

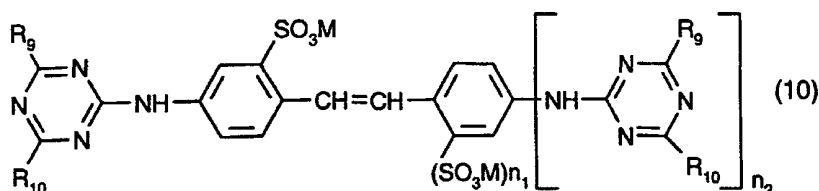
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(54) Title: USE OF UVAS FOR SUPPRESSING THE FLUORESCENCE OF TEXTILE FIBRE MATERIALS TREATED WITH FLUORESCENT WHITENING AGENTS



(57) Abstract: The present invention relates to a process for inhibiting (quenching) the effect of fluorescent whitening agents on cellulosic textile fibre materials treated, being treated or to be treated with fluorescent whitening agents, by the application of certain triazine-based ultra-violet absorption agent (UVAs), preferably those of formula (10) in which M, n_1 , n_2 , R_9 and R_{10} are as defined in claim 2 and to the material so treated and also to processes for decontaminating detergent manufacturing apparatus and recycled industrial laundry water containing residual fluorescent whitening agent (FWAs).

Use of UVAs for suppressing the fluorescence of textile fibre materials treated with fluorescent whitening agents.

The present invention relates to a process for inhibiting (quenching) the effect of fluorescent whitening agents on cellulosic textile fibre materials treated, being treated or to be treated with fluorescent whitening agents, by the application of certain ultra-violet absorption agents (UVAs) and to the material so treated, and to processes for decontaminating detergent manufacturing apparatus and recycled industrial laundry water containing residual fluorescent whitening agent (FWAs).

Processes for quenching the fluorescence of whitened substrates are known. Thus, for example, UK patent application GB-A-No. 2,174,731 teaches a process for quenching or preventing white effects on different substrates by the application of UV absorbers, in which process the UV absorbers employed are derivatives of the benzophenone series or of the unsulfonated benzotriazoles series.

At the present time, commercial detergents and soaps for domestic use usually contain fluorescent whitening agents to impart a whiter appearance to the washed articles. When textiles which have been dyed or printed in a light shade are washed with such a detergent composition, the shade after drying is different from what it was previously, especially in the case of light shades such as blue, pink and beige.

It is known that textiles which have color shades, where the fluorescent whitening effect exerted by fluorescent whitening agents can lead to undesirable shifts in the shade, especially with pastel shades. Those textiles can be washed with color care detergents which mostly do not contain FWAs. To prevent FWA transfer from FWA containing fabrics or from the washing machine itself to those fabrics, a quencher compound can be added to the color care detergent.

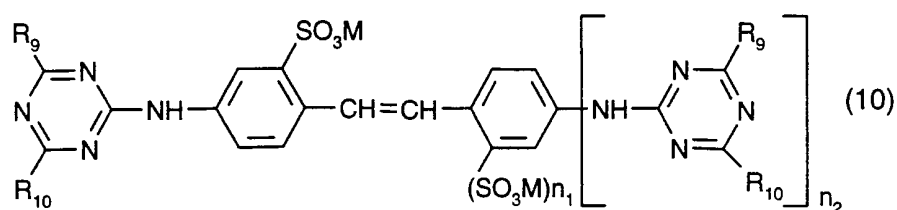
There are also situations where shifts in the shading occur. For example if a set of pastel pink hotel table covers and napkins are washed together then this may result in the items having different shades caused by the fluorescent whitening agent transfer. To reverse this effect, a quencher compound can be added during the wash to the laundry, or added to a detergent or washing aid with which the concerned laundry goods are treated.

It has now been found that certain ultra-violet absorption agents (UVAs) are most suitable for quenching or suppressing the fluorescent effects produced on substrates by treatment with fluorescent whitening agents, before, during or after treatment with the fluorescent whitening agent.

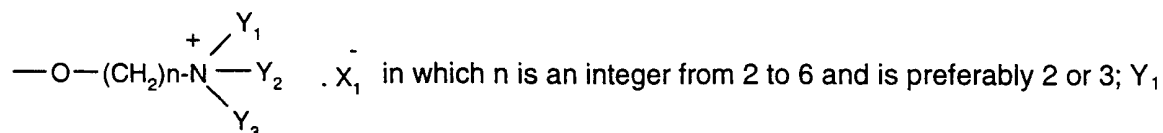
Accordingly, the invention relates to a process for quenching or suppressing the fluorescence of cellulosic textile fibre materials treated, being treated or to be treated, with fluorescent whitening agents, which process comprises applying to said substrates, before or after the treatment with the fluorescent whitening agent, certain ultra-violet absorption agents (UVAs).

The terms "substrates" will be understood as meaning cellulosic textile materials made of cellulosic fibres, by which are meant in turn, for example, yarns, wovens, knits or nonwovens. The textile materials can also consist of blends of fibres.

One preferred class of UV absorbers is that having the formula:



in which M is hydrogen, sodium, potassium, ammonium, mono-, di-, tri- or tetra-C₁-C₄alkylammonium, mono-, di- or tri-C₁-C₄hydroxyalkylammonium or ammonium that is di- or tri-substituted by a mixture of C₁-C₄alkyl and C₁-C₄hydroxyalkyl groups; or

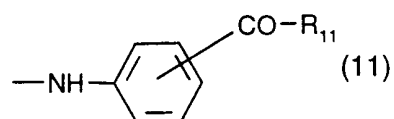


and Y₂, independently, are C₁-C₄alkyl optionally substituted by halogen, cyano, hydroxy or C₁-C₄alkoxy or Y₁ and Y₂, together with the nitrogen atom to which they are each attached, form a 5-7 membered heterocyclic ring, preferably a morpholine, pyrrolidine, piperidine or hexamethyleneimine ring; Y₃ is hydrogen, C₃-C₄alkenyl or C₁-C₄alkyl optionally substituted by cyano, hydroxy or C₁-C₄alkoxy or Y₁, Y₂ and Y₃, together with the nitrogen atom to which they

are each attached, form a pyridine or picoline ring; and X_1^- is a colourless anion, preferably $\text{CH}_3\text{OSO}_3^-$ or $\text{C}_2\text{H}_5\text{OSO}_3^-$;

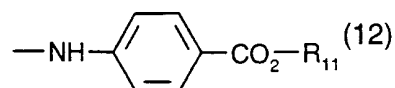
n_1 and n_2 , independently, are 0 or 1, provided that if n_1 is 0, n_2 is 0;

R_9 is optionally substituted aryl or a group having the formula:

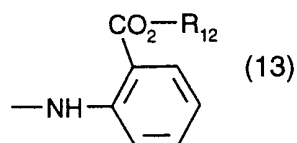


in which R_{11} is optionally substituted alkyl or optionally substituted aryl;

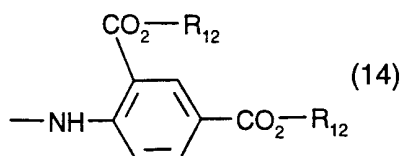
or, when n_2 is 0, R_9 may also be a group having one of the formulae:



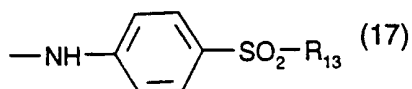
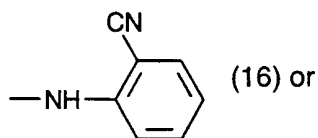
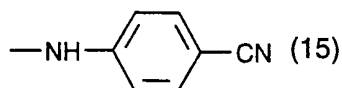
in which R_{11} has its previous significance;

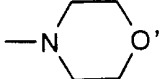


in which R_{12} is M, optionally substituted alkyl or optionally substituted aryl;



in which R_{12} has its previous significance;



in which R_{13} is hydrogen, optionally substituted alkyl or optionally substituted aryl; and R_{10} is hydrogen, halogen, preferably chlorine, optionally substituted alkyl, optionally substituted aryl, , -OH, -NH₂, -N(CH₂CH₂OH)₂, -N[CH₂CH(OH)CH₃]₂, -NH-R₁₂,

-N(R₁₂)₂ or -OR₁₂, in which R₁₂ has its previous significance, or R₁₀ is an aminoacid residue from which a hydrogen atom on the amino group has been removed.

When one or more of R₁₀, R₁₁, R₁₂ and R₁₃ is optionally substituted alkyl, preferred unsubstituted alkyl groups R₁₀, R₁₁, R₁₂ and R₁₃ are C₁-C₁₂-, especially C₁-C₄-alkyl groups. The alkyl groups may be branched or unbranched and may be optionally substituted, e.g. by halogen such as fluorine, chlorine or bromine, by C₁-C₄-alkoxy such as methoxy or ethoxy, by phenyl or carboxyl, by C₁-C₄-alkoxycarbonyl such as acetyl, by a mono- or di-C₁-C₄alkylated amino group or by -SO₃M in which M has its previous significance.

When one or more of R₁₀, R₁₁, R₁₂ and R₁₃ are optionally substituted aryl, they are preferably a phenyl or naphthyl group which may be substituted by C₁-C₄-alkyl, e.g. by methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec.-butyl or tert.-butyl, by C₁-C₄-alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec.-butoxy or tert.-butoxy, by halogen such as fluorine, chlorine or bromine, by C₂-C₅-alkanoylamino, such as acetylamino, propionylamino or butyrylamino, by nitro, sulfo or by di-C₁-C₄alkylated amino.

Preferably, each of the aminoacid residues R₁₀ is the same. Examples of preferred aminoacid residues R₁₀ include those having the formula -NH-CH(CO₂H)-R₁₄ in which R₁₄ is hydrogen or a group having the formula -CHR₁₅R₁₆ in which R₁₅ and R₁₆, independently, are hydrogen or C₁-C₄alkyl optionally substituted by one or two substituents selected from hydroxy, thio, methylthio, amino, carboxy, sulfo, phenyl, 4-hydroxyphenyl, 3,5-diiodo-4-hydroxyphenyl, β-indolyl, β-imidazolyl and NH=C(NH₂)NH-.

Specific examples of aminoacids from which such preferred aminoacid residues R₁₀ are derived include glycine, alanine, sarcosine, serine, cysteine, phenylalanine, tyrosine (4-hydroxyphenylalanine), diiodotyrosine, tryptophan (β-indolylalanine), histidine ((β-imidazolylalanine), α-aminobutyric acid, methionine, valine (α-aminoisovaleric acid), norvaline, leucine (α-aminoisocaproic acid), isoleucine (α-amino-β-methylvaleric acid), norleucine (α-amino-n-caproic acid), arginine, ornithine (α,δ-diaminovaleric acid), lysine (α,ε-

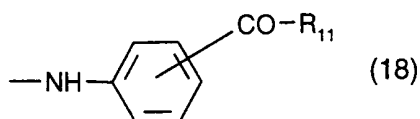
diaminocaproic acid), aspartic acid (aminosuccinic acid), glutamic acid (α -aminoglutaric acid), threonine, hydroxyglutamic acid and taurine, as well as mixtures and optical isomers thereof. Of these aminoacids from which such preferred aminoacid residues R_{10} are derived, glutamic acid and aspartic acid are particularly preferred.

