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(54) Titre : PROCEDE POUR DOTER UNE MATIERE TEXTILE D'UNE PROTECTION UV
(54) Title: METHOD FOR PROVIDING TEXTILE MATERIAL WITH UV PROTECTION

(57) **Abrégé/Abstract:**

The invention relates to a method for providing textile material with UV protection, whereby (a) zinc oxide and/or titanium oxide are applied to the textile material as constituent A, and (b) at least one organic UV absorber is applied to the textile material as constituent B. Constituent B preferably contains at least one compound from the group consisting of phenylbenzotriazoles, dibenzoylmethanes, p-aminobenzoic acid esters, cinnamic acid esters, salicylic acid esters, nitrogen-free 2-hydroxybenzophenones, phenylbenzimidazoles, acrylates, diarylbutadienes, amino-substituted hydroxybenzophenones, and triazines.



Abstract

A method for UV protecting a textile material which comprises applying

- (a) zinc oxide and/or titanium oxide as a component A and
 - (b) one or more organic UV absorbers as a component B
- to said textile material.

Component B preferably comprises one or more compounds selected from the group consisting of

- phenylbenzotriazoles,
- dibenzoylmethanes,
- esters of p-aminobenzoic acid,
- esters of cinnamic acid,
- esters of salicylic acid,
- nonnitrogenous 2-hydroxybenzophenones,
- phenylbenzimidazoles,
- acrylates,
- diarylbutadienes,
- amino-substituted hydroxybenzophenones,
- triazines.+

5

UV protection of textile material

This invention relates to a method for UV protecting textile material, laundry detergent, laundry aftertreatment, and fabric conditioning formulations, finish compositions for UV
10 protecting textile material, the thus finished textile material itself and the use of zinc oxide and/or titanium dioxide together with organic UV absorbers.

The harmful effects of the UV content of sunlight on human skin are not restricted to premature skin aging and the formation of erythemas (skin reddening, sunburn).
15 Excessively long and intensive exposure of the skin to UV radiation also raises the risk of developing skin cancer. The chief culprit responsible for skin reddening and the increased risk of skin cancer is the UV-B-range of UV radiation, i.e., the range from about 280 to about 315 nm. The peak of the erythema action spectrum is located at 308 nm.

20 Textiles scatter or absorb UV radiation and so act as a physical barrier to protect the skin against the harmful effects of sunlight ("textile skin protection"). However, the skin-protecting effect of textiles is dependent on many factors such as fiber type, fabric construction, fabric weight, color, moisture content or nature of finish. Summer clothing in the form of lightweight and light-colored cotton textiles offers only slight and hence
25 inadequate protection against UV radiation.

An excessive dose of UV radiation may not only cause skin damage, but is also crucially responsible for sunlight-induced fading of colored textiles. There is therefore considerable interest in protecting colored textiles as well as human skin against the harmful effects of
30 UV radiation.

It is mainly customary optical brighteners which have hitherto been used to finish and to protect the textiles themselves and also for textile skin protection, especially stilbene- and triazine-based optical brighteners as described for example in EP-A 682 145, GB-A
35 2 313 375 or EP-A 728 749. But the agents are still in need of improvement with regard to

their efficacy and possess a number of disadvantages. Significant disadvantages are their poor formulatability and their inadequate solubility in the respective application medium.

5 WO 97/44422 discloses that sunscreens especially from the group consisting of phenylbenzotriazoles, dibenzoylmethanes, p-aminobenzoic esters, cinnamic esters, salicylic esters, nonnitrogenous 2-hydroxybenzophenones, phenylbenzimidazoles and 2-cyano-3,3-diphenylacrylic esters and also mixtures thereof – without the respective mixing ratios being specified, however – are able to protect dyed textile material against fading. WO 96/03486 describes essentially the same sunscreens as mentioned in WO 97/44422 as
10 agents for protecting dyed textile material against fading. But these agents are likewise still in need of improvement with regard to their efficacy and possess a number of disadvantages. An essential disadvantage is the frequently inadequate UV stability of the abovementioned agents.

15 The incorporation of pigments such as titanium dioxide or zinc oxide in fibers is a tried and tested way of conferring UV protection on textiles comprising these fibers. Especially manufactured fibers comprising polyamide, polyester or polyacrylonitrile are useful for this kind of UV protection. Cellulose fibers less so.

20 JP 03/277699 describes solid detergents, specifically soaps, containing from 0.1 to 15% by weight of zinc oxide. The soaps exhibit good UV absorption and possess a deodorizing effect.

WO 98/42909 describes UV protecting textile fabric by treatment with inorganic particles
25 in combination with a binder that are capable of absorbing, reflecting or scattering UV radiation. These particles may be applied during the washing or laundering of clothing as well as by other methods.

It is an object of the present invention to provide UV absorber systems which are improved
30 in their efficacy and photostability.

We have found that this object is achieved by a method for UV protecting a textile material, which comprises applying

- 35 (a) zinc oxide and/or titanium oxide as a component A and
(b) one or more organic UV absorbers as a component B
to said textile material.

Surprisingly, the combined use of organic UV absorbers and inorganic pigments comprising zinc oxide and/or titanium dioxide in textile finishes, laundry detergents or fabric conditioner compositions leads to a more effective UV protection of the textiles treated with these compositions than the sole use of the organic UV absorbers or inorganic pigments. Not only is skin better and more consistently protected against harmful UV radiation, but colored fabric is provided with improved protection against UV induced color fading.

Component A comprises zinc oxide and/or titanium dioxide as UV absorbing inorganic pigments. Component A can consist of zinc oxide or titanium dioxide each on their own or of mixtures of the two pigments.

Titanium dioxide can be used in its three crystal forms rutile, anatase or brookite, with rutile being preferred. The particle size is generally in the range from 0.01 to 100 μm and preferably in the range from 0.02 to 0.25 μm .

Zinc oxide is generally used in a particle size of from 0.01 to 100 μm . The particle size is preferably in the range from 0.02 to 2 μm and more preferably in the range from 0.08 to 0.25 μm .

The titanium dioxide and zinc oxide pigment particles may be passivated with a layer of inorganic oxides, especially silicon dioxide or aluminum oxide. The pigment surface may further be specifically hydrophilicized or hydrophobicized by treatment with organic compounds or silicones. Useful surface modifiers include for example amines, cationic polymers such as amino-containing polymers, polyols, organophosphates, alkyl phthalates, stearic acid, lauric acid or silicone oils.

Examples of very useful surface modifiers are:

Uvinul[®] TiO₂ (from BASF AG),
Z-COTE[®] (from BASF AG) and
Z-COTE HP1[®] (from BASF AG).

Component B may be commercially available sunscreen having at least one UV absorption maximum in the range from 280 to 450 nm.

In a preferred embodiment, component B comprises such compounds as have at least one UV absorption maximum in the range from 290 to 375 nm.

In a further preferred embodiment, component (B) comprises compounds having at least one UV absorption maximum in the range from 280 to 315 nm (UV-B range) with an E^1_1 value of at least 200, especially at least 250, and at least one UV absorption maximum in the range from 315 to 400 nm (UV-A range) with an E^1_1 value of at least 200, especially at least 250.

