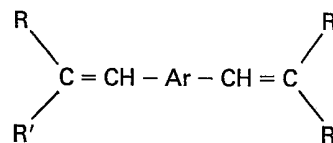


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(54) **Cosmetic compositions for protection against UV radiation**

(57) Cosmetic compositions contain at least one compound of the formula;



where Ar is an m- or p-phenylene or biphenylene optionally substituted by one or more halogen atoms, one or more C₁-C₆ alkyl or alkoxy groups,

R is -H, an ester group -COOR₁, and amide group -CONR₁R₂ or -CN;

R' is -COOR₁, or -CONR₁R₂; in addition when R is -H, R' can be -COOH or its salts,

R₁ is a linear, branched or cyclic, saturated or unsaturated carbon chain containing up to 18 carbon atoms, unsubstituted or substituted by one or more hydroxyl, alkoxy, amino or quaternary ammonium groups, R₂ is -H or a C₁-C₆ group, in a cosmetic medium. The compositions protect skin against UV rays or the agent protects the ingredients of the composition from UV rays.

SPECIFICATION

Cosmetic composition for protection against ultraviolet radiation and its use for this purpose

5 The present invention relates to a cosmetic composition employed as an agent for protecting, particularly human skin, against UV rays. 5

It is known that light rays of wavelengths between 280 and 400 nm permit the browning of human skin and that rays of wavelengths between 280 and 320 nm known under the term UV-B also cause erythemas and cutaneous burns which can be harmful to the development of a suntan.

10 The use of numerous compounds active in the abovementioned wavelengths range of 280 - 320 nm is already known. 10

It is also known that UV-A rays of wavelengths between 320 and 400 nm cause browning of the skin but can also cause a change in the latter, particularly in the case of a sensitive skin or skin continually exposed to solar radiation. It has been found that UV-A rays can augment the action of UV-B rays as has been described by several groups of workers and more particularly by J. WILLIS, A. KLIGMAN and J. EPSTEIN (The Journal of Investigative Dermatology, Vol. 59, no. 6, page 416, 1973) under the name of Photo augmentation. The UV-A rays promote the triggering of the erythemic reaction or augment this reaction in some individuals. Similarly, they can be the cause of phototoxic or photo-allergic reactions.

15 It has therefore appeared desirable to filter the UV-A rays as well. Compounds capable of filtering UV-A rays, particularly dibenzoylmethane derivatives, are known but the number of these compounds remains relatively limited. 20

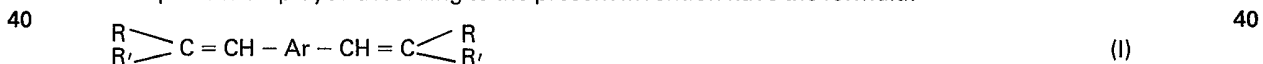
Furthermore, it has appeared advantageous to investigate compounds capable of absorbing UV rays over a wide range, to filter both the UV-A and UV-B rays. This is the case, for example, of the 3-para-oxybenzylidene-2-bornanones of French Patent Application 2,430,938 or of 3-cinnamylidene camphor of U.S. Patent 3,781,417. 25

It is also known that the components present in cosmetic preparations and in particular some colourants of dyeing compositions, coloured hair lacquers, shampoos, hair-setting lotions, makeup products such as tinted creams, nail varnishes and lipsticks, do not always have sufficient light stability and deteriorate under the effect of light radiations.

30 We have therefore investigated compounds capable of absorbing both the UV-A rays and the UV-B rays over the widest possible range of wavelengths and capable of providing protection both to human skin and to various products sensitive to UV radiations; these compounds should possess, in addition to good absorption qualities, good thermal and photochemical stability, as well as a wide range of solubilities in the media usually employed in cosmetics. 30

35 We have found, according to the present invention, that compounds of the formula (I) below have good filtering properties over a wide range of wavelengths extending from 270 to 400 nm and particularly from 305 to 360 nm, whilst possessing excellent thermal and photochemical stability and having the advantage of being neither toxic nor irritant and being harmless to the skin. 35