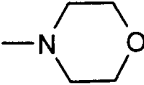
A further preferred example of an aminoacid from which an aminoacid residue R_{10} may be derived is iminodiacetic acid.

Other, less preferred examples of aminoacids from which aminoacid residues R_{10} may be derived include cystine, lanthionine, proline and hydroxyproline.

In each of the compounds of formula (10) it is preferred that they are used in neutral form, i.e. that M is other than hydrogen, preferably a cation formed from an alkali metal, in particular sodium, or from an amine.

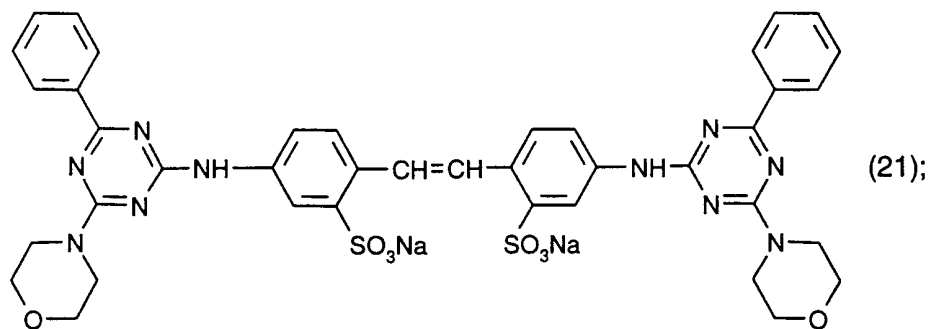
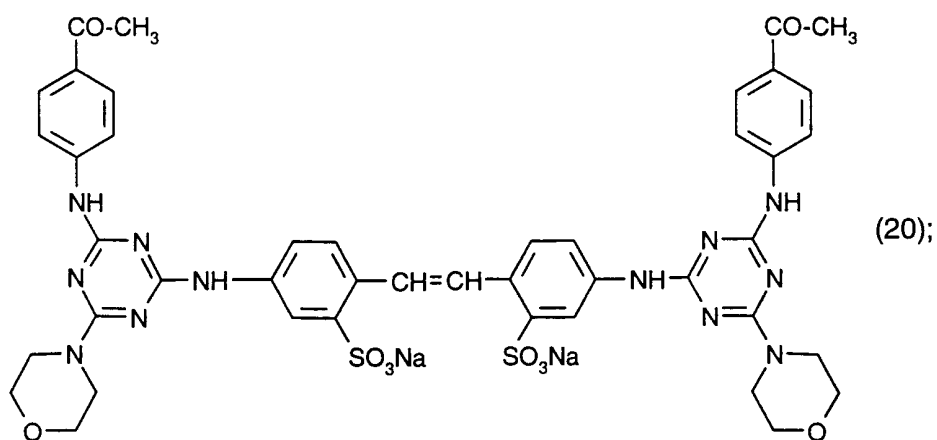
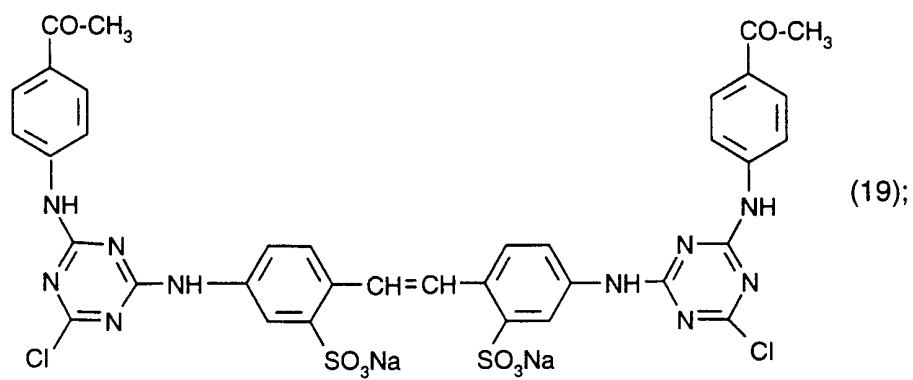
In the compounds of formula (10), preferably R_9 is phenyl, methylphenyl, dimethylphenyl or a group of formula:

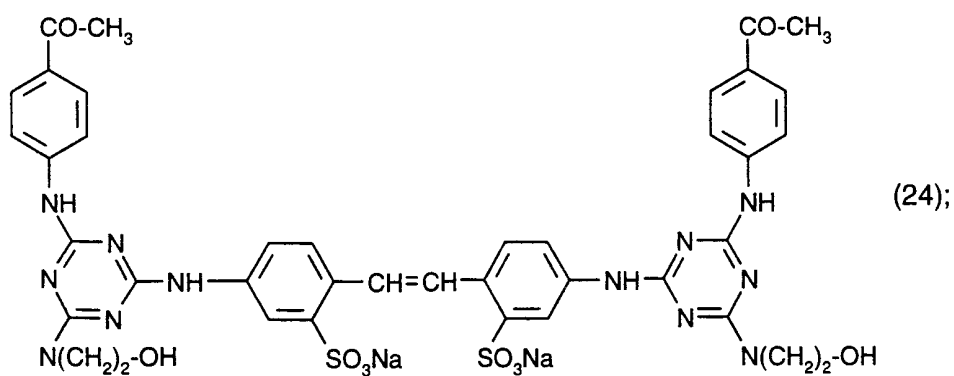
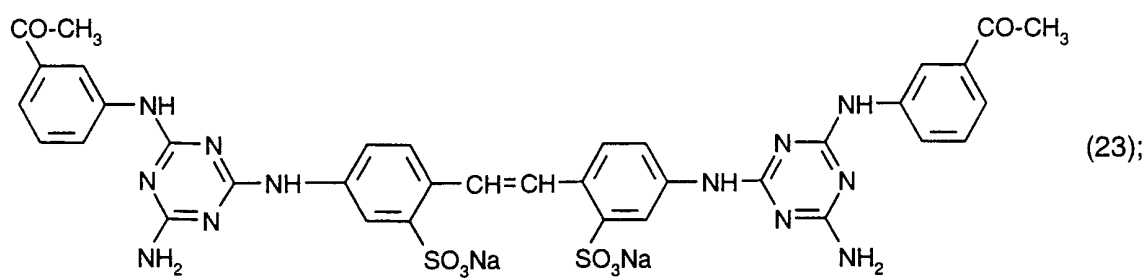
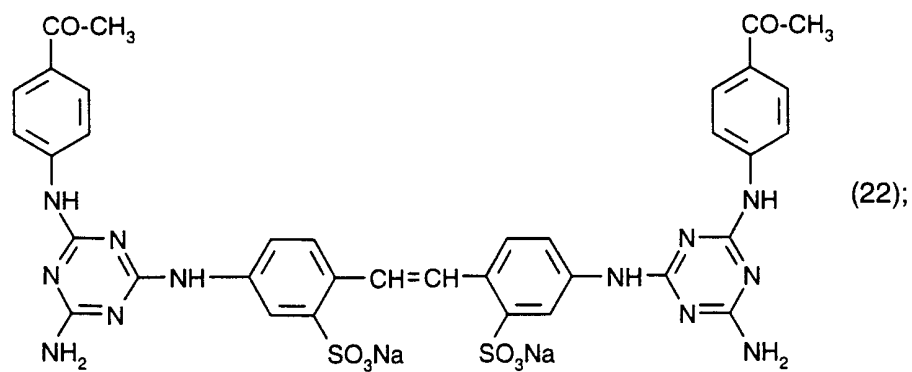


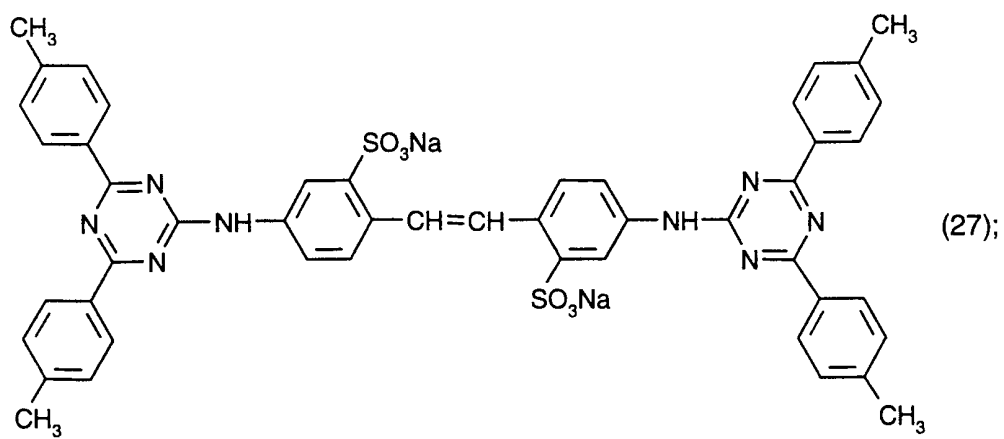
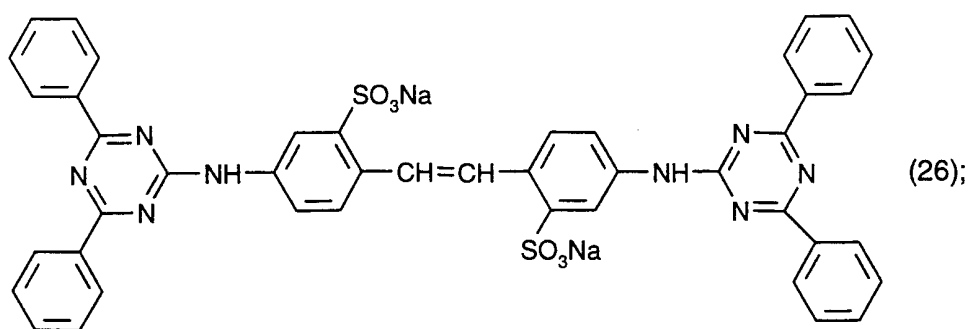
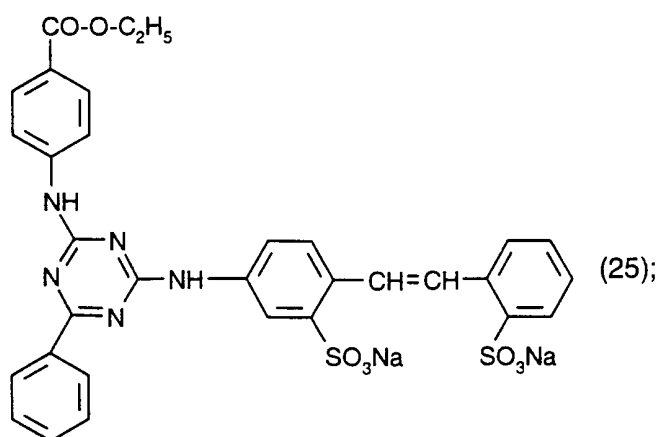
in which R_{11} has its previous significance and is preferably C_1 - C_4 -alkyl, especially methyl or ethyl; and preferably R_{10} is phenyl, methylphenyl, dimethylphenyl, , $-NH_2$, Cl, -

