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Description

The present invention relates to novel compositions allowing photosensitive, thermosensitive and/or oxidation-sensitive compounds to be stabilised against the effects of ultraviolet radiation.

The present invention relates also to the use of said compositions for stabilising especially the colouring and/or the perfumes of a formulation, such as a cosmetic formulation.

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It is known that UV rays (wavelengths from 100 to 400 nm) can initiate free-radical chain reactions which lead to the decomposition of photosensitive molecules. The majority of cosmetic products are formulated with compounds that are sensitive to UV rays, in particular the colorants and perfumes. A portion of UV-B rays (290 to 320 nm) and UV-A rays (320 to 400 nm) can indeed affect the integrity of these photosensitive molecules. Products packed in transparent or semi-transparent packaging are particularly subject to exposure to UV rays. Standard untreated packaging (polyethylene, polypropylene, polyethylene terephthalate, glass, etc.) best protects the formulations from UV-B rays. It is therefore particularly important to provide protection for these products against UV-A.

20

There exists specific packaging which provides more effective protection, especially packaging made of anti-UV-treated polyethylene, polyethylene terephthalate, polypropylene or polyvinyl chloride, but its cost is very high, and phenomena of transfer of the UV filters from the packaging to the formulations are known.

25

A more economical solution consists in adding UV absorbers to the cosmetic formulation. However, these compounds must be chosen carefully in order to ensure protection over the entire UV spectrum, and especially from UV-A. In addition, some UV filters, such as avobenzene, are themselves photosensitive and must be stabilised by other UV absorbers. Finally, these UV absorbers must also be chosen with care in order to ensure that the physico-chemical properties of the formulations (such as colour, odour, transparency, etc.) into which they are incorporated are maintained and to stabilise them for a sufficiently long time to ensure the shelf life of the product.

35

US 7,150,876 describes the use of diethylhexyl syringylidenemalonate as a photostabilising agent for photosensitive compounds, especially avobenzone. However, this product can prove to be expensive.

- 5 US 2012/0039827 describes sunscreen compositions which can comprise ethylhexyl salicylate (A), butyl methoxydibenzoylmethane (B) and diethylhexyl syringylidenemalonate.

10 Accordingly, the object of the present invention is to provide compositions for stabilising photosensitive, thermosensitive and/or oxidation-sensitive compounds, such as colorants, perfumes, antioxidants or ultraviolet filters, against the effects of ultraviolet radiation, at reduced cost.

15 One of the objects of the invention is especially to provide novel compositions for stabilising the colouring and/or perfumes against the harmful effects of ultraviolet radiation.

20 Another object of the invention consists in using novel compositions for stabilising especially the colouring and/or the perfumes of a formulation such as a cosmetic formulation.

The inventors have advantageously shown that the stabilising composition according to the invention allows the colouring and/or the perfumes of a formulation to which it has been added to be stabilised. Better stabilisation has especially been
25 observed with the composition according to the invention comprising the association of three UV absorbers (also called ultraviolet absorber), as compared with compositions comprising only a single UV absorber or two UV absorbers.

30 These stabilisations of the colour and/or the perfumes have advantageously been obtained with a quantity of only approximately 0.3% of the composition according to the invention, which permits a valuable cost/effectiveness compromise.

The compositions according to the invention advantageously make it possible to avoid premature ageing of cosmetic formulations exposed to natural or artificial light,
35 to heat or to the air, which can cause phenomena of oxidation, reduction, catalysis,

etc. These compositions according to the invention therefore in particular allow cosmetic formulations packed in transparent packaging to be protected.

Composition

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The present invention relates to a composition for the stabilisation of at least one photosensitive composition chosen from colorants, perfumes, ultraviolet filters and antioxidants against the effects of ultraviolet radiation, said composition comprising an association of:

- 10
- at least one ultraviolet absorber (A) which is ethylhexyl salicylate;
 - at least one ultraviolet absorber (B) which is butyl methoxydibenzoyl-methane;
 - at least one ultraviolet absorber (C) which is diethylhexyl syringylidene-malonate (C);

15 in proportions of:

- from 70% to 75% by weight of ultraviolet absorber (A), based on the total weight of the ultraviolet absorbers (A), (B) and (C);

- from 15% to 20% by weight of ultraviolet absorber (B), based on the total weight of the ultraviolet absorbers (A), (B) and (C); and

20 - from 9% to 13% by weight of ultraviolet absorber (C), based on the total weight of the ultraviolet absorbers (A), (B) and (C).