Organic UV absorbers B have one or more bands in the UV absorption spectrum. UV absorption maxima for the purposes of the present invention are the bands belonging to the corresponding local or absolute maxima in the UV spectrum of the particular compound, measured in customary organic solvents such as dichloromethane or methanol at room temperature.

The E^1_1 value designates the extinction of the organic UV absorbers B which is measured in solution at a concentration of 1% by weight and a path length of 1 cm. The solvent used for this solution is customarily dichloromethane, although the use of other solvents customary for such UV measurements does not give fundamentally different values.

In a further preferred embodiment, the organic UV absorbers present as component B in the mixture of the invention have an n-octanol/water partition coefficient log P of at least 1.9, especially of at least 2.5, in particular of at least 3.3. Log P can be determined experimentally or arithmetically. Both techniques are described in Chemical Reviews Volume 71, No. 5, pages 52-5-616 (1971).

Preference is given to using organic UV absorbers B selected from the group consisting of

- (I) phenylbenzotriazoles,
- (II) dibenzoylmethanes,
- (III) esters of p-aminobenzoic acid,
- (IV) esters of cinnamic acid,
- (V) esters of salicylic acid,
- (VI) nonnitrogenous 2-hydroxybenzophenones,
- (VII) phenylbenzimidazoles,
- (VIII) acrylates,
- (IX) diarylbutadienes,
- (X) amino-substituted hydroxybenzophenones and
- (XI) triazines.

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Typical UV-absorbing phenylbenzotriazoles (I) are:

- 2,2'-hydroxy-5-methylphenylbenzotriazole,
 5 2,2'-hydroxy-5-tert-octylphenylbenzotriazole,
 2-hydroxy-3-sec-butyl-5-tert-butylbenzotriazole (Tinuvin® 350),
 2-hydroxy-3-dodecyl-5-methylphenylbenzotriazole (Tinuvin® 571),
 2-(2H-benzotriazol-2-yl)-4-methylphenol (Tinuvin® P),
 2-(2H-benzotriazol-2-yl)-4-n-octylphenyl (Tinuvin® 329),
 10 2-(2H-benzotriazol-2-yl)-4,6-di(2'-phenylisopropyl)phenol (Tinuvin® 234),
 2-(2H-benzotriazol-2-yl)-4,6-di(tert-butyl)phenol (Tinuvin® 320),
 2-(6-chloro-2H-benzotriazol-2-yl)-4-methyl-6-tert-butylphenol (Tinuvin® 326),
 2-(6-chloro-2H-benzotriazol-2-yl)-2,6-di-tert-butylphenol (Tinuvin® 327),
 2-(2'-hydroxy-3',5'-di-tert-amylphenyl)-2H-benzotriazole (Tinuvin® 328),
 15 mixture of polyoxyethylene glycol β -[3-(2H-benzotriazol-2-yl)-5-tert-butyl-4-
 hydroxyphenyl] propionate and polyoxyethylene glycol bis β -[3-(2H-benzotriazol-2-yl)-5-
 tert-butyl-4-hydroxyphenyl] propionate having an average molecular weight >600
 (Tinuvin® 1130),
 cocoyl-2-[2'-hydroxy-3'-(cocoyl dimethylbutanoate)-5'-methylphenyl]benzotriazole,
 20 cocoyl 3-[3'-(2H-benzotriazol-2'-yl)-5-tert-butyl-4'-hydroxyphenyl]-
 propionate,
 2,2'-methylenebis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetra-
 methylbutyl)]phenol (Tinuvin® 360),
 2-(2H-1,2,3-benzotriazol-2-yl)-4-methyl-6-(2-methyl-3-{1,3,3,3-
 25 tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl}propyl)phenol.

Typical UV-absorbing dibenzoylmethanes (II) are:

- 3-(4-isopropylphenyl)-3-phenylpropane-1,3-dione (Eusolex® 8020),
 30 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione (Uvinul® BMBM),
 1,3-bis(4-methoxyphenyl)propane-1,3-dione.

Typical UV-absorbing esters of p-aminobenzoic acid (III) are:

- 35 ethyl 4-bis(hydroxypropyl)aminobenzoate (Amerscheen® P),
 2,3-dihydroxypropyl 4-aminobenzoate (Nipa® GMPA),

- menthyl 2-aminobenzoate (Sunarome® UVA),
2-ethylhexyl 4-dimethylaminobenzoate (Escalol® 507),
amyl 4-dimethylaminobenzoate,
ethyl 4-dimethylaminobenzoate,
5 butyl 4-dimethylaminobenzoate,
octyl 4-dimethylaminobenzoate,
lauryl 4-dimethylaminobenzoate,
oleyl 4-dimethylaminobenzoate,
polyethoxyethyl 4-bis(polyethoxy)-4-aminobenzoate (Uvinul® P-25),
10 N-propoxylated ethyl 4-aminobenzoate.

Typical UV-absorbing esters of cinnamic acid (IV) are:

- 2-ethylhexyl 4-methoxycinnamate (Uvinul® MC80, Parsol® MCX),
15 2-ethoxyethyl 4-methoxycinnamate,
propyl 4-methoxycinnamate,
isoamyl 4-methoxycinnamate,
cyclohexyl 4-methoxycinnamate,
isopropyl 4-methoxycinnamate,
20 octyl cinnamate,
ethyl 4-isopropylcinnamate,
ethyl α -cyano- β -phenylcinnamate,
2-ethylhexyl α -cyano- β -phenylcinnamate.

25 Typical UV-absorbing esters of salicylic acid (V) are:

- 2-ethylhexyl salicylate (Sunarome® WMO),
3,3,5-trimethylcyclohexyl 2-hydroxybenzoate,
3,3,5-trimethylcyclohexyl 2-acetamidobenzoate,
30 2-ethylhexyl 2-(4-phenylbenzoyl)benzoate,
4-isopropylbenzyl salicylate,
amyl salicylate,
menthyl salicylate,
homomethyl salicylate,
35 phenyl salicylate,
benzyl salicylate,

isodecyl salicylate.

Typical UV-absorbing nonnitrogenous 2-hydroxybenzophenones (VI) are:

- 5 2-hydroxy-4-methoxybenzophenone (Uvinul® M40),
 2,2'-dihydroxy-4-methoxybenzophenone (Spectra-Sorb® UV-24),
 2,4-dihydroxybenzophenone (Uvinul® 3000),
 2,2',4,4'-tetrahydroxybenzophenone (Uvinul® D-50),
 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (Uvinul® D-49),
 10 2,2-dihydroxy-4,4-dimethoxybenzophenone (Uvinul® 3049),
 2-hydroxy-4-(2-ethylhexyloxy)benzophenone,
 2-hydroxy-4-(n-octyloxy)benzophenone (Uvinul® 3008),
 2-hydroxy-4-methoxy-4'-methylbenzophenone (Mexenone®),
 2-ethylhexyl 4'-phenylbenzophenone-2-carboxylate,
 15 2-hydroxy-3-carboxybenzophenone,
 benzophenone-3 cocoyl acetate ether,
 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (Uvinul® MS 40) and its sodium salt,
 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5,5'-bissulfonic acid and its sodium salt
 (Uvinul® DS 49).