The compounds employed according to the present invention have the formula:



in which

45 Ar denotes an m- or p-phenylene or bi-phenylene radical capable of being substituted by one or more halogen atoms, or one or more C₁-C₆ lower alkyl or lower alkoxy groups, 45

R denotes a hydrogen atom, an ester group -COOR₁, an amide group -CONR₁R₂ or a nitrile (-CN) group,

R' denotes an ester group -COOR₁ or amide group -CONR₁R₂; in addition, when R denotes a hydrogen atom, R' can be an acid group -COOH or a salt thereof,

50 R₁ being a linear, branched or cyclic, saturated or unsaturated carbon chain, substituted if appropriate by one or more hydroxyl, alkoxy, amino or quaternary ammonium groups and capable of containing up to 18 carbon atoms, 50

R₂ being a hydrogen atom or a C₁-C₆ lower alkyl group.

Accordingly the present invention provides a cosmetic composition containing as an agent for protecting against the UV rays at least one compound of the formula (I) above in a cosmetically acceptable medium.

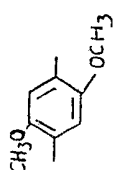
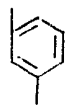
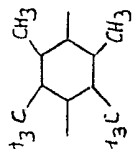
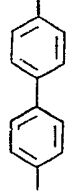
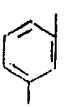
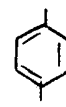
55 Another subject of the present invention is a process for protecting human skin against solar radiation, and particularly the UV-A and/or UV-B rays. 55

In the formula (I) above, the halogen atoms are typically chlorine or bromine atoms, and are preferably chlorine atoms. The lower alkyl group is preferably a C₁-C₄ alkyl group and, in particular, a methyl, ethyl, propyl, isopropyl, butyl, isobutyl or tertiary butyl group. The lower alkoxy group is preferably a C₁-C₄ group and more particularly denotes a methoxy, ethoxy, propoxy or butoxy group. 60

The radical R₁ preferably designates a C₁-C₁₀ radical such as an n-butyl, menthyl, n-octyl, 2-ethylhexyl, 2-hydroxyethyl, 2-ethoxyethyl, 2,3-dihydroxypropyl, 2-aminoethyl, 2-dimethylaminoethyl, 2-diethylaminoethyl, 3-dimethylaminopropyl, or 3-diethylaminopropyl radical or a corresponding quaternary ammonium salt.

Compounds of the formula (I) preferably employed in the cosmetic composition of the invention are the compounds No. 1 to 16 in the following table. This table gives the wavelengths corresponding to the absorption maximum of these compounds (λ_{\max}) as well as their molar extinction coefficient (ϵ) and their analysis.

Compound No.	Ar	R	R'	R ₁	R ₂	Absorption U.V. (nm)	Analysis
1		H	CO ₂ H	-	-	DMSO $\lambda_{\max} = 320 \text{ nm}$ ($\epsilon = 41.300$)	Dosage TBA OH ^o Theory : 9,16 meq/g Found : 9,35 meq/g
2		H	CO ₂ H	-	-	DMSO $\lambda_{\max} = 330 \text{ nm}$ ($\epsilon = 44.000$)	Dosage TBA OH ^o Theory : 6,78 meq/g Found : 6,79 meq/g
3		CO ₂ R ₁	CO ₂ R ₁	n-butyl	-	CHCl ₃ $\lambda_{\max} = 323 \text{ nm}$ ($\epsilon = 37.000$)	Theory Found %C: 67,90 %C: 67,85 %H: 7,98 %H: 8,09
4		CO ₂ R ₁	CO ₂ R ₁	n-butyl	-	CHCl ₃ 395nm($\epsilon = 11.600$) $\lambda_{\max} = 305 \text{ nm}$ ($\epsilon = 20.100$)	Theory Found %C: 65,05 %C: 64,99 %H: 7,85 %H: 7,89
5		CO ₂ R ₁	CO ₂ R ₁	2-ethyl-hexyl	-	CHCl ₃ $\lambda_{\max} = 318 \text{ nm}$ ($\epsilon = 34.200$)	Theory Found %C: 73,17 %C: 73,11 %H: 9,88 %H: 9,93
6		H	CO ₂ R ₁	2-ethyl-hexyl	-	CHCl ₃ $\lambda_{\max} = 325 \text{ nm}$ ($\epsilon = 42.700$)	Theory Found %C: 75,98 %C: 75,96 %H 9,56 %H: 9,65
7		CN	CO ₂ R ₁	ethyl	-	CHCl ₃ $\lambda_{\max} = 345 \text{ nm}$ ($\epsilon = 43.800$)	Theory Found %C: 66,67 %C: 66,65 %H: 4,93 %H: 4,97
8		CN	CO ₂ R ₁	2-ethyl-hexyl	-	CHCl ₃ $\lambda_{\max} = 348 \text{ nm}$ ($\epsilon = 45.000$)	Theory Found %N: 8,56 %N: 8,64 %C: 73,14 %C: 73,24 %H: 8,18 %H: 8,12 %N: 5,69 %N: 5,62
9		CN	CO ₂ R ₁	menthyl	-	Theory CHCl ₃ $\lambda_{\max} = 340 \text{ nm}$ ($\epsilon = 48.000$)	Found %C: 74,97 %C: 74,91 %H: 8,14 %H: 8,16 %N: 5,14 %N: 5,11
10		CONR ₁ R ₂	CONR ₁ R ₂	2-ethyl-hexyl	H	EtOH (nm) $\lambda_{\max} = 318 \text{ nm}$ ($\epsilon = 31.500$)	Theory Found %C: 73,55 %C: 73,69 %H: 10,47 %C: 10,50 %N: 7,46 %N: 7,27

