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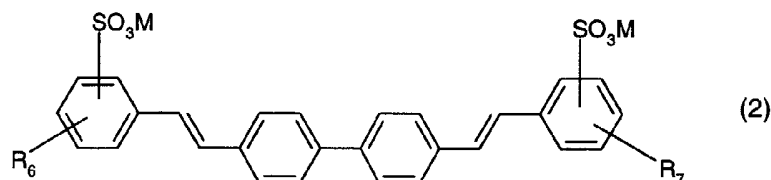
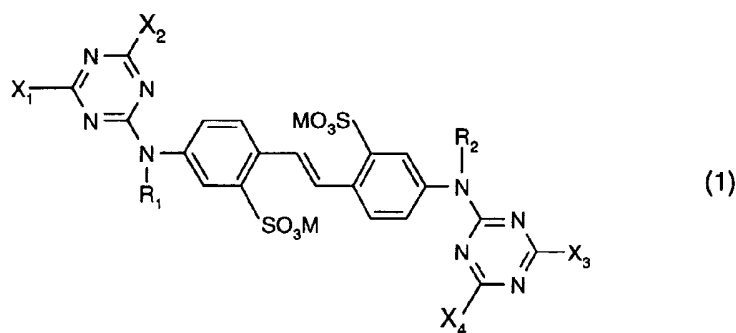
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[Continued on next page]

(54) Title: PROCESS FOR THE TREATMENT OF TEXTILE FIBRE MATERIALS



(57) Abstract: Detergent compositions comprising at least one compound of formula (1), wherein R₁ and R₂ are, independently of each other, hydrogen or unsubstituted or substituted C₁-C₈alkyl, X₁, X₂, X₃ and X₄ are, independently of each other, -N(R₃)R₄ or -OR₅, wherein R₃ and R₄ are hydrogen, cyano, unsubstituted or substituted C₁-C₈alkyl or C₅-C₇cycloalkyl, or R₃ and R₄, together with the nitrogen atom linking them, form a heterocyclic ring, and R₅ is unsubstituted or substituted C₁-C₈alkyl, and M is hydrogen or a cation, together with at least one compound of formula (2), wherein R₆ and R₇, independently of each other, are hydrogen, C₁-C₈alkyl, C₁-C₈alkoxy or halogen, and M is as defined above under formula (1), the novel mixtures of compounds of formulae (1) and (2) and detergent compositions containing compounds embraced by formula (1).



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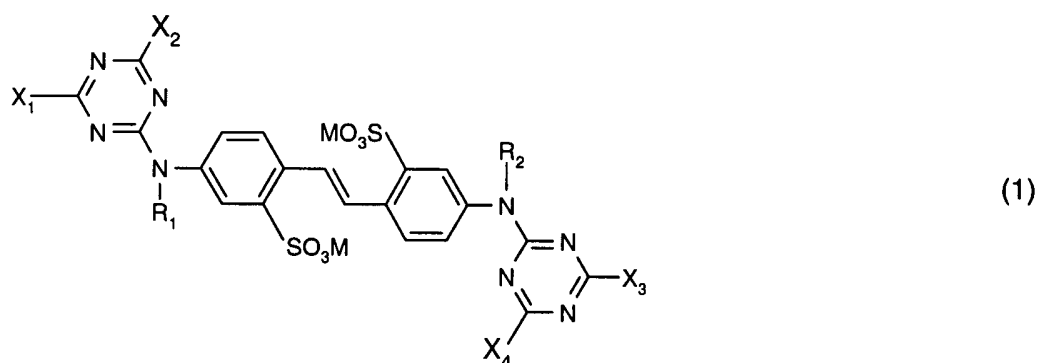
Process for the treatment of textile fibre materials

The present invention is directed to detergent formulations containing certain fluorescent whitening agents or mixtures of fluorescent whitening agents, as well as to mixtures of fluorescent whitening agents.

It is commonly known to use fluorescent whitening agents in detergent formulations. They exhaust during the treatment on to the material to be washed and, by virtue of their special light absorption/emission property, result in elimination of the yellowish shades.

However there is still a need to find improved fluorescent whitening agents for this application. It has now been found that mixtures of the following compounds of formulae (1) and (2), or compounds of formula (1a), possess superior properties with regard to, for example, solubility, build-up properties, light-fastness degree of whiteness, and also possess excellent white aspects in the solid state. The whiteness properties, like whiteness maintenance, can even be enhanced by the use of mixtures of compounds of formulae (1) and (2) or those of formula (1a) in detergents containing cellulase, protease, amylase or lipase enzymes. Favourable results are even obtained at low washing temperatures.

Accordingly, the present invention provides, as a first aspect, a detergent composition comprising
at least one compound of formula



wherein

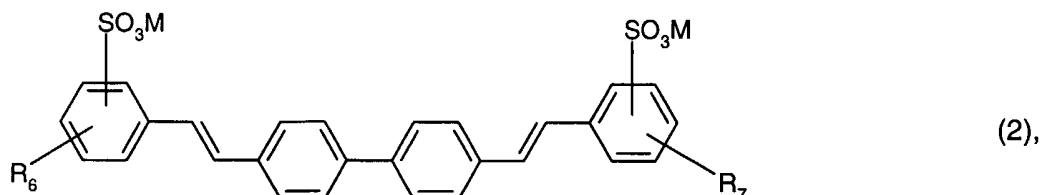
R_1 and R_2 are, independently of each other, hydrogen or unsubstituted or substituted C_1 - C_8 alkyl,

X_1 , X_2 , X_3 and X_4 are, independently of each other, $-N(R_3)R_4$ or $-OR_5$, wherein R_3 and R_4 are hydrogen, cyano, unsubstituted or substituted C_1 - C_8 alkyl or C_5 - C_7 cycloalkyl, or R_3 and R_4 ,

together with the nitrogen atom linking them, form a heterocyclic ring, and R_5 is unsubstituted or substituted C_1 - C_8 alkyl, and

M is hydrogen or a cation,

together with at least one compound of formula



wherein

R_6 and R_7 , independently of each other, are hydrogen, C_1 - C_8 alkyl, C_1 - C_8 alkoxy or halogen, and M is as defined above under formula (1).

Within the scope of the above definitions, C_1 - C_8 alkyl may be methyl, ethyl, n- or isopropyl, n-, sec.- or t-butyl, or linear or branched pentyl, hexyl, heptyl or octyl. Preferred are C_1 - C_4 alkyl groups. In case the alkyl groups are substituted examples of possible substituents are hydroxyl, halogen, like fluorine, chlorine or bromine, sulfo, sulfato, carboxy and C_1 - C_4 alkoxy, like methoxy and ethoxy. Other substituents of such alkyl groups are, for example, cyano, $-CONH_2$ and phenyl. Preferred substituents are hydroxy, carboxy, cyano, $-CONH_2$ and phenyl, especially hydroxy and carboxy. Furthermore, highly preferred substituents are hydroxy and C_1 - C_4 alkoxy, especially hydroxy. The alkyl groups can also be uninterrupted or interrupted by $-O-$ (in case of alkyl groups containing two or more carbon atoms).

Examples for C_5 - C_7 cycloalkyl groups are cyclopentyl and especially cyclohexyl. These groups can be unsubstituted or substituted by, for example, C_1 - C_4 -alkyl, like methyl. Preferred are the corresponding unsubstituted cycloalkyl groups.

Within the scope of the above definitions, C_1 - C_8 alkoxy may be methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec.-butoxy, tert.-butoxy, or linear or branched higher alkoxy groups. Preferred are C_1 - C_4 alkoxy groups, especially methoxy or ethoxy. Highly preferred is methoxy.

Halogen may be fluorine, chlorine, bromine or iodine, preferably chlorine.

If R_3 and R_4 together with the nitrogen atom form a heterocyclic ring such a ring system can be, for example, morpholino, piperidine or pyrrolidine. The heterocyclic ring can be unsubstituted or substituted. An example for such substituents is C_1 - C_4 alkyl, especially methyl.

The cation M is preferably an alkali metal atom, an alkaline earth metal atom, ammonium or a cation formed from an amine. Preferred are Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra- C_1 - C_4 alkylammonium, mono-, di- or tri- C_2 - C_4 -hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1 - C_4 -alkyl and C_2 - C_4 -hydroxyalkyl groups. Highly preferred is sodium.