20

Typical UV-absorbing phenylbenzimidazoles (VII) are:

- 2-phenylbenzimidazole-5-sulfonic acid (Eusolex® 232) and its potassium, sodium and
 triethanolamine salts,
 25 2-[5,6-disulfo-(1H-benzimidazol-2-yl)phenyl]-1H-benzimidazole-
 5,6-disulfonic acid.

Typical UV-absorbing acrylates (VIII) are:

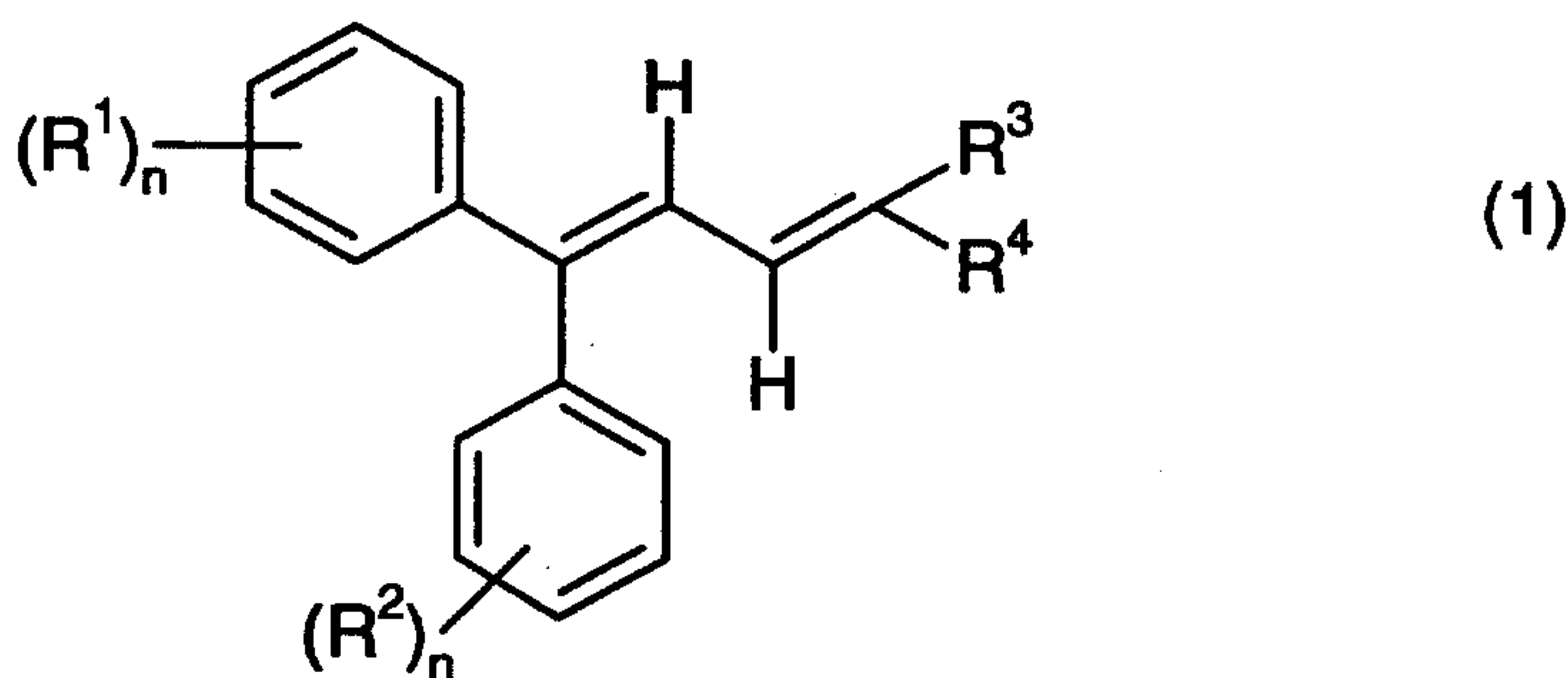
- 30 3-imidazol-4-ylacrylic acid,
 ethyl 3-imidazol-4-ylacrylate,
 2-cyano-3-(4-methoxyphenyl)acrylic acid,
 hexyl 2-cyano-3-(4-methoxyphenyl)acrylate.
- 35 Preferred acrylates include C₆- to C₁₈-alkyl esters or C₅- to C₈-cycloalkylesters of 2-cyano-
 3,3-diphenylacrylic acid. The C₆- to C₁₈-alcohol radical in the cyano-3,3-diphenylacrylic

esters can be linear or singly or multiply branched, and it can be of natural or synthetic origin. Such alcohols can be for example fatty alcohols, oxo alcohols, Ziegler alcohols or Guerbet alcohols. Typical examples of such compounds are n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, isononyl, n-decyl, n-dodecyl, n-tridecyl, isotridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl or eicosyl ester. It is also possible for unsaturated alcohol radicals such as the oleyl, linolyl or linolenyl radical to occur. Mixtures of such esters can also be present.

As C₅- to C₈-cycloalkanol radicals in the cyano-3,3-diphenylacrylic esters there may be mentioned for example cyclopentyl, 2- or 3-methylcyclopentyl, cyclohexyl, 2-, 3- or 4-methylcyclohexyl, dimethylcyclohexyl, cycloheptyl or cyclooctyl radicals.

Preference is given to linear or singly or multiply branched C₈- to C₁₃-alkyl esters of 2-cyano-3,3-diphenylacrylic acid. The corresponding 2-ethylhexyl ester is commercially available as Uvinul® N-539 T from BASF Aktiengesellschaft.

Typical UV-absorbing diarylbutadienes (IX) are especially 4,4-diarylbutadienes of the formula (1) as are described in DE-A 198 28 463 for cosmetic and pharmaceutical preparations:



where the diene system has the Z,Z; Z,E; E,Z or E,E configuration or a mixture thereof, and where the variables independently of one another have the following meanings:

25

R¹ and R²

hydrogen, C₁-C₂₀-alkyl, C₂-C₁₀-alkenyl, C₃-C₁₀-cycloalkyl, C₃-C₁₀-cycloalkenyl, C₁-C₁₂-alkoxy, C₁-C₂₀-alkoxycarbonyl, C₁-C₁₂-alkylamino, C₁-C₁₂-dialkylamino, aryl, hetaryl, unsubstituted or substituted, and