Within the scope of the invention, and unless indicated otherwise, "ultraviolet absorber" (or UV absorber) is understood as meaning a chemical compound

25 capable of absorbing ultraviolet radiation in a range of between 4 and 400 nm, in particular between 200 and 400 nm, and very particularly between 290 and 400 nm (UV-A and UV-B).

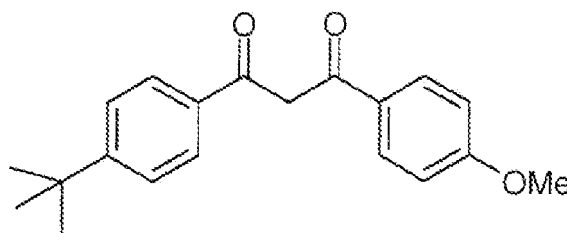
Within the scope of the invention, and unless indicated otherwise, "photosensitive

30 compound" is understood as meaning a compound which can be chemically degraded following exposure to UV radiation coming from natural or artificial light.

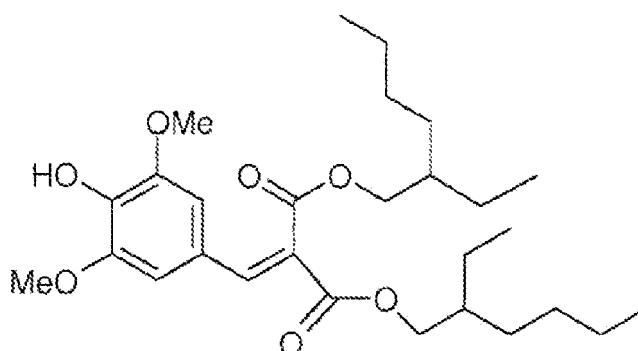
Within the scope of the invention, and unless indicated otherwise, "composition comprising at least one UV absorber" is understood as meaning a composition

35 comprising one UV absorber or a mixture of different UV absorbers.

4-(tert-Butyl)-4'-methoxydibenzoylmethane (also called butyl methoxydibenzoylmethane or avobenzene) has the following formula:



Diethylhexyl syringylidenemalonate has the following formula:



5

Ranges and ratios

The composition as defined hereinbefore comprises:

- 10 - from 70% to 75% by weight of ultraviolet absorber (A), based on the total weight of the ultraviolet absorbers (A), (B) and (C);
- from 15% to 20% by weight of ultraviolet absorber (B), based on the total weight of the ultraviolet absorbers (A), (B) and (C); and
- 15 - from 9% to 13% by weight of ultraviolet absorber (C), based on the total weight of the ultraviolet absorbers (A), (B) and (C).

According to one embodiment, the composition as defined hereinbefore comprises:

- from 71% to 73% by weight of ultraviolet absorber (A), based on the total weight of the ultraviolet absorbers (A), (B) and (C);
- 20 - from 15% to 19% by weight of ultraviolet absorber (B), based on the total weight of the ultraviolet absorbers (A), (B) and (C); and
- from 10% to 13% by weight of ultraviolet absorber (C), based on the total weight of the ultraviolet absorbers (A), (B) and (C).

According to another embodiment, the composition as defined hereinbefore comprises:

- 71.5% by weight of ultraviolet absorber (A), based on the total weight of the ultraviolet absorbers (A), (B) and (C);
- 17% by weight of ultraviolet absorber (B), based on the total weight of the ultraviolet absorbers (A), (B) and (C); and
- 11.5% by weight of ultraviolet absorber (C), based on the total weight of the ultraviolet absorbers (A), (B) and (C).

Other possible components

According to one embodiment, the composition according to the invention further comprises at least one antioxidant compound chosen from the group composed of:

- the thiols and derivatives; the phenols, polyphenols and derivatives, such as the flavonoids, the phenolic acids, the tannins, the anthocyanins; β -carotene (provitamin A); the tocopherols (vitamin E) or esters thereof, such as alpha-tocopherol, gamma-tocopherol, delta-tocopherol.

- According to one embodiment, the ratio between at least one antioxidant compound and the composition of the invention is from 1:15 to 1:1.