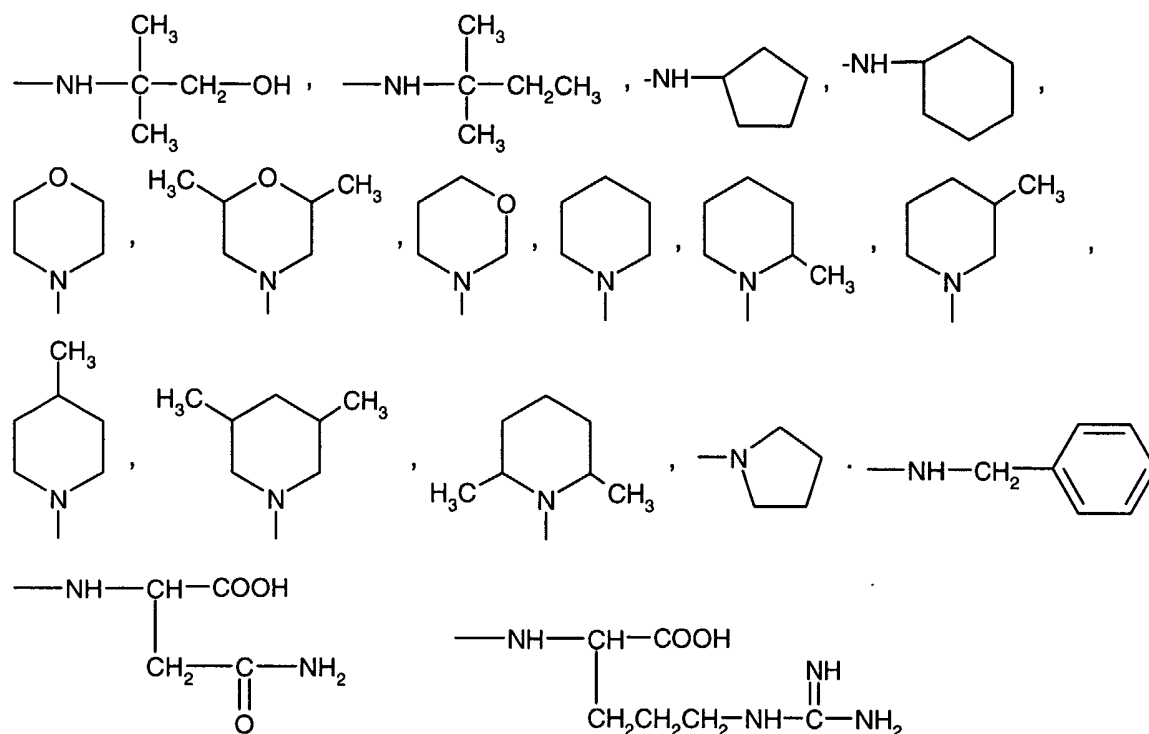
R_1 and R_2 are preferably hydrogen or C_1 - C_4 alkyl, especially hydrogen.

R_3 and R_4 are preferably hydrogen; cyano; C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, $-CONH_2$ or phenyl, especially by hydroxy or carboxy, and wherein the C_1 - C_8 alkyl group is uninterrupted or interrupted by $-O-$; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_7 cycloalkyl, especially cyclohexyl; or R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring.

More preferably, R_3 and R_4 are hydrogen, unsubstituted or hydroxy-substituted C_1 - C_8 alkyl, unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_7 cycloalkyl, or R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring. Highly preferred meanings for R_3 and R_4 are hydrogen, unsubstituted or hydroxy-substituted C_1 - C_8 alkyl, or R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring. Most preferred are unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine rings, especially morpholino, formed by R_3 and R_4 together with the nitrogen atom linking them.

Examples of $-N(R_3)R_4$ groups are $-NH_2$, $-NHCH_3$, $-NHC_2H_5$, $-NH(n-C_3H_7)$, $-NH(i-C_3H_7)$, $-NH(i-C_4H_9)$, $-N(CH_3)_2$, $-N(C_2H_5)_2$, $-N(i-C_3H_7)_2$, $-NH(CH_2CH_2OH)$, $-N(CH_2CH_2OH)_2$, $-N(CH_2CH(OH)CH_3)_2$, $-N(CH_3)(CH_2CH_2OH)$, $-N(C_2H_5)(CH_2CH_2OH)$, $-N(i-C_3H_7)(CH_2CH_2CH_2OH)$, $-NH(CH_2CH(OH)CH_3)$, $-N(C_2H_5)(CH_2CH(OH)CH_3)$,

-NH(CH₂CH₂OCH₃), -NH(CH₂CH₂OCH₂CH₂OH), -NH(CH₂COOH), -NH(CH₂CH₂COOH),
-N(CH₃)(CH₂COOH), -NH(CN),



R₅ is preferably C₁-C₈alkyl, especially C₁-C₄alkyl, which is unsubstituted or substituted by C₁-C₄alkoxy or especially hydroxy. Highly preferred for R₅ is methyl or ethyl, especially methyl.

X₁, X₂, X₃ and X₄ are preferably a radical of formula -N(R₃)R₄.

X_1 and X_3 have preferably the same meanings. In addition it is preferred that X_2 and X_4 have preferably the same meanings. Furthermore, it is preferred that the four radicals X_1 , X_2 , X_3 and X_4 do not have identical meanings.

Preferred are compounds of formula (1), wherein

R₁ and R₂ are hydrogen or C₁-C₄alkyl.

R₃ and R₄ are hydrogen; cyano; C₁-C₈alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, -CONH₂ or phenyl and wherein the C₁-C₈alkyl group is uninterrupted or interrupted by -O-; unsubstituted or C₁-C₄alkyl-substituted C₅-C₇cycloalkyl; or R₃ and R₄, together with the nitrogen atom linking them, form an unsubstituted or C₁-C₄alkyl-substituted morpholino, piperidine or pyrrolidine ring; and

R₅ is C₁-C₈alkyl which is unsubstituted or substituted by hydroxy.

As to R₃, R₄ and R₅ the above preferences apply.

Highly preferred are compounds of formula (1), wherein

X₁ and X₃ are amino, and

X₂ and X₄ are a radical of formula -N(R₃)R₄, wherein R₃ and R₄ are hydrogen; cyano; C₁-C₈alkyl which is unsubstituted or substituted by hydroxy or carboxy, and wherein the C₁-C₈alkyl group is uninterrupted or interrupted by -O-; unsubstituted or C₁-C₄alkyl-substituted cyclohexyl; or R₃ and R₄, together with the nitrogen atom linking them, form an unsubstituted or C₁-C₄alkyl-substituted morpholino, piperidine or pyrrolidine ring.

As to R₃ and R₄ the above preferences apply.

Of particular interest are compounds of formula (1), wherein X₁ and X₃ are amino, and X₂ and X₄ are a radical of formula -N(R₃)R₄, wherein R₃ and R₄ are hydrogen, unsubstituted or hydroxy-substituted C₁-C₈alkyl, unsubstituted or C₁-C₄alkyl-substituted cyclopentyl or cyclohexyl, or R₃ and R₄, together with the nitrogen atom linking them, form an unsubstituted or C₁-C₄alkyl-substituted morpholino, piperidine or pyrrolidine ring. Most interesting compounds of formula (1) are those wherein R₃ and R₄, together with the nitrogen atom linking them, form an unsubstituted or C₁-C₄alkyl-substituted morpholino, piperidine or pyrrolidine ring. As to R₃ and R₄ the above preferences apply.

Further interesting compounds of formula (1) are those of formula (1a) given below.

R₆ and R₇ are preferably hydrogen. Each of the sulfo groups indicated in formula (2) are preferably bonded in ortho position. Interesting compounds of formula (2) are those wherein R₆ and R₇ are hydrogen and each of the sulfo groups indicated in formula (2) are bonded in ortho position.

M is preferably hydrogen, an alkaline- or alkaline earth-metal, or ammonium, especially sodium.

In the mixtures of compounds of formulae (1) and (2) the molar ratio of compound (1) to compound (2) is usually in the range of from 0.1:99.9 to 99.9:0.1, preferably from 1:99 to

99:1 and more preferably from 5:95 to 95:5. Highly preferred is a molar ratio of from 10:90 to 90:10, especially 20:80 to 80:20. Most important is a molar ratio of from 30:70 to 70:30, especially 40:60 to 60:40.

The compounds of formulae (1) and (2) are known or can be prepared in analogy to known processes.

Compounds of formula (1) may be produced by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diaminostilbene-2,2'-disulfonic acid, and amino compounds capable of introducing the groups X_1 , X_2 , X_3 and X_4 . Preferably, 2 moles of cyanuric chloride are initially reacted with 1 mole of 4,4'-diaminostilbene-2,2'-disulfonic acid and then reacting the intermediate obtained in any order with amino compounds capable of introducing the groups X_1 , X_2 , X_3 and X_4 . For the preparation of compounds wherein X_1 and X_3 having the same meaning, and also X_2 and X_4 have the same meaning, it is preferred to react the intermediate obtained first with an amino compound capable of introducing X_1 and X_3 , and, finally with an amino compound capable of introducing X_2 and X_4 . It is also possible to carry out the reaction with the amino compounds in one step by reacting the intermediate with a mixture of amino compounds; in such a case usually corresponding mixtures of compounds of formula (1) are obtained.

Compounds of formula (1) containing a radical of formula $-OR_5$ can for example be prepared by first reacting cyanuric chloride with the corresponding alcohol HOR_5 , reacting the product obtained with 4,4'-diaminostilbene-2,2'-disulfonic acid and then reacting the intermediate with further compounds capable of introducing the remaining groups of X_1 , X_2 , X_3 and X_4 . The last reaction is preferably carried out with the corresponding amines.

Furthermore, the present invention is directed to mixtures of compounds of formulae (1) and (2). As to compounds of formulae (1) and (2) the preferences given above apply.

