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Merocyanine derivatives for cosmetic use

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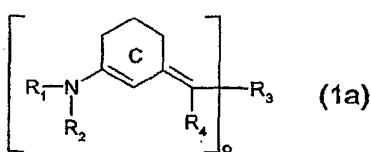
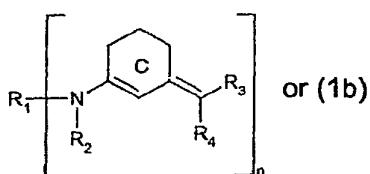
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WO 2005/058269 A1

(54) Title: MEROCYANINE DERIVATIVES FOR COSMETIC USE

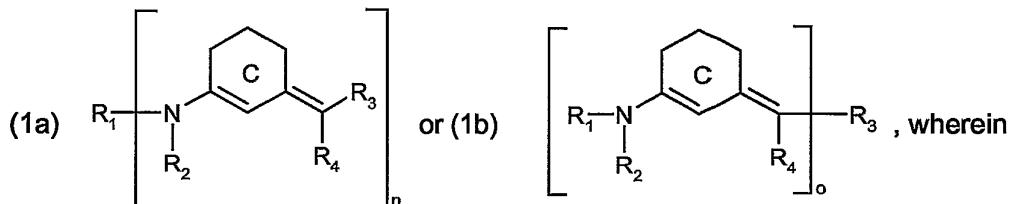


(57) Abstract: Described are merocyanine derivatives of formula (1a) or (1b) wherein n and o are integers from 2 to 4 and aminocyclohexenone intermediates. They are used in protecting human and animal hair and skin from UV radiation.

Merocyanine derivatives for cosmetic use

The present invention relates to the use of merocyanine derivatives in protecting human and animal hair and skin from UV radiation and to cosmetic compositions comprising such compounds.

The compounds for use in accordance with the invention correspond to formula



R₂ is hydrogen; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl; or a cyano group;

R₄ is a cyano group; or -Q₁-R₅;

Q₁ is -COO-; -CONH-; -CO-; -SO₂-; or -CONR₆-;

R₅ is C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; or unsubstituted or C₁-C₆alkyl-substituted C₆-C₂₀aryl;

R₆ is hydrogen; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl;

the cyclohexene radical C is not substituted or substituted by one or more C₁-C₅alkyl;

n is from 2 to 4;

o is from 2 to 4;

if n = 2, in formula (1a)

R₁ is an alkylene, cycloalkylene or phenylene-radical; or R₁ and R₂ simultaneously form an alkylene, cycloalkylene or phenylene radical; and

R₃ is a cyano group; or -Q₁-R₅; or R₃ and R₄ together form a 5- to 7-membered, monocyclic carbocyclic ring, which is optionally interrupted by -O- or -NR₇-;

If o = 2, in formula (1b)

R₃ is an alkylene, cycloalkylene or phenylene radical, which is optionally substituted with C₁-C₄alkyl, C₁-C₄alkoxy, -COR₆, -COOR₆ or -CONHR₆; and

R₁ is hydrogen; a cyano group; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl; or R₁ and R₂ together with the nitrogen atom linking them form a -(CH₂)_m- ring which is optionally interrupted by -O- or by -NR₇-;

R₇ is hydrogen; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl;

m is a number from 3 to 7;

if n = 3, in formula (1a)

R₁ is a trivalent alkyl group, which is optionally interrupted by one or more -O- or -NR₇-groups; and

R₃ is a cyano group; or -Q₁-R₅; or R₃ and R₄ together form a 5- to 7-membered, monocyclic carbocyclic ring;

if o = 3, in formula (1b)

R₃ is an alkylidene, cycloalkylidene or phenylidene radical; and

R₁ is hydrogen; a cyano group; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl; or R₁ and R₂ together with the nitrogen atom linking them form a -(CH₂)_m- ring which is optionally interrupted by -O- or by -NR₇-;

if n = 4, in formula (1a)

R₁ is a tetravalent alkyl group; and

R₃ is a cyano group or -Q₁-R₅; or R₃ and R₄ together form a 5- to 7-membered, monocyclic carbocyclic ring;

if o = 4, in formula (1b)

R₃ is a tetravalent alkyl group; and

R₁ is hydrogen; a cyano group; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl; or R₁ and R₂ together with the nitrogen atom linking them form a -(CH₂)_m- ring which is optionally interrupted by -O- or by -NR₇-.

C₁-C₂₂Alkyl denotes a linear or branched, unsubstituted or substituted alkyl group such as, for example, methyl, ethyl, propyl, isopropyl, n-butyl, n-hexyl, cyclohexyl, n-decyl, n-dodecyl, n-octadecyl, eicosyl, methoxyethyl, ethoxypropyl, 2-ethylhexyl, hydroxyethyl, chloropropyl, N,N-diethylaminopropyl, cyanoethyl, phenethyl, benzyl, p-tert-butylphenethyl, p-tert-octyl-phenoxyethyl, 3-(2,4-di-tert-amylphenoxy)-propyl, ethoxycarbonylmethyl-2-(2-hydroxyethoxy)ethyl or 2-furylethyl.

C₁-C₆alkoxy denotes methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, amyloxy, isoamyloxy or tert-amyloxy.

C_6 - C_{10} aryl denotes, for example, phenyl, tolyl, anisyl, mesityl, chlorophenyl, 2,4-di-tert-
amylphenyl and naphthyl.

Heterocyclic radicals contain one, two, three or four identical or different ring hetero atoms. Special preference is given to heterocycles which contain one, two or three, especially one or two, identical or different hetero atoms. The heterocycles may be mono- or poly-cyclic, for example mono-, bi- or tri-cyclic. They are preferably mono- or bi-cyclic, especially monocyclic. The rings preferably contain 5, 6 or 7 ring members. Examples of monocyclic and bicyclic heterocyclic systems from which radicals occurring in the compounds of formula (1a) and (1b) may be derived are, for example, pyrrole, furan, thiophene, imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, pyridine, pyridazine, pyrimidine, pyrazine, pyran, thiopyran, 1,4-dioxane, 1,2-oxazine, 1,3-oxazine, 1,4-oxazine, indole, benzothiophene, benzofuran, pyrrolidine, piperidine, piperazine, morpholine and thiomorpholine.

When R_5 and R_6 together form a 5- to 7-membered monocyclic carbocyclic or heterocyclic ring, such a ring is, for example, a 1,3-dioxocyclohexane ring such as, for example, a dime-done ring, a 1,3-dioxo-5,5-diethylcyclohexane ring, a 1,3-diaza-2,4,6-trioxocyclohexane ring such as, for example, a barbituric acid ring, a 1,3-dimethylbarbituric acid ring, a 1-phenylbarbituric acid ring, a 1-methyl-3-octylbarbituric acid ring, a 1-ethyl-3-octyloxycarbonylethyl-barbituric acid ring, a 1,2-diaza-3,5-dioxocyclopentane ring such as, for example, a 1,2-diaza-1,2-dimethyl-3,5-dioxocyclopentane ring, a 1,2-diaza-1,2-diphenyl-3,5-dioxocyclopentane ring, or a 2,4-diaza-1-alkoxy-3,5-dioxocyclohexene ring such as, for example, a 2,4-diaza-1-ethoxy-4-ethyl-3,5-dioxocyclohexene ring, a 2,4-diaza-1-ethoxy-4-[3-(2,4-di-tert-
amylphenoxy)propyl]-3,5-dioxocyclohexene ring etc..

Preference is also given to compounds of formula (1a) wherein

R_1 is defined as in formula (1a);

R_2 is hydrogen;

R_3 is a cyano group;

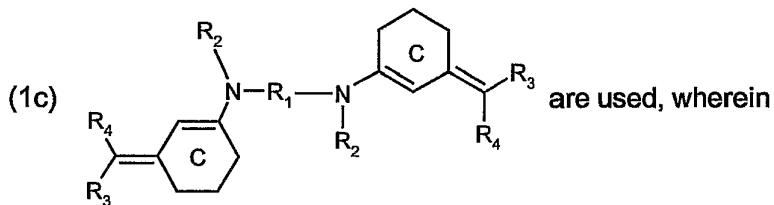
R_4 is $-CONHR_5$; and

R_5 is C_1 - C_{22} alkyl; or C_6 - C_{20} aryl.

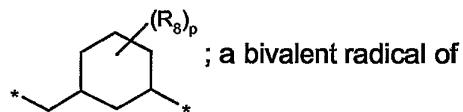
If in formula (1a) $n = 2$,

preference is further given to the use of compounds of formula

- 4 -



R_1 is a $-(CH_2)_m-$ group, not substituted or substituted with one or more than one C_1-C_5 radicals; a bivalent radical of formula (1a₁)



formula (1a₂) ; or R_1 and R_2 together with the 2 linking nitrogen atoms form

a bivalent radical of formula (1a₃) ;

R_8 is hydrogen; or C_1-C_5 alkyl;

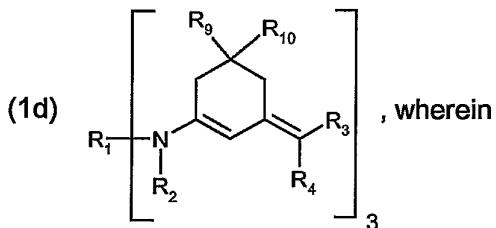
R_3 is a cyano group; or $-Q_1-R_5$;

p is a number from 0 to 3;

the cyclohexene radical C is not substituted or substituted by one or more C_1-C_5 alkyl; and

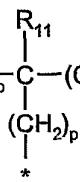
R_2 , R_4 , R_5 , Q_1 and m are defined as in formulae (1a) and (1b).