According to one embodiment, the composition according to the invention further comprises at least one compound having chelating properties chosen from the

- group composed of: ascorbic acid and its esters, such as sodium or calcium ascorbate; 5-6-diacetyl 1-ascorbic acid, 6-palmitoyl 1-ascorbic acid, citric acid and the citrates, such as those of sodium, potassium and calcium; tartaric acid and the tartrates, such as those of sodium, potassium; phytic acid and its salts; the diamino-tetracarboxylic acids such as edetic acid; butylhydroxyanisole and butylhydroxy-toluene; octyl or dodecyl gallates; sodium, potassium or calcium lactates; lecithins; glutathione; enzymes such as catalase, superoxide dismutases and some peroxydases.

According to one embodiment, the ratio between at least one compound having

- chelating properties and the composition of the invention is from 1:15 to 1:6.

According to one embodiment, the composition according to the invention further comprises at least one synthetic or bio-sourced surfactant chosen from the group composed of: the anionic surfactants, such as the carboxylic acid salts, the sulfonated derivatives, the sulfated derivatives and phosphated derivatives;
5 amphoteric surfactants, such as the betaines, the imidazoline derivatives, the polypeptides; and non-ionic surfactants, such as the non-ionic surfactants having an ester bond, an ether bond or an amide bond.

According to one embodiment, the ratio between the composition of the invention
10 and at least one surfactant is from 1:1 to 1:20.

According to one embodiment, the composition according to the invention further comprises at least one solvent chosen from the group composed of: hydrocarbons, especially the aliphatic or aromatic hydrocarbons or the halogenated hydrocarbons,
15 alcohols, glycols, ketones, esters, ethers and glycol ethers.

According to one embodiment, the ratio between the stabilising composition and at least one solvent is from 1:1 to 1:20.

20 According to one embodiment, the composition according to the invention is in liquid form.

Use

25 The present invention relates also to the use of a composition as described hereinbefore for stabilising photosensitive, thermosensitive and/or oxidation-sensitive compounds, such as colorants, perfumes, antioxidants or ultraviolet filters, against the effects of ultraviolet radiation.

30 According to the invention, among the photosensitive compounds there may be mentioned the ultraviolet filters, such as: 4-aminobenzoic acid (PABA), camphor benzalkonium methosulfate, homosalate, 2-hydroxy-4-methoxybenzophenone (benzophenone-3), phenylbenzimidazole sulfonic acid, terephthalylidene dicamphor sulfonic acid, butyl methoxydibenzoylmethane, benzylidene camphor sulfonic acid,
35 octocrylene, polyacrylamidomethyl benzylidene camphor, ethylhexyl methoxycinnamate, PEG-25 4-aminobenzoic acid, isoamyl p-methoxycinnamate, ethylhexyl

triazone, drometrizole trisiloxane, diethylhexyl butamido triazone, 4-methylbenzylidene camphor, 3-benzylidene camphor, ethylhexyl salicylate, ethylhexyl dimethyl PABA, 5-benzoyl-4-hydroxy-2-methoxybenzenesulfonic acid (benzophenone-4), 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid sodium salt (benzophenone-5),
5 methylene bis-benzotriazolyl tetramethylbutylphenol, disodium phenyldibenzimidazole tetrasulfonate, bis-ethylhexyloxyphenol methoxyphenyl triazine, polysilicone-15 or diethylamino hydroxybenzoyl hexyl benzoate.

According to one embodiment, the photosensitive compounds are colorants,
10 perfumes, antioxidants or ultraviolet filters.

According to one embodiment, the present invention relates to the use of a composition as described hereinbefore for stabilising the colouring of a formulation against the effects of ultraviolet radiation.

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According to one embodiment, the present invention relates to the use of a composition as described hereinbefore for stabilising the colorants of a formulation against the effects of ultraviolet radiation. According to one embodiment, the composition according to the invention makes it possible to avoid degradation of the
20 colouring of a formulation by ultraviolet radiation.

According to one embodiment, the present invention relates to the use of a composition as described hereinbefore for stabilising the perfumes of a formulation against the effects of ultraviolet radiation. According to one embodiment, the
25 composition according to the invention makes it possible to avoid degradation of the perfumes of a formulation by ultraviolet radiation.

As examples of perfume ingredients there may be mentioned those included in the list EPA Fragrance Ingredient List of 30 March 2012
30 (<http://www.epa.gov/opprd001/inerts/fmaingredient.pdf>).

As examples of colorants there may be mentioned the organic colorants or the natural colorants, such as madder, carmin soluble, caramel, chlorophyll or curcumin.

