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(54) **Title:** TOPICAL COMPOSITION

(57) **Abstract:** The present invention relates to the use of a phosphate ester emulsifier for reducing the cloth staining tendency of at least one UV filter substance selected from the group consisting of a triazine derivative, an amino substituted hydroxybenzophenone and/ or a benzotriazol derivative. Furthermore, the invention relates to topical compositions comprising a phosphate ester emulsifier and at least one benzotriazol and at least one UV filter substance selected from the group consisting of a triazine derivative and an amino substituted hydroxybenzophenone as well as mixtures thereof.

## Topical composition

The present invention relates to the use of a phosphate ester emulsifier for reducing the cloth staining tendency of at least one UV filter substance selected from the group consisting of a triazine derivative, an amino substituted hydroxybenzophenone and/ or a benzotriazol derivative. Furthermore, the invention relates to topical compositions comprising a phosphate ester emulsifier and at least one benzotriazol derivative and at least one UV filter substance selected from the group consisting of a triazine derivative and an amino substituted hydroxybenzophenone as well as mixtures thereof.

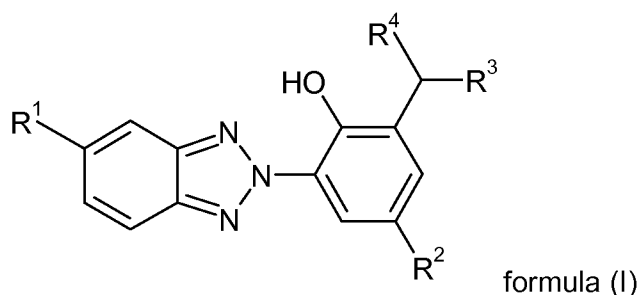
Sun care products have evolved considerably over the years. Earlier formulations were intended to protect the user from UV-B radiation as was once thought that UV-B rays were the most important contributors to wrinkling, skin disease, and skin cancer. However, more recent studies have shown that UV-A radiation is equally or even more important in the development of solar damage and skin diseases, such as lupus erythematosus and melanoma and non-melanoma skin cancer. Thus, today's focus is towards eliminating as much of UVA (320-400 nm) and / or UVB (280-320 nm) light as possible. Consequently, there's a constantly increasing need for sun care products exhibiting high SPF's (Sun Protection Factor) and high UVA protection while being photostable.

Triazine derivatives such as e.g. bis-ethylhexyloxyphenol methoxyphenyl triazine, benzotriazol derivates such as e.g. benzotriazolyl dodecyl p-cresol, dibenzoylmethane derivative such as e.g. methoxy dibenzoylmethane and amino substituted hydroxybenzophenone such as e.g. diethylamino hydroxybenzoyl hexyl benzoate have excellent UV-light absorbing properties and thus contribute significantly to the SPF of a sun care product. However, they have the problem that incorporated into sun care products they tend to stain clothes, which is highly undesirable, in particular as the yellow to brownish stains are not readily removable via conventional laundry.

It was therefore the object of the present invention to remedy the disadvantages of the prior art and to develop sun care products comprising triazine derivatives, benzotriazol derivates and/or amino substituted hydroxybenzophenone which exhibit a reduced cloth staining tendency. Furthermore, such compositions should favourably also exhibit a reduced stickiness resulting in a reduced affinity of sand to the skin.

Surprisingly, it has been found that the use of a phosphate ester emulsifier in contrast to other emulsifiers significantly reduced the staining tendency of these UV-filter substances as well as mixtures thereof on clothes. Furthermore, it has been found that the presence of  
 5 specific benzotriazol derivatives in such compositions resulted in a reduced stickiness.

Thus, the invention relates in one aspect to the use of a phosphate ester emulsifier for reducing the cloth staining tendency of at least one UV filter substance selected from the group consisting of triazine derivatives, an amino substituted hydroxybenzophenone and/ or  
 10 a benzotriazol derivative of formula (I)



wherein

R<sup>1</sup> is hydrogen; C<sub>1-5</sub>alkyl; C<sub>1-5</sub>alkoxy or halogen; preferably hydrogen or chloride; most preferably hydrogen;

15 R<sup>2</sup> is hydrogen; C<sub>1-20</sub>alkyl; C<sub>1-5</sub>alkoxy; C<sub>1-5</sub>alkoxycarbonyl; C<sub>5-10</sub>cycloalkyl; C<sub>6-10</sub>aryl or aralkyl; preferably hydrogen or C<sub>1-5</sub>alkyl; most preferably methyl;

R<sup>3</sup> is C<sub>1-20</sub>alkyl, C<sub>5-10</sub>cycloalkyl, C<sub>1-20</sub>alkoxy or C<sub>5-10</sub>cycloalkoxy, preferably C<sub>5-15</sub>alkyl or C<sub>5-15</sub>alkoxy; and

R<sup>4</sup> is hydrogen or C<sub>1-5</sub>alkyl; preferably hydrogen.

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Topical compositions comprising a phosphate ester emulsifier and at least one benzotriazol derivative of formula (I) and at least one UV filter substance selected from the group consisting of a triazine derivative and an amino substituted hydroxybenzophenone as well as mixtures thereof are novel per se.

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Thus, the invention also relates to a topical composition comprising a phosphate ester emulsifier and at least one benzotriazol derivative of formula (I), characterized in that the composition further comprises at least one UV filter substance selected from the group consisting of a triazine derivative and an amino substituted hydroxybenzophenone as well  
 30 as mixtures thereof.

In yet a further embodiment the invention relates to a method for reducing stains on clothes caused by the use of topical compositions comprising at least one UV filter substance selected from the group consisting of triazine derivatives, an amino substituted hydroxybenzophenone and/ or a benzotriazol derivative of formula (I), said method comprising the use of a phosphate ester emulsifier for the preparation of said topical composition and observing or appreciating the result. It is understood, that the stains are caused by the UV filter substance selected from the group consisting of triazine derivatives, an amino substituted benzophenones and/ or a benzotriazol derivative of formula (I).

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Another subject matter of the invention is directed to a method for reducing the sand adherence on skin after application of a topical composition comprising at least one UV filter substance selected from the group consisting of triazine derivatives, an amino substituted hydroxybenzophenone and a phosphate ester emulsifier, said method comprising the step of incorporating into said composition at least one benzotriazol derivative of formula (I), with all definitions and preferences as given above.