Preference is further given to the use of compounds of formula



- 5 -

R_1 is a trivalent radical of formula (1d₁) $*-(H_2C)_p-C-(CH_2)_p-*$; or



(1d₂) $*-(H_2C)_p-N-(CH_2)_p-*$,

$$\begin{array}{c} | \\ (CH_2)_p \\ | \\ * \end{array}$$

R_2 is hydrogen; or C₁-C₅alkyl;

R_3 and R_4 independently from each other are a cyano group; or $-Q_1-R_5$;

Q_1 is -COO-; -CONH-; -CO-; -SO₂-; -CONR₁₂-;

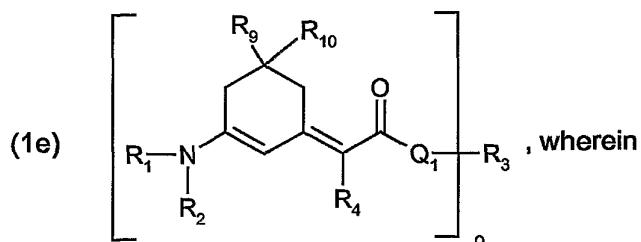
R_5 is C₁-C₅alkyl;

R_9 and R_{10} independently from each other are C₁-C₄alkyl;

R_{11} and R_{12} independently from each other are hydrogen; or C₁-C₅alkyl; and

p is a number from 0 to 5.

Preference is further given to the use of compounds of formula



R_1 and R_2 are each independently of the other C₁-C₂₂alkyl; or a cyano group; or R_1 and R_2 together with the nitrogen atom linking them form a -(CH₂)_m-ring which is optionally interrupted by -O- or by -NR₇-;

R_4 is a cyano group; or $-Q_1-R_5$;

n is 3; or 4;

if $o = 3$

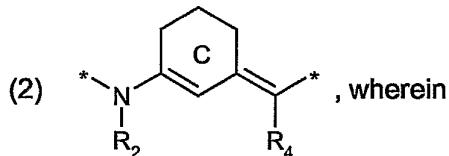
R_3 is a trivalent alkyl radical;

if $o = 4$

R_3 is a tetravalent alkyl radical;

R_5 , R_7 , R_9 , R_{10} , Q_1 and m are defined as in formula (1b).

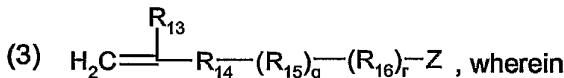
Further preference is given to the use of momomeric, oligomeric or polymeric compound comprising structural elements of formula



at least one of the asterix-marked radicals may be bound to the momomeric, oligomeric or polymeric radical;

the cyclohexene radical C is not substituted or substituted by one or more C₁-C₅alkyl; and R₂ and R₄ are defined as in formula (1a) and (1b)
as UV chromophores.

Preferably, momomeric, oligomeric or polymeric compounds correspond to formula



Z is a radical of formula (2);

R₁₃ is hydrogen; halogen; or C₁-C₅alkyl;

R₁₄ is -CONH-; -COO-; or a phenylene radical;

R₁₅ is C₁-C₂₀alkylene; or C₆-C₂₀arylene;

R₁₆ is -COO-; -OCO-; -CONH-; -NH-CO-O-; -NH-CO-; -SO₂NH-; -NHSO₂-; -SO₂- or -O-;

q is 0; or an integer; and

r is 0; or an integer.

The compounds having structural elements of formula (2) are known and are disclosed for example in US-A-4,749,643, Representatives of these compounds are the examples 3.1 – 3.7 in col. 11 – 13 in this reference.

Representatives of these compounds having structural elements of formula (3) are the examples 2.1 - 2.9 in col. 11 – 13 of this reference.

Further compounds for use in accordance with the invention are listed in Table MC1 herein below:

Table MC1

Com- ound of formula	Structure	λ_{max} [nm]
MC01		366, 398 (EtOH)
MC02		366, 398 (EtOH)
MC03		383 (EtOH)
MC04		
MC05		
MC06		

Table MC1

<u>Com- ound of formula</u>	<u>Structure</u>	<u>λ_{\max} [nm]</u>
MC07		406 (EtOH)
MC08		373 (EtOH)
MC09		
MC10		384 (EtOH)

Table MC1

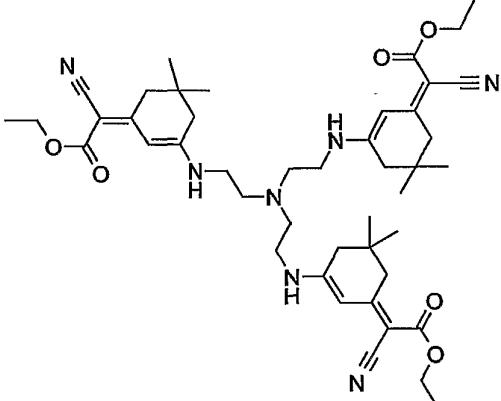
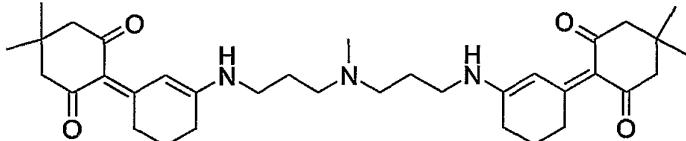
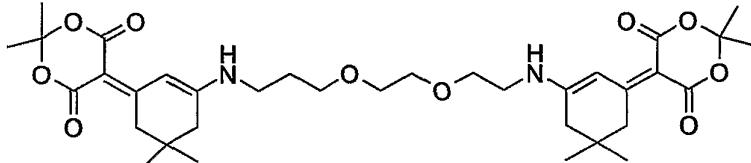
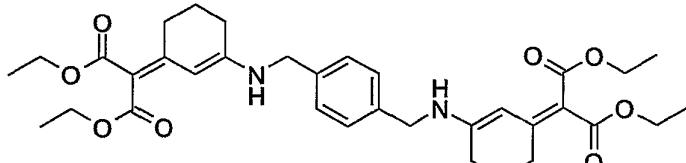
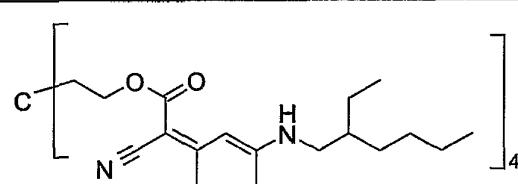
<u>Com- ound of formula</u>	<u>Structure</u>	<u>λ_{\max} [nm]</u>
MC11		
MC12		
MC13		
MC14		
MC15		

Table MC1

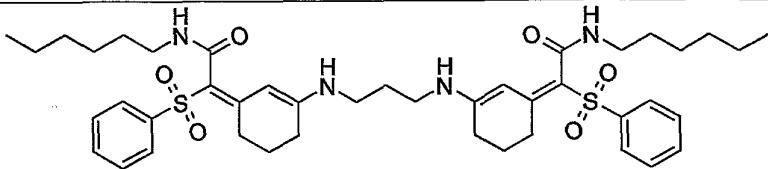
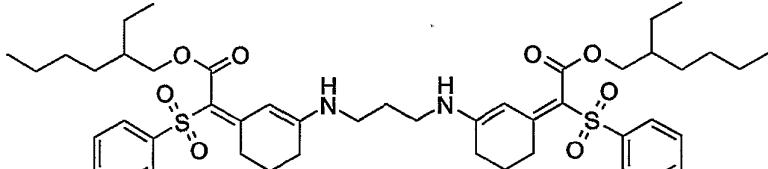
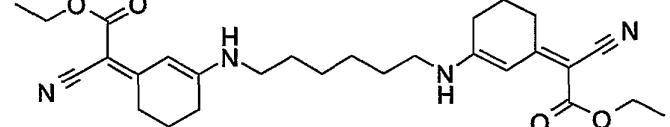
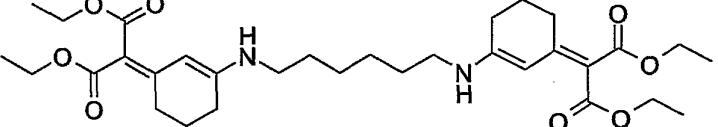
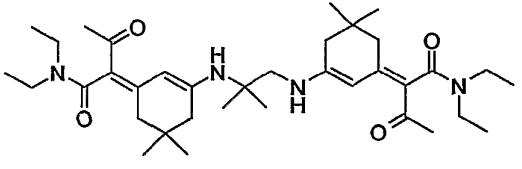
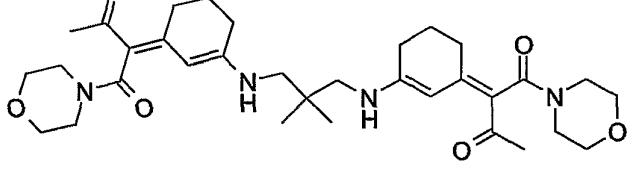
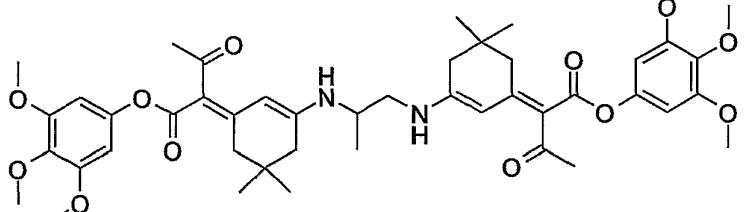
<u>Com- ound of formula</u>	<u>Structure</u>	<u>λ_{\max} [nm]</u>
MC16		
MC17		
MC18		388 (EtOH)
MC19		370 (EtOH)
MC21		
MC21		
MC22		