Compounds of formula (2) wherein R_6 and R_7 are hydrogen and each of the sulfo groups indicated in formula (2) are bonded in ortho position are preferred. In such mixtures, the molar ratio of compound (1) to compound (2) is usually in the range of from 0.1:99.9 to 99.9:0.1, preferably from 1:99 to 99:1 and more preferably from 5:95 to 95:5. Highly preferred is a molar ratio of from 10:90 to 90:10, especially 20:80 to 80:20. Most important is a molar ratio of from 30:70 to 70:30, especially 40:60 to 60:40.

The detergent compositions used preferably comprise

- i) 1-70% of an anionic surfactant and/or a nonionic surfactant;
- ii) 0-75% of a builder;
- iii) 0-30% of a peroxide;
- iv) 0-10% of a peroxide activator; and
- v) 0.001-5% of a mixture of compounds of formulae (1) and (2), each by weight, based on the total weight of the detergent.

More preferably the detergent compositions used comprise

- i) 5-70% of an anionic surfactant and/or a nonionic surfactant;
- ii) 5-70% of a builder;
- iii) 0.5-30% of a peroxide;
- iv) 0.5-10% of a peroxide activator and/or 0.1-2% of a bleaching catalyst; and
- v) 0.01-5% of a mixture of compounds of formulae (1) and (2), each by weight, based on the total weight of the detergent.

In general, an amount of a mixture of compounds of formulae (1) and (2) of 0.001-5%, especially an amount of 0.01-5% is used. Highly preferred is an amount of 0.05-5%, especially 0.05 to 2%. In general, amounts given in percent are to be understood as being percent by weight, based on the total weight, unless otherwise stated.

The detergent may be formulated as a solid, as an aqueous liquid comprising, e.g., 5-50, preferably 10-35% water or as a non-aqueous liquid detergent, containing not more than 5, preferably 0-1 wt.% 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., an alkylbenzenesulfonate, an alkylsulfate, an alkylethersulfate, an olefinsulfonate, an alkanesulfonate, a fatty acid salt, an alkyl or alkenyl ether carboxylate or an α -sulfofatty acid salt or an ester thereof. Preferred are alkylbenzenesulfonates having 10 to 20 carbon atoms in the alkyl group, alkylsulfates having 8 to 18 carbon atoms, alkylethersulfates having 8 to 18 carbon atoms, and fatty acid salts being derived from palm oil or tallow and having 8 to 18 carbon atoms. The average molar number of ethylene oxide added in the alkylethersulfate is preferably 1 to 20, preferably 1 to

10. The salts are preferably derived from an alkaline metal like sodium and potassium, especially sodium. Highly 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, especially sodium.

The nonionic surfactant component may be, e.g., primary and secondary alcohol ethoxylates, especially the C_8 - C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10} - C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

The total amount of anionic surfactant and nonionic surfactant is preferably 5-50% by weight, preferably 5-40% by weight and more preferably 5-30% by weight. As to these surfactants it is preferred that the lower limit is 10% by weight.

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 $NaHSi_mO_{2m+1} \cdot pH_2O$ or $Na_2Si_mO_{2m+1} \cdot pH_2O$ 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.

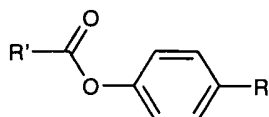
The amount of builders is preferably 5-70% by weight, preferably 5-60% by weight and more preferably 10-60% by weight. As to the builders it is preferred that the lower limit is 15% by weight, especially 20% by weight.

Suitable peroxide components include, for example, the organic and inorganic peroxides (like sodium peroxides) known in the literature and available commercially that bleach textile materials at conventional washing temperatures, for example at from 5 to 95°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 C 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 amount of peroxide is preferably 0.5-30% by weight, preferably 1-20% by weight and more preferably 1-15% by weight. In case a peroxide is used, the lower limit is preferably 2% by weight, especially 5% by weight.

The peroxides, especially the inorganic peroxides, are preferably activated by the inclusion of a bleach activator. Preferred are such compounds that, under perhydrolysis conditions, yield unsubstituted or substituted perbenzo- and/or peroxo-carboxylic acids having from 1 to 10 carbon atoms, especially from 2 to 4 carbon atoms. Suitable compounds include those that carry O- and/or N-acyl groups having the said number of carbon atoms and/or unsubstituted or substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylenediamine (TAED), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N,N-diacetyl-N,N-dimethyl-urea (DDU), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), compounds of formula



wherein R is a sulfonate group, a carboxylic acid group or a carboxylate group, and wherein R' is linear or branched (C₇-C₁₅)alkyl; also activators that are known under the names

SNOBS, SLOBS, NOBS and DOBA, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran and acetylated sorbitol and mannitol and acylated sugar derivatives, especially pentaacetylglucose (PAG), sucrose polyacetate (SUPA), pentaacetylfructose, tetraacetylxylose and octaacetylactose, and acetylated, optionally N-alkylated, glucamine and gluconolactone. The combinations of conventional bleach activators disclosed in German Patent Application DE-A-44 43 177 may also be used. Nitrile compounds that form peroxyimide acids with peroxides are also suitable as bleach activators. Preferred are tetraacetyl ethylenediamine and nonoxoxybenzene sulfonate.

The amount of bleach activator is preferably 0-10% by weight, preferably 0-8% by weight. In case a bleach activator is used, the lower limit is preferably 0.5% by weight, especially 1% by weight.

Bleaching catalysts, which may be added, include, e.g., enzymatic peroxide precursors and/or metal complexes. Preferred metal complexes are manganese, cobalt or iron complexes such as manganese or iron phthalocyanines or the complexes described in EP-A-0509787. In case a bleaching catalyst is used the amount is preferably 0.005 to 2% by weight, more preferably 0.01 to 2% by weight, especially 0.05 to 2% by weight. Highly preferred is an amount of 0.1-2% by weight.

As examples for bleaching catalysts the following are mentioned:

- WO-A-95/30681 (see i.e. formula (I) and the following definition on page 1, lines 7 to 30; especially formula (I) and the following definitions given on page 2, lines 29 to page 11, line 11). Preferred ligands are those given on page 13, line 12 to page 26, line 11.
- WO-A-01/09276 (see i.e. formulae (1), (2) and (3) and the following definitions given on pages 2 and 3).
- WO-A-01/05925 (see i.e. formula (1) and the following definition on page 1, last paragraph to page 2, first paragraph. The preferences given for the metal complexes apply, see especially those of formula (2) on page 3 and those of formula (3) on page 4).
- WO-A-02/088289 (see i.e. formula (1) and the following definition on page 2. The preferences given for the metal complexes apply, see especially the ligands of formula (3) and also the preferences given on page 3, fourth paragraph to page 4, paragraph 7).

Furthermore, the detergent can optionally contain enzymes. Enzymes can be added to detergents for stain removal. The enzymes usually improve the performance on stains that are either protein- or starch-based, such as those caused by blood, milk, grass or fruit juices. Preferred enzymes are cellulases, proteases, amylases and lipases. Preferred enzymes are cellulases and proteases, especially proteases. Cellulases are enzymes which act on cellulose and its derivatives and hydrolyze them into glucose, cellobiose, cellooligosaccharide. Cellulases remove dirt and have the effect of mitigating the roughness to the touch. Examples of enzymes to be used include, but are by no means limited to, the following:

proteases as given in US-B-6,242,405, column 14, lines 21 to 32;

lipases as given in US-B-6,242,405, column 14, lines 33 to 46;

amylases as given in US-B-6,242,405, column 14, lines 47 to 56; and

cellulases as given in US-B-6,242,405, column 14, lines 57 to 64.

The enzymes can optionally be present in the detergent. When used, the enzymes are usually present in an amount of 0.01-5% by weight, preferably 0.05-5% and more preferably 0.1-4% by weight, based on the total weight of the detergent.

Further preferred additives for the detergents according to the invention are polymers that, during the washing of textiles, inhibit staining caused by dyes in the washing liquor that have been released from the textiles under the washing conditions (dye fixing agents, dye transfer inhibitors). Such polymers are preferably polyvinylpyrrolidones, polyvinylimidazoles or polyvinylpyridine N-oxides which may have been modified by the incorporation of anionic or cationic substituents, especially those having a molecular weight in the range from 5000 to 60 000, more especially from 10 000 to 50 000. Such polymers are usually used in an amount of from 0.01 to 5 %, preferably 0.05 to 5 % by weight, especially 0.1 to 2 % by weight, based on the total weight of the detergent. Preferred polymers are those given in WO-A-02/02865 (see especially page 1, last paragraph and page 2, first paragraph).

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; photobleaching

agents; pigments; and/or shading agents. These constituents should, of course, be stable to any bleaching system employed. Such auxiliaries can be present in an amount of, for example, 0.1 to 20% by weight, preferably 0.5 to 10 % by weight, especially 0.5 to 5 % by weight, based on the total weight of the detergent.

The detergent compositions can take a variety of physical forms including powder, granular, tablet and liquid forms. Examples thereof are conventional powder heavy-duty detergents, compact and supercompact heavy-duty detergents and tablets, like heavy-duty detergent tablets. One important physical form is the so-called concentrated granular form adapted to be added to a washing machine.