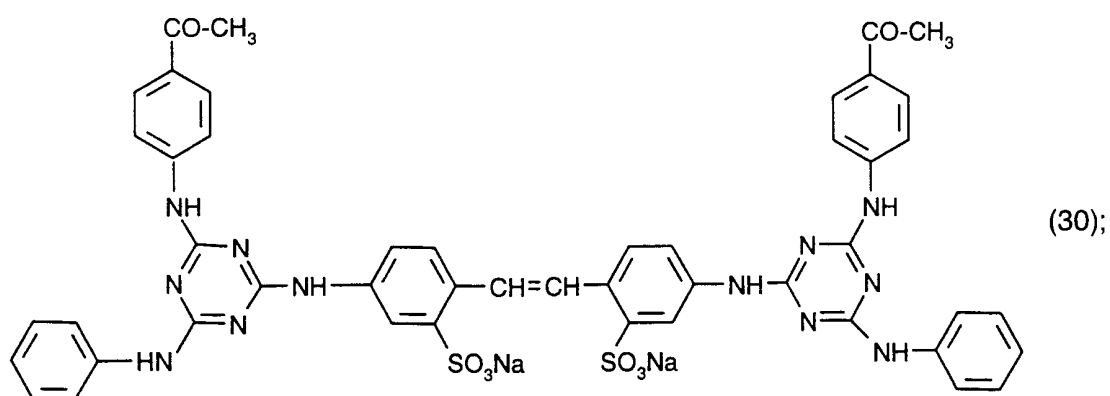
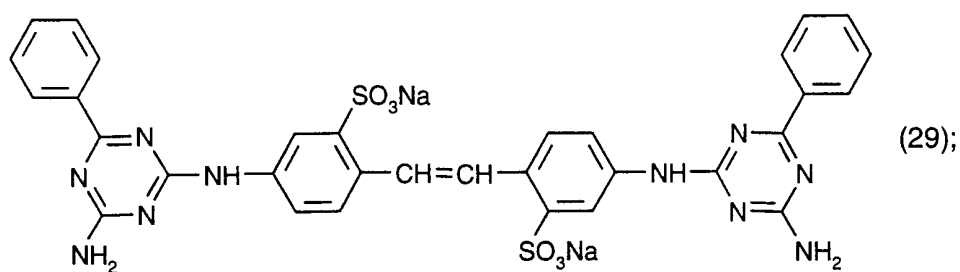
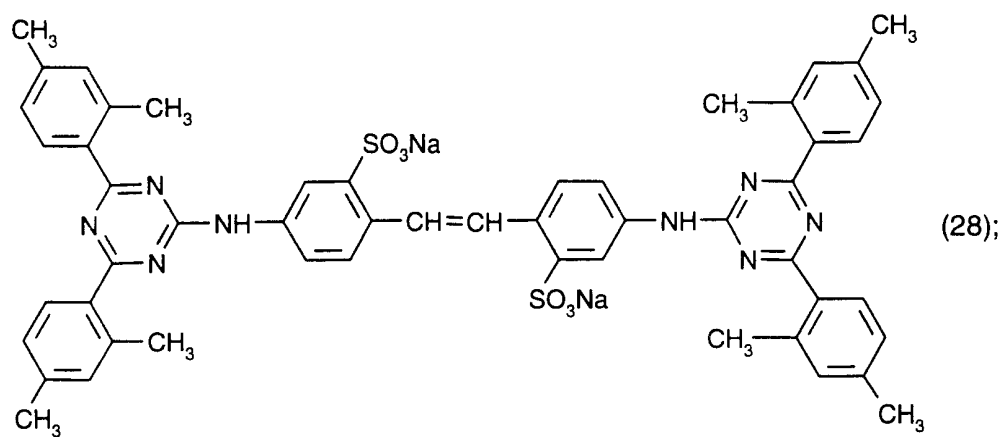
$N(CH_2CH_2OH)_2$ or $-N[CH_2CH(OH)CH_3]_2$.

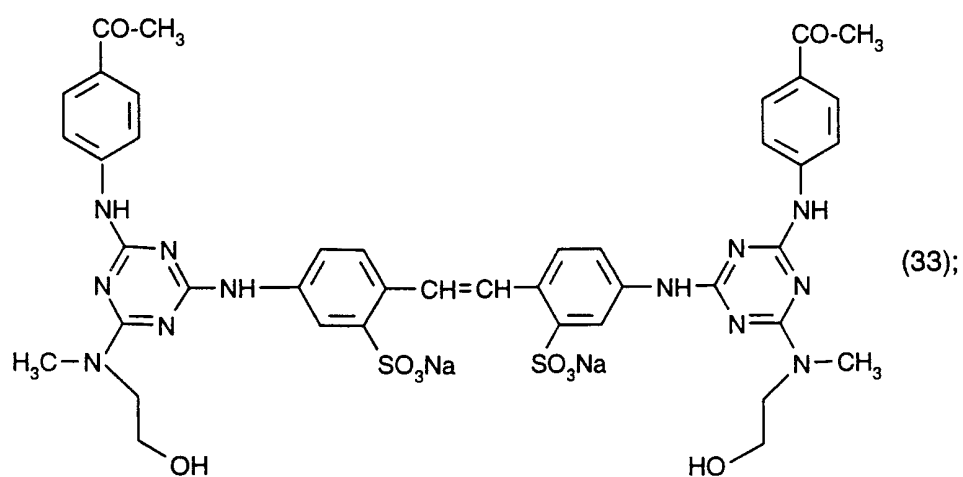
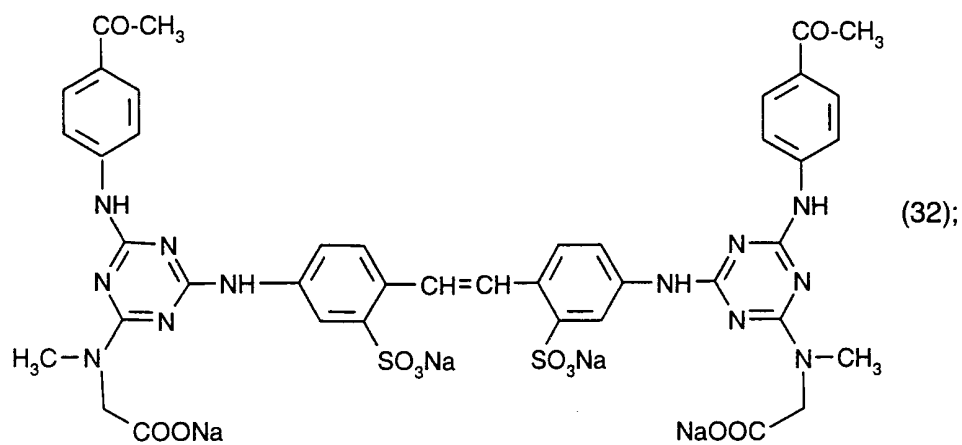
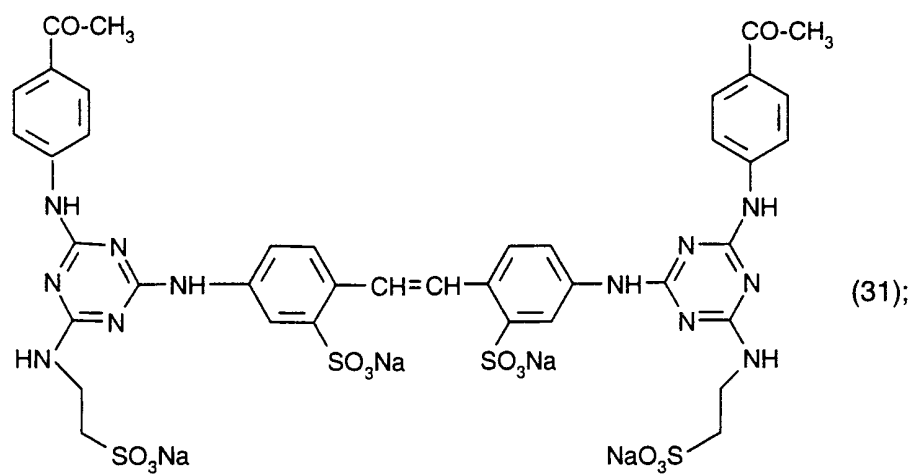
Preferred compounds of formula (10) are those having the formula:

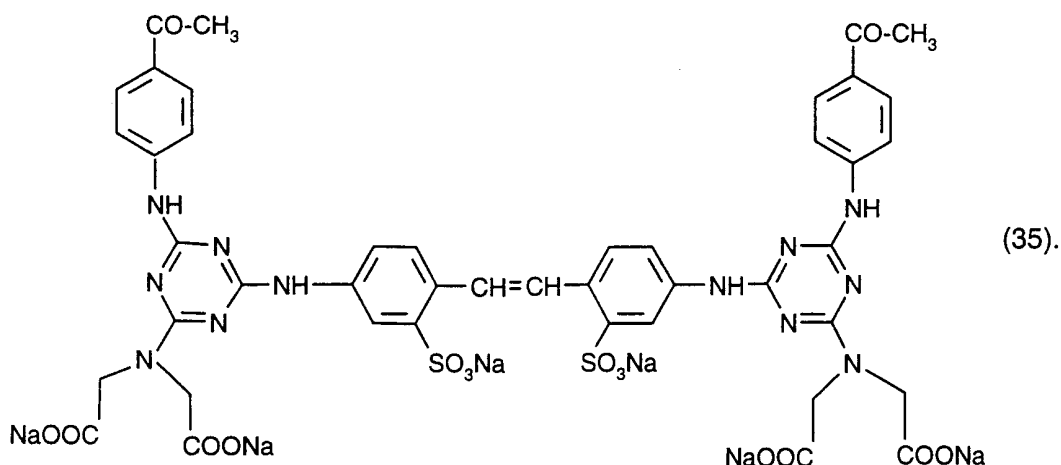
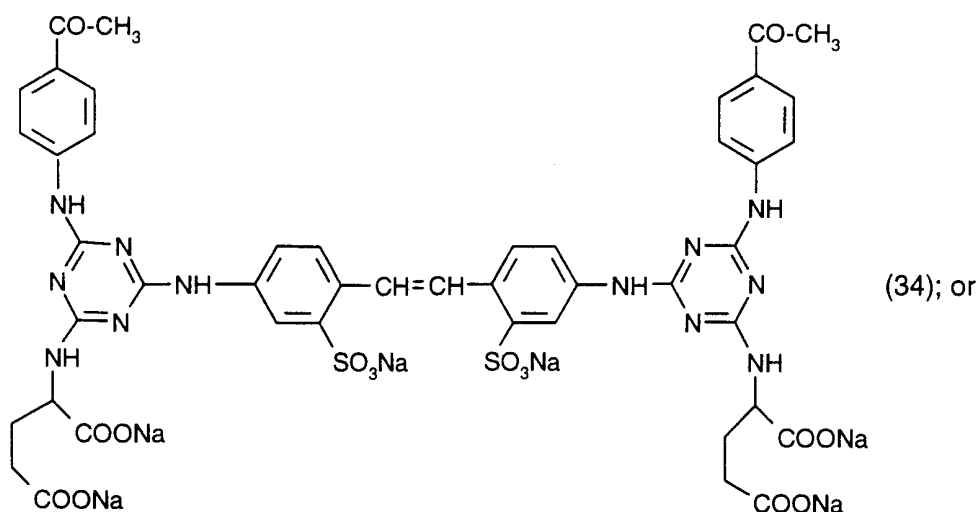








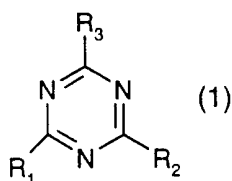




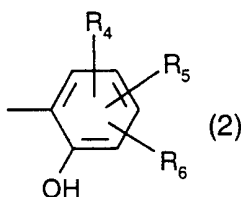
The compounds of formula (10) may be produced by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of an aminostilbene-sulfonic acid, an amino compound capable of introducing a group R_9 and a compound capable of introducing a group R_{10} , in which R_9 and R_{10} each have their previous significance. Unsymmetrical compounds of formula (10), namely those in which n_2 is zero, may be produced by the method described in GB-A-2,298,422.

The starting materials are known compounds which are readily available.

A second preferred class of triazine UVA's is that having the formula:



in which at least one of R_1 , R_2 and R_3 is a radical of formula:



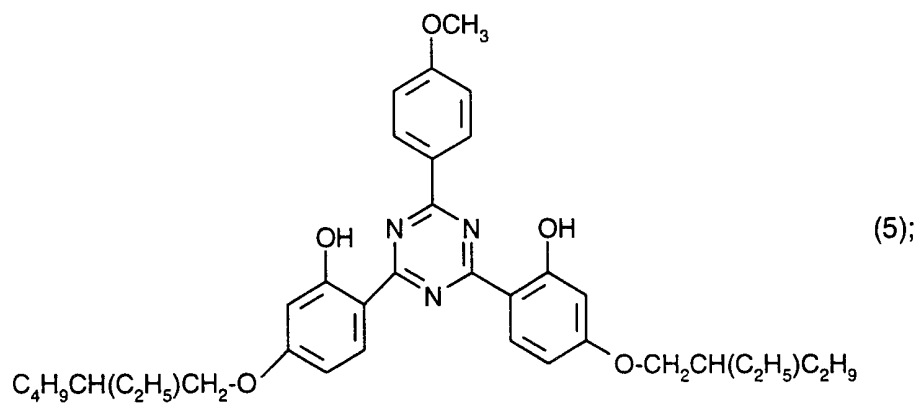
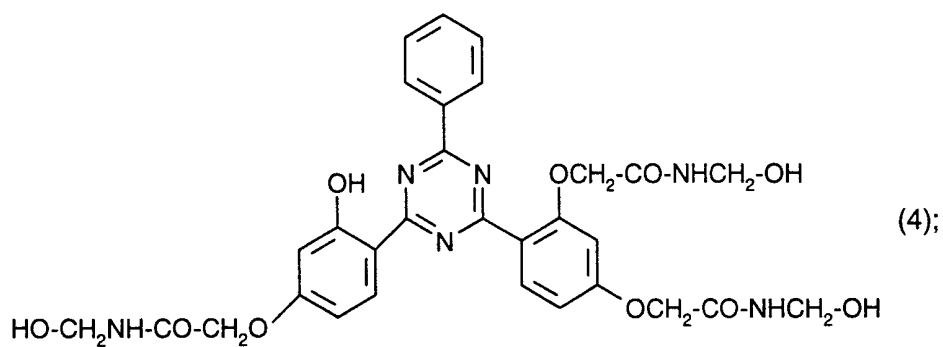
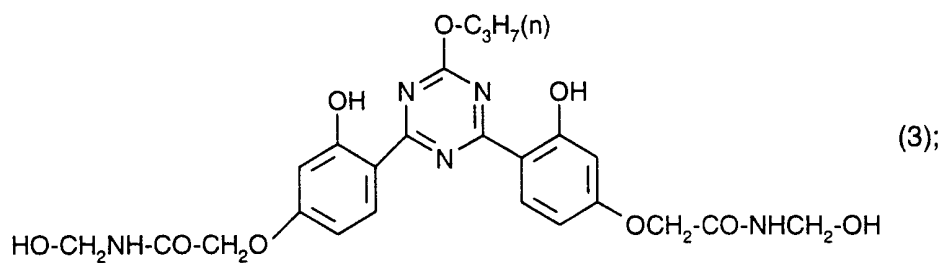
in which R_4 , R_5 and R_6 , independently, are hydrogen; C_1 - C_{12} alkoxy; hydroxy; $-O-CH_2-CO-NH-CH_2OH$; SO_3M in which M has its previous significance and the remaining substituent(s) R_1 , R_2 and R_3 are, independently, halogen, preferably chlorine, C_1 - C_{12} alkoxy or phenyl, the phenyl substituent being optionally substituted by one or more of hydroxy, C_1 - C_{12} -alkoxy, $-O-CH_2-CO-NH-CH_2OH$, SO_3M in which M has its previous significance.

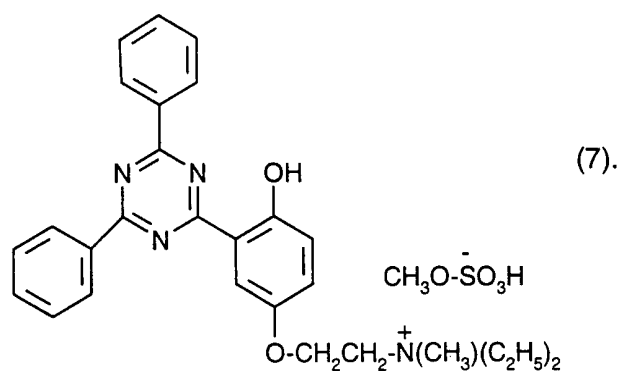
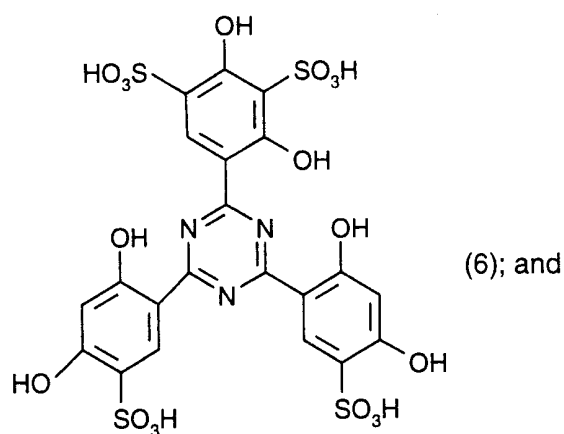
In the compounds of formula (1), C_1 - C_4 alkyl groups Y_1 , Y_2 and Y_3 may be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert.-butyl, methyl and ethyl being preferred

C_1 - C_{12} Alkoxy groups R_1 , R_2 , R_3 , R_4 , R_5 and R_6 may be, e.g., methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, tert.-butoxy, n-amyloxy, n-hexoxy, n-heptoxy, n-octoxy, isooctoxy, n-nonyloxy, n-decoxy, n-undecyloxy or n-dodecyloxy, methoxy and ethoxy being preferred.

The alkyl radicals in the mono-, di-, tri- or tetra- C_1 - C_4 alkylammonium groups M are preferably methyl. Mono-, di- or tri- C_1 - C_4 hydroxyalkylammonium groups M are preferably those derived from ethanolamine, di-ethanolamine or tri-ethanolamine. When M is ammonium that is di- or tri-substituted by a mixture of C_1 - C_4 alkyl and C_1 - C_4 hydroxyalkyl groups, it is preferably N-methyl-N-ethanolamine or N,N-dimethyl-N-ethanolamine. M is preferably, however, hydrogen or sodium.

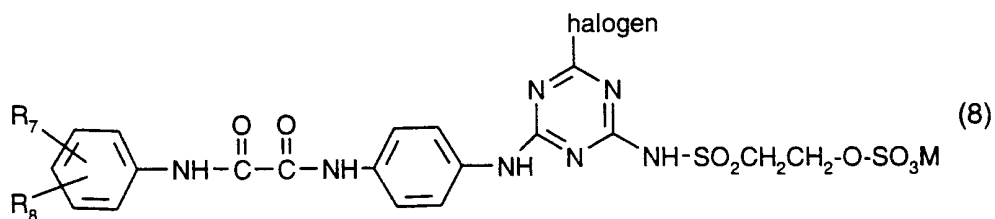
Preferred compounds of formula (1) are those having the formulae:





The compounds of formula (1) are known and may be prepared e.g. by the method described in U.S. Patents 3118887 and 5197991.

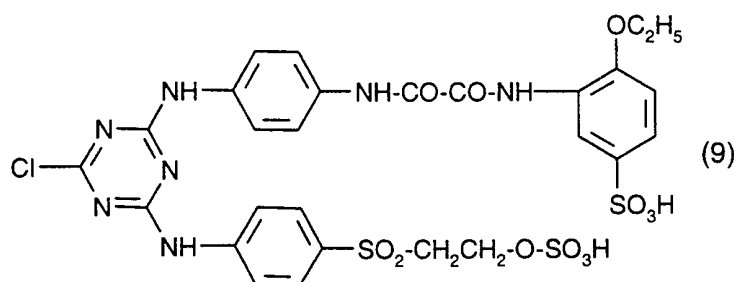
A third preferred class of triazine UVAs is that having the formula:



in which M has its previous significance and R_7 and R_8 are C_1 - C_{12} -alkoxy or SO_3M in which M has its previous significance. Preferably halogen is chlorine.