30

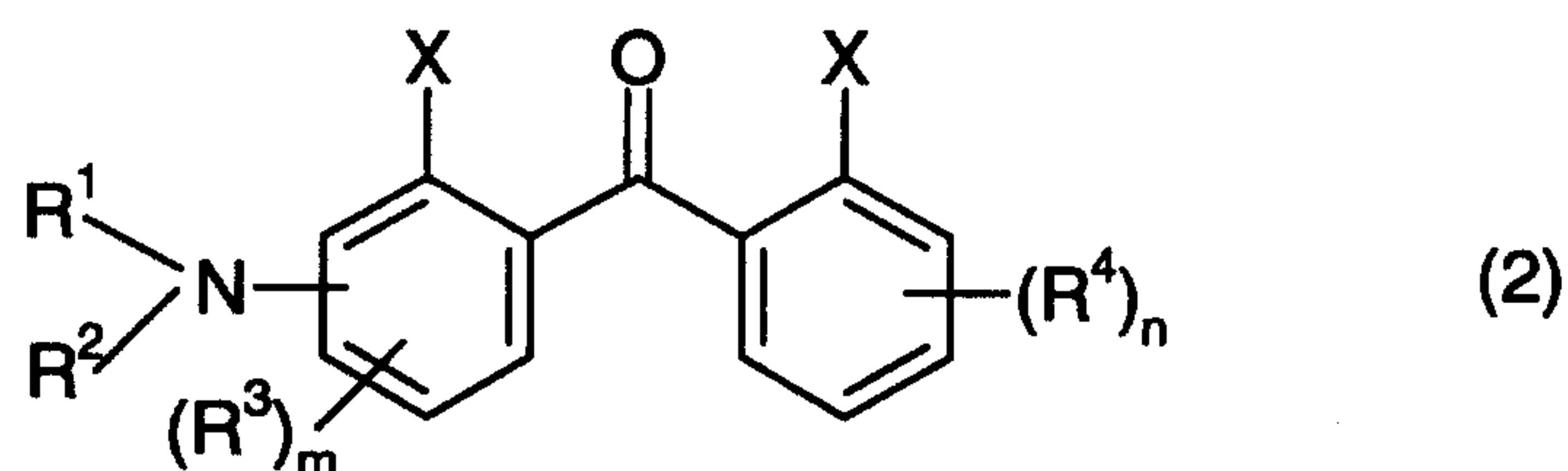
substituents which confer solubility in water and are selected from the group consisting of carboxylate, sulfonate or ammonium radicals;

- 5 R^3 hydrogen, $COOR^5$, COR^5 , $CONR^5R^6$, CN;
- R^4 $COOR^6$, COR^6 , $CONR^5R^6$;
- 10 R^5 hydrogen, $[X]_o-R^7$, C₁-C₆-alkylene-SO₃Y, C₁-C₆-alkylene-PO₃Y, C₁-C₆-alkylene-N(R⁸)₃⁺ A⁻;
- R^6 $[X]_o-R^7$, C₁-C₆-alkylene-SO₃Y, C₁-C₆-alkylene-PO₃Y, C₁-C₆-alkylene-N(R⁸)₃⁺ A⁻;
- X -CH₂-CH₂-Z-, -CH₂-CH₂-CH₂-Z-, -CH(CH₃)-CH₂-Z-, -CH₂-CH₂-CH₂-CH₂-Z-, -CH₂-CH(CH₂-CH₃)-Z-;
- 15 A Cl, Br, I, SO₄R⁹;
- Y hydrogen, Na⁺, K⁺, Mg²⁺, Ca²⁺, Li⁺, Al³⁺, N(R⁸)₄⁺;
- 20 Z O, NH;
- R^7 and R^8
- hydrogen, C₁-C₆-alkyl, C₂-C₆-alkenyl, C₁-C₆-acyl;
- 25 R^9 hydrogen, C₁-C₆-alkyl, C₂-C₆-alkenyl;
- n 1 to 3;
- 30 o 1 to 150.

With regard to a more particular specification of the structures of the 4,4-diarylbutadienes of the formula (1) and examples of such compounds (1), the disclosure in DE-A 198 28 463 is expressly incorporated herein by reference. A typical example of a representative of such a compound (IX) is 1,1-bis(neopentyloxycarbonyl)-4,4-diphenyl-

1,3-butadiene.

Typical UV-absorbing amino-substituted hydroxybenzophenones (X) are in particular those of the formula (2) as are described in German patent application 199 17 906.9 for
5 cosmetic and pharmaceutical preparations:



in which the variables independently of one another have the following meanings:

10

R^1 and R^2 are hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{10} -alkenyl, C_3 - C_{10} -cycloalkyl, C_3 - C_{10} -cycloalkenyl, where the substituents R^1 and R^2 together with the nitrogen atom to which they are bonded can form a 5- or 6-membered ring;

15

R^3 and R^4 are C_1 - C_{20} -alkyl, C_2 - C_{10} -alkenyl, C_3 - C_{10} -cycloalkyl, C_3 - C_{10} -cycloalkenyl, C_1 - C_{12} -alkoxy, C_1 - C_{20} -alkoxycarbonyl, C_1 - C_{12} -alkylamino, C_1 - C_{12} -dialkylamino, aryl, heteroaryl, optionally substituted, and substituents which confer solubility in water and are selected from the group consisting of a nitrile group, carboxylate, sulfonate or ammonium radicals;

20

X is hydrogen, $COOR^5$, $CONR^6R^7$;

R^5 to R^7 are hydrogen, C_1 - C_{20} -alkyl, C_2 - C_{10} -alkenyl, C_3 - C_{10} -cycloalkyl, C_3 - C_{10} -cycloalkenyl, $-(Y-O)_o-Z$, aryl;

25

Y is $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-\text{CH}(\text{CH}_3)-\text{CH}_2-$;

Z is $-\text{CH}_2-\text{CH}_3$, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$, $-\text{CH}(\text{CH}_3)-\text{CH}_3$;

30

m is from 0 to 3;

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n is from 0 to 4;

o is from 1 to 20.

5 With regard to a more particular specification of the structures of the amino-substituted hydroxybenzophenones of the formula II and examples of such compounds II, the disclosure in German patent application 199 17 906.9 is expressly incorporated herein by reference. A typical example of a representative of such a compound (X) is n-hexyl 2-(4'-diethylamino-2'-hydroxybenzoyl) benzoate.

10

Typical UV-absorbing triazines (XI) are:

2,4,6-trianilino-4-(carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine (Uvinul® T-150),
 2-ethylhexyl 4-[[4-{4-[tert-butylamino)carbonyl]anilino}-6-(4-{[2-
 15 ethylhexyl)oxy]carbonyl}anilino)-1,3,5-triazin-2-yl]amino}benzoate,
 2-(4-methoxyphenyl)-4,6-di[4-(2-ethylhexyloxy)-2-hydroxyphenyl]-1,3,5-triazine.

Representatives of the compounds (B) of the type (I) to (VIII) and (XI) are incidentally described in WO 97/44422 and WO 96/03486.

20

As well as compounds of type (I) to (XI), useful organic UV absorbers B further include for example the following:

3-(4-methylbenzylidene)bornan-2-one (Eusolex® 6300),
 25 5-(3,3-dimethyl-2-norbornylidene)-3-penten-2-one,
 3-benzylidenebornan-2-one,
 digalloyl trioleate,
 2-hydroxy-1,4-naphthalenedione,
 5-methyl-2-phenylbenzoxazole,
 30 dibenzaldehydeamine,
 dianisoylmethane,
 methyleugenol,
 2-amino-6-hydroxypurine,
 N-(4-ethoxycarbonylphenyl)-N'-methyl-N'-phenylformamidine (Givosorb® UV1),
 35 N-(4-ethoxycarbonylphenyl)-N'-ethyl-N'-phenylformamidine (Givosorb® UV2),
 3-(4'-methylbenzylidene)camphor (Uvinul® MBC95),

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N¹-(2-ethoxyphenyl)-N²-(2-ethylphenyl)ethanediamide,
 N¹-(2-ethoxyphenyl)-N²-(4-dodecaphenyl)ethanediamide,
 2-ethylhexyl 2-cyano-(3-oxo-2,3-dihydro-1H-isoindol-1-ylidene)ethanoate,
 1,1-dicyano-2-(4-butyloxy)phenyl-2-phenylethene.