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In a particular preferred embodiment the compositions according to the present invention furthermore comprise a dibenzoylmethane derivative, such as particularly butyl methoxy dibenzoylmethane.

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The term "C<sub>x-y</sub>alkyl" as used herein refers to straight-chain or branched alkyl radicals having x to y carbon atoms such as e.g. methyl, ethyl, n-propyl, 1-methylethyl, n-butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylpropyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl, 1-ethyl-2-methylpropyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl or n-eicosyl without being limited thereto.

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The term C<sub>5-10</sub>cycloalkyl denotes to unsubstituted or C<sub>1-10</sub>alkyl (mono- or poly-)substituted, in particular C<sub>1-5</sub>alkyl (mono- or poly-)substituted cyclic, bicyclic or tricyclic hydrocarbon residues such as in particular cyclopentyl, cyclohexyl, cycloheptyl or decahydronaphthyl.

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Preferably, C<sub>5-10</sub>cycloalkyl denotes to unsubstituted or C<sub>1-2</sub>alkyl (mono- or poly-)substituted cyclopentyl, cyclohexyl or cycloheptyl such as in particular to unsubstituted or (mono- or poly-)methyl substituted cyclohexyl such as most in particular cyclohexyl or 3,3,5-trimethyl-cyclohexyl.

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The term "C<sub>x-y</sub>alkoxy" as used herein denotes to linear or branched alkoxy-, respectively unsubstituted or (mono- or poly-)substituted cycloalkoxy radicals having from x to y carbon atoms such as e.g. methoxy, ethoxy, propoxy, butyloxy or pentyloxy, 2,5,5-trimethylhexyloxy, 3,5,5-trimethylhexyloxy, isoamyloxy, 2-ethylhexyloxy or 3,3,5-

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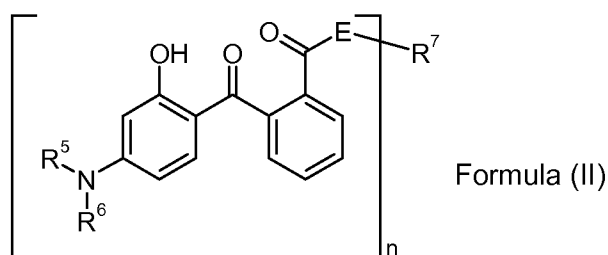
The term C<sub>6-10</sub>aryl refers e.g. to naphthyl or phenyl radicals, preferably phenyl.

The term "cloth" as used herein refers to any textile product made of materials such as

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Particular suitable amino substituted hydroxybenzophenone derivatives encompass

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wherein

R<sup>5</sup> and R<sup>6</sup> independently of each other are hydrogen; C<sub>1</sub>-C<sub>20</sub>alkyl; C<sub>2</sub>-C<sub>20</sub>alkenyl; C<sub>5</sub>-C<sub>10</sub>cycloalkyl or C<sub>5</sub>-C<sub>10</sub>cycloalkenyl; or R<sup>5</sup> and R<sup>6</sup>, together with the nitrogen atom they are

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bound to, form a 5 to 6 membered ring;

n is an integer from 1 or 2;

E is -O- or -N(R<sup>8</sup>)-and

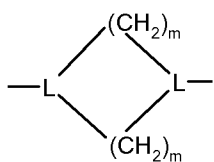
R<sup>8</sup> is hydrogen; C<sub>1</sub>-C<sub>5</sub>alkyl; or C<sub>1</sub>-C<sub>5</sub>hydroxyalkyl;

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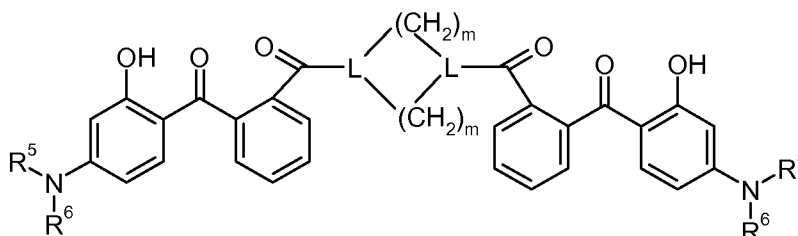
with the proviso that

- when  $n = 1$  then  $R^7$  is  $C_1$ - $C_{20}$ alkyl;  $C_2$ - $C_{20}$ alkenyl;  $C_1$ - $C_5$ hydroxyalkyl;  $C_5$ - $C_{10}$ cycloalkyl;  $C_5$ - $C_{10}$ cycloalkenyl;  $C_{6-10}$ aryl; or aralkyl optionally substituted by O, N or S; or a  $C_1$ - $C_5$  aminocarbonyl or alkylcarbonyl radical;

- when  $n = 2$  then  $R^7$  is an  $C_1$ - $C_{20}$ alkyl;  $C_5$ - $C_{10}$ cycloalkyl-;  $C_2$ - $C_{20}$ alkenyl- or aryl-diradical or  
 5  $R^7$  with E forms a diradical of formula (III) resulting in a compound of formula (IV)



formula (III)



formula (IV)

wherein L is N (nitrogen) and  
 m is an integer between 1 and 3.

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A particular suitable amino substituted hydroxybenzophenone derivative according to the present invention is diethylamino hydroxybenzoyl hexyl benzoate [IUPAC Name: Hexyl 2-[4-(diethylamino)-2-hydroxybenzoyl]benzoate] sold under the tradename Uvinul<sup>®</sup> A plus by BASF SE Ludwigshafen.

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Another suitable amino substituted hydroxybenzophenone derivative according to the present invention is 1,1'-(1,4-piperazinediyl)bis[1-[2-[4-(diethylamino)-2-hydroxybenzoyl]phenyl]-methanone [CAS No 919803-06-8] which is e.g. disclosed in WO 2007071584.

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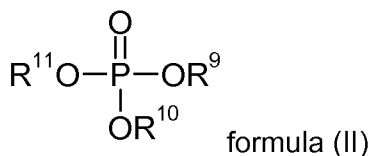
Compounds according to formula (II) and their preparation are e.g. disclosed in EP1046391, EP1133980, DE10012408 and WO 2007071584.

Particularly suitable triazine derivatives are ethylhexyl triazone (Uvinul<sup>®</sup> T-150), diethylhexyl butamido triazone (Uvasorb<sup>®</sup> HEB) and bis-ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb<sup>®</sup> S) such as most preferably bis-ethylhexyloxyphenol methoxyphenyl triazine.