C₁-C₁₂Alkoxy groups R₇ and R₈ may be, e.g., methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, tert.-butoxy, n-amyloxy, n-hexoxy, n-heptoxy, n-octoxy, isooctoxy, n-nonyloxy, n-decoxy, n-undecyloxy or n-dodecyloxy, methoxy and ethoxy being preferred.

A preferred compound of formula (8) is that having the formula:



The compounds of formula (8) are known and may be prepared e.g. by the method described in U.S. Patents 3118887 and 5197991.

Mixtures of UV absorbers can also be used.

The UV absorber is preferably applied to the substrate from an aqueous medium.

In the process of this invention, the UV absorber can be applied to the substrate and fixed thereon by all known methods of dyeing or printing, for example by treatment in a long bath in the temperature range from 20°C to 140°C, by impregnation and batching at room temperature or elevated temperature, for example in the range from 20°C to 90°C for 30 minutes to 48 hours, depending on the temperature, by padding and fixing by treatment with saturated steam, superheated steam, hot air, or by treatment with high frequency or contact heat. The UV absorber can also be applied by heat transfer printing. The UV absorber can further be fixed on the substrate in combination with organic polymers, for example in the form of aqueous or non-aqueous surface coatings, or by the method of pigment printing.

The method of applying and fixing the UV absorber and the amount of UV absorber employed depends on the substrate, the dye used, the fluorescent whitening agents and their fastness properties, and on the properties of the UV absorber. In general, good quenching effects are obtained when the UV absorber is used in an amount of 0.01 to 10% by weight,

based on the weight of the substrate. Preferably the UV absorber is used in an amount of 0.1 to 2% by weight, based on the weight of the substrate.

As already mentioned, the UV absorber can be applied after treatment with a fluorescent whitening agent or before, during or after dyeing or printing a substrate treated with a fluorescent whitening agent.

The method of applying the UV absorber to the substrate after dyeing or printing the substrate involves adding the substrate to a bath containing a liquor, wherein the liquor to goods ratio is preferably 1 to 20.

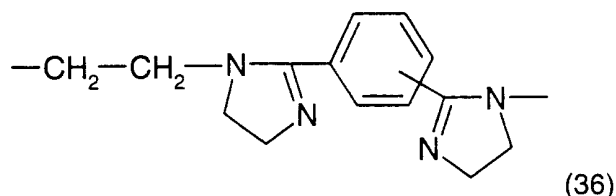
The after treatment liquor contains 0.01 to 10% by weight of UV absorber, based on the weight of the substrate. Preferably the UV absorber is used in an amount of 0.1 to 2% by weight, based on the weight of the substrate.

The temperature of the after treatment liquor is in the range of 30 to 90°C, preferably 50 to 70°C. The after treatment liquor also contains a salt, such as sodium sulfate.

Treatment with the UV absorber can also be effected before, during or after dyeing or printing, before the substrate is treated with a fluorescent whitening agent. This last mentioned procedure is used, for example, for treating articles of clothing which are washed after use and may be conducted by washing the cellulosic textile fibre material with a detergent containing at least one UVA compound as described previously.

The detergent treatment according to the present invention is preferably effected by washing the cellulosic textile fibre material at least once with the detergent composition at a temperature ranging from 10 to 100°C, especially from 15 to 60°C.

Further compounds which are suitable for use in detergent compositions include a water-soluble acid addition salt or quaternary ammonium salt of a compound containing the group of formula (36),



wherein the benzene radical is attached to the other two parts of the group at its m- or p-positions, which compound is produced by the acylation of an excess of a polyethylenepolyamine of formula (37),



in which p is an integer 2 to 5, by isophthalic or terephthalic acid or a functional derivative thereof in a molar ratio exceeding 1.5:1, subsequently cyclising the product to afford imidazoline groups, and optionally reacting the product further by way of partial or full alkylation and/or by way of acylation in a molar ratio of initial to present acylating agent of 1:0.3 to 1:1.0, with a bifunctional acylating agent which is a saturated aliphatic dicarboxylic acid of formula (38),

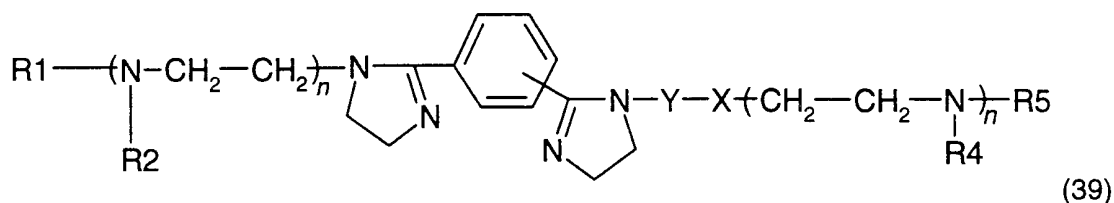


in which q is an integer 1 to 6, or a functional derivative thereof, or a functional derivative of carbonic acid.

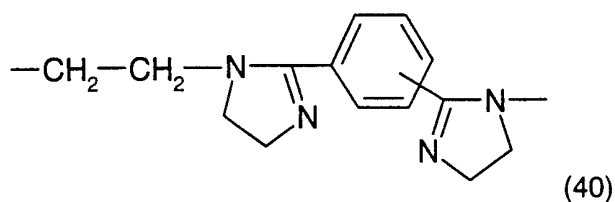
The functional derivatives of isophthalic or terephthalic acid contemplated include the anhydride, acid halides and esters thereof. The alkyl groups incorporated in the compound through alkylation or quaternary ammonium salt formation are selected from methyl and ethyl, either of which may be substituted by a phenyl or naphthyl group. Suitable functional derivatives of the saturated aliphatic dicarboxylic acids of formula (38) include their diesters, particularly dimethyl esters, and of carbonic acid include a halide or ester thereof, a mixed halide-ester, and urea. Examples of such carbonic acid derivatives besides urea, are phosgene, diethyl carbonate and ethyl chlorocarbonate. Acids from which the acid addition salts of the compounds can be produced include inorganic acids, e.g. hydrochloric, hydrobromic and sulphuric acids, aromatic sulphonic acids, e.g. benzenesulphonic and p-toluenesulphonic acids, and C₁-C₂ alkylsulphuric acids. The anions of the acid addition salts,

and also of the quaternary ammonium salts are preferably those of a strong inorganic acid, e.g. Cl^- , Br^- and SO_4^{2-} , or of a strong mixed organic-inorganic acid, e.g. CH_3SO_4^- , $\text{C}_2\text{H}_5\text{SO}_4^-$ and the benzene- and toluenesulphonic acid anions. Especially preferred are anions of strong inorganic acids, particularly Cl^- , and the preferred salts are the acid addition salts, especially with hydrochloric acid.

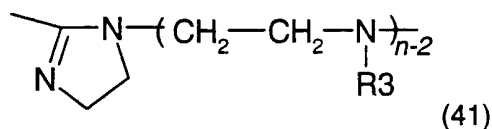
It is believed that the compounds predominantly possess the general formula (39),



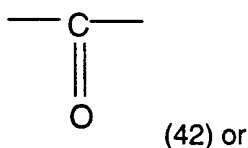
in which X is the group of formula (40),

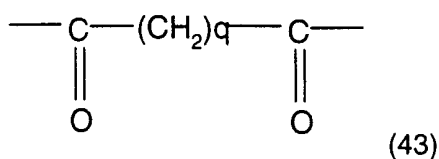


wherein the benzene radical is attached to the other two parts of the group at its m- or p-positions; n is an integer 1 to 4, Y is, when n is 1, the group $-\text{CO}-\text{NH}-$, or, when n is 2 to 4, the group of formula (41),

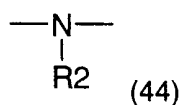


either each of R1, R2, R3, R4 and R5, independently, is hydrogen, methyl, ethyl or methyl or ethyl substituted by phenyl or naphthyl, or R2, R3 and R4 are as defined above, R1 is a bond, and R5 is the group

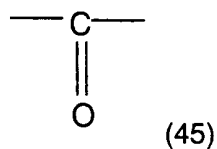




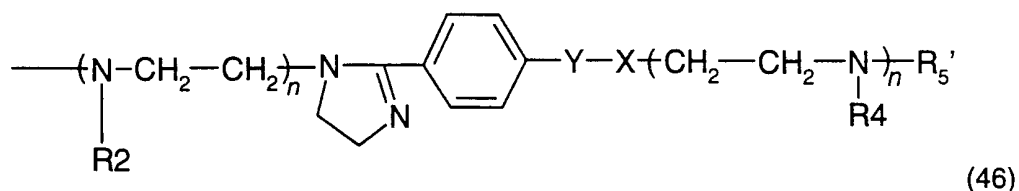
wherein q is an integer 1 to 6, and the group of formula (36) is the repeating unit of an oligomeric or polymeric compound, the moiety



at the end of one terminal unit being terminated by hydrogen, methyl, ethyl or methyl or ethyl substituted by phenyl or naphthyl, and the moiety

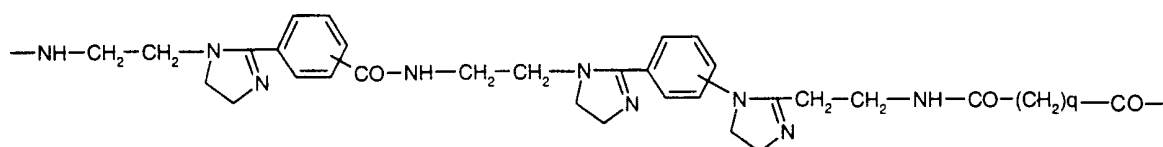


at the end of the other terminal unit being terminated by the group of formula (46),



wherein X, n, Y, R₂ and R₄ are as defined above, and R₅' is hydrogen, methyl, ethyl or methyl or ethyl substituted by phenyl or naphthyl, and the benzene radicals are attached to the other parts of the compound or group at their m- or p-positions.

Of the compounds of formula (36), an especially preferred class is constituted by those compounds which contain the repeating unit of formula (47),

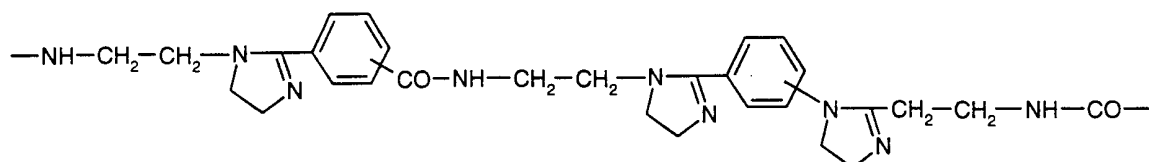


(47)

in which q is as defined above.