Compound No.	Ar	R	R'	R ₁	R ₂	Absorption U.V. (nm)	Analysis Dosage TBA OH ⁶
11		CONR ₁ R ₂	CONR ₁ R ₂	2-ethyl-hexyl	H	EtOH λ max = 305 nm (ε = 16.000) EtOH 380 nm λ max (ε = 14.300)	Theory Found %C: 71,07 %C: 70,32 %H: 10,19 %H: 10,23 %N: 6,91 %N: 6,57
12		CONR ₁ R ₂	CONR ₁ R ₂	2-ethyl-hexyl	H	EtOH = 278 nm λ max (ε = 14.200)	Theory Found %C: 73,55 %C: 73,37 %H: 10,47 %C: 10,56 %N: 7,46 %N: 7,52
13		CN	CONR ₁ R ₂	n-octyl	H	CHCl ₃ = 315 nm λ max (ε = 13.300)	Theory Found %C: 74,68 %C: 74,55 %H: 9,22 %H: 9,23 %N: 10,25 %N: 10,15
14		CONR ₁ R ₂	CONR ₁ R ₂	2-ethyl-hexyl	H	EtOH = 328 nm λ max (ε = 42.000)	Theory Found %C: 75,50 %C: 75,29 %H: 9,99 %H: 10,06 %N: 6,77 %N: 9,66
15		CONR ₁ R ₂	CN	n-octyl	H	CHCl ₃ = 296 nm λ max ε = 39070	Theory Found %C: 73,43 %C: 73,42 %H: 8,63 %H: 8,67 %N: 11,42 %N: 11,21
16		H	CONR ₁ R ₂	n-butyl	n-butyl	EtOH = 322 nm λ max ε = 38400	Theory Found %C: 71,95 %C: 71,94 %H: 10,06 %N: 10,08 %N: 5,99 %N: 5,86

The compounds of the formula (I) employed according to the invention are generally liposoluble except for the acids which, when neutralised, may be soluble in water.

The acids employed according to the invention such as those of Examples 1 and 2 can be obtained by condensing the corresponding dialdehydes, for example terephthalaldehyde or 4,4'-diformyldiphenyl, with malonic acid in pyridine in the presence of piperidine.

The diesters such as the compound of Example 6 can be obtained by esterifying the above acids with an alcohol in the presence of sulphuric acid.