Table MC1

<u>Com- ound of formula</u>	<u>Structure</u>	<u>λ_{\max} [nm]</u>
MC23		
MC24		391 (EtOH)
MC25		378 (EtOH)
MC26		

Table MC1

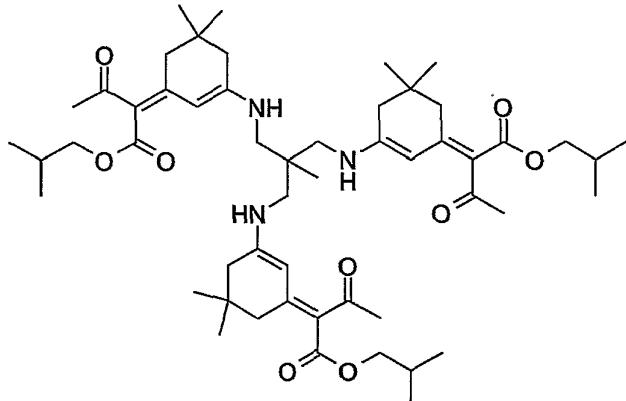
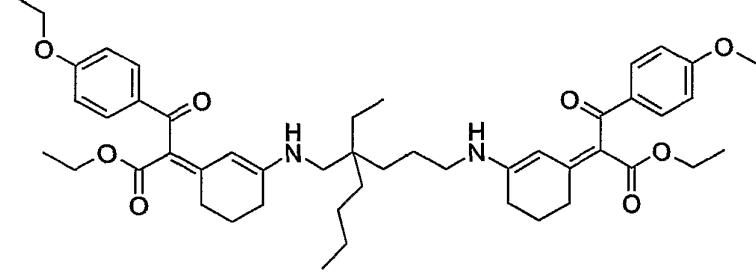
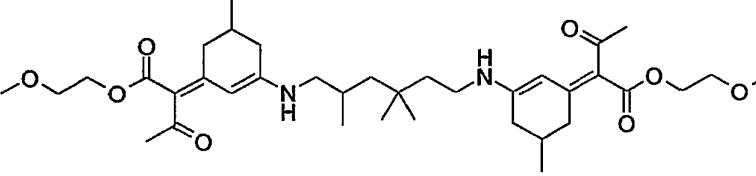
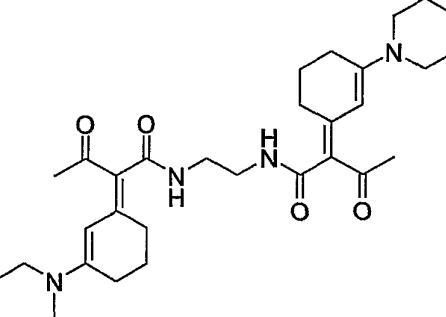
<u>Com- ound of formula</u>	<u>Structure</u>	<u>λ_{\max} [nm]</u>
MC27	 <p>Chemical structure of compound MC27: A bis(2-((2,6-diisopropylphenyl)methyl)amino)cyclohexanecarboxylate derivative. It features a central cyclohexane ring substituted with two 2-((2,6-diisopropylphenyl)methyl)amino groups and two carboxylate groups at the 1 and 4 positions.</p>	
MC28	 <p>Chemical structure of compound MC28: A bis(4-((2,6-diisopropylphenyl)methyl)phenyl)amine derivative. It consists of a central nitrogen atom bonded to two 4-((2,6-diisopropylphenyl)methyl)phenyl groups.</p>	
MC29	 <p>Chemical structure of compound MC29: A bis(2-((2,6-diisopropylphenyl)methyl)phenyl)amine derivative. It features a central nitrogen atom bonded to two 2-((2,6-diisopropylphenyl)methyl)phenyl groups.</p>	
MC30	 <p>Chemical structure of compound MC30: A bis(2-((2,6-diisopropylphenyl)methyl)phenyl)amine derivative. It consists of a central nitrogen atom bonded to two 2-((2,6-diisopropylphenyl)methyl)phenyl groups.</p>	

Table MC1

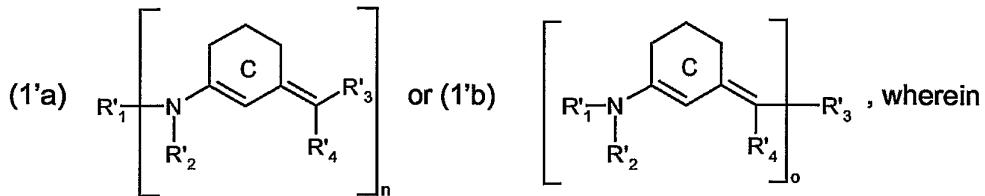
<u>Com- ound of formula</u>	<u>Structure</u>	λ_{\max} [nm]
MC31		
MC32		
MC33		
MC34		357/388 (EtOH)

Table MC1

<u>Com- ound of formula</u>	<u>Structure</u>	<u>λ_{\max} [nm]</u>
MC35		389 (EtOH)
MC36		401 (EtOH)
MC37		383 (Acetonitrile)

The merocyanine compounds of formula (1a) and (1b) used in accordance with the invention are, in some cases, known compounds but also include novel compounds.

The novel compounds correspond to formula



R'_{2} is hydrogen; C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; unsubstituted or C_1 - C_6 alkyl- or C_1 - C_6 alkoxy-substituted C_6 - C_{20} aryl; a cyano group; or R'_{1} and R'_{2} together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by $-O-$ or by $-NR'_{7}-$;

R'_{4} is $-Q'_{1}-R'_{5}$;

Q'_{1} is $-COO-$; $-CONH-$; $-CO-$; $-SO_2-$; or $-CONR'_{6}-$;

R'_{5} is C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; or unsubstituted or C_1 - C_6 alkyl-substituted C_6 - C_{20} aryl;

R'_{6} is hydrogen; C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; unsubstituted or C_1 - C_6 alkyl- or C_1 - C_6 alkoxy-substituted C_6 - C_{20} aryl;

R'_{7} is hydrogen; C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; unsubstituted or C_1 - C_6 alkyl- or C_1 - C_6 alkoxy-substituted C_6 - C_{20} aryl;

the cyclohexene radical C is not substituted or substituted by one or more C_1 - C_6 alkyl;

m is from 3 to 7;

n is from 2 to 4;

o is from 2 to 4;

if $n = 2$, in formula (1'a)

R'_{1} is an alkylene, cycloalkylene or phenylene-radical; or R'_{1} and R'_{2} simultaneously form an alkylene, cycloalkylene or phenylene radical; and

R'_{3} is a cyano group or $-Q'_{1}-R'_{5}$; or R'_{3} and R'_{4} together form a 5- to 7-membered, monocyclic carbocyclic ring;

If $o = 2$, in formula (1'b)

R'_{3} is an alkylene, cycloalkylene or phenylene radical; and

R'_{1} is hydrogen; a cyano group; C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; unsubstituted or C_1 - C_6 alkyl- or C_1 - C_6 alkoxy-substituted C_6 - C_{20} aryl; or R'_{1} and R'_{2} together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by $-O-$ or by $-NR'_{7}-$;

if $n = 3$, in formula (1'a)

R'_{1} is a trivalent alkyl group, which is optionally interrupted by one or more $-O-$ or $-NR'_{7}-$ groups; and

R'_{3} is a cyano group or $-Q'_{1}-R'_{5}$; or R'_{3} and R'_{4} together form a 5- to 7-membered, monocyclic carbocyclic ring;

if σ = 3, in formula (1'b)

R'_3 is an alkylidene, cycloalkylidene or phenylidene radical; and

R'_1 is hydrogen; a cyano group; C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; unsubstituted or C_1 - C_6 alkyl- or C_1 - C_6 alkoxy-substituted C_6 - C_{20} aryl; or R'_1 and R'_2 together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by -O- or by $-NR'_7-$;

if n = 4, in formula (1'a)

R'_1 is a tetravalent alkyl group; and

R'_3 is a cyano group or $-Q'_1-R'_5$; or R'_3 and R'_4 together form a 5- to 7-membered, monocyclic carbocyclic ring;

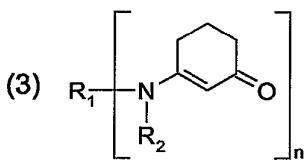
if σ = 4, in formula (1'b)

R'_3 is a tetravalent alkyl group; and

R'_1 is hydrogen; a cyano group; C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; unsubstituted or C_1 - C_6 alkyl- or C_1 - C_6 alkoxy-substituted C_6 - C_{20} aryl; or R'_1 and R'_2 together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by -O- or by $-NR'_7-$.