35 More particularly, there may be mentioned as colorants: Acid Black 1, Acid Black 52, Acid Blue 3, Acid Blue 9, Acid Blue 9 Ammonium Salt, Acid Blue 62, Acid Blue 74,

Acid Green 1, Acid Green 25, Acid Green 50, Acid Orange 6, Acid Orange 7, Acid
 Red 18, Acid Red 27, Acid Red 33, Acid Red 51, Acid Red 73, Acid Red 87, Acid
 Red 92, Acid Red 95, Acid Red 184, Acid Red 195, Acid Violet 9, Acid Violet 43,
 Acid Yellow 3, Acid Yellow 23, Acid Yellow 73, Basic Blue 6, Acid Yellow 73 Sodium
 5 Salt, Aka2, Aka3, Aka102, Aka104(1), Aka105(1), Aka106, Aka201, Aka202,
 Aka203, Aka204, Aka205, Aka206, Aka207, Aka208, Aka213, Aka214, Aka215,
 Aka218, Aka219, Aka220, Aka221, Aka22, Aka225, Aka226, Aka227, Aka228,
 Aka230(1), Aka230(2), Aka231, Aka232, Aka401, Aka404, Aka405, Aka501,
 Aka502, Aka503, Aka504, Aka505, Annatto, Anthocyanins, Ao1, Ao2, Ao201,
 10 Ao202, Ao203, Ao204, Ao205, Ao403, Ao404, Astaxanthin, Basic Blue 6, Basic Blue
 41, Basic Yellow 11, Beetroot, Blue 1, Blue 4, Brilliant Black 1, Bromocresol Green,
 Bromothymol Blue, Brown 1, Capsanthin/Capsorubin, Caramel, Carmine, Beta-
 Carotene, Carotenoids, Chlorophyllin-Copper Complex, CI 10006, CI 10020, CI
 10316, CI 11680, CI 11710, CI 11725, CI 11920, CI 12010, CI 12085, CI 12120, CI
 15 12150, CI 12370, CI 12420, CI 12480, CI 12490, CI 12700, CI 13015, CI 14270, CI
 14700, CI 14720, CI 14815, CI 15510, CI 15525, CI 15580, CI 15620, CI 15630, CI
 15800, CI 15850, CI 15865, CI 15880, CI 15980, CI 15985, CI 16035, CI 16185, CI
 16230, CI 16255, CI 16290, CI 17200, CI 18050, CI 18130, CI 18690, CI 18736, CI
 18820, CI 18965, CI 19140, CI 20040, CI 20170, CI 20470, CI 21100, CI 21108, CI
 20 21230, CI 24790, CI 26100, CI 27290, CI 27755, CI 28440, CI 40215, CI 40800, CI
 40820, CI 40825, CI 40850, CI 42045, CI 42051, CI 42053, CI 42080, CI 42090, CI
 42100, CI 42170, CI 42510, CI 42520, CI 42735, CI 44045, CI 44090, CI 45100, CI
 45190, CI 45220, CI 45350, CI 45370, CI 45380, CI 45396, CI 45405, CI 45410, CI
 45425, CI 45430, CI 47000, CI 47005, CI 50325, CI 50420, CI 51319, CI 58000, CI
 25 59040, CI 60724, CI 60725, CI 60730, CI 61565, CI 61570, CI 61585, CI 62045, CI
 69800, CI 69825, CI 71105, CI 73000, CI 73015, CI 73360, CI 73385, CI 73900, CI
 73915, CI 74100, CI 74160, CI 74180, CI 74260, CI 75100, CI 75120, CI 75125, CI
 75130, CI 75135, CI 75170, CI 75300, CI 75470, CI 75810, CI 77000, CI 77002, CI
 77004, CI 77007, CI 77015, CI 77120, CI 77163, CI 77220, CI 77231, CI 77267, CI
 30 77268:1, CI 77288, CI 77289, CI 77346, CI 77400, CI 77480, CI 77713, CI 77742,
 CI 77745, CI 77820, CI 77947, Cochineal, Crocus Sativus Flower Extract, Curry
 Red, Daidai201, Daidai203, Daidai204, Daidai205, Daidai206, Daidai207,
 Daidai401, Daidai402, Daidai403, Dihydroxyacetone, Direct Blue 86, Dunaliella
 Bardawil Powder, Erythulose, Ext. Violet 2, Ext. Yellow 7, Ext. Yellow 7 Lake, Fast
 35 Green FCF, Fluorescent Brightener 230, Fluorescent Brightener 236, Gardenia
 Florida Extract, Green 3, Green 5, Green 6, Green 8, Haematococcus Pluvialis