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Particular suitable phosphate esters emulsifiers are compounds of formula (II)

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wherein R<sup>9</sup>, R<sup>10</sup> and R<sup>11</sup> may be hydrogen, an alkyl of from 1 to 22 carbons, preferably from 12 to 18 carbons; or an alkoxyated alkyl having 1 to 22 carbons, preferably from 12 to 18 carbons, and having 1 or more, preferably from 2 to 25, most preferably 2 to 12, moles ethylene oxide, with the provision that at least one of R<sup>9</sup>, R<sup>10</sup> and R<sup>11</sup> is an alkyl or alkoxyated alkyl as previously defined but having at least 6 alkyl carbons in said alkyl or alkoxyated alkyl group.

Monoesters in which R<sup>9</sup> and R<sup>10</sup> are hydrogen and R<sup>11</sup> is selected from alkyl groups of 10 to 18 carbons and alkoxyated fatty alcohols of 10 to 18 carbons and 2 to 12 moles ethylene oxide are preferred. Among the preferred phosphate ester emulsifier are C<sub>8-10</sub> Alkyl Ethyl Phosphate, C<sub>9-15</sub> Alkyl Phosphate, Cetareth-2 Phosphate, Cetareth-5 Phosphate, Ceteth-8 Phosphate, Ceteth-10 Phosphate, Cetyl Phosphate, C<sub>6-10</sub> Pareth-4 Phosphate, C<sub>12-15</sub> Pareth-2 Phosphate, C<sub>12-15</sub> Pareth-3 Phosphate, DEA-Cetareth-2 Phosphate, DEA-Cetyl Phosphate, DEA-Oleth-3 Phosphate, Potassium cetyl phosphate, Deceth-4 Phosphate, Deceth-6 Phosphate and Trilaureth-4 Phosphate. A particular advantageous phosphate ester emulsifier according to the invention is potassium cetyl phosphate e.g. commercially available as Amphisol® K at DSM Nutritional Products Ltd Kaiseraugst as the overall staining tendency of the UV filter substances or mixtures thereof such as in particular the benzotriazol derivative is decreased.

The amount of the at least one benzotriazol derivative of formula (I) in the compositions according to the present invention is preferable selected in the range of 1 to 20 wt.-%, such as preferably 2 to 20 wt.-%, such as more preferably in the range of 2 to 15 wt.-% and in particular in the range of 4 to 10 wt.-%, and most in particular in the range of 4 to 8 wt.-% based on the total weight of the composition.

The amount of the amino substituted hydroxybenzophenone derivative such as in particular of diethylamino hydroxybenzoyl hexyl benzoate in the compositions according to the invention is preferable selected in the range of 0.5 to 10 wt.-%, more preferable selected in the range of 0.5 to 8 wt.-%, in particular in the range of 1 to 5 wt.-% and most particular in the range of 3 to 5 wt.-% based on the total weight of the composition.

The amount of the triazine derivative such as in particular of bis-ethylhexyloxyphenol methoxyphenyl triazine in the compositions according to the invention is preferably selected in the range of 0.5 to 8 wt.-%, in particular in the range of 1 to 5 wt.-%, most particular in the range of 2 to 4 wt.-% based on the total weight of the composition.

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The phosphate ester emulsifier is preferably used in an amount of 0.5 to 10 wt.-% such as in particular in the range of 0.5 to 5 wt.-% such as most in particular in the range of 1 to 4 wt.-% based on the total weight of the composition.

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In a particular embodiment of the present invention the benzotriazol derivative is selected from compounds of formula (I) wherein  $R^1$  and  $R^4$  are hydrogen,  $R^2$  is methyl and  $R^3$  is  $C_{5-10}$ alkoxy such as preferably  $C_{6-10}$ alkoxy, or  $C_6$ cycloalkoxy such as in particular 2,5,5-trimethylhexyloxy, 3,5,5-trimethylhexyloxy, isoamyloxy, 2-ethylhexyloxy or 3,3,5-trimethyl-cyclohexyloxy. Such compounds and their preparation are e.g. disclosed in

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EP Application No.: 10150832.3 (PCT publication: WO2011/086124). Particularly preferred according to the present invention is a compound of formula (I), wherein  $R^1$  and  $R^4$  are hydrogen,  $R^2$  is methyl and  $R^3$  is 2-ethylhexyloxy (i.e. 2-(2H-Benzotriazol-2-yl)-6-(2-ethylhexyloxymethyl)-4-methyl-phenol).

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In another particular embodiment of the present invention the compound of formula (I) is a compound wherein  $R^1$  and  $R^4$  are hydrogen,  $R^2$  is methyl and  $R^3$  is undecyl ( $C_{11}H_{23}$ ) which is commercially available as Tinogard TL [INCI Name: benzotriazolyl dodecyl p-cresol; IUPAC Name: 2-(2H-benzotriazol-2-yl)-6-dodecyl-4-methyl-phenol] at BASF SE Ludwigshafen.

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In a further particular embodiment the benzotriazol derivative of formula (I) is benzotriazolyl dodecyl p-cresol, the triazine derivative is bis-ethylhexyloxyphenol methoxyphenyl triazine and the amino substituted hydroxybenzophenone derivative is diethylamino hydroxybenzoyl hexyl benzoate. It is particularly preferred if the topical composition furthermore comprises

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butyl methoxydibenzoylmethane.

In another particular embodiment the benzotriazol derivative of formula (I) is selected from compounds of formula (I) wherein  $R^1$  and  $R^4$  are hydrogen,  $R^2$  is methyl and  $R^3$  is  $C_{5-10}$ alkoxy such as in particular  $C_{6-10}$ alkoxy, or  $C_6$ cycloalkoxy such as most in particular

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2,5,5-trimethylhexyloxy, 3,5,5-trimethylhexyloxy, isoamyloxy, 2-ethylhexyloxy or

3,3,5-trimethyl-cyclohexyloxy such as in particular 2-(2H-Benzotriazol-2-yl)-6-(2-ethylhexyloxymethyl)-4-methyl-phenol and the triazine derivative is bis-ethylhexyloxyphenol methoxyphenyl triazine and the amino substituted hydroxybenzophenone derivative is diethylamino hydroxybenzoyl hexyl benzoate. It is particularly preferred if the topical composition furthermore comprises butyl methoxydibenzoylmethane.

