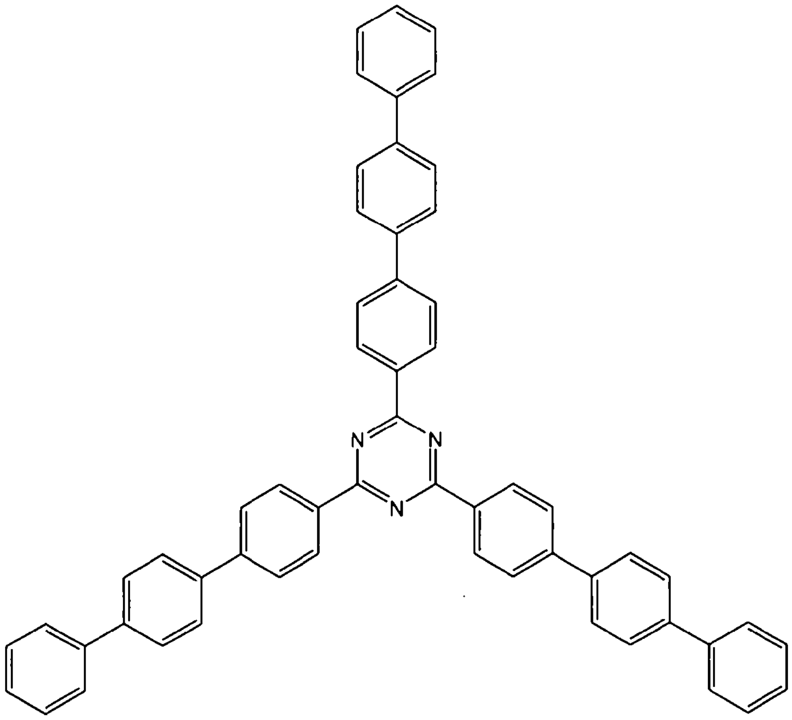
24. Cosmetic preparation according to claim 7 comprising the UV filter combination (S) comprising

(s_1) at least one symmetrical triazine derivatives of formula (1); and

(s_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.

25. Cosmetic composition according to any one of claims 7 to 24 wherein the compound of formula (1), formula (6)

or formula (9)



is present in the composition in the micronized state.

26. Use of compounds of formula (1) according to claim 1 or a cosmetic preparation comprising same substantially as hereinbefore described with reference to the examples.