Of importance are also the so-called compact (or supercompact) detergents. In the field of detergent manufacture, a trend has developed recently towards the production of compact detergents, which contain increased amounts of active substance. In order to minimize energy expenditure during the washing process, the compact detergents are required to operate efficiently at temperatures as low as 40°C, or even at room temperatures, e.g. at 25°C. Such detergents usually contain only low amounts of fillers or processing aids, like sodium sulfate or sodium chloride. The amount of such fillers is usually 0-10% by weight, preferably 0-5 % by weight, especially 0-1 % by weight, based on the total weight of the detergent. Such detergents usually have a bulk density of 650-1000 g/l, preferably 700-1000 g/l and especially 750-1000 g/l.

The detergents can also be present in the form of tablets. Relevant characteristics of tablets are ease of dispensing and convenience in handling. Tablets are the most compact delivery of solid detergents and have a bulk density of, for example, 0.9 to 1.3 kg/litre. To enable fast disintegration laundry detergent tablets generally contain special disintegrants:

- Effervescent such as carbonate/hydrogencarbonate/citric acid;
- swelling agents like cellulose, carboxymethyl cellulose, cross-linked poly(N-vinylpyrrolidone);
- quickly dissolving materials such as Na (K) acetate, or Na (K) citrate;
- rapidly dissolving water-soluble rigid coating such as dicarboxy acids.

The tablets can also contain combinations of any of the above disintegrants.

The detergent may also be formulated 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 wt.% of water. Non-aqueous liquid detergent compositions can contain other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers. The detergents can also be present as the so-called "unit liquid dose" form.

This detergent treatment of textiles can be conducted as a domestic treatment in normal washing machines.

The textile fibres treated may be natural or synthetic fibres or mixtures thereof. Examples of natural fibres include vegetable fibres such as cotton, viscose, flax, rayon or linen, preferably cotton and animal fibres such as wool, mohair, cashmere, angora and silk, preferably wool. Synthetic fibres include polyester, polyamide and polyacrylonitrile fibres. Preferred textile fibres are cotton, polyamide and wool fibres, especially cotton fibres. Preferably, textile fibres treated according to the method of the present invention have a density of less than 200 g/m².

According to this process usually an amount of 0.01 to 3.0% by weight, especially 0.05 to 3.0% by weight, based on the weight of the textile fibre material, of a mixture of compounds of formulae (1) and (2) is used.

The process is usually conducted in the temperature range of from 5 to 100°C, especially 5 to 60°C. Preferred is a temperature range of 5 to 40°C, especially 5 to 35°C and more preferably 5 to 30°C.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 11. Laundry products are typically at pH 9-11.

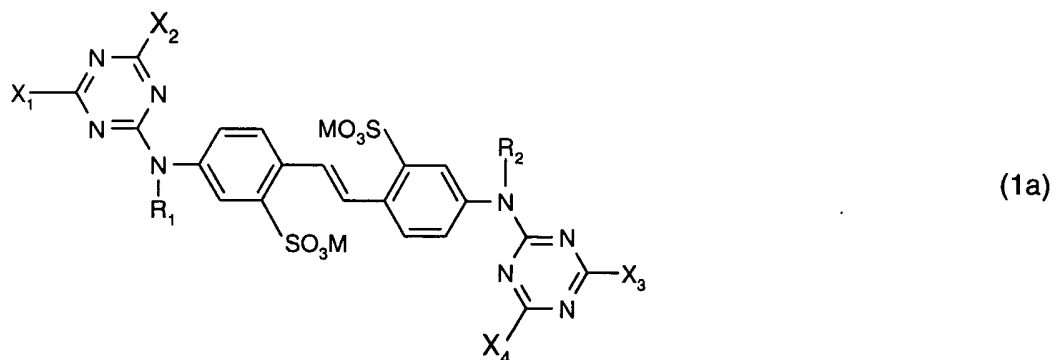
Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accordance with the invention. By an effective amount of the detergent composition it is meant, e.g., from 20 g to 300 g of product dissolved or dispersed in a wash solution of volume from 5 to 85 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods. Examples are

- top-loading, vertical axis U.S.-type automatic washing machines using about 45 to 83 liters of water in the wash bath, a wash cycle of about 10 to about 14 minutes and a wash water temperature of about 10 to about 50°C;
- front-loading, horizontal-axis European-type automatic washing machine using about 8 to 15 liters of water in the wash bath, a wash cycle of about 10 to about 60 minutes and a wash water temperature of about 30 to about 95°C;
- top-loading, vertical-axis Japanese-type automatic washing machine using about 26 to 52 liters of water in the wash bath, a wash cycle of about 8 to about 15 minutes and a wash water temperature of about 5 to about 25°C.

The liquor ratio is preferably 1:4 to 1:40, especially 1:4 to 1:15. Highly preferred is a liquor ratio of 1:4 to 1:10, especially 1:5 to 1:9.

Furthermore, the present invention is directed to a detergent composition comprising at least one compound of formula



wherein

R₁ and R₂ are, independently of each other, hydrogen or unsubstituted or substituted

C₁-C₈alkyl,

X₁, X₂, X₃ and X₄ are, independently of each other, -N(R₃)R₄ or -OR₅, wherein R₃ and R₄ are hydrogen; cyano; C₁-C₈alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, -CONH₂ or phenyl and wherein the C₁-C₈alkyl group is uninterrupted or interrupted by -O-; unsubstituted or C₁-C₄alkyl-substituted C₅-C₇cycloalkyl; or R₃ and R₄, together with the nitrogen atom linking them, form an unsubstituted or C₁-C₄alkyl-substituted morpholino, piperidine or pyrrolidine ring;

R₅ is C₁-C₈alkyl which is unsubstituted or substituted by hydroxy, and

M is hydrogen or a cation,

and wherein the detergent contains at least one enzyme selected from the group consisting of cellulase, protease, amylase and lipase.

As to the compounds of formula (1a) as well as to the substituents thereof the meanings and preferences given above for compounds of formula (1) apply.

Of interest are compounds of formula (1a), wherein R₁ and R₂ are, independently of each other, hydrogen or unsubstituted or substituted C₁-C₈alkyl,

X₁, X₂, X₃ and X₄ are, independently of each other, -N(R₃)R₄ or -OR₅, wherein R₃ and R₄ are hydrogen, unsubstituted or hydroxy-substituted C₁-C₈alkyl, unsubstituted or C₁-C₄alkyl-substituted C₅-C₇cycloalkyl, or R₃ and R₄, together with the nitrogen atom linking them, form an unsubstituted or C₁-C₄alkyl-substituted morpholino, piperidine or pyrrolidine ring, and R₅ is unsubstituted or hydroxy-substituted C₁-C₈alkyl, and

M is hydrogen or a cation.

Highly preferred are corresponding detergent compositions which contain enzymes as well as peroxide, peroxide activator and/or bleaching catalyst.

Preferred are detergent compositions comprising

- i) 1-70% of an anionic surfactant and/or a nonionic surfactant;
- ii) 0-75% of a builder;
- iii) 0-30% of a peroxide;
- iv) 0-10% of a peroxide activator;
- v) 0.001-5% of a compound of formula (1a); and
- vi) 0.05-5% of at least one enzyme selected from the group consisting of cellulase, protease, amylase and lipase, especially protease.

Highly preferred are detergent compositions comprising

- i) 5-70% of an anionic surfactant and/or a nonionic surfactant;
- ii) 5-70% of a builder;
- iii) 0.5-30% of a peroxide;
- iv) 0.5-10% of a peroxide activator and/or 0.1-2% of a bleaching catalyst;
- v) 0.01-5% of a compound of formula (1a); and
- vi) 0.05-5% of at least one enzyme selected from the group consisting of cellulase, protease, amylase and lipase, especially protease.

As to the enzymes, the detergents and the ingredients thereof the definitions and preferences given above apply. The compounds of formula (1a) can be used in the same way as given above for the mixture of compounds of formulae (1) and (2).

A further object of the present invention is to provide a process for the domestic washing treatment of a textile fibre material wherein the textile fibre material is contacted with an aqueous solution of a detergent comprising a compound of formula (1a) as defined above, and wherein the detergent contains at least one enzyme selected from the group consisting of cellulase, protease, amylase and lipase, and wherein the temperature of the solution is between 5°C and 40°C, preferably between 5°C and 30°C, throughout the process.

As to the compounds of formula (1a) as well as for the detergents and the washing process the definitions and preferences given above apply.

The above washing treatment of textile fibers can also be conducted with the mixture of compounds of formulae (1) and (2).