In another particular embodiment the compositions according to the present invention are substantially free of a polyglycerol based UV-filter such as e.g. disclosed in [EP Application No's] EP09178503.0, EP09178501.4, EP09178502.2 EP09178495.9, EP09178506.3, EP09178505.5 or EP10150832.3 which are obtainable by a process comprising the steps of ring-opening polymerization of  $x$  mol equivalents of glycidol using 1 mol equivalent of a polyol starter unit with  $y$  mol equivalents hydroxyl-groups, followed by block copolymerization with  $z$  X ( $x+y$ ) mole equivalents of propylene oxide to form a hyperbranched polyether-polyol backbone carrying ( $x+y$ ) mol equivalents hydroxyl-groups followed by partial or total esterification, respectively partial or total etherification of the hydroxyl groups with a UV-light absorbing chromophore such as particularly with *p*-dimethylamino benzoic acid, 3-[1-(4-Hydroxymethyl-phenyl)-meth-(E)-ylidene]-1,7,7-trimethyl-bicyclo[2.2.1]heptan-2-one, 2-(4-diethylamino-2-hydroxybenzoyl)benzoic acid, *p*-alkoxycinnamic acid, 2-cyano-3,3-diphenylacrylic acid as well as mixtures thereof and wherein  $x$  is an integer selected in the range from 3-16,  $y$  is an integer selected in the range from 1-6, and  $z$  is an integer selected in the range from 0-10.

Particular suitable dibenzoylmethane derivatives to be used in the topical compositions according to the present invention encompass 2-methyldibenzoylmethane, 4-methyldibenzoylmethane, 4-isopropyldibenzoylmethane, 4-*tert*.-butyldibenzoylmethane, 2,4-dimethyldibenzoylmethane, 2,5-dimethyldi-benzoylmethane, 4,4'-diisopropyldibenzoylmethane, 4,4'-dimethoxydibenzoylmethane, 4-*tert*.-butyl-4'-methoxydibenzoylmethane, 2-methyl-5-isopropyl-4'-methoxydibenzoyl-methane, 2-methyl-5-*tert*-butyl-4'-methoxydibenzoylmethane, 2,4-dimethyl-4'-methoxydi-benzoylmethane, 2,6-dimethyl-4-*tert*-butyl-4'-methoxydibenzoylmethane such as most in particular 4-(*tert*.-butyl)-4'-methoxydibenzoylmethane (INCI Name: butyl methoxy dibenzoylmethane; IUPAC Name: 1-(4-Methoxyphenyl)-3-(4-*tert*-butylphenyl)propane-1,3-dione) which is e.g. commercially available as PARSOL® 1789 at DSM Nutritional Products Ltd Kaiseraugst.

The amount of the dibenzoylmethane derivative such as in particular of butyl methoxydibenzoylmethane in the compositions according to the invention is preferable selected in the range of 2 to 8 wt.-%, in particular in the range of 3 to 6 wt.-%, most  
5 particular in the range of 3 to 5 wt.-% based on the total weight of the composition.

The term "topical" is understood here to mean external application to keratinous substances, which are in particular the skin, scalp, eyelashes, eyebrows, nails, mucous membranes and hair.

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As the compositions according to the invention are intended for topical application, they comprise a physiologically acceptable medium, that is to say a medium compatible with keratinous substances, such as the skin, mucous membranes, and keratinous fibres. In particular the physiologically acceptable medium is a cosmetically acceptable carrier.

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The term cosmetically acceptable carrier refers to all carriers and/or excipients and/ or diluents conventionally used in cosmetic compositions.

Preferred topical compositions according to the invention are skin care preparations,  
20 decorative preparations, and functional preparations.

Examples of skin care preparations are, in particular, light protective preparations, anti-ageing preparations, preparations for the treatment of photo-ageing, body oils, body lotions, body gels, treatment creams, skin protection ointments, skin powders, moisturizing gels,  
25 moisturizing sprays, face and/or body moisturizers, skin-tanning preparations (i.e. compositions for the artificial/sunless tanning and/or browning of human skin), for example self-tanning creams as well as skin lightening preparations.

Examples of decorative preparations are, in particular, lipsticks, eye shadows, mascaras,  
30 dry and moist make-up formulations, rouges and/or powders.

Examples of functional preparations are cosmetic or pharmaceutical compositions containing active ingredients such as hormone preparations, vitamin preparations, vegetable extract preparations, anti-ageing preparations, and/or antimicrobial (antibacterial  
35 or antifungal) preparations without being limited thereto.

In a particular embodiment the topical compositions according to the invention are light-protective preparations (sun care products), such as sun protection milks, sun protection lotions, sun protection creams, sun protection oils, sun protection sprays, sun blocks or tropical's or day care creams with a SPF (sun protection factor). Of particular interest are sun protection creams, sun protection lotions, sun protection milks and sun protection preparations.

The topical compositions according to the present invention are advantageously in the form of an oil-in-water (O/W) emulsion comprising an oily phase dispersed in an aqueous phase in the presence of an O/W phosphate ester emulsifier. The preparation of such O/W emulsions is well known to a person skilled in the art and illustrated in the examples.

In a particular embodiment, the invention relates to topical compositions in the form of O/W emulsions comprising an oily phase dispersed in an aqueous phase in the presence of an O/W phosphate ester emulsifier wherein the benzotriazol derivative of formula (I) is benzotriazolyl dodecyl p-cresol, the triazine derivative is bis-ethylhexyloxyphenol methoxyphenyl triazine and the amino substituted hydroxybenzophenone derivative is diethylamino hydroxybenzoyl hexyl benzoate and the O/W emulsifier potassium cetyl phosphate. It is particularly preferred if the topical composition furthermore comprises butyl methoxydibenzoylmethane.

In a further embodiment, the invention relates to topical compositions in the form of O/W emulsions comprising an oily phase dispersed in an aqueous phase in the presence of an O/W phosphate ester emulsifier wherein the benzotriazol derivative of formula (I) is a compound of formula (I) wherein  $R^1$  and  $R^4$  are hydrogen,  $R^2$  is methyl and  $R^3$  is 2,5,5-trimethylhexyloxy, 3,5,5-trimethylhexyloxy, isoamyloxy, 2-ethylhexyloxy or 3,3,5-trimethyl-cyclohexyloxy such as in particular 2-(2H-Benzotriazol-2-yl)-6-(2-ethylhexyloxymethyl)-4-methyl-phenol, the triazine derivative is bis-ethylhexyloxyphenol methoxyphenyl triazine and the amino substituted hydroxybenzophenone derivative is diethylamino hydroxybenzoyl hexyl benzoate and the O/W emulsifier is potassium cetyl phosphate. It is particularly preferred if the topical composition furthermore comprises butyl methoxydibenzoylmethane.