5

Particularly preferred organic UV absorbers B, which are used together with zinc oxide and/or titanium dioxide, include the compounds:

1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione (Uvinul® BMBM),
 10 polyethoxyethyl 4-bis(polyethoxy)-4-aminobenzoate (Uvinul® P-25),
 2-ethylhexyl 4-methoxycinnamate (Uvinul® MC80),
 2-hydroxy-4-methoxybenzophenone (Uvinul® M40),
 2,4-dihydroxybenzophenone (Uvinul® 3000),
 2,2',4,4'-tetrahydroxybenzophenone (Uvinul® D-50),
 15 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (Uvinul® D-49),
 2,2-dihydroxy-4,4-dimethoxybenzophenone (Uvinul® 3049),
 2-hydroxy-4-(2-ethylhexyloxy)benzophenone,
 2-hydroxy-4-(n-octyloxy)benzophenone (Uvinul® 3008),
 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (Uvinul® MS 40) and salts thereof,
 20 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5,5'-bissulfonic acid and salts thereof
 (Uvinul® DS49),
 2'-ethylhexyl 2-cyano-3,3-diphenylacrylate (Uvinul® N 539 T),
 ethyl 2-cyano-3,3-diphenylacrylate (Uvinul® 3035),
 1,1-bis(neopentyloxycarbonyl)-4,4-diphenyl-1,3-butadiene,
 25 n-hexyl 2-(4'-diethylamino-2'-hydroxybenzoyl)benzoate,
 2,4,6-trianilino-4-(carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine (Uvinul® T-150),
 3-(4'-methylbenzylidene)camphor (Uvinul® MBC95).

It may occasionally be of advantage for components A and B to be used together with
 30 antioxidants and/or free-radical traps. Antioxidants and free-radical traps which may be
 used here include all compounds customarily used for stabilizing food and feed but also for
 stabilizing plastics or lubricants. A list of such compounds may be found for example in
 Kirk-Othmer, Encyclopedia of Chemical Technology, fourth edition, volume 3, p. 424-447
 or in Ullmann's Encyclopedia of Industrial Chemistry, sixth edition, 2000 Electronic
 35 Release, chapters antioxidants and food additives.

However, they include in particular:

- 5 - substituted phenols, hydroquinones, pyrocatechols and gallates such as 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-methoxyphenol, 3-tert-butyl-4-methoxyphenol, 2,2'-methylenebis(4-methyl-6-tert-butylphenol), propyl, octyl and dodecyl gallate or tert-butylhydroquinone (TBHQ), butylated hydroxyanisoles (BHA) and butylated hydroxytoluene (BHT),
- 10 - Irganox® antioxidants (from Ciba-Geigy) such as Irganox® 1010 (tetrakis(methylene 3,5-di-tert-butyl-4-hydroxycinnamate)-methane), Irganox® 1035 (thiodiethylene bis(3,5-di-tert-butyl-4-hydroxycinnamate)) and Irganox® 1076 (octadecyl propane(3-benzene-3',5'-di-tert-butyl-4'-hydroxybenzyl)phosphonate),
- 15 - trihydroxybutyrophenone (THBP),
- α -tocopherol and its natural or synthetic derivatives such as acetyl- α -tocopherol,
- ascorbic acid and ascorbic acid derivatives, especially esterification products with
20 long-chain fatty acids such as ascorbyl palmitate,
- diazabicyclooctane (DABCO),
- chroman derivatives such as long-chain esters of 2,5,7,8-tetramethyl-6-
25 hydroxychroman-2 acid,
- aromatic amines such as ethoxyquin,
- organic sulfides such as 3,3'-thiodipropionic acid and dilauryl thiodipropionate,
30
- sterically hindered amines, for example of the tetramethylpiperidine type such as Uvinul® 4049H, Uvinul® 4050H and Uvinul® 5050H from BASF AG,
- free radicals of the N-oxyl type such as 4-hydroxytetramethylpiperidine N-oxide,
35 esterification products thereof with carboxylic acids and further derivatives,

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- hydroxylamines such as those of dialkylamines and hydroxylamine ether derivatives of tetramethylpiperidine compounds,
- ascorbic, lactic, citric and tartaric acids and salts thereof.

5

The inorganic pigments A and organic UV absorbers B cooperate very well as UV absorbers possessing textile fiber affinity and mutually reinforce their effect. First, they protect, when applied to a textile material, the human skin against harmful UV radiation. Secondly, they protect dyed textile material against fading. The two protective effects preferably occur simultaneously.

10

Textile materials with which the components A and B have affinity and where they develop their protective effect include in particular apparel articles, i.e., articles which are worn on the human skin, but also house and garden articles comprising dyed textiles such as awnings and sunshades which are exposed to intensive solar irradiation. This textile material to be protected preferably comprises cellulose (cotton), for example apparel textiles comprising cotton or cotton-polyester blends.

15

The present invention also provides for the use of zinc oxide and/or titanium dioxide together with organic UV absorbers on textile material to protect human skin against harmful UV radiation and/or to protect dyed textile material against fading.

20

The mixture containing the components A and B is customarily applied to the textile material in the form of an aqueous liquor containing the components A and B alongside further ingredients, for example by spraying or dipping and squeezing off. The components A and B can be applied to the textile material in the course of textile finishing during the manufacture of the textile material, in the course of laundering, in the course of laundry pretreatment and/or laundry aftertreatment.

25

The UV protection factor UPF of the textile material is increased as a result.

30

The UV protection factor or Ultraviolet Radiation Protection Factor UPF of textiles is determined in accordance with the Australian/New Zealand standard AS/NZS 4399:1996 using an in vitro method. It measures the UV transmission of the textile object. The spectral transmission can be used to determine the protection factor directly using the following equation:

35

- 15 -

$$UPF = \frac{\int_{\lambda=280nm}^{400nm} S_{\lambda} \times E_{\lambda} \times d_{\lambda}}{\int_{\lambda=280nm}^{400nm} S_{\lambda} \times E_{\lambda} \times T_{\lambda} \times d_{\lambda}}$$

where:

5

S_{λ} is the spectral irradiation of the sun in the UV region at the wavelength λ ,
 E_{λ} is the spectral erythema action of the UV radiation at the wavelength λ , and
 T_{λ} is the spectral transmissivity of the textile object at the wavelength λ .

10 The present invention also provides a laundry detergent formulation comprising from 0.01% to 20% by weight, preferably from 0.1% to 10% by weight, particularly preferably from 0.1 to 5% by weight of the components A and B alongside further customary ingredients. The weight ratio of component A to component B is preferably in the range from 20 : 1 to 1 : 10, particularly preferably in the range from 8 : 1 to 1 : 5 and specifically
 15 preferably in the range from 3 : 1 to 1 : 1. In this connection, the components A and B can be added separately to the formulation or a ready-prepared mixture of A and B can be incorporated into the formulation.