The preparation of the compounds of formula (1a) and (1b) may be carried out according to known methods of the prior art as described for example in US-A-4,749,643 on col. 13, line 66 – col. 14, line 57 and the references cited therein.

The compounds of formula (1a) can be prepared starting from 1-aminocyclohexanone-3 of the general formula



wherein R_1 , R_2 and n are defined as in formula (1a) by condensation of dihydroxyresorcines with primary or secondary amine compounds. After alkylation with dimethylsulfate or other suitable alkylating agents like diethylsulfate and subsequent reaction with a suitable methylene-active compound compounds of formula (1a) are obtained.

The alkylation reaction of the starting compounds of formula (3) with suitable alkylating agents like dimethylsulfate may be carried out in a suitable solvent, preferably dimethylsulfoxide, *N*-methylpyrrolidone, dimethylformamide or dimethylacetamide. Protic solvents like methanol, ethanol, iso-butanol, tert-butanol or iso-propanol are also suitable. The reaction

may also be carried out in aliphatic or aromatic solvents like hexane, toluene or xylol. Ether compounds like diethylether and tetrahydrofurane or halogenated solvents like chloroform or dichlormethane are also suitable solvents as well as mixtures of these solvents.

The reaction may be carried out at temperatures between -80°C and the boiling point of the reaction mixture, preferably from 60 to 120°C.

The intermediates of formula (3), wherein

R_2 is hydrogen; C_1-C_{22} alkyl; cyclo- C_3-C_8 alkyl; unsubstituted or C_1-C_6 alkyl- or C_1-C_6 alkoxy-substituted C_6-C_{20} aryl; or R_1 and R_2 together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by -O- or $-NR_3-$;

R_3 is hydrogen; C_1-C_{22} alkyl; cyclo- C_3-C_8 alkyl; or unsubstituted or C_1-C_6 alkyl-substituted C_6-C_{20} aryl;

m is from 3 to 7;

n is from 2 to 4;

the cyclohexene radical C is unsubstituted or substituted by one or more C_1-C_5 alkyl;

when $n = 2$,

R_1 and R_2 simultaneously form an alkylene, cycloalkylene or phenylene radical;

when $n = 3$,

R_1 is a trivalent alkyl group, which is optionally interrupted by one or more -O- or $-NR_3-$ groups;

when $n = 4$,

R_1 is a tetravalent alkyl group which is optionally interrupted by one or more -O- or $-NR_3-$ groups;

are novel and are a further subject matter of the present invention.

They are useful intermediates for the preparation of UV absorbers and represent themselves UV-B absorbers for protecting human and animal hair and skin from UV radiation.

Further compounds for use in accordance with the invention are listed in Table MC1a herein below:

Table MC1a

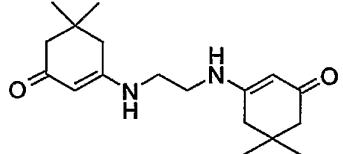
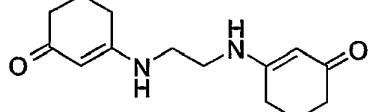
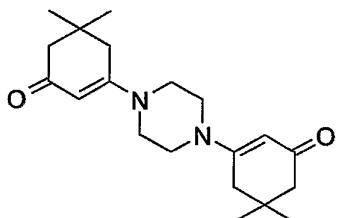
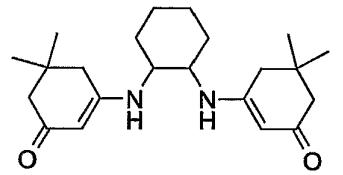
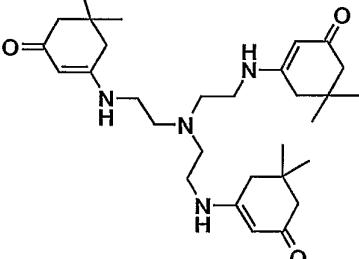
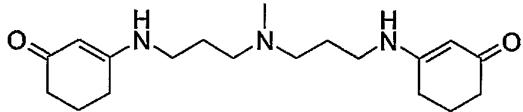
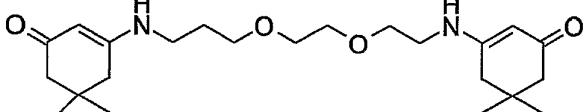
<u>Com- ound of formula</u>	<u>Structure</u>	<u>λ_{\max} [nm]</u>
MC01a		296 (EtOH)
MC04a		
MC06a		309 (EtOH)
MC08a		295 (Acetonitril)
MC11a		
MC12a		
MC13a		

Table MC1a

<u>Com- ound of formula</u>	<u>Structure</u>	<u>λ_{max} [nm]</u>
MC14a		

The compounds of the formulae (1a) and (1b) 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 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 merocyanine derivatives of formula (1a) and (1b) 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.

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

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

The UV absorbers according to 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).

The cosmetic formulations or pharmaceutical compositions according to the present invention may additionally contain one or more than one further UV filter.

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.

Preference is given to the use of mixing ratios of the UV absorber of formula (1a) and (1b) according to the present invention and optionally further light-protective agents from 1:99 to 99:1, preferably from 1:95 to 95:1 and most preferably from 10:90 to 90:10, based on weight. Of special interest are mixing ratios of from 20:80 to 80:20, preferably from 40:60 to 60:40 and most preferably approximately 50:50. Such mixtures can be used, inter alia, to improve the solubility or to increase UV absorption.

Suitable UV filter substances which can be additionally used with the UV absorbers according to the present invention are for example 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-benzylidenebornan-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-phenylenedimethylene)-bis(7,7-dimethyl-2-oxo-bicyclo[2.2.1]heptane-1-methane-sulfonic acid) and salts, 3-(4'-sulfo)benzylidene-bornan-2-one and salts; camphorbenzal-konium 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-ethylhexyl-oxy)-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'-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, Fe2O3, Ce2O3, Al2O3, ZrO2. (surface coatings: polymethyl-methacrylate, methicone (methylhydrogenpolysiloxane as described in CAS 9004-73-3), di-methicone, 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. aminoxybenzophenone 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,

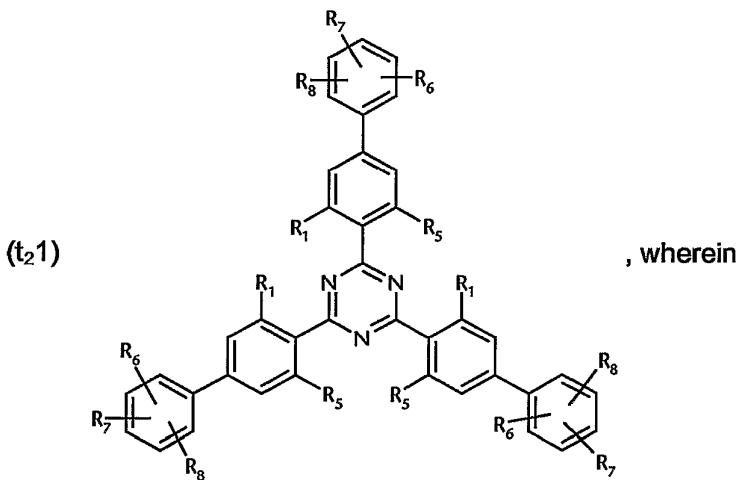
Marcel Dekker, Inc. , New York and Basle or in Cosmetics & Toiletries (107), 50ff (1992) also can be used as additional UV protective substances.

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

- UV-filter combinations (T) comprising

(t₁) at least one merocyanine derivative of formula (1a) or (1b); and

(t₂) a triazine compound of formula



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

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; biphenyl; 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; or $-COOH$.

Most preferred are UV-filter combinations comprising

(t₃) the compound of formula (MC02); and

(t₄) 1,3,5-Triazine, 2,4,6-tris[1,1'-biphenyl]-4-yl- (9Cl).

The compounds of formula (1a) and (1b) may also be used as an anti-wrinkle perception modifier.

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 and 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 oils, emulsifiers, super-fattening agents, surfactants, consistency regulators/thickeners and rheology modifiers, polymers, biogenic active ingredients, deodorizing active ingredients, anti-dandruff agents, antioxidants, hydrotropic agents, preservatives and bacteria-inhibiting agents, perfume oils, colorants, polymeric beads or hollow spheres as SPF enhancers,

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, bath preparations, cosmetic personal care preparations, foot-care preparations, light-protective preparations, skin-tanning preparations, depigmenting preparations, deodorants, antiperspirants, preparations for cleansing and caring for blemished skin, shaving preparations, fragrance preparations or cosmetic hair-treatment preparations

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.