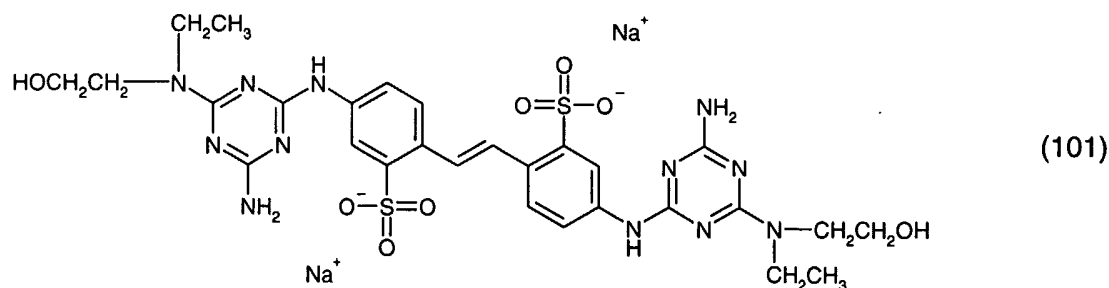
The compounds and mixtures used according to the present invention are particularly advantageous in that they exhibit not only extremely high whitening ability, but, in addition, in many cases highly desirable water solubilities and also possess excellent white aspects in the solid state. A further advantage of the present invention is that the detergent composition delivers improved whiteness performance and fabric feel. Furthermore the compounds and especially the mixtures show very good results with respect to exhaustion properties.

The compounds have the advantage that they are also effective in the presence of active chlorine donors, such as, for example, hypochlorite and can be used without substantial loss of the effects in washing baths with non-ionic washing agents, for example alkylphenol polyglycol ethers. Also in the presence of perborate or peracids and activators, for example tetraacetylglycoluril or ethylenediamine-tetraacetic acid are the compounds and mixtures of compounds stable both in pulverulent washing agent and in washing baths. In addition, they impart a brilliant appearance in daylight.

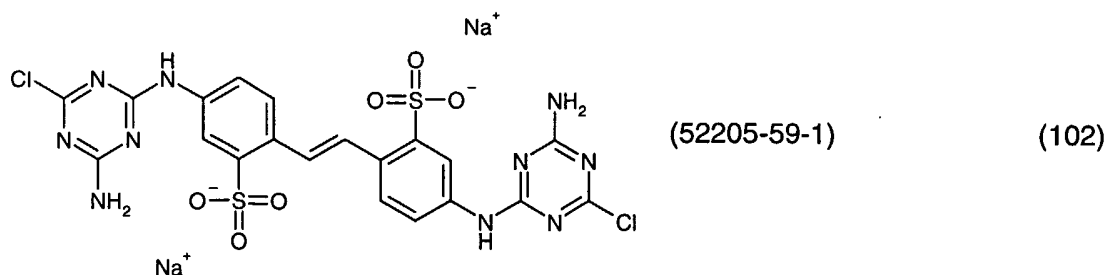
Compounds of the formula (1) and mixtures of compounds of formulae (1) and (2) have also been found to be useful for the fluorescent whitening of textile materials, in which connection polyamides, wool and cotton should be singled out particularly. The textile fibres treated according to this embodiment of the present invention may be natural or synthetic fibres or mixtures thereof. Examples of natural fibres include vegetable fibres such as cotton, viscose, flax, rayon or linen, preferably cotton and animal fibres such as wool, mohair, cashmere, angora and silk, preferably wool. Synthetic fibres include polyester, polyamide and polyacrylonitrile fibres. Preferred textile fibres are cotton, polyamide and wool fibres. Preferably, textile fibres treated according to the present invention have a density of less than 1000 g/m^2 , especially less than 500 g/m^2 and most preferred less than 250 g/m^2 .

The following Examples serve to illustrate the invention; parts and percentages are by weight, unless otherwise stated.

Preparation Example 1:



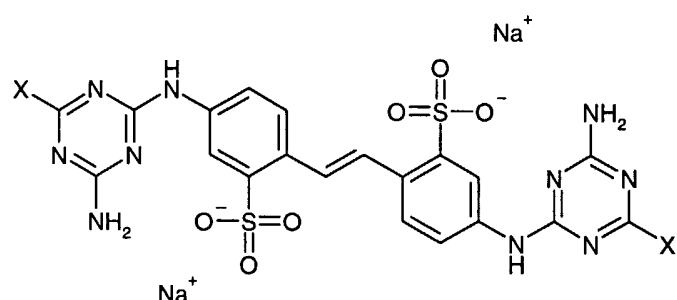
In a 1 liter flask 0.05 mole of the compound of formula



are mixed with 600ml of water and heated to a temperature of 60°C. Then 9.2g of 2-ethylaminoethanol are added and the reaction mixture is heated to a temperature of 98°C; during heating the pH is maintained at a value between 8.5 and 9 by addition of a 4-molar aqueous solution of sodium hydroxide. The reaction mixture is cooled to 50°C and the pH is adjusted to a value of 4.5 by addition a 6-molar aqueous solution of hydrochloric acid. The precipitate is filtered off, washed with 100ml of a 10% aqueous sodium chloride solution and dried in vacuum. In this way, there are obtained 30.5g of a yellowish product.

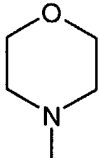
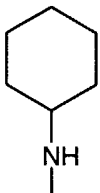
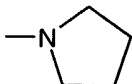
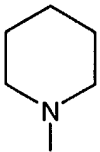
Preparation Examples 2 to 15:

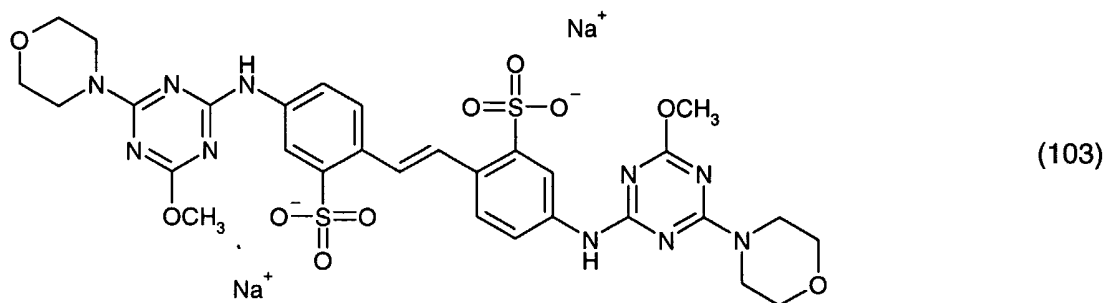
The following compounds of formula



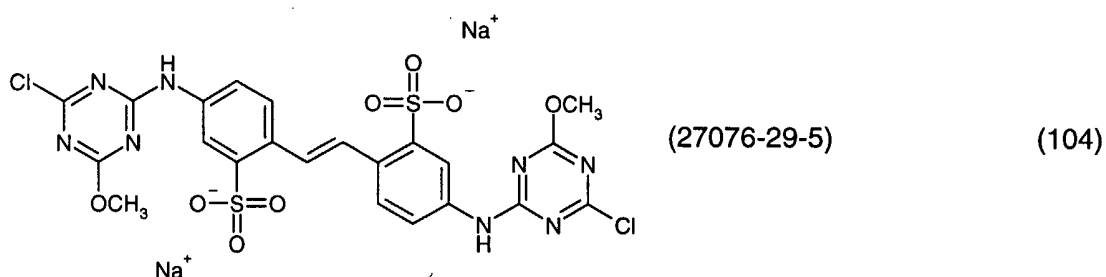
can be prepared in analogy to the process given in Preparation Example 1, by replacing 9.2 g of 2-ethylaminoethanol with an equimolar amount of the corresponding amine. X is as defined in the following Table 1. Compounds which precipitate after cooling to 50°C are isolated directly as sodium salts without addition of hydrochloric acid and then dried in vacuum.

Table 1

Example	X
2	$-\text{N}(\text{C}_2\text{H}_5)_2$
3	
4	$-\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$
5	
6	$-\text{NHCH}_2\text{CH}_2\text{OH}$
7	$-\text{NHCH}_2\text{CH}_2\text{OCH}_3$
8	$-\text{NHCH}_2\text{CH}_2\text{COOH}$
9	$-\text{NHCH}_2\text{CH}_3$
10	$-\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$
11	$-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$
12	
13	
14	$-\text{NHCH}_2\text{COOH}$
15	$\begin{array}{c} \text{---NH---CH---COOH} \\ \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{---NH---C(=NH)---NH}_2 \end{array}$

Preparation Example 16:

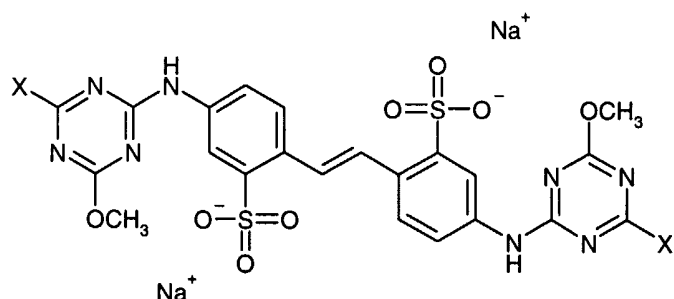
In a 1 litre flask 0.05 mole of the compound of formula



are mixed with 600ml of water and heated to a temperature of 60°C. Then 9.5g of morpholine are added and the reaction mixture is heated to a temperature of 98°C; during heating the pH is maintained at a value between 8.5 and 9 by addition of a 4-molar aqueous solution of sodium hydroxide. The reaction mixture is cooled to 40°C and the precipitate is filtered off, washed with 100ml of a 10% aqueous sodium chloride solution and dried in vacuum. In this way, there are obtained 30g of a yellow product.