The tetraesters such as the compounds of Examples 3 to 5 can also be prepared in known manner by condensing the corresponding dialdehyde, for example 2,5-dimethoxyterephthalaldehyde or terephthalaldehyde, with a malonate such as n-butyl malonate or 2-ethylhexyl malonate. The dialdehydes are commercial products or can be prepared by conventional methods, for example by chloromethylation followed by the Sommelet reaction. The malonates can be synthesized from malonic acid and the corresponding alcohols in benzene or toluene in the presence of sulphuric acid by eliminating the water formed in the course of the esterification.

The cyanoesters according to the invention such as those of Examples 7 to 9 can be prepared by the condensation of the corresponding dialdehydes with cyanoacetates in ethanol in the presence of potassium fluoride. The cyanoacetates can themselves be prepared by the esterification of cyanoacetic acid with the corresponding alcohols in toluene in the presence of sulphuric acid, or are commercial products.

The diamides according to the invention such as the compound of Example 16, can be obtained by reacting the chloride of the corresponding diacid with an amine in methylene chloride.

The tetra-amides according to the invention, such as the compounds of Examples 10 to 12 and 14, can be obtained by the condensation of a malonamide, for example N-2-ethylhexyl malonamide, with an aromatic dialdehyde, for example terephthalaldehyde, isophthalaldehyde, 2,5-dimethoxyterephthalaldehyde or 4,4'-diformyldiphenyl, in the presence of piperidine acetate in toluene under reflux over a period of about twenty hours.

The cyanoamides according to the invention, such as the compounds of Examples 13 and 15, can be obtained by the condensation of a cyanoacetamide, such as N-octylcyanoacetamide, with an aromatic dialdehyde such as tetramethyl terephthalaldehyde or isophthalaldehyde in ethanol, in the presence of potassium fluoride.

According to a first embodiment of the present invention the cosmetic composition forming the subject of the present application is a composition intended to protect human skin against ultraviolet rays. It can therefore be presented in the diverse forms usually employed for this type of composition. It can be presented, in particular, in the form of a solution, lotion, gel, an emulsion such as a cream or a milk, a solid stick or may be packaged as an aerosol.

It may also contain cosmetic adjuvants usually employed in this type of composition such as thickeners, softeners, humectants, super-fattening agents, emollients, wetting agents, surfactants, preservatives, anti-foams, perfumes, oils, waxes, colourants and/or pigments intended to colour the composition itself or the skin.

The compound of the formula (I) is present particularly in an amount, by weight, of 0.1 to 15% relative to the total weight of the composition.

A monoalcohol or a lower (typically of 1 to 6 carbon atoms) polyol or a mixture thereof or an aqueous alcohol solution may be employed as a solubilising solvent. The monoalcohols or polyols which are particularly preferred are ethanol, isopropanol, propylene glycol or glycerol.

In one embodiment of the invention the composition is an emulsion in the form of a protective cream or milk comprising, in addition to the compound of the formula (I), a fatty alcohol, ethoxylated or glycerolated fatty alcohol, fatty acid ester and particularly a fatty acid triglyceride, fatty acid, lanolin, natural or synthetic oil, or wax, in the presence of water.

In another embodiment the composition is a lotion such as an oil-alcohol lotion based on a lower alcohol such as ethanol, or a glycol such as propylene glycol and/or a polyol such as glycerol and a fatty acid ester such as a fatty acid triglyceride.

The composition of this invention can also be in the form of an aqueous-alcoholic gel comprising one or more lower alcohols such as ethanol, propylene glycol or glycerol, and a thickener, in the presence of water.

The cosmetic sunscreen compositions containing at least one compound of the formula (I) may also contain other sunlight filters specific for the UV-B radiation and/or the UV-A radiation and compatible with the compounds according to the invention. It is therefore possible to obtain a formulation filtering all of the UV-B and UV-A radiations.

The compounds according to the invention may be associated, in particular, with UV-B filters formed by liposoluble compounds or oils having filtering properties such as coffee oil. Suitable lipophilic UV-B sunlight filters which may be mentioned include salicylic acid derivatives such as 2-ethylhexyl salicylate, homomenthyl salicylate, derivatives of cinnamic acid such as 2-ethylhexyl p-methoxycinnamate, 2-ethoxyethyl p-methoxycinnamate, derivatives of p-aminobenzoic acid such as amyl p-aminobenzoate, 2-ethylhexyl p-dimethylaminobenzoate, benzophenone derivatives such as 2-hydroxy-4-methoxybenzophenone, camphor derivatives such as 3-(4'-methylbenzylidene) camphor, if appropriate in combination with 4-isopropylidibenzoyl methane or 3-benzylidene camphor.