20 Laundry detergent formulations according to the invention can be solid or liquid formulations.

Solid laundry detergent formulations according to the invention generally include as further customary ingredients

25 (c) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant as component C,

(d) from 0 to 50% by weight of one or more inorganic builders as component D,

30 (e) from 0 to 20% by weight of one or more organic cobuilders E,

(f) from 0 to 60% by weight of other customary ingredients such as cationic surfactants, standardizing agents, enzymes, perfume, complexing agents, corrosion inhibitors, bleaching agents, bleach activators, bleach catalysts, dye transfer inhibitors, soil

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antiredeposition agents, soil release polyesters, colorants, dissolution improvers and/or disintegrants as component F,

components A to F adding up to 100% by weight.

5

The solid laundry detergent formulations of the invention are customarily present in powder, granule, extrudate or tablet form.

Liquid laundry detergent formulations according to the invention generally include as further customary constituents

10

(c) from 0.1 to 40% by weight of at least one nonionic and/or anionic surfactant as component C,

(d) from 0 to 20% by weight of one or more inorganic builders as component D,

15

(e) from 0 to 10% by weight of one or more organic cobuilders as component E,

(f) from 0 to 40% by weight of other customary ingredients such as cationic surfactants, sodium carbonate, enzymes, perfume, complexing agents, corrosion inhibitors, bleaching agents, bleach activators, bleach catalysts, dye transfer inhibitors, soil antiredeposition agents, soil release polyesters, colorants, nonaqueous solvents, hydrotropes, thickeners and/or alkanolamines as component F, and

20

(g) from 0 to 99.85% by weight of water as component G,

25

components A to G adding up to 100% by weight.

Useful anionic surfactants are in particular:

30

- fatty alcohol sulfates of fatty alcohols having from 8 to 22 and preferably from 10 to 18 carbon atoms, for example C₉- to C₁₁-alcohol sulfates, C₁₂- to C₁₄-alcohol sulfates, C₁₂- to C₁₈-alcohol sulfates, lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate;

35

- sulfated alkoxyated C₈- to C₂₂-alcohols (alkyl ether sulfates). Compounds of this kind are prepared for example by first alkoxyating a C₈- to C₂₂-alcohol, preferably a C₁₀- to C₁₈-alcohol, for example a fatty alcohol, and then sulfating the alkoxylation product. The alkoxylation is preferably carried out using ethylene oxide;

5

- linear C₈- to C₂₀-alkylbenzenesulfonates (LAS), preferably linear C₉- to C₁₃-alkylbenzenesulfonates and -alkyltoluenesulfonates,

- alkanesulfonates such as C₈- to C₂₄- and preferably C₁₀- to C₁₈-alkanesulfonates,

10

- soaps such as for example the sodium and potassium salts of C₈- to C₂₄-carboxylic acids.

15

The anionic surfactants mentioned are preferably included in the laundry detergent in the form of salts. Suitable cations in these salts are alkali metal ions such as sodium, potassium and lithium and ammonium ions such as hydroxyethylammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium.

Useful nonionic surfactants are in particular:

20

- alkoxyated C₈- to C₂₂-alcohols such as fatty alcohol alkoxyates or oxo alcohol alkoxyates. These may have been alkoxyated with ethylene oxide, propylene oxide and/or butylene oxide. Useful surfactants here include all alkoxyated alcohols which contain at least two molecules of one of the aforementioned alkylene oxides. Here it is possible to use block polymers of ethylene oxide, propylene oxide and/or butylene oxide or addition products which contain the aforementioned alkylene oxides in random distribution. Nonionic surfactants generally contain from 2 to 50 and preferably from 3 to 20 mol of at least one alkylene oxide per mole of alcohol. The alkylene oxide component is preferably ethylene oxide. The alcohols preferably have from 10 to 18 carbon atoms. Depending on the nature of the alkoxylation catalyst used to make them, alkoxyates have a broad or narrow alkylene oxide homologue distribution;

30

- alkylphenol alkoxyates such as alkylphenol ethoxyates having C₆- to C₁₄-alkyl chains and from 5 to 30 alkylene oxide units;

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- alkylpolyglucosides having from 8 to 22 and preferably from 10 to 18 carbon atoms in the alkyl chain and generally from 1 to 20 and preferably from 1.1 to 5 glucoside units;
- 5 - N-alkylglucamides, fatty acid amide alkoxyates, fatty acid alkanolamide alkoxyates and also block copolymers of ethylene oxide, propylene oxide and/or butylene oxide.

Useful inorganic builders are in particular:

- 10 - crystalline or amorphous aluminosilicates having ion-exchanging properties such as zeolites in particular. Useful zeolites include in particular zeolites A, X, B, P, MAP and HS in their sodium form or in forms in which sodium has been partly replaced by other cations such as lithium, potassium, calcium, magnesium or ammonium;
- 15 - crystalline silicates such as in particular disilicates or sheet-silicates, for example δ - $\text{Na}_2\text{Si}_2\text{O}_5$ or β - $\text{Na}_2\text{Si}_2\text{O}_5$. The silicates can be used in the form of their alkali metal, alkaline earth metal or ammonium salts, preferably as sodium, lithium and magnesium silicates;
- 20 - amorphous silicates such as sodium metasilicate or amorphous disilicate;
- carbonates and bicarbonates. These can be used in the form of their alkali metal, alkaline earth metal or ammonium salts. Preference is given to sodium, lithium and magnesium carbonates or bicarbonates, especially sodium carbonate and/or sodium
25 bicarbonate;
- polyphosphates such as pentasodium triphosphate.

Useful organic cobuilders include in particular low molecular weight, oligomeric or
30 polymeric carboxylic acids.

- Useful low molecular weight carboxylic acids include for example citric acid, hydrophobically modified citric acid such as for example agaric acid, malic acid, tartaric acid, gluconic acid, glutaric acid, succinic acid, imidodisuccinic acid,
35 oxydisuccinic acid, propanetricarboxylic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid, alkyl- and alkenylsuccinic acids and

aminopolycarboxylic acids such as for example nitrilotriacetic acid, β -alaninediacetic acid, ethylenediaminetetraacetic acid, serinediacetic acid, isoserinediacetic acid, N-(2-hydroxyethyl)iminodiacetic acid, ethylenediaminedisuccinic acid and methyl- and ethylglycinediacetic acid;

- 5 - useful oligomeric or polymeric carboxylic acids include for example homopolymers of acrylic acid, oligomaleic acids, copolymers of maleic acid with acrylic acid, methacrylic acid, C₂-C₂₂-olefins such as for example isobutene or long-chain α -olefins, vinyl alkyl ethers having C₁-C₈-alkyl groups, vinyl acetate, vinyl propionate, methacrylic esters of C₁-C₈-alcohols and styrene. Preference is given to using the
10 homopolymers of acrylic acid and also copolymers of acrylic acid with maleic acid. Polyaspartic acids are also useful as organic cobuilders. Oligomeric and polymeric carboxylic acids are used in acid form or as sodium salt.