The topical compositions according to the present invention furthermore advantageously contain at least one co-surfactant such as e.g. selected from the group of mono- and diglycerides and/ or fatty alcohols. The co-surfactant is generally used in an amount selected in the range of 0.1 to 10 wt.-%, such as in particular in the range of 0.5 to 5 wt.-%, such as most in particular in the range of 1 to 3 wt.-%, based on the total weight of the composition. Particular suitable co-surfactants are selected from the list of alkyl alcohols such as cetyl alcohol (Lorol C16, Lanette 16), cetearyl alcohol (Lanette O), stearyl alcohol (Lanette 18), behenyl alcohol (Lanette 22), glyceryl stearate, glyceryl myristate (Estol 3650), hydrogenated coco-glycerides (Lipocire Na10) as well as mixtures thereof. If the phosphate ester emulsifier is potassium cetyl phosphate a particular suitable co-surfactant is cetearyl alcohol.

The compositions in form of O/W emulsions according to the invention can be provided, for example, in all the formulation forms for O/W emulsions, for example in the form of serum, milk, spray or cream, and they are prepared according to the usual methods. The compositions which are subject-matters of the invention are intended for topical application and can in particular constitute a dermatological or cosmetic composition, for example intended for protecting human skin against the adverse effects of UV radiation (antiwrinkle, anti-ageing, moisturizing, anti-sun protection and the like).

According to an advantageous embodiment of the invention the compositions constitute cosmetic composition and are intended for topical application to the skin.

Finally, a subject-matter of the invention is a method for the cosmetic treatment of keratinous substances such as in particular the skin, characterized in that a composition as defined above is applied to the said keratinous substances such as in particular to the skin. The method is in particular suitable to protect the skin against the adverse effects of UV-radiation such as in particular sun-burn and/ or photoageing.

In accordance with the present invention, the compositions according to the invention may comprise further ingredients such as ingredients for skin lightening; tanning prevention; treatment of hyperpigmentation; preventing or reducing acne, wrinkles, lines, atrophy and/or inflammation; chelators and/or sequestrants; anti-cellulites and slimming (e.g. phytanic acid), firming, moisturizing and energizing, self tanning, soothing, as well as agents to improve elasticity and skin barrier and/or further UV-filter substances and carriers and/or

excipients or diluents conventionally used in topical compositions. If nothing else is stated, the excipients, additives, diluents, etc. mentioned in the following are suitable for topical compositions according to the present invention. The necessary amounts of the cosmetic and dermatological adjuvants and additives can, based on the desired product, easily be  
5 determined by the skilled person. The additional ingredients can either be added to the oily phase, the aqueous phase or separately as deemed appropriate. The mode of addition can easily be adapted by a person skilled in the art.

The cosmetically active ingredients useful herein can in some instances provide more than  
10 one benefit or operate via more than one mode of action.

The topical cosmetic compositions of the invention can also contain usual cosmetic adjuvants and additives, such as preservatives/ antioxidants, fatty substances/ oils, water, organic solvents, silicones, thickeners, softeners, emulsifiers, sunscreens, antifoaming  
15 agents, moisturizers, aesthetic components such as fragrances, surfactants, fillers, sequestering agents, anionic, cationic, nonionic or amphoteric polymers or mixtures thereof, propellants, acidifying or basifying agents, dyes, colorings/colorants, abrasives, absorbents, essential oils, skin sensates, astringents, antifoaming agents, pigments or nanopigments, e.g. those suited for providing a photoprotective effect by physically blocking out ultraviolet  
20 radiation, or any other ingredients usually formulated into cosmetic compositions. Such cosmetic ingredients commonly used in the skin care industry, which are suitable for use in the compositions of the present invention are e.g. described in the CTFA Cosmetic Ingredient Handbook, Second Edition (1992), The Cosmetic, Toiletry and Fragrance Association, Inc. or International Cosmetic Ingredient Dictionary and Handbook, Vol. 4,  
25 2008 (ISBN-10: 1882621433) without being limited thereto.

The necessary amounts of the cosmetic and dermatological adjuvants and additives can – based on the desired product – easily be chosen by a skilled person in this field and will be illustrated in the examples, without being limited hereto.  
30

Of course, one skilled in this art will take care to select the above mentioned optional additional compound or compounds and/or their amounts such that the advantageous properties intrinsically associated with the combination in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions.  
35

The topical compositions according to the invention in general have a pH in the range of 3 to 10, preferably a pH in the range of 4 to 8 and most preferably a pH in the range of 4 to 7. The pH can easily be adjusted as desired with suitable acids such as e.g. citric acid or bases such as NaOH, Triethanolamine (TEA Care), Tromethamine (Trizma Base) and  
 5 Aminomethyl Propanol (AMP-Ultra PC 2000) according to standard methods in the art.

The following examples are provided to further illustrate the compositions and effects of the present invention. These examples are illustrative only and are not intended to limit the scope of the invention in any way.

10

**Example 1**Compositions

The compositions as outlined in table 1 and 2 were prepared according to standard methods in the art.