Suitable water-soluble sunlight filters filtering the UV-B rays which may be used with the liposoluble or water-soluble filters of the invention, provided they are compatible with the latter, include the benzylidene camphor derivatives described in French Patents No. 2,199,971, 2,236,515 and 2,383,904 and, more particularly, 4-(2-oxo-3-bornylidenemethyl)-phenyltrimethylammonium methylsulphate, and the salts of 4-(2-oxo-3-bornylidenemethyl)benzenesulphonic acid, 2-methyl-5-(2-oxo-3-bornylidenemethyl) benzenesulphonic acid and 2-phenylbenzimidazole-5-sulphonic acid.

The compounds used in this invention may also be associated with UV-A filters among which there may be mentioned dibenzoylmethane derivatives.

The sunscreen compositions according to the invention may be presented in the form of solutions, lotions, emulsions such as a cream or a milk, in the form of oils, oily gels, aqueous-alcoholic or alcoholic gels, or may be packaged as aerosols or solid sticks. They may incorporate the abovementioned cosmetic adjuvants usually employed in compositions of this type.

The present invention also provides cosmetic compositions, coloured or uncoloured, containing at least one compound of the formula (I) as an agent for protection against ultraviolet rays.

These compositions may be in the form of, say, haircare compositions such as hair lacquers, hairsetting and, if appropriate, conditioning or untangling lotions, shampoos, colouring shampoos, hair dyeing compositions, makeup products such as nail varnishes, skin conditioning creams, foundations, or lipsticks, as well as any other cosmetic compositions which, on account of its constituents, may present problems of stability to light during storage.

The invention also provides a process for protecting human skin against UV-A rays and/or UV-B rays consisting in applying to the skin an effective quantity of a cosmetic composition containing at least one compound of the formula (I), associated if appropriate with other agents absorbing the UV-A and/or UV-B rays in a cosmetically acceptable medium.

The following Examples further illustrate the present invention.

25	<i>Example 1</i>		25
	<i>Protective day cream</i>		
	Compound No. 4: 2,5-dimethoxy-1,4-phenylene-bis(butyl α -carboxybutyl acrylate)	1 g	
	Polyoxyethyleneated fatty alcohols	7 g	
30	Fatty acid triglycerides	30 g	30
	Glycerol monostearate	2 g	
	Silicone oil	1.5 g	
	Cetyl alcohol	1.5 g	
	Preservatives	0.3 g	
35	Perfume	0.6 g	35
	Demineralised water q.s.	100 g	

To prepare this cream the fatty materials are heated to 80-85°C; the filter of formula (I) is added. Water is heated to 80-85°C and the fatty phase is added with vigorous stirring to the aqueous phase; stirring is continued for 10 to 15 minutes, then the mixture is allowed to cool with moderate stirring and the perfume is added at approximately 40°C.

	<i>Example 2</i>		
	<i>Protective day cream</i>		
45	Compound No. 7: p-phenylenebis(ethyl α -cyanoacrylate)	0.5 g	45
	Benzylidene camphor	0.5 g	
	Triglycerides of fatty acids (C ₈ to C ₁₂)	31 g	
	Glycerol monostearate	6 g	
	Stearic acid	2 g	
50	Cetyl alcohol	1.2 g	50
	Lanolin	4 g	
	Preservatives	0.3 g	
	Propanediol	2 g	
	Triethanolamine	0.5 g	
55	Perfume	0.5 g	55
	Demineralised water q.s.	100 g	

The fatty materials are heated to 80-85°C and the filters are added; the fatty phase is added with vigorous stirring to water (containing the water-soluble compounds) previously heated to 80-85°C. After 15 minutes vigorous stirring, the mixture is allowed to cool with moderate stirring.