Useful bleaching agents include for example adducts of hydrogen peroxide with inorganic
15 salts such as for example sodium perborate monohydrate, sodium perborate tetrahydrate or sodium carbonate perhydrate or percarboxylic acids such as phthalimidopercaproic acid.

Suitable bleaching activators are e.g. N,N,N',N' - tetraacetyl ethylendiamine (TAED), sodium p-nonanoyloxybenzenesulfonate or N-methylmorpholiniumacetonitrilmethyl-
20 sulfate.

Enzymes preferably used in laundry detergents are proteases, lipases, amylases, cellulases, oxidases or peroxidases.

25 Suitable dye transfer inhibitors are e.g. homopolymers and copolymers of 1-vinylpyrrolidone, 1-vinylimidazole or 4-vinylpyridine-N-oxide. Homopolymers and copolymers of 4-vinylpyridine reacted with chloroacetic acid are also suitable dye transfer inhibitors.

30 The present invention further provides laundry aftertreatment and laundry conditioning compositions comprising from 0.01% to 20% by weight, preferably from 0.1 to 10% by weight and particularly preferably from 0.1% to 5% by weight of components A and B as well as other customary constituents. The weight ratio of component A to component B is preferably in the range from 20 : 1 to 1 : 10, more preferably in the range from 8 : 1 to 1 : 5
35 and especially in the range from 3 : 1 to 1 : 1. In this connection, the components A and B

can be added separately to the formulation or a ready-prepared mixture of A and B can be incorporated into the formulation.

5 The laundry aftertreatment and laundry conditioning compositions of the invention generally include as further customary constituents

- c) from 0.1 to 40% by weight of at least one cationic surfactant as component C,
- d) from 0 to 30% by weight of one or more nonionic surfactants as component D,
- 10 e) from 0 to 30% by weight of further customary ingredients such as scents, colorants, stabilizers, fiber and color protection additives, viscosity modifiers, soil release additives, soil antiredeposition agents, dye transfer inhibitors, complexing agents, corrosion control additives, bactericides, preservatives, nonaqueous solvents,
- 15 hydrotropes and/or alkanolamines as component E,
- f) from 0 to 25% by weight of cationic polymers as binders as component F, and
- g) water to 100% by weight as component G.

20

Useful cationic polymers (component F) include all natural or synthetic cationic polymers containing amino and/or ammonium groups and being soluble or dispersible in water. Examples of such cationic polymers are polyethyleneimines, amidated, alkoxyated and/or alkylated polyethyleneimines, crosslinked polyethyleneimines, polyamidoamines, 25 alkoxyated and/or alkylated polyamidoamines, crosslinked polyamidoamines, ethyleneimine-grafted crosslinked polyamidoamines, amine-epichlorohydrin polycondensates, polyvinylamines, alkoxyated polyvinylamines, partially hydrolyzed polyvinylformamides, polyallylamines, polydimethyldiallylammonium chlorides, polymers containing 1-vinylimidazole units such as poly-1-vinylimidazole or poly-(1- 30 vinylimidazole-co-1-vinylpyrrolidone), polymers containing quaternary vinylimidazole units, condensates of imidazole and epichlorohydrin, polymers containing basic methacrylamide or methacrylic ester units, polymers containing basic quaternary methacrylamide or methacrylic ester units and/or lysine condensates.

35 The term "cationic polymers" also comprehends amphoteric addition polymers which have a net cationic charge, i.e., the polymers contain both anionic and cationic monomers in

copolymerized form, but the molar fraction of the cationic units present in the polymers is greater than that of the anionic units.

Preferred cationic surfactants (component C) are selected from the group consisting of the quaternary diesterammonium salts, the quaternary tetraalkylammonium salts, the quaternary diamidoammonium salts, the amidoamine esters and imidazolium salts. These are preferably present in the fabric conditioners in an amount of from 3 to 30% by weight. Examples are quaternary diesterammonium salts having two C₁₁- to C₂₂-alk(en)yl-carbonyloxy(mono- to pentamethylene) radicals and two C₁- to C₃-alkyl- or hydroxyalkyl radicals on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

Quaternary diesterammonium salts are further in particular those which have a C₁₁- to C₂₂-alk(en)ylcarbonyloxytrimethylene radical bearing a C₁₁- to C₂₂-alk(en)ylcarbonyloxy radical on the central carbon atom of the trimethylene group and three C₁- to C₃-alkyl- or hydroxyalkyl radicals on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

Quaternary tetraalkylammonium salts are in particular those which have two C₁- to C₆-alkyl radicals and two C₈- to C₂₄-alk(en)yl radicals on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

Quaternary diamidoammonium salts are in particular those which have two C₈- to C₂₄-alk(en)ylcarbonylaminoethylene radicals, a substituent selected from hydrogen, methyl, ethyl and polyoxyethylene having up to 5 oxyethylene units and as fourth radical a methyl group on the quaternary nitrogen atom and, for example, chloride, bromide, methosulfate or sulfate as counterion.

Amidoamino esters are in particular tertiary amines bearing a C₁₁- to C₂₂-alk(en)ylcarbonylamino (mono- to trimethylene) radical, a C₁₁- to C₂₂-alk(en)ylcarbonyloxy (mono- to trimethylene) radical and a methyl group as substituents on the nitrogen atom.

Imidazolinium salts are in particular those which bear a C₁₄- to C₁₈-alk(en)yl radical in position 2 of the heterocycle, a C₁₄- to C₁₈-alk(en)ylcarbonyl(oxy or amino)ethylene radical on the neutral nitrogen atom and hydrogen, methyl or ethyl on the nitrogen atom

carrying the positive charge, while counterions here are for example chloride, bromide, methosulfate or sulfate.

5 The present invention also provides for the use of zinc oxide and/or titanium dioxide together with organic UV absorbers in laundry detergent, laundry aftertreatment and laundry conditioning compositions.

The present invention also provides a finishing composition for UV protection of textile materials comprising the components A and B.

10

The finishing compositions according to the invention are present for example as finishes in the narrower sense in the course of the manufacture of the textiles or in the form of an aqueous wash liquor or as a liquid textile treatment composition. It is accordingly possible for example to treat the textiles with the finishing composition in connection with the
15 manufacture of the textiles. Textiles never treated or only inadequately treated with a finish may be treated for example in the home before or after washing with a textile treatment composition containing the inorganic pigments A and the organic UV absorbers B. But it is also possible to treat the textiles with the components (A) and (B) in the main wash cycle or after the main wash cycle in the conditioning rinse cycle of the washing machine, partly
20 using the above-described formulations.

The examples hereinbelow illustrate the present invention.