Powder, Haematoxylon Campechianum Wood Extract, Henna, Katsu201, Ki4, Ki5, Ki201, Ki202(1), Ki202(2), Ki203, Ki204, Ki205, Ki401, Ki402, Ki403(1), Ki404, Ki405, Ki406, Ki407, Kuro401, Lactoflavin, Lawsone, Midori3, Midori201, Midori202, Midori204,k Midori205, Midori401, Midori402, Murasaki201, Murasaki401, Natural
5 Red 26, Ninhydrin, Orange 4, Orange 5, Orange 10, Orange 11, Ponceau SX, Pyrophyllite, Red 4, Red 17, Red 21, Red 22, Red 27, Red 28, Red 30, Red 31, Red 33, Red 34, Red 36, Red 40, Solvent Green 3, Solvent Green 7, Solvent Orange 1, Solvent Red 1, Solvent Red 3, Solvent Red 23, Solvent Red 24, Solvent Red 43, Solvent Red 48, Solvent Red 49:1, Solvent Red 72, Solvent Red 73, Solvent Violet
10 13, Solvent Yellow 18, Solvent Yellow 29, Solvent Yellow 33, Solvent Yellow 44, Sunset Yellow, Vat Red 1, Violet 2, Yellow 5, Yellow 6, Yellow 7, Yellow 8, Yellow 10, Yellow 11.

According to a preferred embodiment there may be mentioned as colorants Blue 1
15 (CI 42090), Red 33 (CI 17200), Red 4 (CI 14700) and Ext. Violet 2 (CI 60730).

In particular, the present invention relates to the use of a composition as described hereinbefore for stabilising the colorants or the perfumes in all types of cosmetic formulations, more particularly care or hygiene products, perfumes or eaux de
20 toilette. Preferably, the cosmetic formulations are shampoos, shower gels, mouthwashes, lotions, serums or gels.

In order to protect the colouring from the effects of UV rays, the above-mentioned stabilising composition is added to a formulation in an appropriate quantity. That
25 quantity will depend on the nature of the colorants, on the nature of the perfume, on the presence of compounds which may cause phenomena of oxidation, reduction or catalysis, and on the presence of various photosensitive compounds, but also on the degree of exposure of the formulation to UV rays. It will therefore be dependent especially on the transparency of the container to UV rays and on the shelf life of the
30 formulation.

According to one embodiment, the composition according to the invention is introduced into a formulation in a content of from 0.01% to 3%, preferably from 0.05% to 2% and more particularly from 0.1% to 1% by weight, based on the total
35 weight of the formulation.

The present invention relates also to a method for stabilising photosensitive, thermosensitive and/or oxidation-sensitive compounds, such as colorants, perfumes, antioxidants or ultraviolet filters, said method comprising adding a stabilising composition as described hereinbefore to a formulation comprising said

5 photosensitive compounds.

Examples

Suppliers

- 10 - Ethylhexyl salicylate: Merck, Ashland, Symrise, DSM
- Avobenzene: Merck, Ashland, Symrise, DSM
- Diethylhexyl syringylidenemalonate: Merck
- Blue 1 (CI 42090): Sensient Cosmetic Technologies
- Red 33 (CI 17200): Sensient Cosmetic Technologies
- 15 - Red 4 (CI 14700): Sensient Cosmetic Technologies
- Ext. Violet 2 (CI 60730): Sensient Cosmetic Technologies
- Perfume I: Sensient Fragrances
- Perfume II: Sensient Fragrances
- Perfume III: Sensient Fragrances

20

Colorants

- A₁: Blue 1 – CI 42090
- B₁: Red 33 – CI 17200
- C₁: Red 4 – CI 14700
- 25 - D₁: Ext. Violet 2 – CI 60730

Perfumes

- Perfume I: vanilla note (commercial name: Vanilla)
- Perfume II: balsamic, spicy, musk notes (commercial name: Baby)
- 30 - Perfume III: floral, vanilla, amber notes (commercial name: Blue)

ORAC index measurement:

- 35 Spectrofluorimetric analysis carried out by mixing the sample with dilute fluorescein, at a temperature of 37°C, in a cuvette of the spectrophotometer. At t = 0, the free

radical source AAPH (2,2'-azobis(2-amidinopropane) dihydrochloride) was added to the mixture. The reduction in fluorescence was measured every 100 seconds.