15

**Table 1 Amphisol formulations according to the invention**

Tradename	INCI Name	1A	2A	3A	4A	5A	6A	7A	8A	9A	10A
		Wt.-%									
Phenonip	Preservative	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Keltrol CG-T	Xanthan Gum	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Finsolv TN	C12-15 Alkyl Benzoate	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00
Amphisol® K	Potassium Cetyl Phosphate	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
Lanette O	Cetearyl Alcohol	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Tinosorb® S	Bis-Ethylhexyloxy phenol Methoxy phenyl Triazine	4.00		4.00						4.00	
Tinogard® TL	Benzotriazolyl dodecyl p-Cresol		8.00	4.00	4.00	8.00	2.00	8.00			
PARSOL® 1789	Butyl Methoxy-dibenzoylmethane				4.00	4.00	4.00	4.00	4.00		4.00
Uvinul® A Plus	Diethylamino Hydroxy-benzoyl Hexyl Benzoate					4.00			4.00		
	2-(2H-Benzotriazol-2-yl)-6-(2-ethylhexyl-oxy-methyl)-4-methyl-phenol*									4.00	8.00
Water		Ad 100									

\*benzotriazol derivative of formula (I): 2-(2H-Benzotriazol-2-yl)-6-(2-ethylhexyloxymethyl)-4-methyl-phenol (i.e. a compound of formula (I), wherein R<sup>1</sup> and R<sup>4</sup> are hydrogen, R<sup>2</sup> is methyl and R<sup>3</sup> is 2-ethylhexyloxy)

**Table 2 Pemulen TR2 formulations (Reference)**

Tradename	INCI Name	1B	2B	3B	4B	5B	6B	7B	8B	9B	10B
		Wt.-%									
Phenonip	Preservative	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Keltrol CG-T	Xanthan Gum	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Finsolv TN	C12-15 Alkyl Benzoate	30.0	30.0	30.0	30.0	30.0	30.00	30.0	30.00	30.0	30.0
Pemulen TR2	Acrylates/C10-30 Alkyl Acrylate Crosspolymer	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
TEA Care		0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	4.00		4.00						4.00	
Tinogard® TL	Benzotriazolyl dodecyl p-Cresol		8.00	4.00	4.00	8.00	2.00	8.00			
PARSOL® 1789	Butyl Methoxy-dibenzoylmethane				4.00	4.00	4.00	4.00	4.00		4.00
Uvinul® A Plus	Diethylamino Hydroxy-benzoyl Hexyl Benzoate					4.00			4.00		
	2-(2H-Benzo-triazol-2-yl)-6-(2-ethylhexyloxy-methyl)-4-methyl-phenol*									4.00	8.00
Water		Ad 100									

\*benzotriazol derivative of formula (I): 2-(2H-Benzotriazol-2-yl)-6-(2-ethylhexyloxymethyl)-4-methyl-phenol (i.e. a compound of formula (I), wherein R<sup>1</sup> and R<sup>4</sup> are hydrogen, R<sup>2</sup> is methyl and R<sup>3</sup> is 2-ethylhexyloxy)

### Wash trials

On a textile cloth (Jersey by the company Testex „Prüf Textilien“ Windheckenweg 53, D-53902 Bad Münstereifel) squares of 5 cm x 5 cm size were indicated. Afterwards 1 ml of the

10

respective formulation was applied homogenously onto this filed. Afterwards, the cloth was dried for 30min at 40°C before the residual emulsion was removed with a paper towel. Then the cloth was washed at 40°C with a washing powder (Persil Color Megaperls) in a washing machine using a washing program for fine textiles. After taking the cloth out of the washing machine it was air-dried.

15

Lab Measurement

The treated cloth is laid onto one layer of the white, untreated textile cloth and the L,a,b value is determined with a Minolta Spectrophotometer CM-3600d.

The reference is an untreated cloth, treated in the same manner as the samples.

- 5 The  $\Delta E$  value is calculated according to the following formula:

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

Table 3: Results

Sample	Emusifier	UV-filters, [c wt.-%]	$\Delta E$
1A	Amphisol <sup>®</sup> K	Tinosorb <sup>®</sup> S [4 wt.-%]	<b>5.8</b>
1B (Reference)	Pemulen TR2	Tinosorb <sup>®</sup> S [4 wt.-%]	<b>6.8</b>
2A	Amphisol <sup>®</sup> K	Tinogard <sup>®</sup> TL [8 wt.-%]	<b>4.7</b>
2B (Reference)	Pemulen TR2	Tinogard <sup>®</sup> TL [8 wt.-%]	<b>5.7</b>
3A	Amphisol <sup>®</sup> K	Tinosorb <sup>®</sup> S [4 wt.-%]; Tinogard <sup>®</sup> TL [4 wt.-%]	<b>6.3</b>
3B (Reference)	Pemulen TR2	Tinosorb <sup>®</sup> S [4 wt.-%]; Tinogard <sup>®</sup> TL [4 wt.-%]	<b>7.6</b>
4A	Amphisol <sup>®</sup> K	Tinogard <sup>®</sup> TL [4 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>7.6</b>
4B (Reference)	Pemulen TR2	Tinogard <sup>®</sup> TL [4 wt.-%] PARSOL 1789 [4 wt.-%]	<b>8.0</b>
5A	Amphisol <sup>®</sup> K	Tinogard <sup>®</sup> TL [8 wt.-%] Uvinul <sup>®</sup> A plus [4 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>9.5</b>
5B (Reference)	Pemulen TR2	Tinogard TL [8 wt.-%] Uvinul A plus [4 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>9.7</b>
6A	Amphisol <sup>®</sup> K	Tinogard <sup>®</sup> TL [2 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>7.3</b>
6B (Reference)	Pemulen TR2	Tinogard <sup>®</sup> TL [2 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>7.6</b>
7A	Amphisol <sup>®</sup> K	Tinogard <sup>®</sup> TL [8 wt.-%]	<b>7.8</b>

		PARSOL <sup>®</sup> 1789 [4 wt.-%]	
7B (Reference)	Pemulen TR2	Tinogard <sup>®</sup> TL [8 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>8.9</b>
8A	Amphisol <sup>®</sup> K	Uvinul A plus [4 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>9.0</b>
8B (Reference)	Pemulen TR2	Uvinul A plus [4 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>10.3</b>
9A	Amphisol <sup>®</sup> K	Tinosorb <sup>®</sup> S [4 wt.-%]; 2-(2H-Benzo-triazol-2-yl)-6-(2-ethylhexyl-oxy-methyl)-4-methyl-phenol [4 wt.-%]	<b>6.51</b>
9B (Reference)	Pemulen TR2	Tinosorb <sup>®</sup> S [4 wt.-%]; 2-(2H-Benzo-triazol-2-yl)-6-(2-ethylhexyl-oxy-methyl)-4-methyl-phenol [4 wt.-%]	<b>7.33</b>
10A	Amphisol <sup>®</sup> K	2-(2H-Benzo-triazol-2-yl)-6-(2-ethylhexyl-oxy-methyl)-4-methyl-phenol [8 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>8.33</b>
10B (Reference)	Pemulen TR2	2-(2H-Benzo-triazol-2-yl)-6-(2-ethylhexyl-oxy-methyl)-4-methyl-phenol [8 wt.-%] PARSOL <sup>®</sup> 1789 [4 wt.-%]	<b>9.00</b>

As can be retrieved from the table the use of a phosphate ester emulsifier leads to a reduced staining tendency of the respective UV-filter substances respectively mixtures thereof.