Example 1 – Application of the UV protectant as a laundry aftertreatment in the
25 conditioning rinse bath and determination of the UV protection factor UPF

White woven cotton fabric having a basis weight of 100 g/m² and a UV protection factor (UPF) of 4.1 was washed at a water hardness of 3 mmol/l. The laundering process was a main wash cycle at 40 °C with a commercially available laundry detergent (Ariel® Color) and a subsequent conditioning rinse. The conditioner used was a commercially available
30 formulation (Downy from Lenor®) in a dosage of 1000 ppm, based on the liquor. The fabric conditioner formulation included either no UV absorber or in each case 100 or 200 ppm, based on the liquor, of an inventive UV absorber combination, added before the conditioning rinse. The liquor ratio was 12.5:1. After the conditioning rinse cycle, the
35 fabric was removed and its UV protection factor was determined in the dried state. Subsequently the fabric was tested for photostability. The fabric sample was exposed in a

SUNTEST[®] CPS tabletop accelerated lighting unit from Heraeus, Hanau, for 4 and 24 hours under outdoor conditions using a WG 295 filter at the maximum radiative power output of the instrument. The UV protection factor was redetermined after 4 and 24 hours of exposure.

5

The inorganic pigments used were as follows:

- Z-COTE[®], an amphiphilic zinc oxide from BASF AG
- Uvinul[®] TiO₂ from BASF AG

10

The organic UV absorbers were used as follows:

- A = 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (Uvinul[®] N-539 T)
- B = 2-hydroxy-4-(n-octyloxy)benzophenone (Uvinul[®] 3008)

15

The results are summarized in table 1.

Table 1

	UPF	Δ	UPF after 4 h exposure	Δ	UPF after 24 h exposure	Δ
no additive	4.3		4.2		4.2	
50 ppm of ZnO	4.7	0.4	4.5	0.3	4.6	0.4
100 ppm of ZnO	5.5	1.2	5.5	1.3	5.4	1.2
50 ppm of A	8.5	4.2	7.2	3.0	5.5	1.2
100 ppm of A	13.4	9.1	11.4	7.2	8.5	4.3
50 ppm of A + 50 ppm of ZnO	12.3	8.0	11.8	7.6	10.3	6.1
100 ppm of A + 100 ppm of ZnO	19.2	14.9	18.4	14.2	16.5	12.3
100 ppm of TiO ₂	5.0	0.7	4.9	0.7	4.8	0.6
100 ppm of A + 100 ppm of TiO ₂	17.6	13.3	17.5	13.3	14.5	10.3
100 ppm of B	10.1	5.8	9.0	4.8	7.4	3.2
100 ppm of B + 100 ppm of TiO ₂	14.8	10.5	14.5	10.3	12.4	8.2

$$\Delta = \text{UPF (with additive)} - \text{UPF (without additive)}$$

The results clearly show the synergistic effect on the combined use of UV absorbers A and B with zinc oxide and titanium dioxide respectively. It is similarly clear that the pigment oxides have a positive effect on the photostability of the organic UV absorbers A and B. Zinc oxide and titanium dioxide increase the UV protection factor of the cotton fabric only insignificantly when used alone in either case.

Example 2 – Application as a laundry aftertreatment in the conditioning rinse bath and determination of the photostability of dyed cotton fabric used

A woven cotton fabric dyed with Reactive Black 5 to 1/3 standard depth was treated in the conditioning rinse cycle with a commercially available formulation (Downy from Lenor®, 1000 ppm, based on the liquor) in the presence of an inventive UV absorber combination (in each case 200 ppm, based on the liquor) in a liquor ratio of 12.5:1. After the conditioning rinse cycle, the dyed fabrics were removed and tested for photostability in the dried state.

Photostability was measured as follows:

The samples were exposed in a SUNTEST® tabletop accelerated lighting unit from Heraeus, Hanau for 8 or 24 hours under outdoor conditions using a WG 295 filter at the maximum radiative power output of the instrument. A spectrophotometer with an integration sphere Lambda 900 from Perkin Elmer was used to measure the reflectance spectra of the dyes before and after exposure. These reflectance spectra were converted in line with the Kubelka-Munk theory into K/S spectra (K = absorption coefficient, S = scattering coefficient). The photostabilities were evaluated with reference to the K/S values after 8 or 24 hour exposure relative to the K/S values prior to exposure (K/S in each case at the maximum of the K/S spectra). The higher the value in % reported in table 2, the higher the photostability.

The inorganic pigment used was Z-COTE® from BASF AG.

The organic UV absorbers used were as follows:

C = n-hexyl 2-(4'-diethylamino-2'-hydroxybenzoyl)benzoate

D = 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione (Uvinul® BMBM)

Table 2

5

	K/S (8 h) / K/S (0 h) x 100%	K/S (24 h) / K/S (0 h) x 100%
no additive	77.2%	57.7%
400 ppm of ZnO	82.0%	63.7%
400 ppm of C	81.3%	62.0%
200 ppm of C + 200 ppm of ZnO	85.5%	68.8%
400 ppm of D	80.8%	61.0%
200 ppm of D + 200 ppm of ZnO	84.9%	67.0%

The results clearly show the synergistic effect on the combined use of C or D with zinc oxide.

We claim:-

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1. A method for UV protecting a textile material, which comprises applying
 - (a) zinc oxide and/or titanium oxide as a component A and
 - (b) one or more organic UV absorbers as a component Bto said textile material.
- 10
2. A method as claimed in claim 1, wherein said component A comprises UV absorbers having an absorption maximum in the range from 280 to 450 nm.
- 15
3. A method as claimed in claim 1 or 2, wherein said component B comprises one or more compounds selected from the group consisting of
 - phenylbenzotriazoles,
 - dibenzoylmethanes,
 - esters of p-aminobenzoic acid,
 - 20 - esters of cinnamic acid,
 - esters of salicylic acid,
 - nonnitrogenous 2-hydroxybenzophenones,
 - phenylbenzimidazoles,
 - acrylates,
 - 25 - diarylbutadienes,
 - amino-substituted hydroxybenzophenones,
 - triazines.
- 30
4. A method as claimed in any of claims 1 to 3, wherein the weight ratio of said component A to said component B is in the range from 20 : 1 to 1 : 10.
5. A method as claimed in any of claims 1 to 4, wherein said components A and B are applied to said textile material in the form of an aqueous liquor containing said components A and B alongside further ingredients.

6. A method as claimed in any of claims 1 to 5, wherein said components A and B are applied to said textile material in the course of textile finishing during the manufacture of said textile material, in the course of laundering and/or in the course of laundry aftertreatment.
- 5
7. A laundry detergent formulation comprising from 0.01 to 20% by weight, based on their total, of said components A and B as defined in any of claims 1 to 4 as well as further customary constituents.
- 10
8. A laundry aftertreatment and laundry conditioning formulation comprising from 0.01 to 20% by weight, based on their total, of said components A and B as defined in any of claims 1 to 4 as well as further customary constituents.
- 15
9. A laundry aftertreatment and laundry conditioning formulation as claimed in claim 8, comprising from 1 to 50% by weight of one or more cationic surfactants selected from the group consisting of quaternary diesterammonium salts, quaternary tetraalkylammonium salts, quaternary diamidoammonium salts, amidoamino esters and imidazolines.
- 20
10. A finishing composition for UV protecting a textile material, comprising a mixture of said components A and B as defined in any of claims 1 to 4.
11. Textile material comprising a mixture of said components A and B as defined in any of claims 1 to 4.
- 25
12. The use of zinc oxide and/or titanium dioxide together with organic UV absorbers on textile material to protect the human skin against harmful UV radiation and/or to protect dyed textile material against fading.