Example 1: Preparation of the stabilising compositions

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The ethylhexyl salicylate was premixed with the diethylhexyl syringylidenemalonate, and then the mixture was heated to 45°C. The avobenzone was then incorporated into the mixture at the temperature of 45°C in small fractions, with stirring.

10 The following compositions were prepared:

Composition 1 (comparative)	%
Ethylhexyl salicylate	84.5
Avobenzone	8.5
Diethylhexyl syringylidenemalonate	7

Composition 2 (comparative)	%
Ethylhexyl salicylate	76
Avobenzone	17
Diethylhexyl syringylidenemalonate	7

Composition 3 (comparative)	%
Ethylhexyl salicylate	75.5
Avobenzone	8.5
Diethylhexyl syringylidenemalonate	16

Composition 4 (comparative)	%
Ethylhexyl salicylate	67
Avobenzone	17
Diethylhexyl syringylidenemalonate	16

Composition 5 (comparative)	%
Ethylhexyl salicylate	73.5
Avobenzone	14
Diethylhexyl syringylidenemalonate	11.5

15

Composition 6 (comparative)	%
Ethylhexyl salicylate	77
Avobenzone	11.5
Diethylhexyl syringylidenemalonate	11.5

Composition 7	%
Ethylhexyl salicylate	71.5
Avobenzone	17
Diethylhexyl syringylidenemalonate	11.5

Example 2: Preparation of foaming product formulations

- 5 Foaming product formulations were prepared using 0.1% of an aqueous 0.01% solution of a colorant A₁, B₁, C₁ or D₁; 0.1% of perfume I, II or III; and 0.3% of a stabilising composition chosen from one of stabilising compositions 1 to 7 above.

Foaming product formulation:

Formulation	% by weight, based on the total weight of the composition
Phase A	
Sodium lauryl ether sulfate (Texapon® NSO IS)	30
Cocamidopropyl betaine (Dehyton® K COS)	22.5
Phase B	
Stabilising composition	0.3
Preservative	0.3
Perfume	0.1
Phase C	
Sodium lauryl ether sulfate (Texapon® NSO IS)	10
Cocamidopropyl betaine (Dehyton® K COS)	7.5
Phase D	
Water	qs 100
Phase E	
0.01% aqueous colorant solution	0.1

10

Procedure:

- phases A, B and C were premixed independently of one another;
 - phase B was incorporated into phase C, and the whole was mixed;
 - 15 - the mixture of phases B and C obtained was in turn incorporated into phase A;
 - phase D was added slowly to the mixture of phases A, B and C;
 - once the mixture is homogeneous, phase E was added.
- 20 Several formulations were prepared by combining a perfume, a colorant and a stabilising composition as follows:
- perfume I + colorant A₁, B₁, C₁ or D₁ + composition 1 / 2 / 3 / 4 / 5 / 6 or 7
 - perfume II + colorant A₁, B₁, C₁ or D₁ + composition 1 / 2 / 3 / 4 / 5 / 6 or 7
 - perfume III + colorant A₁, B₁, C₁ or D₁ + composition 1 / 2 / 3 / 4 / 5 / 6 or 7

Each series was prepared in triplicate and placed:

- in darkness (controls);
- in a UV accelerated ageing chamber (Suntest) for 24 hours and 48 hours;
- 5 - in natural light.

The Suntest is a CPS+ model from Atlas / Ametek provided with a 1500 W xenon lamp equipped with a window glass filter which allows natural sunlight to be simulated behind glazing having a thickness of 3 mm. The lighting intensity was
10 fixed at its maximum level (60 W/m²).

After passing through the Suntest, the discoloration and degradation of the perfume were evaluated for each of the samples.

The discoloration was evaluated by means of a spectrophotometer in transmission
15 mode, CM-5 model from Konica Minolta. The ΔE values of the samples after 24 hours' and 48 hours' exposure to UV were measured. The ΔE value corresponds to the colour difference between the samples and the control (which has not been exposed to the Suntest) in the L*a*b colour space, according to the following formula:

$$20 \quad \Delta E^* = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}$$

where:

L_1, a_1, b_1 are the coordinates in the L*a*b colour space of the first colour to be
25 compared (control), and L_2, a_2, b_2 are those of the second (sample).

The smaller the ΔE values, the less the colouring of the formulations has degraded.