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

Preparation Examples

Example 1: Preparation of the compound MC 20:

1a. Preparation of the preliminary stage (compound MC 01a)



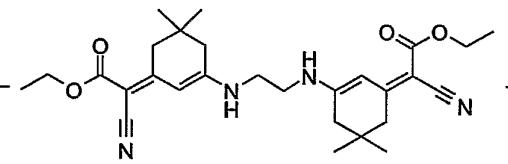
A mixture of 6.04 g ethylenediamine and 31.15 g dimedone in 200 ml toluene is heated under reflux conditions using a water separator for three hours.

After cooling down the mixture the product is filtered off, washed with minor amounts of ethyl acetate and dried in vacuum at 80°C.

The yield is nearly quantitative.

Mp. > 250 °C.

Example 1b. Preparation of the compound MC2



7.61 g of the compound MC14a are dissolved in 375 ml N-methylpyrrolidone at 100°C and mixed dropwise with 6.50 g dimethylsulfate.

The reaction mixture is stirred for 60 minutes at 100°C.

After cooling down to 80°C a mixture of 5.81 g cyan acidic acidethylester, 5.14 g triethylamine and 4.3 ml isopropanol is added slowly dropwise. The reaction mixture is stirred at a temperature of 100°C for 90 minutes.

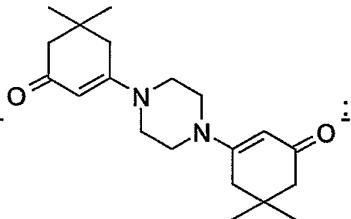
After cooling down of the reaction mixture the raw product is filtered off.

Subsequent column chromatography with a mixture of toluene and methanol (6:4) over silica gel delivers 1.28 g (10 % o. th.) of a pure product which is dried in vacuum at 80°C.

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λ_{max} (acetonitril) = 389 nm.

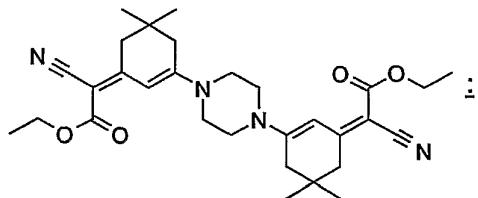
Example 2a: Preparation of compound MC06a



A mixture of 9.06 g dimedone and 2.78 g piperazine in 64 ml toluene is heated under reflux conditions using a water separator for five hours.

After cooling down the mixture the product is filtered off, washed with minor amounts of ethyl acetate and dried in vacuum at 80°C. Yield: 75 %.

Example 2b: Preparation of the compound MC07



3,34 g dimethylsulfate are added dropwise to 4.33 g of the compound MC 06a (prepared in Example 2a). The reaction mixture is stirred for 60 minutes at 100°C.

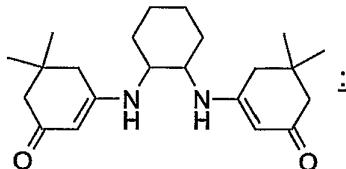
After cooling down to 80°C a mixture of 2.89 g ethyl cyano acetate and 5,21 g of triethylamine is added dropwise. The reaction mixture is stirred at a temperature of 110°C for 90 minutes.

After cooling down and the addition of 300 ml water the raw product is filtered off.

Subsequent column chromatography with a mixture of toluene and methanol (6:4) over silica gel delivers 4.5 g (65 % o. th.) of a pure product, which is dried in vacuum at 80°C.

λ_{max} (ethanol) = 406 nm.

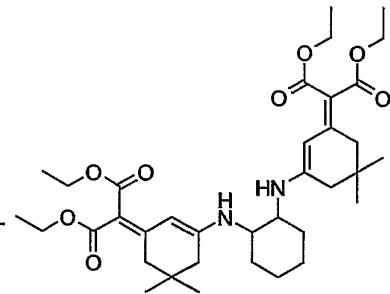
Example 3a: Preparation of compound MC08a



A mixture of 9,06 g dimedone and 4,30 g 1,2-diamino-cyclohexane in 64 ml toluene is heated under reflux conditions using a water separator for three hours.

After cooling down the mixture the product is filtered off, washed with minor amounts of ethyl acetate and dried in vacuum at 80°C yielding 95 % product.

Example 3b. Preparation of the compound MC10



22,86 g of dimethylsulfate are added dropwise to 16,99 g of the compound MC 06a. The reaction mixture is stirred for 60 minutes at 100°C.

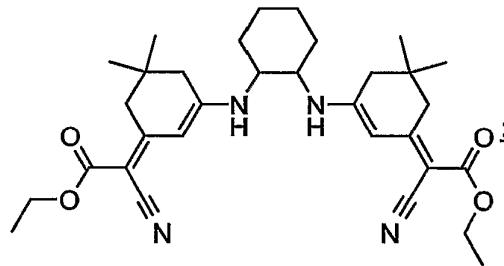
After cooling down to 80°C the mixture is treated with 13,50 g of triethylamine and stirred for 10 minutes. Then a mixture of 16,72 g diethylmalonate and 28,89 g DBU is added slowly dropwise. The reaction mixture is stirred at a temperature of 100°C for 90 minutes.

After cooling down and the addition of 300 mL of water the raw product is filtered off.

Subsequent column chromatography with a mixture of toluene and methanol (6:4) over silica gel delivers 21.28 g (70 % o. th.) of a pure product which is dried in vacuum at 80°C.

λ_{max} (ethanol) = 373 nm.

Example 3c: Preparation of the compound MC09



17.93 g (0.05 mol) MC09a are heated with 30 ml dimethylsulfate in an oil bath up to 100°C and stirred for 40 min at this temperature. The reaction mixture is cooled down to 60°C, a mixture of 11.93 g (0.103 mol) ethyl cyano acetate and 8.25 g (0.120 mol) sodium ethanolate are added in 50 ml ethanol and stirred for 40 minutes at 110°C, wherein ethanol is distilled off during the reaction. The mixture is cooled down, the compound precipitated with H2O and extracted by suction.

The subsequent column chromatography (Kieselgel) with a 9:1-mixture of toluene and acetone delivers the pure product which is dried in vacuum at 80°C

Yield: 23.3 g (85 % d. Th.).

Example 4: Preparation of micronized UV absorbers

100 parts of the compound of formula MC 2 are milled together with zirconium silicate balls (diameter: 0,1 to 4 mm) as grinding aids, a dispersing agent (15 parts of C₈-C₁₆polyglucoside) and water (85 parts) in a ball mill to a mean particle size of d₅₀ = 200nm. With this method a micropigment dispersion of a UV absorber is obtained.

Application ExamplesExample 5: UV-A/UV-B Daily Care UV Protection Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
	Ethylhexyl Methoxycinnamate	5.00
Part B	Water	qs to 100
	Glycerin	2.00
	UV-absorber dispersion as described in example 4	3.00
	Disodium EDTA	0.10
Part C	Water	20.00
	Diazolidinyl Urea (and) Iodopropynyl Butylcarbamate	0.15
	Propylene Glycol	4.00
Part D	Sodium Acrylates Copolymer (and) Paraffinium Liquidum (and) PPG-1 Trideceth-6	1.50
	Cyclopentasiloxane	4.50
	PEG-12 Dimethicone	2.00
	Tocopheryl Acetate	0.45
	Water (and) Citric Acid	qs
Part E	Fragrance	qs

Manufacturing instruction:

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 6: UV Day Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Cetyl Phosphate	1.75
	C12-C15 Alkyl Benzoate	5.00
	Cetearyl Alcohol/ PEG-20 Stearate	2.00
	Ethoxydiglycol Oleate	2.00
	Stearic Acid	1.50
	Ethylhexyl Methoxycinnamate	3.00
	Isononyl Isononanoate	2.00
Part B	Aqua	qs to 100
	Xanthan Gum	0.35
	UV-absorber dispersion as described in example 4	5.00
	Disodium EDTA	0.20
	Propylene Glycol	2.00
	Diazolidinyl Urea (and) Methylparaben (and) Propylparaben (and) Propylene Glycol	0.70
Part C	Glycerin	1.50
	Cyclopentasiloxane (and) Dimethiconol	1.00
	Ethoxydiglycol	3.00
Part D	Dimethicone	2.00
	Triethanolamine	qs

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. 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 7: Sun Protection Emulsion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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 4	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 8: Every Day Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
Part B	Aqua	20.00
	UV-absorber dispersion as described in example 4	3.00
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 9: Sprayable Sunscreen Emulsion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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 4	12.00
Part D	Titanium Dioxide (and) Silica (and) Sodium Polyacrylate	8.00
	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 Ultra Turrax 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 10: Daily Care Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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 4	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 11: Daily Care with UV Protection

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
	Propylene Glycol	7.50

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	1.00
Part C	Aqua	30.00
	UV-absorber dispersion as described in example 4	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 12: O/W Every Day UV Protection Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
	UV-absorber dispersion as described in example 4	8.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben Steareth-10 Allyl Ether/Acrylates Copolymer	0.70 1.50
Part E	Water (and) Sodium Hydroxide	qs

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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 13: O/W Every Day UV Protection

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
	UV-absorber dispersion as described in example 4	8.00
Part D	Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Butylparaben (and) Propylparaben (and) Isobutylparaben Steareth-10 Allyl Ether/Acrylates Copolymer	0.70 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 14: Sunscreen Cream