More preferably, the compounds contain the repeating unit of formula (47) in which q is 4.

Another especially preferred class of the compounds is constituted by those compounds which contain the repeating unit of formula (48),



(48)

In each of the above two classes of compounds, the benzene nuclei in the units of formulae (47) and (48) are linked at their m- or p-positions, preferably at their p-positions.

The detergent composition used comprises;

- i) 5-90%, preferably 5-70% of an anionic surfactant and/or a nonionic surfactant;
- ii) 5-70%, preferably 5-40% of a builder;
- iii) 0-30%, preferably 1-12% of a peroxide;
- iv) 0-10%, preferably 1-6% of a peroxide activator and/or 0-1%, preferably 0.1-0.3% of a bleaching catalyst;
- v) 0.005-2%, preferably 0.01-1% of at least one compound of formula (1), (8) or (10) or a water-soluble acid addition salt of quaternary ammonium salt of a compound produced by the acylation of an excess of a polyethylenepolyamine of formula $H(HN-CH_2-CH_2)_p-NH_2$ in which p is an integer 2 to 5, with isophthalic or terephthalic acid or a functional derivative thereof in a molar ratio exceeding 1.5:1, subsequently cyclizing the product to afford imidazoline groups, and optionally reacting the product further by: a) full alkylation, b) partial alkylation followed by acylation in a molar ratio of initial to present acylating agent of 1:0.3 to 1:1.0, with a bifunctional acylating agent which is a saturated aliphatic dicarboxylic acid of formula, $HOOC-(CH_2)_q-COOH$ in which q is an integer 1 to 6, or a

functional derivative thereof, or a functional derivative of carbonic acid, (c) acylation as described above with respect to (b), (d) acylation as described above with respect to (b) followed by alkylation, or (e) partial alkylation, which alkylation or quaternary ammonium salt formation is effected with an alkylating agent yielding a methyl, ethyl or phenyl- or naphthyl-substituted methyl or ethyl group, and which quaternary ammonium salt does not contain a nitrogen atom bearing more than two phenyl- or naphthyl-substituted methyl or ethyl groups and

- vi) 0.005-10%, preferably 0.1-5% of one or more auxiliaries, each by weight, based on the total weight of the detergent.

The said detergent compositions are also new and, as such form a further aspect of the present invention.

The detergent may be formulated as a solid, as an aqueous liquid comprising 5-50%, preferably 10-35% water or as a non-aqueous liquid detergent, containing not more than 5%, preferably 0-1% of water, and based on a suspension of a builder in a non-ionic surfactant, as described, e.g., in GB-A-2158454.

The anionic surfactant component may be, e.g., a sulphate, sulphonate or carboxylate surfactant, or a mixture of these.

Preferred sulphates are alkyl sulphates having 12-22 carbon atoms in the alkyl radical, optionally in combination with alkyl ethoxy sulphates having 10-20 carbon atoms in the alkyl radical.

Preferred sulphonates include alkyl benzene sulphonates having 9-15 carbon atoms in the alkyl radical.

In each case, the cation is preferably an alkali metal, especially sodium.

Preferred carboxylates are alkali metal sarcosinates of formula $R-CO(R_1)CH_2COOM_1$ in which R is alkyl or alkenyl having 9-17 carbon atoms in the alkyl or alkenyl radical, R_1 is C_1 - C_4 alkyl and M_1 is alkali metal.

The nonionic surfactant component may be, e.g., a condensate of ethylene oxide with a C₉-C₁₅ primary alcohol having 3-8 moles of ethylene oxide per mole.

The builder component may be an alkali metal phosphate, especially a tripolyphosphate; a carbonate or bicarbonate, especially the sodium salts thereof; a silicate or disilicate; an aluminosilicate; a polycarboxylate; a polycarboxylic acid; an organic phosphonate; or an aminoalkylene poly (alkylene phosphonate); or a mixture of these.

Preferred silicates are crystalline layered sodium silicates of the formula $\text{NaHSi}_m\text{O}_{2m+1} \cdot p\text{H}_2\text{O}$ or $\text{Na}_2\text{Si}_m\text{O}_{2m+1} \cdot p\text{H}_2\text{O}$ in which m is a number from 1.9 to 4 and p is 0 to 20.

Preferred aluminosilicates are the commercially-available synthetic materials designated as Zeolites A, B, X, and HS, or mixtures of these. Zeolite A is preferred.

Preferred polycarboxylates include hydroxypolycarboxylates, in particular citrates, polyacrylates and their copolymers with maleic anhydride.

Preferred polycarboxylic acids include nitrilotriacetic acid and ethylene diamine tetra-acetic acid.

Preferred organic phosphonates or aminoalkylene poly(alkylene phosphonates) are alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates.

Any peroxide component may be any organic or inorganic peroxide compound, described in the literature or available on the market, which bleaches textiles at conventional washing temperatures, e.g. temperatures in the range of from 5°C to 90°C. In particular, the organic peroxides are, for example, monoperoxides or polyperoxides having alkyl chains of at least 3, preferably 6 to 20, carbon atoms; in particular diperoxydicarboxylates having 6 to 12 carbon atoms, such as diperoxyperazates, diperoxypersebacates, diperoxyphthalates and/or diperoxydodecanedioates, especially their corresponding free acids, are of interest. It is preferred, however, to employ very active inorganic peroxides, such as persulphate, perborate and/or percarbonate. It is, of course, also possible to employ mixtures of organic and/or inorganic peroxides. The peroxides, especially the inorganic peroxides, are preferably activated by the inclusion of an activator such as tetraacetyl ethylenediamine or

nonoylbenzene sulfonate. Bleaching catalysts which may be added include, e.g., enzymatic peroxide precursors and/or metal complexes. Preferred metal complexes are manganese or iron complexes such as manganese or iron phthalocyanines or the complexes described in EP-A-0509787.

The detergents used will usually contain one or more auxiliaries such as soil suspending agents, for example sodium carboxymethylcellulose; salts for adjusting the pH, for example alkali or alkaline earth metal silicates; foam regulators, for example soap; salts for adjusting the spray drying and granulating properties, for example sodium sulphate; perfumes; and also, if appropriate, antistatic and softening agents; such as smectite clays; enzymes, such as amylases and proteases; photobleaching agents; pigments; and/or shading agents. These constituents should be stable to any bleaching system employed.

Depending on the particular process, the white effects are quenched or suppressed locally or over the whole area of the substrate. These white effects are produced with commercially available fluorescent whitening agents, for example the known anionic or cationic fluorescent whitening agents and disperse fluorescent whitening agents used in detergent compositions.

Exemplary of such fluorescent whitening agents are derivatives of bis(triazinylamino)stilbenedisulfonic acid, triazolyl derivatives of stilbenesulfonic acids, bis(stilbene) compounds, pyrazoline, coumarin, bis(benzimidazolyl), bis(oxazolyl), naphthalimide, cyanine, benzoxazolyl and oxacyanine derivatives.

Examples of cellulosic fibres treated according to the method of the present invention may include vegetable fibres such as cotton, viscose, flax, rayon or linen, and animal fibres such as wool, mohair, cashmere, angora and silk. Preferred cellulosic textile fibres are those consisting of cotton.

In the detergent-making machines like spray towers may be required to produce, alternately, detergent containing and not containing fluorescent whitening agents.

Problems arise when, after the machine has been used to produce FWA containing detergents, it is subsequently required for the production of FWA-free, like color care, detergents. In these circumstances, residual FWA on the machine parts contaminates the color care detergent which is subsequently produced. It is possible to clean the spray tower, but this is expensive and impairs production capacity.

A quencher compound can be used in a separate process to clean the spray tower in between two batches, or it can be added to the detergent which is subsequently produced.

In the industrial laundry saving water is a key issue. Therefore there are a lot of different technologies to re-use water. In continuous washing machines e.g. fresh water may be applied only for the last rinse, flows from the last rinse to the first rinse, and is collected in a tank under the machine. Then it may be pumped into the pre-wash bath. Washing extractors also can have such water collecting tanks for the re-use of liquor.

Problems in such washing systems which work with water re-circulation arise when the re-used liquor still contains residual FWA which contaminates fabrics which are supposed to be washed without FWA.

To prevent FWA transfers during washing, a quencher compound can be added to the re-use water, e.g. into the water collecting tank.

A further area of application of the present invention is for the removal of FWA residues from hard surfaces such as floors, walls, tables, chairs etc. In the show business area, for example in discos, fluorescent soap bubbles containing FWA's are used for producing special effects under UV light. This usage naturally results in residual FWA being deposited on the furniture, floors and walls, which can readily be eliminated by application of the process of the present invention.

The following Examples further illustrate the present invention.

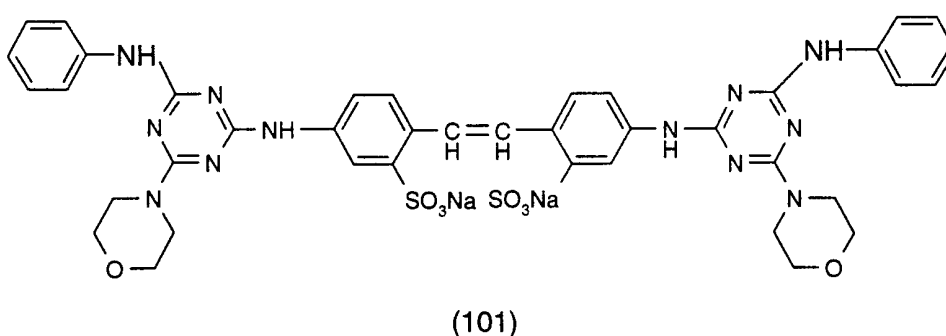
Example 1

Pre-brightened fabric is treated with detergent containing quencher ; decrease of degree of whiteness is measured.