Preparation Examples 17 to 19:

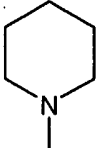
The following compounds of formula



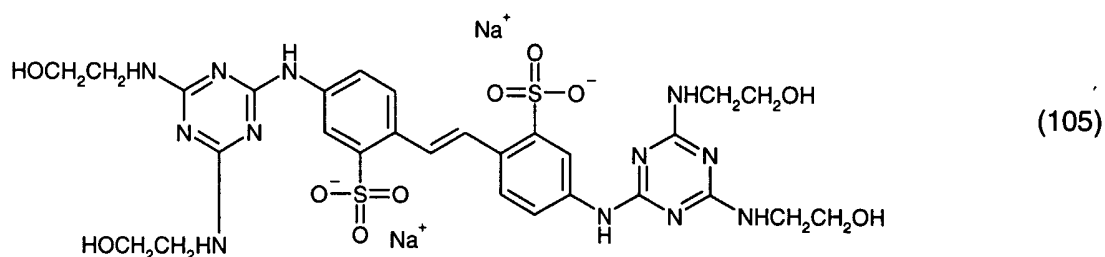
can be prepared in analogy to the process given in Preparation Example 16, by replacing 9.5 g of morpholine with an equimolar amount of the corresponding amine. X is as defined in the

following Table 2. Compounds having high solubility are treated with a 6-molar aqueous solution of hydrochloric acid in order to adjusted the pH to a value of 4.5 before cooling to 50°C.

Table 2

Example	X
17	$-\text{N}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$
18	
19	$-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$

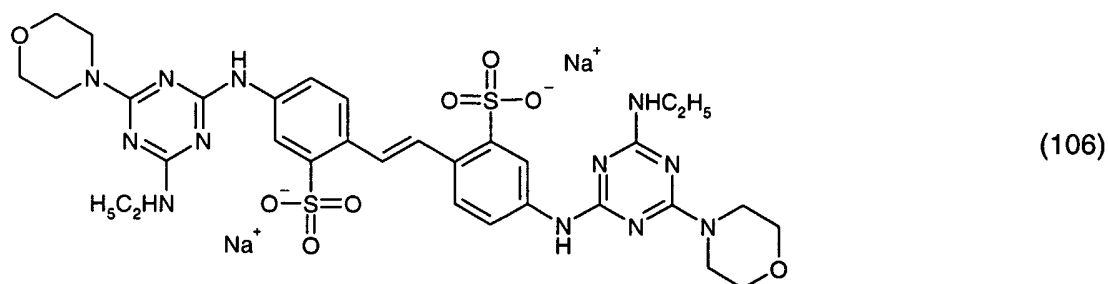
Preparation Example 20:



In a 2 litre flask 130ml of methylethylketone, 80ml of deionised water, 150g of ice and 18.5g cyanuric chloride are mixed. Over a period of 30 minutes 185 ml of a solution of 4,4'-diaminostilbene-2,2'-disulfonic acid (as disodium salt) in water (concentration of 100g/l) are added dropwise, the temperature being between -8 und $+5^{\circ}\text{C}$. The pH is maintained at a value between 4.5 and 5 by addition of an aqueous sodium carbonate solution. A yellowish suspension is obtained. Then, by use of a dropping funnel, 27.2g of ethanolamine (99%) are added. The pH increases to a value of 10 and then drops to a lower value, whereby the temperature increases to 10 to 15°C . Then the reaction mixture is warmed to a temperature of 45°C and held at this temperature for 20 minutes. During heating to 98°C within 30 minutes a mixture of methylethylketone and water is distilled off; the pH is maintained at a value between 8.5 and 9 by addition of an aqueous sodium hydroxide solution. After no further addition of aqueous sodium hydroxide solution is necessary in order to maintain the pH at a constant value the reaction mixture is cooled to 50°C . The pH is adjusted to a value

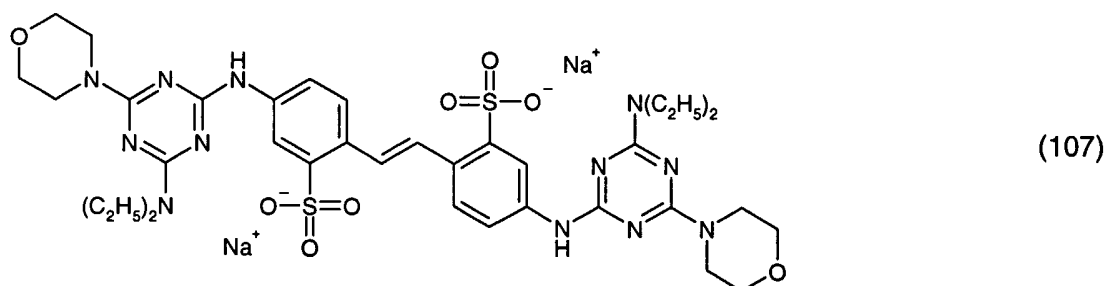
of 5.5 and a yellowish crystalline precipitate can be filtered off. After drying 29g of a yellowish product are obtained.

Preparation Example 21:

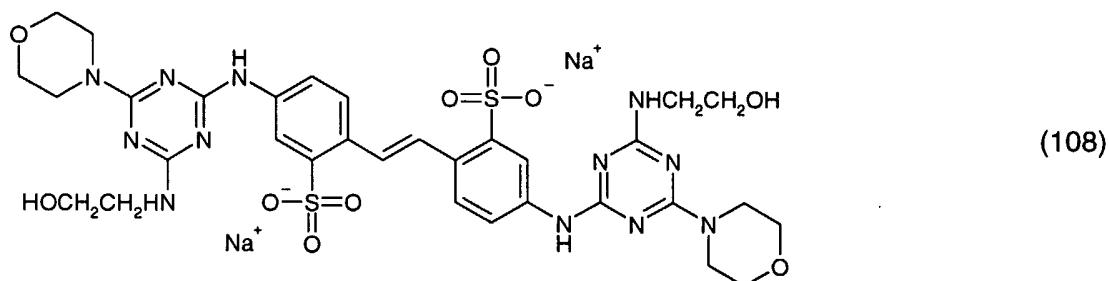


In a 1 litre pressure vessel 0.037 mole of N,N'-bis-(4-morpholino-6-chloro-1,3,5-triazine-2-yl)-4,4'-diaminostilbene-2,2'-disulfonic acid (as disodium salt) are suspended in 500 ml of water. 15 g of an aqueous solution of ethylamine (70%) are added and the reaction mixture is heated to a temperature of 100 to 105°C and stirred for 4.5 hours. The reaction mixture is cooled to 25°C and the precipitate is filtered off, washed with 100ml of a 10% aqueous sodium chloride solution and dried in vacuum at 70°C. In this way there are obtained 25.8g of a yellowish powder.

Preparation Example 22:



The compound of formula (107) can be prepared in analogy to the process given in Preparation Example 21, by replacing 15 g of an aqueous solution of ethylamine (70%) with a corresponding solution containing an equimolar amount of diethylamine.

Preparation Example 23:

In a 1 liter flask 0.05 mole of N,N'-bis-(4-morpholino-6-chloro-1,3,5-triazine-2-yl)-4,4'-diaminostilbene-2,2'-disulfonic acid (as disodium salt) are suspended in 600ml of water and heated to a temperature of 60°C. 6.4g of ethanolamine are added and the reaction mixture is heated to a temperature of 98°C. The pH is maintained at a value between 8.5 and 9 by addition of a 4-molar aqueous sodium hydroxide solution. The reaction mixture is cooled to 25°C and 10% by volume of sodium chloride are added. The precipitate is filtered off, washed with 100ml of a 10% aqueous sodium chloride solution and dried in vacuum at 70°C. In this way there are obtained 41.8g of a yellowish powder.

Application Example 1:

General procedure:

A wash liquor is prepared by dissolving 0.8 g of a washing powder in 200 ml of tap water. 10 g of bleached cotton fabric is added to the bath and washed at 40°C over 15 minutes and then rinsed, spin-dried and ironed at 160°C.