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
	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 4	12.00
Part D	Phenyl Trimethicone	1.50
	Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	0.70
	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 15: UVA/UVB Daily Care Lotion, type O/W

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Glyceryl Stearate (and) PEG-100 Stearate	5.00
	Stearyl Alcohol	1.00
	Tripalmitin	0.70
	Mineral Oil	15.00

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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 4	8.00
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 16: UVA/UVB Daily Care Lotion, type O/W

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Oleth-3 Phosphate	0.60
	Steareth-21	2.50
	Steareth-2	1.00
	Cetyl Alcohol	0.80
	Stearyl Alcohol	1.50
	Tri behenin	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
Part D	Sodium Acrylates Copolymer (and) Mineral Oil (and) PPG-1 Trideceth-6	1.50
Part E	UV-absorber dispersion as described in example 4	10.00

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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 17: UV-A/UV-B Every Day Protection Lotion O/W

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
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 UV-absorber dispersion as described in example 4	1.00 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 18: Sprayable Sunscreen Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
	Titanium Dioxide (and) Alumina (and) Silica (and) Sodium Polyacrylate	2.50
Part C	Water	30.00
	UV-absorber dispersion as described in example 4	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 19: O/W Every Day UV Protection Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
	UV-absorber dispersion as described in example 4	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 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 20: Water resistant Sunscreen Emulsion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Polyglyceryl-10 Pentastearate (and) Behenyl Alcohol (and) Sodium Stearyl Lactylate	2.50
	VP/Eicosene Copolymer	1.50
	Stearyl Alcohol	1.50

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
	Squalane	4.00
	C12-15 Alkyl Benzoate	7.50
	Octocrylene	1.50
	4-Methylbenzylidene Camphor	3.00
	Ethylhexyl Methoxycinnamate	2.00
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 4	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 21: UVA/UVB Sun Protection Lotion, O/W type

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
	Cetyl Alcohol	1.00
	Dimethicone	0.10
	Ethylhexyl Methoxycinnamate	5.00
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 4	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 is adjusted with part F to 7.00 and part G is added.

Example 22: UVA/UVB Sun Protection Lotion, O/W type

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
	Cetyl Alcohol	1.00
	Dimethicone	0.10
	Ethylhexyl Methoxycinnamate	5.00
Part B	Water	qs to 100
	Glycerin	3.00

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part C	Steareth-10 Allyl Ether/Acrylates Copolymer	0.50
Part D	UV-absorber dispersion as described in example 4	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 23: Sunscreen Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
	VP/Eicosene Copolymer	2.00
Part B	Water	qs to 100
	UV-absorber dispersion as described in example 4	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

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
	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. Part F is added at room temperature.

Example 24: W/O Sunscreen Lotion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
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
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 4	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 25: Skin Protection Sunscreen Lotion W/O

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	Polyglyceryl-2 Dipolyhydroxystearate	3.00
	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 4	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 26: O/W emulsion

	<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
Part A	UV absorber of formula (MC10)	3 g
	sesame oil	10 g
	glyceryl stearate	4 g
	stearic acid	1 g
	cetyl alcohol	0.5 g
	polysorbate 20	0.2 g
Part B	propylene glycol	4 g
	propylparaben	0.05 g

<u>INCI-Name</u>	<u>% w/w (as supplied)</u>
methylparaben	0.15 g
triethanolamine	0.1 g
carbomer 934	0.1 g
<u>water</u>	ad 100 ml

Preparation of the emulsionPhase (A):

Firstly, the UV absorber is dissolved in sesame oil. The other components of (A) are added thereto and combined.

Phase (B):

Propylparaben and methylparaben are dissolved in propylene glycol. 60 ml of water are then added, heating to 70°C is carried out and then carbomer 934 is emulsified therein.

Emulsion:

(A) is slowly added to (B) with vigorous application of mechanical energy. The volume is adjusted to 100 ml by the addition of water.

Example 27: Daily care cream, type O/W

	<u>INCI name</u>	<u>% w/w (as used)</u>
Part A	Glyceryl stearate (and) cetearyl alcohol (and) cetyl palmitate (and) cocoglycerides	4.0
	Ceteareth-12	4.0
	Cetearyl alcohol	2.0
	Dicaprylyl ether	4.5
	Ethylhexyl stearate	4.0
	Hexyl laurate	3.5
	Ethylhexyl triazone	1.0
	Benzylidene malonate polysiloxane	2.0
	HDI(trimethylol hexyl-lactone crosspolymer (and) silica	5.0
	Stearyl dimethicone	1.0
	Dimethicone	2.0
	Cetyl alcohol	0.8

	<u>INCI name</u>	<u>% w/w (as used)</u>
	compound of formula (MC10)	2.0
Part B	Water	q.s. to 100
	Water (and) scleroglucan (and) phenoxyethanol	2.0
	Glycerol	2.0
Part C	Steareth-10 allyl ether/acrylate copolymer	0.45
	Phenoxyethanol (and) methylparaben (and) ethylparaben (and) butylparaben (and) propylparaben (and) isobutylparaben	0.7
Part D	Aqua (and) tocopheryl acetate (and) caprylic/capric triglyceride (and) polysorbate 80 (and) lecithin	4.0
Part E	Water (and) sodium hydroxide	q.s.
	Fragrance	q.s.

Preparation procedure:

Part A and part B are heated separately to 80°C. Part A is poured into part B, whilst stirring continuously. Afterwards the mixture is homogenized with an Ultra Turrax at 11 000 rpm for 20 sec.. The mixture is cooled to 60°C and part C is added. At a temperature below 30°C, part D is added and the pH value is adjusted with sodium hydroxide to between 6.5 and 7.0. Finally, fragrance is added.

Example 28: Sun-protection cream, type O/W

	<u>INCI name</u>	<u>% w/w (as used)</u>
Part A	Polyglyceryl-3 methylglucose distearate	2.0
	Decyl oleate	5.7
	Isopropyl palmitate	5.8
	Caprylic/capric triglyceride	6.5
	compound of formula (MC10)	2.0
	Ethylhexyl methoxycinnamate	5.0
	Cetyl alcohol	0.7
Part B	Glycerol	3.0
	Carbomer	0.3
	Water	q.s. to 100
Part C	Phenoxyethanol (and) methylparaben (and) ethylparaben (and) butylparaben (and) propylparaben (and) isobutylparaben	0.5
Part D	Methylene bis-benzotriazolyl tetramethylbutylphenol (and) aqua (and) decyl glucoside (and) propylene glycol (and) xanthan gum	8.0

	<u>INCI name</u>	<u>% w/w (as used)</u>
	Water	20.0
Part E	Water (and) sodium hydroxide	q.s.
	Fragrance	q.s.

Preparation procedure

Part A and part B are heated separately to 75°C. Part A is poured into part B whilst stirring. The mixture is homogenised with an Ultra Turrax at 11 000 rpm for 15 sec. The mixture is cooled to 60°C and part C and part D are incorporated. The mixture is homogenised again for a short time (5 sec./11 000 rpm) and further cooled, with moderate stirring. At room temperature, the pH is adjusted with sodium hydroxide solution to between 5.5 and 6.0. Finally, fragrance is added.

Example 29: Daily care UV-protection lotion

	<u>INCI name</u>	<u>% w/w (as used)</u>
Part A	Oleth-3 phosphate	0.6
	Steareth-21	2.5
	Steareth-2	1.0
	Cetyl alcohol	0.8
	Stearyl alcohol	1.5
	Tri behenin	0.8
	Isohexadecane	8.0
	compound of formula (MC10) or (MC37)	5.0
Part B	Water	q.s. to 100
	Glycerol	2.0
	Methylene bis-benzotriazolyl tetramethylbutylphenol (and) aqua (and) decyl glucoside (and) propylene glycol (and) xanthan gum	3.0
	Disodium EDTA	0.1
Part C	Water	20.0
	Diazolidinyl urea (and) iodopropynyl butylcarbamate	0.15
	Propylene glycol	4.0
Part D	Sodium acrylate copolymer (and) liquid paraffin (and) PPG-1 trideceth-6	1.5
	Cyclopentasiloxane	4.5

	<u>INCI name</u>	<u>% w/w (as used)</u>
	PEG-12 dimethicone	2.0
	Tocopheryl acetate	0.45
	Water (and) citric acid	q.s.
Part E	Fragrance	q.s.

Preparation procedure

Heat part A and part B separately to 75°C. Pour part A into part B, whilst stirring continuously. Immediately after emulsification, incorporate in the mixture SF 1202 and SF 1288 from part D. Afterwards homogenise with an Ultra Turrax at 11 000 rpm for 30 sec.. Allow to cool to 65°C and incorporate SALCARE® SC91. At a temperature below 50°C, add part C. At 35°C or below, incorporate vitamin E acetate and subsequently adjust the pH with citric acid. At room temperature, add part E.