Conditions of pre-brightening:

Fabric:	bleached, white, non-brightened cotton fabric
Wash temperature:	70°C

Wash liquor: 10 : 1
 Wash time: 30 minutes
 Wash cycles: 1
 Drying: hanging in drying cabinet at 40°C
 Brightener: the following amounts of a compound of formula (101) in solution of 0.01% concentration are applied:
 4 ml (40 mg FWA /kg fabric) $\Rightarrow$ Degree of whiteness (Ganz) = 120
 13 ml (130 mg FWA /kg fabric) $\Rightarrow$ Degree of whiteness (Ganz)=160



Wash conditions:

Dosage: 25g "Compact Color" / kg detergent
 Wash temperature: 60°C
 Wash liquor: 5 : 1
 Wash time: 15 minutes
 Wash cycles: 1
 Drying: hanging in drying cabinet at 40°C
 Conc. of quencher: 0.05%, 0.10%, 0.50%, 1.00% in the detergent

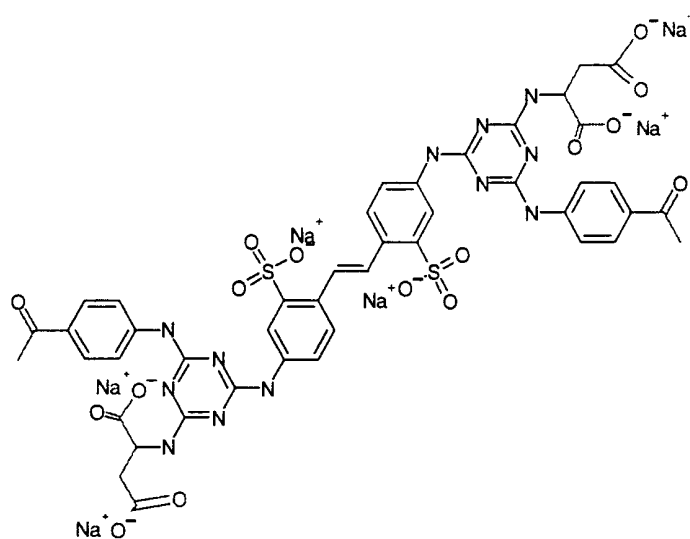
A wash liquor is prepared by dissolving 25 g/kg of "Color Compact" and the specific concentration (shown in Table 1) of quencher of formula (102), in 50 mls of tap water. 10 g of bleached cotton fabric is added to the bath and washed at 60°C over 15 minutes and then rinsed, spin-dried, dried hanging in the cabinet at 40°C and ironed cautiously on the left side at 100°C.

Formulation of the used detergent "Color Compact" according to EEC recommendation:

> 30% zeolite (Na-Al-silicate)

15 - 30%	Na-carbonate
5 - 15%	anionic surfactants
< 5%	nonionic surfactants, sodium bicarbonate, soap, polycarboxylate, enzymes, perfume
	(Does not contain FWA and PVP)

Results (see Table 1):



(102)

The quencher of formula (102) shows significant effects already after 1 wash cycle. The more quencher is incorporated in the detergent, the stronger the decrease of degree of whiteness. At a higher initial whiteness level stronger effects are achieved if the same quencher level is applied:

With a high amount of quencher of 1% at an initial whiteness of 121 a decrease of whiteness of $\Delta 59$ is achieved; at $W=161$ a difference of $\Delta 89$.

Table 1:

Effects of different concentrations of quencher in "Color Compact" detergent on prebrightened fabric, a) with 40 mg FWA (101)/kg fabric and b) with 130 mg FWA (101)/kg fabric, after 1 wash cycle (Initial whiteness of cotton before prebrightening: $W=76$)

Quencher Concentration	Initial degree of whiteness	Degree of whiteness after 1 wash cycle	ΔW
a) 0,05%	122	108	14
a) 0,10%	120	98	22
a) 0,50%	119	75	44
a) 1,00%	121	62	59
b) 0,05%	162	142	20
b) 0,10%	162	132	30
b) 0,50%	161	92	69
b) 1,00%	161	72	89

The whiteness of the washed samples is measured with a DCI/SF 500 spectrophotometer according to Ganz method. The Ganz method is described in detail in the Ciba-Geigy Review, 1973/1, and also in the article "Whiteness Measurement", ISCC Conference on Fluorescence and the Colorimetry of Fluorescent Materials, Williamsburg, February 1972, published in the Journal of Color and Appearance, 1, No. 5 (1972).

Example 2

Application field spray tower. In detergent containing brightener quencher is incorporated; detergent powder aspect and white effects on cotton are evaluated

Conditions:

Into the detergent "Color Compact" containing 0,07% of a compound of formula (101), the following concentrations of the quencher of formula (102) are incorporated via slurry:

- a. 0,07%
- b. 0,14%
- c. 0,28%

The slurries are dried over night at 70°C, 70% performance and about 425 mbar. After powdering the aspect of the detergent is evaluated visually under UV light.

To evaluate white effects on cotton of the quenched detergent one wash cycle is conducted as follows.

Wash conditions:

Dosage:	25g "Color Compact" / kg detergent
Wash temperature:	60°C
Wash liquor:	1:5
Wash time:	15 minutes
Wash cycles:	1
Drying:	hanging in drying cabinet at 40°C
Conc. of quencher:	0.07% and 0.14% in the detergent

A wash liquor is prepared by dissolving 25 g/kg of "Color Compact" and the specific concentration of quencher in 50 mls of tap water. 10 g of bleached cotton fabric is added to the bath and washed at 60°C over 15 minutes and then rinsed, spin-dried, dried hanging in the cabinet at 40°C and ironed cautiously on the left side at 100°C.

Results of detergent powder aspect:

The detergents containing quencher show a significantly lower fluorescence than the detergent without quencher.

Results of wash tests: (see table 2):

At the higher quencher level a slightly lower degree of whiteness on cotton is achieved compared to washing without quencher.

Table. 2: Effects of different concentrations of quencher in detergent containing brightener after 1 wash cycle with unbrightened cotton

Concentration of quencher	Degree of whiteness of cotton (Initial W = 76)
0,07%	93
0,14%	88
0,28%	nn

Example 3

Application field Industrial Laundry:

Different amounts of quencher are added to wash liquor containing brightener; evaluated are the fluorescence of the liquor and white effects on cotton

The following solutions are made:

- a. 26 mg compound of formula (101) / l
- b. 26 mg compound of formula (102) / l (no fluorescence)
- c. 26 mg compound of formula (101) / l + 26 mg compound of formula (102) / l
- d. 26 mg compound of formula (101) / l + 52 mg compound of formula (102) / l
- e. 26 mg compound of formula (101) / l + 104 mg compound of formula (102) / l
- f. 26 mg compound of formula (101) / l + 208 mg compound of formula (102) / l

The solutions are assessed visually under UV-Light.

Wash conditions:

Fabric:	bleached white unbrightened cotton fabric
Dosage:	25g "Color Compact" / kg detergent
Wash temperature:	60°C
Wash liquor:	1:5
Wash time:	15 minutes
Wash cycles:	1
Drying:	hanging in drying cabinet at 40°C
Liquor:	50 ml of the above described solutions

A wash liquor is prepared by dissolving 25 g/kg "Color Compact" in 50 mls of the specific described solutions. 10 g of bleached cotton fabric is added to the bath and washed at 60°C over 15 minutes and then rinsed, spin-dried, dried hanging in the cabinet at 40°C and ironed cautiously on the left side at 100°C.

Results (see table 3):

Visual assessment of the quenched solutions:

The fluorescence of the liquor is reduced as a function of the quencher concentration.

Wash test:

Table 3: Effects of different amounts of quencher in wash liquor containing brightener after 1 wash cycle on unbrightened cotton

Wash Liquor Contains:	Degree of whiteness (Initial W = 76)
26 mg compound (101) / l	161
26 mg compound (102) / l	58
26 mg / l compound (101) 26 mg / l compound (102)	134
26 mg / l compound (101) 52 mg / l compound (102)	122
26 mg / l compound (101) 104 mg / l compound (102)	108
26 mg / l compound (101) 208 mg / l compound (102)	120

Significant quenching effects can be observed as shown by the change in Ganz whiteness (ΔW):

identical amounts of brightener and quencher :	$\Delta W = -27$
double the amount of quencher with respect to the brightener:	$\Delta W = -39$
four times the amount of quencher with respect to the brightener:	$\Delta W = -53$
eight times the amount of quencher with respect to the brightener:	$\Delta W = -41$

Example 4

Cotton fabrics, dyed with 0.1% of a reactive blue dye are treated as follows:

A. 100 parts of cotton fabric are treated in a liquor to goods ratio of 1:20 over 20 minutes at 60° in a bath containing 0.1 parts of a quencher of formula (102) and 5 g/l sodium sulfate and subsequently rinsed and dried.

B. 100 parts of cotton fabric are treated as in example A but without the addition of the quencher of formula (102).

Each sample is divided into 2 pieces, one of which is washed, the other is used for comparison purposes. Washing is carried out at 50 °C for 15 minutes at a liquor to goods ratio of 1:20 with 4 g/l of a standard detergent powder containing a fluorescent whitening agent comprising of:

8.0 %	Sodium - Alkylbenzene sulphonate
2.9 %	Tallow alcohol-tetradecan-ethyleneglycolether (14 EO units)
3.5 %	Na-Soap
43.8 %	Na-Triphosphate
7.5 %	Na-Silicate
1.9 %	Mg-Silicate
1.2 %	CMC
0.2 %	EDTA
21.2 %	Na-Sulfate
0.2 %	Fluorescent whitening agent
9.6 %	Water

After washing the washed fabrics of A and B are visually compared to the unwashed fabrics of A and B.

Under UV-light the washed piece of B shows a strong fluorescence compared to the unwashed piece of B, while on the other hand the washed piece of A shows only a very slight fluorescence compared to the unwashed piece.

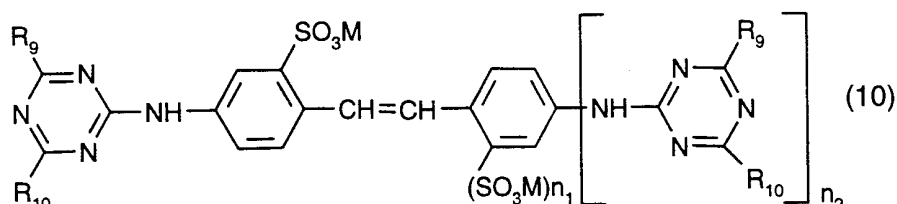
Using daylight as light source, a difference in hue of the washed and unwashed pieces of B could be observed, whereas no difference in hue could be observed for the washed and unwashed pieces of A.

Thus, the application of the quencher of formula (102) onto the cotton fabric, yields a strong reduction of fluorescence and an avoidance of change in hue, if fluorescent whitening agents exhaust on the fabric during the washing process.

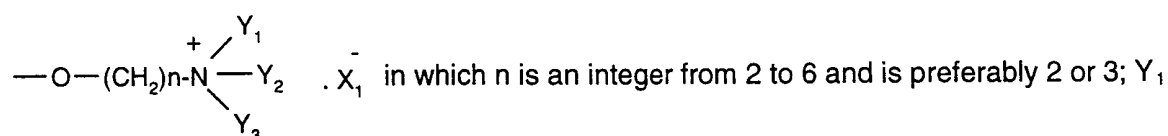
The use of the quencher of formula (47) as a component of the present detergent, also results in the application of this quencher onto the cotton fabric, and also yields a strong reduction of fluorescence and an avoidance of change in hue, if fluorescent whitening agents exhaust on the fabric during the washing process.