### 5 **Example 2 Sand repellent properties**

50 mg of the respective formulation as outlined in table 4 were applied on PMMA Schönberg plates (5x5cm). Plates are dried at 43°C for 15 minutes. 2.5 g sand were distributed on the plates. For removal of excess sand the plates were tilt (about 45°, left and right side). The sticky sand residue on each plate was determined through weighting. The

10 results are presented in table 4.

The reduction in the sand adherence was determined as:

$$\Delta \text{ Adherence [\%]} = \{(\text{Adherence Sample [mg]} - \text{Adherence Reference [mg]}) / \text{Adherence Sample [mg]}\} * 100\%.$$

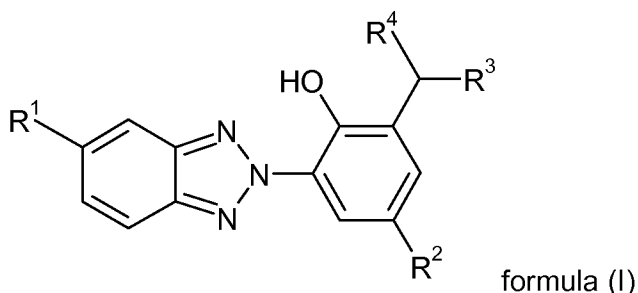
**Table 4**

Trade Name	9A (Reference)	9B	10A (Reference)	10B
	Wt.-%			
Phenonip	0.80	0.80	0.80	0.80
Keltrol CG-T	0.30	0.30	0.30	0.30
Finsolv TN	30.00	30.00	30.00	30.00
Ampisol K	5.00	5.00	5.00	5.00
Lanette O	1.50	1.50	1.50	1.50
Tinogard TL		4.00		4.00
Tinosorb S	4.00	4.00		
Uvinul A plus			4.00	4.00
Water	Ad 100			
Sand adherence [mg]	1.37	1.32	1.45	1.32
$\Delta$ Adherence [%]	-4%		-10%	

As can be retrieved from the results in table 4, the compositions according to the present invention exhibit a reduced sand-adherence.

## Claims

1. A topical composition comprising a phosphate ester emulsifier and a benzotriazol derivative of formula (I)



5 wherein

R<sup>1</sup> is hydrogen; C<sub>1-5</sub>alkyl; C<sub>1-5</sub>alkoxy or halogen; preferably hydrogen or chloride, most preferably hydrogen;

R<sup>2</sup> is hydrogen; C<sub>1-20</sub>alkyl; C<sub>1-5</sub>alkoxy; C<sub>1-5</sub>alkoxycarbonyl; C<sub>5-10</sub>cycloalkyl; C<sub>6-10</sub>aryl or aralkyl; preferably hydrogen or C<sub>1-5</sub>alkyl, most preferably methyl;

10 R<sup>3</sup> is C<sub>1-20</sub>alkyl, C<sub>5-10</sub>cycloalkyl, C<sub>1-20</sub>alkoxy or C<sub>5-10</sub>cycloalkoxy, preferably C<sub>5-15</sub>alkyl or C<sub>5-15</sub>alkoxy; and

R<sup>4</sup> is hydrogen or C<sub>1-5</sub>alkyl, preferably hydrogen;

15 characterized in that the composition further comprises at least one UV filter substance selected from the group consisting of a triazine derivative and an amino substituted hydroxybenzophenone as well as mixtures thereof.

2. The topical composition according to claim 1, characterized in that the benzotriazol derivative is used in an amount selected in the range of 1 to 20 wt.-% based on the total weight of the composition.

20

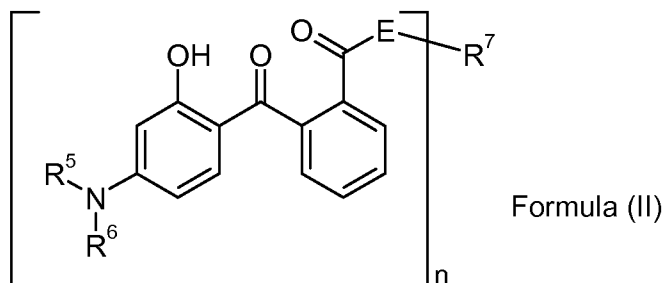
3. The topical composition according to claim 1 or 2, characterized in that the benzotriazol derivative is used in an amount selected in the range of 2 to 20 wt.-% based on the total weight of the composition.

25

4. The topical composition according to any one of claims 1 to 3, characterized in that the benzotriazol compound of formula (I) is a compound wherein R<sup>1</sup> and R<sup>4</sup> are hydrogen, R<sup>2</sup> is methyl and R<sup>3</sup> is 2,5,5-trimethylhexyloxy, 3,5,5-trimethylhexyloxy, isoamyloxy, 2-ethylhexyloxy, 3,3,5-trimethyl-cyclohexyloxy or undecyl.

5. The topical composition according to any one of claims 1 to 4, characterized in that the triazine derivative is selected from the group consisting of ethylhexyl triazone, diethylhexyl butamido triazone and bis-ethylhexyloxyphenol methoxyphenyl triazine.