Example 30: Sun-protection cream, type O/W

	<u>INCI name</u>	<u>% w/w (as used)</u>
Part A	Polyglyceryl-3 methylglucose distearate	2.0
	Decyl oleate	5.7
	Isopropyl palmitate	5.8
	Caprylic/capric triglyceride	6.5
	compound of formula (MC14) or (MC37)	2.0
	Ethylhexyl methoxycinnamate	5.0
	Cetyl alcohol	0.7
Part B	Glycerol	3.0
	Carbomer	0.3
	Water	q.s. to 100
Part C	Phenoxyethanol (and) methylparaben (and) ethylparaben (and) butylparaben (and) propylparaben (and) isobutylparaben	0.5
Part D	Methylene bis-benzotriazolyl tetramethylbutylphenol (and) aqua (and) decyl glucoside (and) propylene glycol (and) xanthan gum	8.0
	Water	20.0
Part E	Water (and) sodium hydroxide	q.s.
	Fragrance	q.s.

Preparation procedure:

Part A and part B are heated separately to 75°C. Part A is poured into part B whilst stirring. The mixture is homogenised with an Ultra Turrax at 11 000 rpm for 15 sec.. The mixture is cooled to 60°C, and part C and part D are incorporated. The mixture is homogenised again for a short time (5 sec./11 000 rpm). After further cooling, with moderate stirring, the pH is adjusted with sodium hydroxide at room temperature. A solution between pH 5.50 and 6.00 is obtained. Finally, fragrance is added.

Example 31: Sun-protection cream, type O/W

	<u>INCI name</u>	<u>% w/w (as used)</u>
Part A	Polyglyceryl-3 methylglucose distearate	2.0
	Decyl oleate	5.7
	Isopropyl palmitate	5.8
	Caprylic/capric triglyceride	6.5
	Mixture of the compound of formula (MC10) (50 %) or (MC37) (50 %) and Uvinul A Plus CAS Reg. No. 302776-68-7 (50 %)	2.0
	Ethylhexyl methoxycinnamate	5.0
	Cetyl alcohol	0.7
Part B	Glycerol	3.0
	Carbomer	0.3
	Water	q.s. to 100
Part C	Phenoxyethanol (and) methylparaben (and) ethylparaben (and) butylparaben (and) propylparaben (and) isobutylparaben	0.5
Part D	Methylene bis-benzotriazolyl tetramethylbutylphenol (and) aqua (and) decyl glucoside (and) propylene glycol (and) xanthan gum	8.0
	Water	20.0
Part E	Water (and) sodium hydroxide	q.s.
	Fragrance	q.s.

Preparation procedure:

Part A and part B are heated separately to 75°C. Part A is poured into part B whilst stirring. The mixture is homogenised with an Ultra Turrax at 11 000 rpm for 15 sec.. After cooling 60°C, part C and part D are incorporated. The mixture is homogenised again for a short time (5 sec./11 000 rpm). After further cooling, with moderate stirring, the pH is adjusted at room

temperature with sodium hydroxide solution to between 5.50 and 6.00. Finally, fragrance is added.

Example 32: Sun-protection cream, type O/W

	<u>INCI name</u>	<u>% w/w (as used)</u>
Part A	Polyglyceryl-3 methylglucose distearate	2.0
	Decyl oleate	5.7
	Isopropyl palmitate	5.8
	Caprylic/capric triglyceride	6.5
	Mixture of compound of formula (MC10) (50 %) or (MC37) (50 %) and benzylidene camphor, CAS Reg. No. 36861-47-9 (50 %)	2.0
	Ethylhexyl methoxycinnamate	5.0
	Cetyl alcohol	0.7
Part B	Glycerol	3.0
	Carbomer	0.3
	Water	q.s. to 100
Part C	Phenoxyethanol (and) methylparaben (and) ethylparaben (and) butylparaben (and) propylparaben (and) isobutylparaben	0.5
Part D	Methylene bis-benzotriazolyl tetramethylbutylphenol (and) aqua (and) decyl glucoside (and) propylene glycol (and) xanthan gum	8.0
	Water	20.0
Part E	Water (and) sodium hydroxide	q.s.
	Fragrance	q.s.

Preparation procedure

Part A and part B are heated separately to 75°C. Part A is poured into part B whilst stirring. The mixture is homogenised with an Ultra Turrax at 11 000 rpm for 15 sec.. After cooling to 60°C, part C and part D are incorporated. The mixture is homogenised again for a short time (5 sec./11 000 rpm). After further cooling, with moderate stirring, the pH is adjusted at room temperature with sodium hydroxide. A solution between pH 5.50 and 6.00 is obtained.

Finally, fragrance is added.

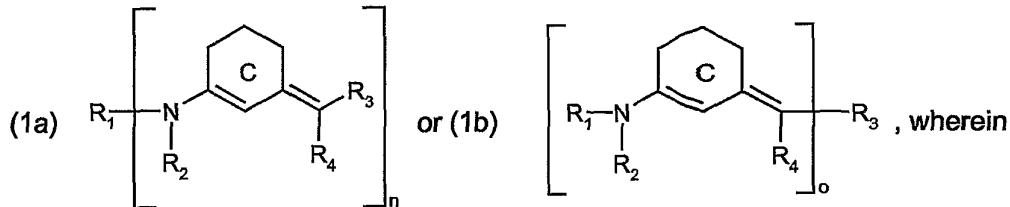
- 50a -

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.

What is claimed is:

1. Use of a compound of formula



R₂ is hydrogen; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl; or a cyano group;

R₄ is a cyano group; or -Q₁-R₅;

Q₁ is -COO-; -CONH-; -CO-; -SO₂-; or -CONR₆-;

R₅ is C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; or unsubstituted or C₁-C₆alkyl-substituted C₆-C₂₀aryl;

R₆ is hydrogen; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl;

the cyclohexene radical C is not substituted or substituted by one or more C₁-C₅alkyl;

n is from 2 to 4;

o is from 2 to 4;

if n = 2, in formula (1a)

R₁ is an alkylene, cycloalkylene or phenylene-radical; or R₁ and R₂ simultaneously form an alkylene, cycloalkylene or phenylene radical; and

R₃ is a cyano group or -Q₁-R₅; or R₃ and R₄ together form a 5- to 7-membered, monocyclic carbocyclic ring, which is optionally interrupted by -O- or -NR₇-;

If o = 2, in formula (1b)

R₃ is an alkylene, cycloalkylene or phenylene radical, which is optionally substituted with C₁-C₄alkyl, C₁-C₄alkoxy, -COR₆, -COOR₆ or -CONHR₆; and

R₁ is hydrogen; a cyano group; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl; or R₁ and R₂ together with the nitrogen atom linking them form a -(CH₂)_m- ring which is optionally interrupted by -O- or by -NR₇-;

R₇ is hydrogen; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl;

m is a number from 3 to 7;

if n = 3, in formula (1a)

R_1 is a trivalent alkyl group, which is optionally interrupted by one or more $-O-$ or $-NR_7-$ groups; and

R_3 is a cyano group or $-Q_1-R_5$; or R_3 and R_4 together form a 5- to 7-membered, monocyclic carbocyclic ring;

if $o = 3$, in formula (1b)

R_3 is an alkylidene, cycloalkylidene or phenylidene radical; and

R_1 is hydrogen; a cyano group; C_1-C_{22} alkyl; cyclo- C_3-C_8 alkyl; unsubstituted or C_1-C_6 alkyl- or C_1-C_6 alkoxy-substituted C_6-C_{20} aryl; or R_1 and R_2 together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by $-O-$ or by $-NR_7-$;

if $n = 4$, in formula (1a)

R_1 is a tetravalent alkyl group; and

R_3 is a cyano group; or $-Q_1-R_5$; or R_3 and R_4 together form a 5- to 7-membered, monocyclic carbocyclic ring;

if $n = 4$, in formula (1b)

R_3 is a tetravalent alkyl group; and

R_1 is hydrogen; a cyano group; C_1-C_{22} alkyl; cyclo- C_3-C_8 alkyl; unsubstituted or C_1-C_6 alkyl- or C_1-C_6 alkoxy-substituted C_6-C_{20} aryl; or R_1 and R_2 together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by $-O-$ or by $-NR_7-$;

in protecting human and animal hair and skin from UV radiation.

2. Use according claim 1, wherein in formula (1a)

R_1 is defined as in formula (1a);

R_2 is hydrogen;

R_3 is a cyano group;

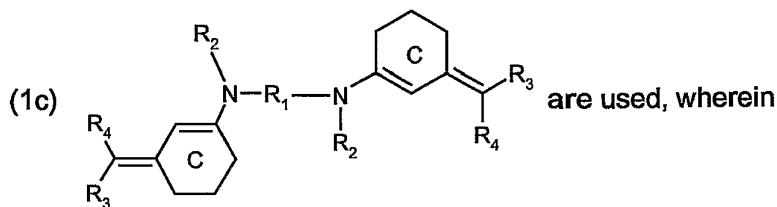
R_4 is $-CONHR_5$; and

R_5 is C_1-C_{22} alkyl; or C_6-C_{20} aryl.