Claims

1. A process for quenching or suppressing the fluorescence of cellulosic textile fibre materials treated, being treated or to be treated, with fluorescent whitening agents, which process comprises applying to said substrates, before, during or after the treatment with the fluorescent whitening agent, the step of applying a liquor containing a triazine UVA compound.
2. A process according to claim 1 in which the triazine UVA compound is a compound having the formula:

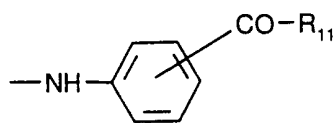


in which M is hydrogen, sodium, potassium, ammonium, mono-, di-, tri- or tetra-C₁-C₄alkylammonium, mono-, di- or tri-C₁-C₄hydroxyalkylammonium or ammonium that is di- or tri-substituted by a mixture of C₁-C₄alkyl and C₁-C₄hydroxyalkyl groups; or

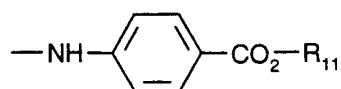


and Y₂, independently, are C₁-C₄alkyl optionally substituted by halogen, cyano, hydroxy or C₁-C₄alkoxy or Y₁ and Y₂, together with the nitrogen atom to which they are each attached, form a 5-7 membered heterocyclic ring, preferably a morpholine, pyrrolidine, piperidine or hexamethyleneimine ring; Y₃ is hydrogen, C₃-C₄alkenyl or C₁-C₄alkyl optionally substituted by cyano, hydroxy or C₁-C₄alkoxy or Y₁, Y₂ and Y₃, together with the nitrogen atom to which they are each attached, form a pyridine or picoline ring; and X₁⁻ is a colourless anion, preferably CH₃OSO₃⁻ or C₂H₅OSO₃⁻; n₁ and n₂, independently, are 0 or 1, provided that if n₁ is 0, n₂ is 0; R₉ is optionally substituted aryl or a group having the formula:

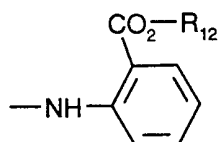
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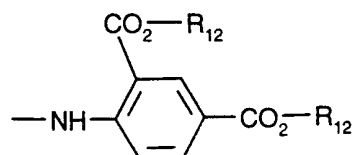
in which R_{11} is optionally substituted alkyl or optionally substituted aryl;
 or, when n_2 is 0, R_9 may also be a group having one of the formulae:



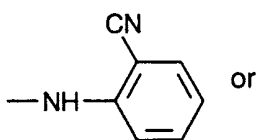
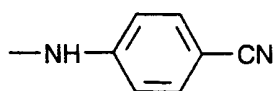
in which R_{11} is optionally substituted alkyl or optionally substituted aryl;

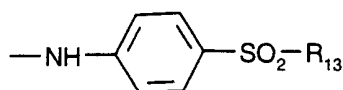


in which R_{12} is M, optionally substituted alkyl or optionally substituted aryl;

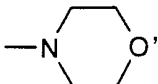


in which R_{12} has its previous significance;





in which R_{13} is hydrogen, optionally substituted alkyl or optionally substituted aryl; and

R_{10} is hydrogen, halogen, optionally substituted alkyl, optionally substituted aryl, ,

-OH,

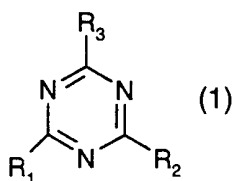
■ NH_2 , $\text{-N(CH}_2\text{CH}_2\text{OH)}_2$, $\text{-N[CH}_2\text{CH(OH)CH}_3\text{]}_2$, -NH-R_{12} , $\text{-N(R}_{12}\text{)}_2$ or -OR_{12} , in which R_{12} has its previous significance, or R_{10} is an aminoacid residue from which a hydrogen atom on the amino group has been removed.

■

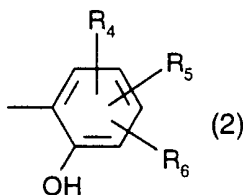
3. A process according to claim 2 in which R_{10} is an aminoacid residue derived from taurine, sarcosine, glutamic acid or iminodiacetic acid.

4. A process according to claim 2 in which R_{10} is chloro, amino, phenyl, methylphenyl, dimethylphenyl, morpholino or an aminoacid residue from which a hydrogen atom on the amino group has been removed.

5. A process according to claim 1 in which the triazine UVA compound is a compound having the formula:

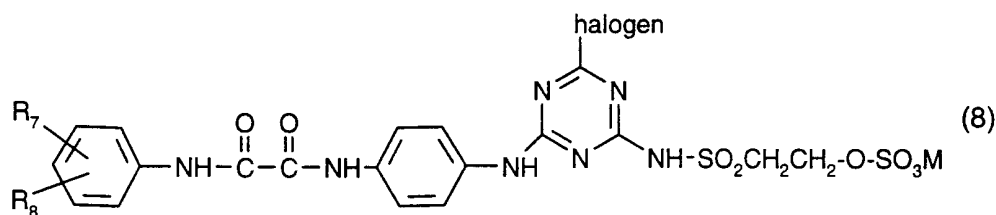


in which at least one of R_1 , R_2 and R_3 is a radical of formula:



in which R_4 , R_5 and R_6 , independently, are hydrogen; C_1 - C_{12} alkoxy; hydroxy; $-O-CH_2-CO-NH-CH_2OH$; SO_3M in which M has its previous significance and the remaining substituent(s) R_1 , R_2 and R_3 are, independently, halogen, C_1 - C_{12} alkoxy or phenyl, the phenyl substituent being optionally substituted by one or more of hydroxy, C_1 - C_{12} alkoxy, $-O-CH_2-CO-NH-CH_2OH$, SO_3M in which M has its previous significance.

6. A process according to claim 1 in which the triazine UVA compound is a compound having the formula:



in which M has its previous significance and R_7 and R_8 are C_1 - C_{12} -alkoxy or SO_3M in which M is as previously defined.

7. A process according to any of the preceding claims in which the triazine-based ultra-violet absorption agent used as a quencher compound is used in an amount ranging from 0.01 to 10% by weight, based on the weight of the substrate.

8. A process according to any of the preceding claims in which the triazine-based ultra-violet absorption agent used as a quencher compound is used in an amount ranging from 0.1 to 2% by weight, based on the weight of the substrate.

9. A process according to any of the preceding claims in which the triazine-based ultra-violet absorption agent used as a quencher compound is used by washing the cellulosic textile

fibre material with a detergent containing at least one triazine-based ultra-violet absorption agent.

10. A process according to claim 9 in which the detergent treatment is effected by washing the cellulosic textile fibre material at least once with the detergent composition at a temperature ranging from 10 to 100°C.

11. A process according to claim 10 in which the detergent treatment is effected by washing the cellulosic textile fibre material at least once with the detergent composition at a temperature ranging from 15 to 60°C.

12. A process according to any of the preceding claims in which the cellulosic textile fibre material is cotton.

13. A substrate when treated according to a process claimed in any of the preceding claims.

14. A detergent composition comprising;

- i) 5-90% of an anionic surfactant and/or a nonionic surfactant;
- ii) 5-70% of a builder;
- iii) 0-30% of a peroxide;
- iv) 0-10% of a peroxide activator and/or 0-1%, preferably 0.1-0.3% of a bleaching catalyst;
- v) 0.005-2% of at least one compound of formula (1), (8), (10) or a water-soluble acid addition salt of quaternary ammonium salt of a compound produced by the acylation of an excess of a polyethylenepolyamine of formula $H(HN-CH_2-CH_2)_p-NH_2$ in which p is an integer 2 to 5, with isophthalic or terephthalic acid or a functional derivative thereof in a molar ratio exceeding 1.5:1, subsequently cyclizing the product to afford imidazoline groups, and optionally reacting the product further by: a) full alkylation, b) partial alkylation followed by acylation in a molar ratio of initial to present acylating agent of 1:0.3 to 1:1.0, with a bifunctional acylating agent which is a saturated aliphatic dicarboxylic acid of formula, $HOOC-(CH_2)_q-COOH$ in which q is an integer 1 to 6, or a functional derivative thereof, or a functional derivative of carbonic acid, (c) acylation as described above with respect to (b), (d) acylation as described above with respect to (b) followed by alkylation, or (e) partial alkylation, which alkylation or quaternary ammonium salt formation is effected with an alkylating agent yielding a methyl, ethyl or phenyl- or naphthyl-substituted

methyl or ethyl group, and which quaternary ammonium salt does not contain a nitrogen atom bearing more than two phenyl- or naphthyl-substituted methyl or ethyl groups;

vi) 0.005-10% of one or more auxiliaries, each by weight, based on the total weight of the detergent.

15. A detergent composition comprising;

- i) 5-70% of an anionic surfactant and/or a nonionic surfactant;
- ii) 5-40% of a builder;
- iii) 1-12% of a peroxide;
- iv) 1-6% of a peroxide activator and/or 0-1%, preferably 0.1-0.3% of a bleaching catalyst;
- v) 0.01-1% of at least one compound of formula (1), (8), (10) or a water-soluble acid addition salt of quaternary ammonium salt of a compound produced by the acylation of an excess of a polyethylenepolyamine of formula $H(HN-CH_2-CH_2)_p-NH_2$ in which p is an integer 2 to 5, with isophthalic or terephthalic acid or a functional derivative thereof in a molar ratio exceeding 1.5:1, subsequently cyclizing the product to afford imidazoline groups, and optionally reacting the product further by: a) full alkylation, b) partial alkylation followed by acylation in a molar ratio of initial to present acylating agent of 1:0.3 to 1:1.0, with a bifunctional acylating agent which is a saturated aliphatic dicarboxylic acid of formula, $HOOC-(CH_2)_q-COOH$ in which q is an integer 1 to 6, or a functional derivative thereof, or a functional derivative of carbonic acid, (c) acylation as described above with respect to (b), (d) acylation as described above with respect to (b) followed by alkylation, or (e) partial alkylation, which alkylation or quaternary ammonium salt formation is effected with an alkylating agent yielding a methyl, ethyl or phenyl- or naphthyl-substituted methyl or ethyl group, and which quaternary ammonium salt does not contain a nitrogen atom bearing more than two phenyl- or naphthyl-substituted methyl or ethyl groups;
- vi) 0.1-5% of one or more auxiliaries, each by weight, based on the total weight of the detergent.

16. A process in which a triazine UVA compound is used to clean a spray tower in between two batches of detergent manufacture.

17. A process in which a triazine UVA compound is added to the re-use water in an industrial laundry process.