5 6. The topical composition according to any one of claims 1 to 5, characterized in that amino substituted hydroxybenzophenone derivative is a compound of formula (II)



wherein

10  $R^5$  and  $R^6$  independently of each other are hydrogen;  $C_1$ - $C_{20}$ alkyl;  $C_2$ - $C_{20}$ alkenyl;  $C_5$ - $C_{10}$ cycloalkyl or  $C_5$ - $C_{10}$ cycloalkenyl; or  $R^5$  and  $R^6$ , together with the nitrogen atom they are bound to, form a 5 to 6 membered ring;

$n$  is an integer from 1 or 2;

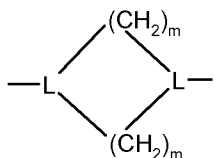
$E$  is  $-O-$  or  $-N(R^8)-$  and

$R^8$  is hydrogen;  $C_1$ - $C_5$ alkyl; or  $C_1$ - $C_5$ hydroxyalkyl;

15 with the proviso that

- when  $n = 1$  then  $R^7$  is  $C_1$ - $C_{20}$ alkyl;  $C_2$ - $C_{20}$ alkenyl;  $C_1$ - $C_5$ hydroxyalkyl;  $C_5$ - $C_{10}$ cycloalkyl;  $C_5$ - $C_{10}$ cycloalkenyl;  $C_{6-10}$ aryl; or aralkyl optionally substituted by O, N or S; or a  $C_1$ - $C_5$  aminocarbonyl or alkylcarbonyl radical;

20 - when  $n = 2$  then  $R^7$  is an  $C_1$ - $C_{20}$ alkyl;  $C_5$ - $C_{10}$ cycloalkyl-;  $C_2$ - $C_{20}$ alkenyl- or aryl-diradical or  $R^7$  with  $E$  forms a diradical of formula (III)



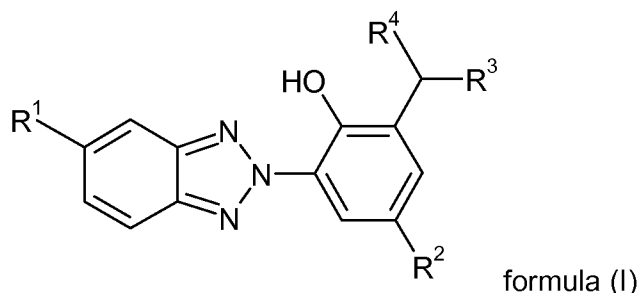
formula (III)

wherein  $L$  is  $N$  (nitrogen) and

$m$  is an integer between 1 and 3.

7. The topical composition according to claim 6, characterized in that the amino substituted hydroxybenzophenone derivative is diethylamino hydroxybenzoyl hexyl benzoate or 1,1'-(1,4-piperazinediyl)bis[1-[2-[4-(diethylamino)-2-hydroxybenzoyl]phenyl]-methanone.
8. The topical composition according to any one of claims 1 to 7, characterized in that the amount of the triazine derivative and of the amino substituted hydroxybenzophenone is selected, independently of each other, in the range of 0.5 to 8 wt.-% based on the total weight of the composition.
9. The topical composition according to any one of claims 1 to 8, characterized in that the phosphate ester emulsifier is potassium cetyl phosphate.
10. The topical composition according to any one of claims 1 to 9, characterized in that the amount of phosphate ester emulsifier is selected in the range of 0.5 to 5wt.-% based on the total weight of the composition.
11. The topical composition according to any one of claims 1 to 10, characterized in that the topical composition further comprises butyl methoxydibenzoylmethane.
12. The topical composition according to claim 11, characterized in that the amount of the dibenzoylmethane derivative is selected in the range of 2 to 8 wt.-% based on the total weight of the composition.
13. The topical composition according to any one of claims 1 to 12, characterized in that the topical composition is an O/W emulsion comprising an oily phase dispersed in an aqueous phase in the presence of an O/W emulsifier.
14. The topical composition according to any one of claims 1 to 13, characterized in that the composition comprises at least one co-surfactant in an amount selected in the range of 0.1 to 10 wt.-% based on the total weight of the composition.

15. Use of a phosphate ester emulsifier for reducing cloth staining tendency of at least one UV filter substance selected from the group consisting of a triazine derivative, an amino substituted hydroxybenzophenone and/ or a benzotriazol derivative of formula (I)



5 wherein

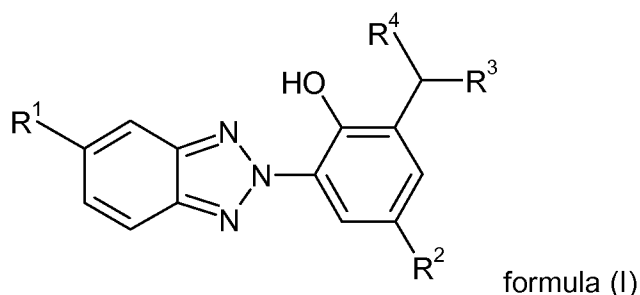
$R^1$  is hydrogen;  $C_{1-5}$ alkyl;  $C_{1-5}$ alkoxy or halogen; preferably hydrogen or chloride; most preferably hydrogen;

$R^2$  is hydrogen;  $C_{1-20}$ alkyl;  $C_{1-5}$ alkoxy;  $C_{1-5}$ alkoxycarbonyl;  $C_{5-10}$ cycloalkyl;  $C_{6-10}$ aryl or aralkyl; preferably hydrogen or  $C_{1-5}$ alkyl; most preferably methyl;

10  $R^3$  is  $C_{1-20}$ alkyl;  $C_{5-10}$ cycloalkyl;  $C_{1-20}$ alkoxy or  $C_{5-10}$ cycloalkoxy, preferably  $C_{5-15}$ alkyl or  $C_{5-15}$ alkoxy; and

$R^4$  is hydrogen or  $C_{1-5}$ alkyl; preferably hydrogen

16. Method for reducing stains on clothes caused by the use of topical compositions  
 15 comprising at least one UV filter substance selected from the group consisting of a triazine derivative, an amino substituted hydroxybenzophenone and/ or a benzotriazol derivative of formula (I)



wherein

20  $R^1$  is hydrogen;  $C_{1-5}$ alkyl;  $C_{1-5}$ alkoxy or halogen; preferably hydrogen or chloride; most preferably hydrogen;

$R^2$  is hydrogen;  $C_{1-20}$ alkyl;  $C_{1-5}$ alkoxy;  $C_{1-5}$ alkoxycarbonyl;  $C_{5-10}$ cycloalkyl;  $C_{6-10}$ aryl or aralkyl; preferably hydrogen or  $C_{1-5}$ alkyl; most preferably methyl;

25  $R^3$  is  $C_{1-20}$ alkyl,  $C_{5-10}$ cycloalkyl;  $C_{1-20}$ alkoxy or  $C_{5-10}$ cycloalkoxy; preferably  $C_{5-15}$ alkyl or  $C_{5-15}$ alkoxy; and

R<sup>4</sup> is hydrogen or C<sub>1-5</sub>alkyl; preferably hydrogen

said method comprising the use of a phosphate ester emulsifier for the preparation of said topical composition and observing or appreciating the result.