The following washing powders A and B are used (amounts given in the following Tables 3a and 3b are in g):

Table 3a (Ingredients of washing powders A and B)

	A	B
Sodium laurylbenzene-sulfonate (LAS)	10g	10g
Sodium lauryl ether sulfate (AES)	3g	3g
Dobanol 23-6.5 (nonionic alcoholethoxylate)	4g	4g
Sodium tripolyphosphate	30g	-----
Zeolite A	-----	20g

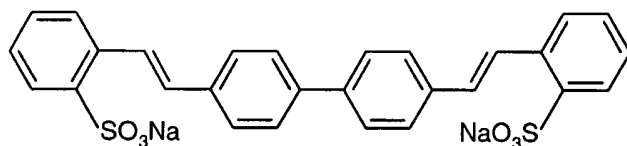
Sodium carbonate	15g	15g
Sodium silicate	5g	5g
Sodium sulfate	11g	17g
Cellulase	1.5g	-----
Protease	-----	1.5g
Polycarboxylate (co-builder)	-----	4g
Carboxymethylcellulose	2g	2g
Perfume	0.1g	0.1g
Water	5g	5g
Fluorescent whitener or mixture of fluorescent whitener used	Xg	Xg

Table 3b (Washing powders used)

	Amount of fluorescent whitener or mixture of fluorescent whitener used	Washing powder
Compound of Prep. Ex. 1	0.2g	A
Compound of Prep. Ex. 2	0.1g	B
Compound of Prep. Ex. 3	0.3g	A
Compound of Prep. Ex. 4	0.2g	A
Compound of Prep. Ex. 5	0.4g	A
Compound of Prep. Ex. 12	0.15g	B
Compound of Prep. Ex. 13	0.1g	B
Compound of Prep. Ex. 16	0.3g	B
Mixture of compound of Prep. Ex. 6 and compound of formula (109) [7:3 weight ratio]	0.2g	A
Mixture of compound of Prep. Ex. 12 and compound of formula (109) [7:3 weight ratio]	0.4g	B
Mixture of compound of Prep. Ex. 14 and compound of formula (109) [7:3 weight ratio]	0.3g	A
Mixture of compound of Prep. Ex. 17 and compound of formula (109) [1:1 weight ratio]	0.2g	B

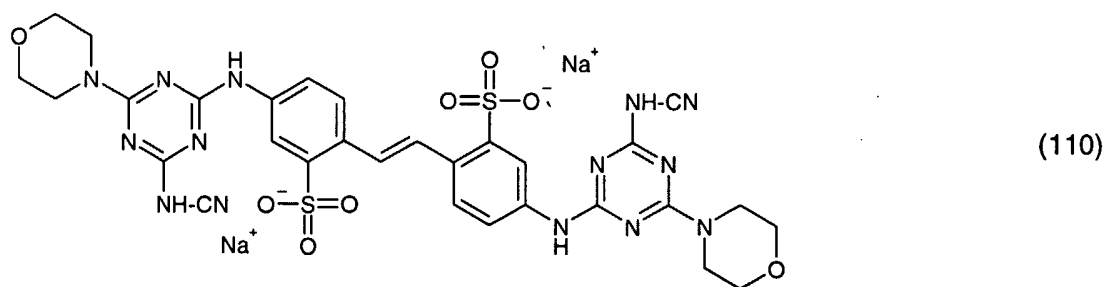
Mixture of compound of Prep. Ex. 18 and compound of formula (109) [1:2 weight ratio]	0.5g	B
Mixture of compound of Prep. Ex. 1 and compound of formula (109) [1:5 weight ratio]	0.3g	B
Mixture of compound of Prep. Ex. 2 and compound of formula (109) [5:1 weight ratio]	0.2g	B
Mixture of compound of Prep. Ex. 3 and compound of formula (109) [1:1 weight ratio]	0.2g	B
Mixture of compound of Prep. Ex. 20 and compound of formula (109) [3:7 weight ratio]	0.1g	A
Mixture of compound of Prep. Ex. 21 and compound of formula (109) [1:9 weight ratio]	0.1g	B
Mixture of compound of Prep. Ex. 22 and compound of formula (109) [9:1 weight ratio]	0.2g	B
Mixture of compound of Prep. Ex. 23 and compound of formula (109) [1:1 weight ratio]	0.4g	B
Mixture of compound of formula (110) and compound of formula (109) [1:1 weight ratio]	0.3g	B

Constitution of compound of formula (109):



(109)

Constitution of compound of formula (110):



The cotton fabrics washed with the detergents given in Table 3b according to the general procedure show good whiteness properties.

Application Example 2:

General procedure:

A wash liquor is prepared by dissolving 0.8 g of a washing powder in 200 ml of tap water. 10 g of bleached cotton fabric is added to the bath and washed at 30°C over 15 minutes and then rinsed, spin-dried and ironed at 160°C.

The following washing powders are used (amounts given in the following Tables 4a and 4b are percent by weight, based on the total weight of the detergent):

Table 4a (Ingredients of washing powders C and D)

	C	D
Sodium laurylbenzene-sulfonate (LAS)	8%	8%
Sodium lauryl ether sulfate (AES)	3%	3%
Dobanol 23-6.5 (nonionic alcoholethoxylate)	5%	5%
Zeolite A	20%	20%
Polycarboxylate (co-builder)	5%	5%
Soda ash	18%	18%
Sodium silicate	4%	4%
Sodium sulfate	5%	5%
Hydroxyethanediphosphonic acid (complexing agent)	0.5%	0.5%
Cellulase	1.5%	-----
Protease	-----	1.5%
Carboxymethylcellulose	1%	1%

Sodium perborate monohydrate	15%	15%
TAED	5%	5%
Soap	2%	2%
Fluorescent whitener or mixture of fluorescent whitener used	X%	X%

In each of the above detergents a sufficient amount of water is used to give 100%.

Table 4b (Washing powders used)

	Amount of fluorescent whitener or mixture of fluorescent whitener used	Washing powder
Compound of Prep. Ex. 1	0.2%	C
Compound of Prep. Ex. 3	0.2%	C
Compound of Prep. Ex. 7	0.2%	D
Compound of Prep. Ex. 8	0.2%	C
Compound of Prep. Ex. 9	0.4%	C
Compound of Prep. Ex. 10	0.2%	C
Compound of Prep. Ex. 11	0.2%	C
Compound of Prep. Ex. 17	0.4%	C
Compound of Prep. Ex. 20	0.5%	C
Compound of formula (110)	0.3%	D
Mixture of compound of Prep. Ex. 1 and compound of formula (109) [10:1 weight ratio]	0.2%	D
Mixture of compound of Prep. Ex. 3 and compound of formula (109) [5:1 weight ratio]	0.4%	C
Mixture of compound of Prep. Ex. 5 and compound of formula (109) [1:5 weight ratio]	0.15%	C
Mixture of compound of Prep. Ex. 11 and compound of formula (109) [1:1 weight ratio]	0.2%	C
Mixture of compound of Prep. Ex. 15 and compound of formula (109) [1:9 weight ratio]	0.4%	C
Mixture of compound of Prep. Ex. 16 and	0.3%	D

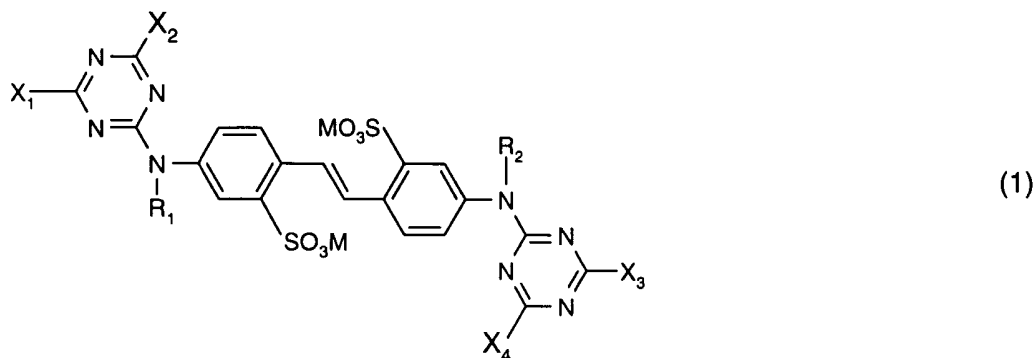
compound of formula (109) [9:1 weight ratio]		
Mixture of compound of Prep. Ex. 19 and compound of formula (109) [1:5 weight ratio]	0.2%	D

As to the constitution of compounds of formulae (109) and (110) see Application Example 1.

The cotton fabrics washed with the detergents given in Table 4b according to the general procedure show good whiteness properties.

What is claimed is:

1. A detergent composition comprising at least one compound of formula



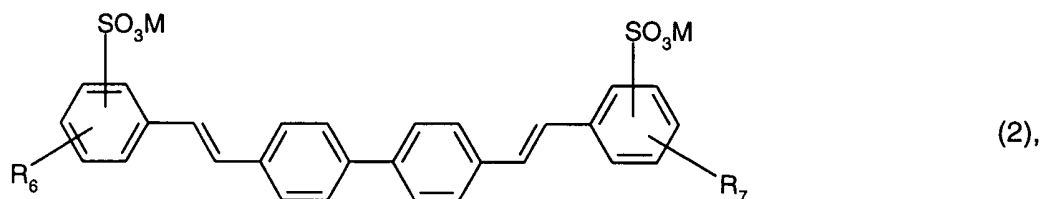
wherein

R_1 and R_2 are, independently of each other, hydrogen or unsubstituted or substituted C_1 - C_8 alkyl,

X_1 , X_2 , X_3 and X_4 are, independently of each other, $-N(R_3)R_4$ or $-OR_5$, wherein R_3 and R_4 are hydrogen, cyano, unsubstituted or substituted C_1 - C_8 alkyl or C_5 - C_7 cycloalkyl, or R_3 and R_4 , together with the nitrogen atom linking them, form a heterocyclic ring, and R_5 is unsubstituted or substituted C_1 - C_8 alkyl, and

M is hydrogen or a cation,

together with at least one compound of formula



wherein

R_6 and R_7 , independently of each other, are hydrogen, C_1 - C_8 alkyl, C_1 - C_8 alkoxy or halogen, and M is as defined above under formula (1).