*Example 3**Protective milk*

	Compound No. 3: p-phenylenebis(butyl α -carboxybutyl acrylate)	0.5 g	
	Octyl p-dimethylaminobenzoate	0.5 g	
5	Cetyl stearyl alcohol	2 g	5
	Cetyl alcohol	2 g	
	Triglycerides of fatty acids (C ₈ to C ₁₂)	20 g	
	Lanolin	4 g	
	Stearic acid	0.5 g	
10	Preservatives	0.3 g	10
	Carbopol 934 (crosslinked polyacrylic acid sold by the GOODRICH CHEMICAL Company)	0.15g	
	Triethanolamine	0.2 g	
	Perfume	0.4 g	
	Demineralised water q.s.	100 g	
15			15

The emulsion is prepared in the same manner as in Example 1.

*Example 4**Oil-alcohol sunscreen lotion*

20	Compound No. 5: phenylenebis(2-ethylhexyl α -carboxy-2-ethylhexylacrylate)	3.5 g	20
	2-Ethylhexyl p-methoxycinnamate	2 g	
	Perfume	0.5 g	
	96° ethanol	47.5 g	
	Triglycerides of fatty acids (C ₈ to C ₁₂)q.s.	100 g	
25			25

The mixture of the various components is heated to 40-45°C to homogenise and produce a clear lotion.

*Example 5**Sunscreen cream*

30	Compound No. 6: p-phenylenebis(2-ethylhexyl acrylate)	3 g	30
	4-[(2-Oxo-3-bornylidene)-methyl]-phenyl trimethylammonium methyl sulphate	2.5 g	
	Polyoxyethyleneated fatty alcohols	7 g	
	Triglycerides of fatty acids (C ₈ -C ₁₂)	30 g	
	Glycerol monostearate	2 g	
35	Silicone oil	1.5 g	35
	Cetyl alcohol	1.5 g	
	Preservatives	0.3 g	
	Perfume	0.6 g	
	Demineralised water q.s.	100 g	
40			40

The preparation of this cream is similar to that of Example 1; in this case the 4[(2-oxo-3-bornylidene)-methyl]-phenyl trimethylammonium methyl sulphate is dissolved in water

Example 6

45	<i>Sunscreen cream</i>		45
	Compound No. 4: 2,5-dimethoxy-1,4-phenylenebis-(butyl α -carboxybutylacrylate)	2.5 g	
	Benzylidene camphor	4 g	
	Triglycerides of fatty acids (C ₈ to C ₁₂)	31 g	
	Glycerol monostearate	6 g	
50	Stearic acid	2 g	50
	Cetyl alcohol	1.2 g	
	Lanolin	4 g	
	Preservatives	0.3 g	
	Propanediol	2 g	
55	Triethanolamine	0.5 g	55
	Perfume	0.4 g	
	Demineralised water q.s.	100 g	

The filters are dissolved in the fatty phase. The compound No. 4 may be replaced with 2.5 g of compound No. 3.

60

*Example 7**Sunscreen oil*

The following ingredients are mixed, and, if necessary, heated to 40-45°C for homogenising:

	Compound No. 5: p-phenylenebis(2-ethylhexyl α-carboxy-2-ethylhexylacrylate)	3 g	
5	Octyl p-dimethylaminobenzoate	3 g	5
	Cocoa butter	2.5 g	
	Antioxidants	0.05g	
	Perfume	0.5 g	
10	Triglycerides of fatty acids (C ₈ to C ₁₂)q.s.	100 g	10

*Example 8**Sunscreen gel*

	Compound No. 12: m-phenylenebis (α-carbamyl-2-ethylhexyl N-2-ethylhexylacrylamide)	2 g	
15	2-Ethylhexyl p-methoxycinnamate	2.5 g	15
	Cocoa butter	5 g	
	Antioxidants	0.05g	
	Silica	10 g	
	Perfume	0.5 g	
20	Triglycerides q.s.	100 g	20

This fatty gel is prepared by heating the fatty materials to 40-45°C and the silica is then added with vigorous stirring, followed by the filters.