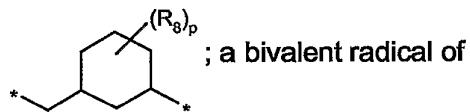
3. Use according to claim 1, wherein

if $n = 2$,

compounds of formula



R_1 is a $-(CH_2)_m-$ group, not substituted or substituted with one or more than one C_1-C_5 radicals; a bivalent radical of formula (1a₁)



formula (1a₂) ; or R_1 and R_2 together with the 2 linking nitrogen atoms form

a bivalent radical of formula (1a₃) ;

R_8 is hydrogen; or C_1-C_5 alkyl;

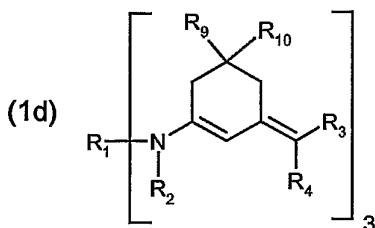
R_3 is a cyano group; or $-Q_1-R_5$;

p is a number from 0 to 3;

the cyclohexene radical C is not substituted or substituted by one or more C_1-C_5 alkyl; and

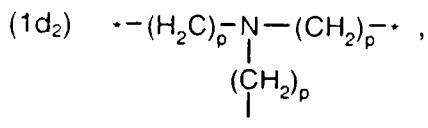
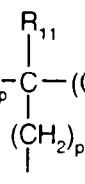
R_2 , R_4 , R_5 , Q_1 and m are defined as in claim 1.

4. Use according to claim 1, wherein compounds of formula



are used, wherein

R₁ is a trivalent radical of formula (1d₁) $\cdot\text{--}(\text{H}_2\text{C})_p\text{--}\overset{\cdot}{\underset{\cdot}{\text{C}}}\text{--}(\text{CH}_2)_p\text{--}\cdot\cdot$; or



R₂ is hydrogen; or C₁-C₅alkyl;

R₃ and R₄, independently from each other are a cyano group; or -Q₁-R₅;

Q₁ is -COO-; -CONH-; -CO-; -SO₂-; -CONR₁₂-;

R₅ is C₁-C₅alkyl;

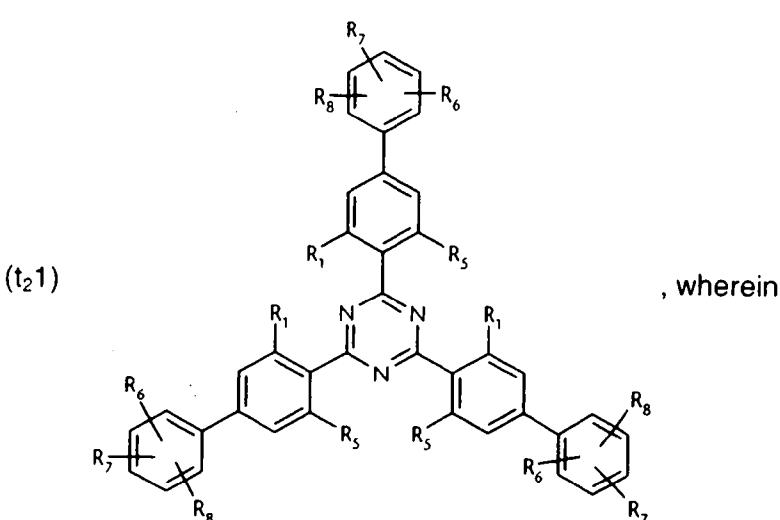
R₉ and R₁₀ independently from each other are C₁-C₄alkyl;

R₁₁ and R₁₂ independently from each other are hydrogen; or C₁-C₅alkyl; and

p is a number from 0 to 5.

5. Use according to any one of claims 1 to 4, wherein an additional UV absorber is used.

6. Use according to claim 5 wherein the additional UV absorber is selected from the triazine compounds of formula

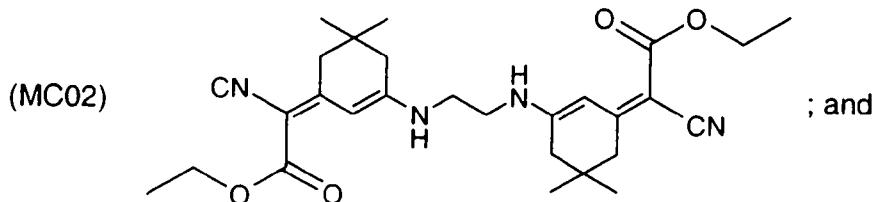


R₁ and R₅ are hydrogen; C₁-C₁₈alkyl; or C₆-C₁₂aryl; and

R₆, R₇ and R₈, independently from each other are hydrogen; hydroxy; halogen; C₁-C₁₈alkyl; C₁-C₁₈alkoxy; C₆-C₁₂aryl; biphenyl; C₆-C₁₂aryloxy; C₁-C₁₈alkylthio; carboxy; -COOM; C₁-C₁₈-alkylcarboxyl; aminocarbonyl; or mono- or di-C₁-C₁₈alkylamino; C₁-C₁₀acylamino; or -COOH.

7. Use according to claim 6, wherein a UV filter combination comprising

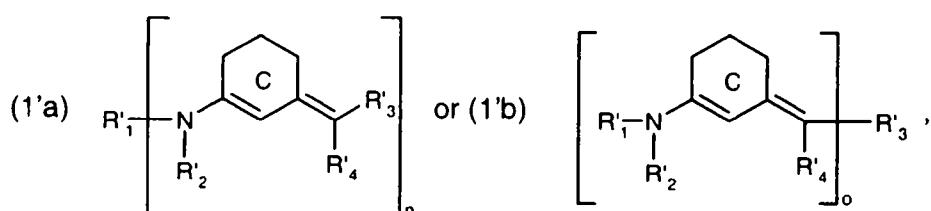
(t₃) the compound of formula



(t₄) 1,3,5-Triazine, 2,4,6-tris[1,1'-biphenyl]-4-yl- (9CI).

is used.

8. Compounds of formula



R₂' is hydrogen; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₂₀aryl; a cyano group; or R₁', and R₂' together with the nitrogen atom linking them form a -(CH₂)_m- ring which is optionally interrupted by -O- or by -NR₇;

R'_4 is $-Q'_1 - R'_5$:

Q'_1 is $-COO-$; $-CONH-$; $-CO-$; $-SO_2-$; or $-CONR'$.

R₅ is C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; or unsubstituted or C₁-C₆alkyl-substituted C₆-C₂₀aryl;

R'_6 is hydrogen; C_1-C_{22} alk
substituted C_6-C_7 aryl;

R₇ is hydrogen; C₁-C₂₂alkyl; cyclo-C₃-C₈alkyl; unsubstituted or C₁-C₆alkyl- or C₁-C₆alkoxy-substituted C₆-C₁₂aryl;

the cyclohexene radical C is not substituted, $\rho = 0$ with $\rho = 0$.

THE CYCLOHEXENE RING

WISDOMS 107,

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is from 2 to 4,

R' is an alkylene, cycloalkylene or phenylene-radical; or R'₁ and R'₂ simultaneously form an alkylene, cycloalkylene or phenylene-radical.

R'_3 is a cyano group or $-Q'_1-R'_5$; or R'_3 and R'_4 together form a 5- to 7-membered, mono-cyclic ring system;

If $\alpha = 2$, in formula (1'b)

R'_3 is an alkylene, cycloalkylene or phenylene radical; and

R'_1 is hydrogen; a cyano group; C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; unsubstituted or C_1 - C_6 alkyl- or C_1 - C_6 alkoxy-substituted C_6 - C_{20} aryl; or R'_1 and R'_2 together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by $-O-$ or by $-NR'_7-$;

if $\alpha = 3$, in formula (1'a)

R'_1 is a trivalent alkyl group, which is optionally interrupted by one or more $-O-$ or $-NR'_7-$ groups; and

R'_3 is a cyano group or $-Q'_1-R'_5$; or R'_3 and R'_4 together form a 5- to 7-membered, monocyclic carbocyclic ring;

if $\alpha = 3$, in formula (1'b)

R'_3 is an alkylidene, cycloalkylidene or phenylidene radical; and

R'_1 is hydrogen; a cyano group; C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; unsubstituted or C_1 - C_6 alkyl- or C_1 - C_6 alkoxy-substituted C_6 - C_{20} aryl; or R'_1 and R'_2 together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by $-O-$ or by $-NR'_7-$;

if $\alpha = 4$, in formula (1'a)

R'_1 is a tetravalent alkyl group; and

R'_3 is a cyano group or $-Q'_1-R'_5$; or R'_3 and R'_4 together form a 5- to 7-membered, monocyclic carbocyclic ring;

if $\alpha = 4$, in formula (1'b)

R'_3 is a tetravalent alkyl group; and

R'_1 is hydrogen; a cyano group; C_1 - C_{22} alkyl; cyclo- C_3 - C_8 alkyl; unsubstituted or C_1 - C_6 alkyl- or C_1 - C_6 alkoxy-substituted C_6 - C_{20} aryl; or R'_1 and R'_2 together with the nitrogen atom linking them form a $-(CH_2)_m-$ ring which is optionally interrupted by $-O-$ or by $-NR'_7-$.

9. A cosmetic preparation comprising at least one compound of formula (1a) or (1b) according to claim 1 with cosmetically acceptable carriers or adjuvants.

10. Compounds of the formula (1'a) or (1'b) as defined in claim 8, substantially as hereinbefore described with reference to the Examples.