Results obtained for the formulations prepared using compositions 2, 4 and 7:

30

Perfume	Colorant	Time (h)	Control (ΔE)	Composition 2 (ΔE)	Composition 4 (ΔE)	Composition 7 (ΔE)
Perfume I	A ₁	24	47.23	3.9	3.65	2.73
		48	47.04	13.33	4.58	3.42
	B ₁	24	53.92	13.36	10.97	8.4
		48	53.66	29.46	21.38	21.93
	C ₁	24	33.78	1.95	2.68	2.3
		48	33.79	3.38	4.39	3.68

	D ₁	24	25.22	2.9	3.74	2.98
		48	24.66	15.67	10.56	11.45
Perfume II	A ₁	24	47.59	1.93	2.6	2.46
		48	46.91	34.61	21.61	10.95
	B ₁	24	53.7	13.51	11.1	10.81
		48	53.45	47.09	52.33	23.29
	C ₁	24	34.22	1.56	1.77	2.07
		48	34.21	3.51	3.52	3.64
	D ₁	24	26.81	1.95	2.44	2.9
		48	25.56	19.76	16.31	9.69
Perfume III	A ₁	24	48.77	2.19	2.47	2.29
		48	48.7	23.72	3.93	3.97
	B ₁	24	54.99	13.19	10.63	9.93
		48	54.91	53.03	19.01	20.4
	C ₁	24	33.99	1.45	1.57	1.57
		48	33.84	4.09	3.1	2.7
	D ₁	24	23.95	2.33	2.22	2.22
		48	23.49	18.34	6.59	7.56

Example 3, comparative: Comparison of foaming product formulations

- 5 The following compositions a, b and c were prepared:

Composition a	%
Ethylhexyl salicylate	83
Avobenzone	17

Composition b	%
Ethylhexyl salicylate	88.5
Diethylhexyl syringylidenemalonate	11.5

Composition c	%
Diethylhexyl syringylidenemalonate	100

- 10 Six different formulations were prepared using these compositions a, b and c, according to the procedure of Example 2, said formulations comprising perfume II and colorants B or D.

- 15 Compositions a and b were incorporated in an amount of 0.3% into the foaming product formulation, that is to say in the same proportions as the stabilising

compositions 2, 4 and 7. Composition c was incorporated in an amount of 0.15% into the foaming product formulation.

ΔE results obtained for the formulations prepared using compositions 2, 4, 7, a, b

5 and c:

Colorant B:

	Blank (without stabilising composition of the invention)	Composition					
		2	4	7	a	b	c
24 h	53.7	13.51	11.1	10.81	35.49	36.70	12.45
48 h	53.45	47.09	52.33	23.29	55.40	54.98	54.35

Colorant D:

	Blank (without stabilising composition of the invention)	Composition					
		2	4	7	a	b	c
24 h	26.81	1.95	2.44	2.9	12.81	25.98	5.46
48 h	25.56	19.76	16.31	9.69	26.36	30.34	18.12

10

These results demonstrated that the stabilising compositions according to the invention, comprising the association ethylhexyl salicylate/avobenzene/diethylhexyl syringylidenemalonate, permit better stabilisation of the colouring as compared with compositions comprising only the association of two compounds: ethylhexyl salicylate/avobenzene or ethylhexyl salicylate/diethylhexyl syringylidenemalonate.

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Composition c was incorporated in an amount of 0.15% into the foaming product formulation, which is close to the use percentage recommended by the supplier of the diethylhexyl syringylidenemalonate (0.10%). However, comparable, or even better, results were obtained, in terms of stabilisation of the colouring, with the stabilising compositions of the invention.

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The samples were evaluated as follows:

- 15

20

	Blank (without composition)	Composition 7	Composition c
Darkness	+++	+++	++
72 h Suntest	+	++	0

	Blank (without composition)	Composition 7	Composition c
Darkness	+++	+++	++
72 h Suntest	+	++	0

	Blank (without composition)	Composition 7	Composition c
Darkness	+++	+++	++
72 h Suntest	+	++	0

Example 5: Synergistic effect

The following compositions c, d and e were prepared:

5

Composition c	%
Diethylhexyl syringylidenemalonate	100

Composition d	%
Ethylhexyl salicylate	100

Composition e	%
Avobenzone	100

10 The ORAC index of composition no. 7 (Example 1) and of comparative compositions c, d and e was measured by spectrofluorimetry. The results are compiled in the following table:

Compositions	ORAC index ($\mu\text{mol Te/kg}$)
Composition no. 7 (Example 1)	102 240
Composition c (comparative, compound (C) on its own)	7430
Composition d (comparative, compound (A) on its own)	2013
Composition e (comparative, compound (B) on its own)	13487

15 The results show a synergistic effect of composition no. 7 according to the invention as compared with compositions c, d and e. The ORAC index of composition no. 7 (comprising the combination of ethylhexyl salicylate, avobenzone and diethylhexyl syringylidenemalonate) of 102 240 $\mu\text{mol Te/kg}$ in fact far exceeds the sum of the ORAC indices of compositions c, d and e:

20
$$71.5 \cdot 2013 / 100 + 17 \cdot 13487 / 100 + 11.5 \cdot 7430 / 100 = 4586.5 < 102\,240$$

The ORAC index allows the antioxidant nature of the compositions studied to be demonstrated. Thus, composition no. 7 advantageously has an antioxidant power which is greater than the sum of the oxidant powers of compositions c, d and e.

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Example 6: Comparative study

The following compositions f, g, h, i and j were prepared:

Composition f	%
Ethylhexyl salicylate	90
Avobenzone	5
Diethylhexyl syringylidenemalonate	5

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Composition g	%
Ethylhexyl salicylate	65
Avobenzone	30
Diethylhexyl syringylidenemalonate	5

Composition h	%
Ethylhexyl salicylate	70
Avobenzone	5
Diethylhexyl syringylidenemalonate	25

Composition i	%
Ethylhexyl salicylate	56
Avobenzone	22
Diethylhexyl syringylidenemalonate	22

Composition j	%
Homosalate	60
Avobenzone	20
Diethylhexyl syringylidenemalonate	20

- 15 These comparative compositions differ from the compositions according to the invention by virtue of the proportion of compounds (A), (B) or (C) and/or the nature of compound (A).

20 The ORAC index of composition no. 7 (Example 1) and of the comparative compositions f, g, h, i and j was measured. The results are compiled in the following table:

Compositions	ORAC index (μmol Te/kg)
Composition no. 7 (Example 1)	102 240
Composition f (comparative)	< 2000
Composition g (comparative)	< 2000
Composition h (comparative)	4810
Composition i (comparative)	3925
Composition j (comparative)	4270

The results show that composition no. 7 according to the invention has an ORAC index which is very much higher than that of the comparative compositions f, g, h, i and j. Thus, composition no. 7 advantageously has an antioxidant nature which is

5 far superior to that of compositions f, g, h, i and j.

P a t e n t k r a v

1. Sammensætning til stabilisering af mindst én lysfølsom forbindelse, der er udvalgt blandt farvestoffer, parfumer, ultraviolette filtre eller antioxidanter, mod virkningerne fra ultraviolette strålinger, hvor sammensætningen omfatter en kombination af ethyl-hexyl-salicylat (A), butylmethoxydibenzoylmethan (B) og diethylhexylsyringylidenmalonat (C) i følgende forhold:

- fra 70 til 75 vægt% af (A), i forhold til den samlede vægt af (A), (B) og (C);
- fra 15 til 20 vægt% af (B), i forhold til den samlede vægt af (A), (B) og (C); og
- fra 9 til 13 vægt% af (C), i forhold til den samlede vægt af (A), (B) og (C).

2. Sammensætning ifølge krav 1, omfattende:

- fra 71 til 73 vægt% af (A), i forhold til den samlede vægt af (A), (B) og (C);
- fra 15 til 19 vægt% af (B), i forhold til den samlede vægt af (A), (B) og (C); og
- fra 10 til 13 vægt% af (C), i forhold til den samlede vægt af (A), (B) og (C).

3. Sammensætning ifølge krav 2, omfattende

- 71,5 vægt% af (A), i forhold til den samlede vægt af (A), (B) og (C);
- 17 vægt% af (B), i forhold til den samlede vægt af (A), (B) og (C); og
- 11,5 vægt% af (C), i forhold til den samlede vægt af (A), (B) og (C).

4. Anvendelse af en sammensætning ifølge et hvilket som helst af kravene 1 til 3, til stabilisering af lysfølsomme, temperaturfølsomme og/eller oxidationsfølsomme forbindelser, så som farvestoffer, parfumer, antioxidanter eller ultraviolette filtre mod virkningerne fra ultraviolette strålinger.

5. Anvendelse ifølge krav 4, hvor de lysfølsomme forbindelser er farvestoffer eller parfumer.