25 *Example 9* 25*Aqueous-alcoholic sunscreen gel*

	Carbopol 934	0.7 g	
	Triethanolamine	0.35g	
	Propylene glycol	25 g	
30	96° ethanol	25 g	30
	Compound No. 1: p-phenylenebis-acrylic acid in the form of triethanolamine salt	1 g	
	Diethanolamine salt of p-methoxy-cinnamic acid	2.5 g	
	Preservative	0.3 g	
	Perfume	0.4 g	
35	Demineralised water q.s.	100 g	35

The Carbopol is dispersed in water with vigorous stirring, then triethanolamine is added, followed by the solvents and water in which the filters have previously been dissolved.

The same results are obtained by replacing the compound No. 1 by the compound No. 2 in the form of triethanolamine salt. 40 40

Examples 10 and 11

In these examples, the compounds of the formula (I) are employed to protect coloured compositions against the sun.

45 45

*Example 10**Coloured shampoo*

	Triethanolamine lauryl sulphate	10 g	
	0.05% strength solution of Orasol BLW blue	1 cc	
50	Compound No. 2: p-biphenylenebisacrylic acid in the form of triethanolamine salt	0.5 g	50
	Perfume, preservative q.s.		
	Water q.s	100 g	

55 *Example 11* 55*Coloured hairsetting lotion*

	Vinylpyrrolidone copolymer (of average molecular weight of 40,000, sold under the designation K30 by GAF)	2 g	
	CR 1 solid red W 3000 (CI No. 27,290)	0.02g	
60	Compound No. 11: 2,5-dimethoxy-1,4-phenylenebis(2-carbamyl-2-ethylhexyl N-2-ethylhexylacrylamide)	0.3 g	60
	96° ethanol	60 g	
	Water q.s.	100 g	

*Example 12**Sunscreen stick*

Compound No. 13: 2,3,5,6-tetramethyl-1,4-phenylenebis(α -cyano-N-octylacrylamide)	2 g	
Benzylidene camphor	2 g	
5 Carnauba wax	20 g	5
Ozokerite	20 g	
Lanolin	26 g	
Vaseline oil	30 g	
10 The fatty materials are melted and the filters are dispersed therein.		10

*Example 13**Sunscreen stick*

Compound No. 10: p-phenylenebis(α -carbonyl-2-ethylhexyl N-2-ethylhexylacrylamide)	1 g	
15 p-Methylbenzylidene camphor	1.5 g	15
Beeswax	12.5 g	
Ozokerite	28 g	
Carnauba wax	10 g	
Paraffin	10 g	
20 Lanolin	12 g	20
Paraffin oil	25 g	

Example 14

25 <i>Sunscreen oil</i>		25
Compound No. 15: m-phenylenebis(α -cyano-N-octylacrylamide)	1 g	
p-Methylbenzylidene camphor	2 g	
Cocoa butter	2.5 g	
Antioxidants, perfume q.s.		
30 Triglycerides of fatty acids, C ₈ -C ₁₂ q.s.	100 g	30

This oil is prepared in the same manner as in Example 7

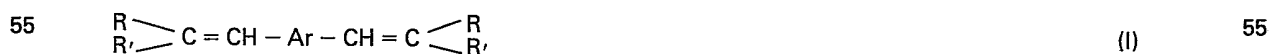
Example 15

35 <i>Protective day cream</i>		35
Compound No. 16: p-phenylenebis(N,N-dibutylacrylamide)	0.3 g	
Benzylidene camphor	0.3 g	
Triglycerides of fatty acids, C ₈ -C ₁₂	31 g	
Glycerol monostearate	6 g	
40 Stearic acid	2 g	40
Cetyl alcohol	1.2 g	
Lanolin	4 g	
Propanediol	2 g	
Triethanolamine	0.5 g	
45 Perfume, preservatives q.s.		45
Demineralised water q.s.	100 g	

This cream is prepared as in Example 2.

50 CLAIMS 50

1. A composition suitable for use in cosmetics which comprises at least one compound of the formula



in which

- 60 Ar denotes an m- or p-phenylene or biphenylene radical, optionally substituted by one or more halogen atoms, or C₁-C₆ alkyl or alkoxy groups, 60
- R denotes a hydrogen atom, an ester group -COOR₁, and amide group -CONR₁R₂ or a -CN group;
- R' denotes an ester group -COOR₁ or amide group -CONR₁R₂ or, where R denotes a hydrogen atom, in addition an acid group -COOH or a salt thereof,

R_1 being a linear, branched or cyclic, saturated or unsaturated, hydrocarbon radical containing up to 18 carbon atoms, optionally substituted by one or more hydroxyl, alkoxy, amino or quaternary ammonium groups,

R_2 being a hydrogen atom or a C_1-C_6 alkyl group, and a cosmetically acceptable diluent or carrier.

- 5 2. A composition according to Claim 1, in which R denotes a hydrogen atom and R' an acid group
-COOH or amide group -CONR₁R₂, or R denotes an amide group -CONR₁R₂ or -CN group and R' an ester
group COOR₁ or amide group -CONR₁R₂, or R denotes an ester group -COOR₁ and R' an amide group
-CONR₁R₂, R₁ and R₂ being as defined in Claim 1. 5
3. A composition according to Claim 1, in which the compound of the formula (I) is: p-phenylenebis(butyl
10 α -carboxybutylacrylate), 2,5-dimethoxy-1,4-phenylenebis(butyl α -carboxybutylacrylate), p-phenylenebis(2-ethylhexyl α -carboxy-2-ethylhexylacrylate) or p-phenylenebis(2-ethylhexylacrylate). 10
4. A composition according to Claim 2, in which the compound of the formula (I) is p-phenylenebis-
acrylic acid, p-biphenylenebis-acrylic acid, p-phenylenebis-(ethyl α -cyanoacrylate), p-phenylenebis-(2-
ethylhexyl α -cyanoacrylate), p-phenylenebis-(menthyl α -cyanoacrylate), p-phenylenebis-(α -carbonyl-2-
15 ethylhexyl N-2-ethylhexylacrylamide), 2,5-dimethoxy-1,4-phenylenebis(α -carbonyl-2-ethylhexyl N-2-ethylhexylacrylamide), 2,3,5,6-tetra-methyl-1,4-phenylenebis(α -cyano-N-octylacrylamide), p-biphenylene-
15 (α -carbonyl-2-ethylhexyl N-2-ethylhexylacrylamide), m-phenylene-bis(α -carbonyl-2-ethylhexyl N-2-ethylhexylacrylamide), m-phenylene-bis(α -cyano-N-octylacrylamide), or p-phenylene-bis(N,N-dibutylacrylamide).
5. A composition according to any one of Claims 1 to 4, in which the compound of the formula (I) is
20 present in an amount from 0.1 to 15% by weight relative to the total weight of the composition. 20
6. A composition according to any one of Claims 1 to 5, which additionally comprises one or more fatty
alcohols, ethoxylated or glycerolated fatty alcohols, fatty acid esters, fatty acids, lanolin, natural or synthetic
oils, or waxes.
7. A composition according to any one of Claims 1 to 6, which additionally comprises a monoalcohol or a
25 lower polyol or a mixture thereof. 25
8. A composition according to any one of Claims 1 to 7, which additionally comprises at least one
thickener, softening agent, super-fattening agent, emollient, humectant, wetting agent, surfactant, preserva-
tive, anti-foam agent, perfume, oil, wax, colourant and/or pigment.
9. A composition according to any one of Claims 1 to 8 which is in the form of an anti-sun composition
30 and comprises at least one compound of the formula (I) and one or more water-soluble or liposoluble
sunlight filters having a filtering effect in respect of the UV-B rays and/or one or more sunlight filters filtering
the UV-A rays. 30
10. A composition according to Claim 9 in which the sunlight filter is a camphor derivative, coffee oil, a
35 salicylic acid derivative, a cinnamic acid derivative a p-aminobenzoic acid derivative or a benzophenone
derivative or a benzoylmethane derivative. 35
11. A composition according to any one of Claims 1 to 8, which is in the form of a coloured or uncoloured
cosmetic composition, being a hair care composition, a make-up product or a cream for treating the skin.
12. A composition according to Claim 1 substantially as described in any one of the Examples.
- 40 13. A process for protecting human skin against ultraviolet rays, which comprises applying thereto a
composition as claimed in any one of Claims 1 to 10 and 12. 40