2. A composition according to claim 1, wherein

R_1 and R_2 are hydrogen or C_1 - C_4 alkyl,

R_3 and R_4 are hydrogen; cyano; C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, $-CONH_2$ or phenyl and wherein the C_1 - C_8 alkyl group is uninterrupted or interrupted by $-O-$; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_7 cycloalkyl; or R_3 and R_4 ,

together with the nitrogen atom linking them, form an unsubstituted or C₁-C₄alkyl-substituted morpholino, piperidine or pyrrolidine ring; and

R₅ is C₁-C₈alkyl which is unsubstituted or substituted by hydroxy.

3. A composition according to claim 1 or 2, wherein

X₁, X₂, X₃ and X₄ are a radical of formula -N(R₃)R₄.

4. A composition according to any of claims 1 to 3, wherein

X₁ and X₃ are amino, and

X₂ and X₄ are a radical of formula -N(R₃)R₄, wherein R₃ and R₄ are hydrogen; cyano; C₁-C₈alkyl which is unsubstituted or substituted by hydroxy or carboxy, and wherein the C₁-C₈alkyl group is uninterrupted or interrupted by -O-; unsubstituted or C₁-C₄alkyl-substituted cyclohexyl; or R₃ and R₄, together with the nitrogen atom linking them, form an unsubstituted or C₁-C₄alkyl-substituted morpholino, piperidine or pyrrolidine ring.

5. A composition according to claim 4, wherein

R₃ and R₄, together with the nitrogen atom linking them, form an unsubstituted or C₁-C₄alkyl-substituted morpholino, piperidine or pyrrolidine ring, preferably a morpholino ring.

6. A composition according to any of claims 1 to 5, wherein

R₆ and R₇ are hydrogen and each of the sulfo groups indicated in formula (2) are bonded in ortho position.

7. A process according to any of claims 1 to 6, wherein

M is hydrogen, an alkaline- or alkaline earth-metal, or ammonium, preferably sodium.

8. A composition according to any of claims 1 to 7, comprising

i) 1-70% of an anionic surfactant and/or a nonionic surfactant;

ii) 0-75% of a builder;

iii) 0-30% of a peroxide;

iv) 0-10% of a peroxide activator; and

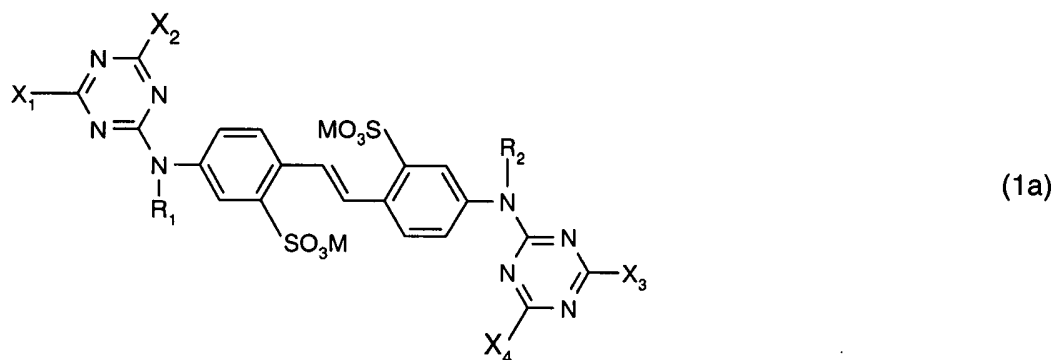
v) 0.001-5% of a mixture of compounds of formulae (1) and (2).

9. A composition according to claim 8, comprising

- i) 5-70% of an anionic surfactant and/or a nonionic surfactant;
- ii) 5-70% of a builder;
- iii) 0.5-30% of a peroxide;
- iv) 0.5-10% of a peroxide activator and/or 0.1-2% of a bleaching catalyst; and
- v) 0.01-5% of a mixture of compounds of formulae (1) and (2).

10. A composition according to any of claims 1 to 9 in which the detergent composition comprises at least one enzyme selected from the group consisting of cellulase, protease, amylase and lipase, preferably protease.

11. A detergent composition comprising at least one compound of formula



wherein

R_1 and R_2 are, independently of each other, hydrogen or unsubstituted or substituted C_1 - C_8 alkyl,

X_1 , X_2 , X_3 and X_4 are, independently of each other, $-N(R_3)R_4$ or $-OR_5$, wherein R_3 and R_4 are hydrogen; cyano; C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, $-CONH_2$ or phenyl and wherein the C_1 - C_8 alkyl group is uninterrupted or interrupted by $-O-$; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_7 cycloalkyl; or R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring;

R_5 is C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy, and

M is hydrogen or a cation,

and wherein the detergent contains at least one enzyme selected from the group consisting of cellulase, protease, amylase and lipase.

12. A composition according to claim 11, wherein

X_1 , X_2 , X_3 and X_4 are a radical of formula $-N(R_3)R_4$.

13. A composition according to any of claims 11 and 12, wherein

X_1 and X_3 are amino,

X_2 and X_4 are a radical of formula $-N(R_3)R_4$, wherein R_3 and R_4 are hydrogen; cyano or C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy or carboxy, and wherein the C_1 - C_8 alkyl group is uninterrupted or interrupted by $-O-$; unsubstituted or C_1 - C_4 alkyl-substituted cyclohexyl; or R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring, and

M is hydrogen, an alkaline- or alkaline earth-metal, or ammonium, preferably sodium.

14. A composition according to claim 13, wherein

R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring, preferably a morpholino ring.

15. A composition according to any of claims 11 to 14, wherein the composition comprises a peroxide, a peroxide activator and/or a bleaching catalyst.

16. A composition according to any of claims 11 to 15, comprising

i) 1-70% of an anionic surfactant and/or a nonionic surfactant;

ii) 0-75% of a builder;

iii) 0-30% of a peroxide;

iv) 0-10% of a peroxide activator;

v) 0.001-5% of a compound of formula (1a); and

vi) 0.05-5% of at least one enzyme selected from the group consisting of cellulase, protease, amylase and lipase.

17. A composition according to any of claims 11 to 16, comprising

i) 5-70% of an anionic surfactant and/or a nonionic surfactant;

ii) 5-70% of a builder;

iii) 0.5-30% of a peroxide;

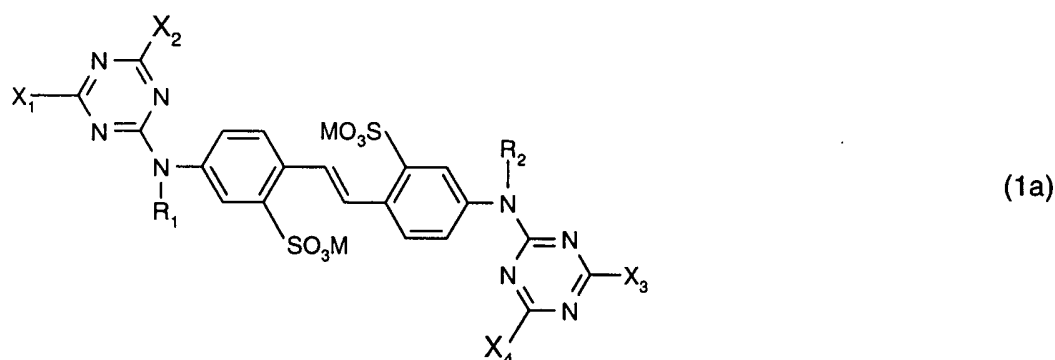
iv) 0.5-10% of a peroxide activator and/or 0.1-2% of a bleaching catalyst;

v) 0.01-5% of a compound of formula (1a); and

vi) 0.05-5% of at least one enzyme selected from the group consisting of cellulase, protease, amylase and lipase.

18. A composition according to any of claims 11 to 17, wherein the enzyme is a protease enzyme.

19. A process for the domestic washing treatment of a textile fibre material wherein the textile fibre material is contacted with an aqueous solution of a detergent comprising a compound of formula



wherein

R_1 and R_2 are, independently of each other, hydrogen or unsubstituted or substituted C_1 - C_8 alkyl,

X_1 , X_2 , X_3 and X_4 are, independently of each other, $-N(R_3)R_4$ or $-OR_5$, wherein R_3 and R_4 are hydrogen; cyano; C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, $-CONH_2$ or phenyl and wherein the C_1 - C_8 alkyl group is uninterrupted or interrupted by $-O-$; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_7 cycloalkyl; or R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring;

R_5 is C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy, and

M is hydrogen or a cation,

and wherein the detergent contains at least one enzyme selected from the group consisting of cellulase, protease, amylase and lipase,

and wherein the temperature of the solution is between 5°C and 40°C , preferably between 5°C and 30°C , throughout the process.

20. A process according to claim 19, wherein

X_1 , X_2 , X_3 and X_4 are a radical of formula $-N(R_3)R_4$.

21. A process according to any of claims 19 and 20, wherein

X_1 and X_3 are amino,

X_2 and X_4 are a radical of formula $-N(R_3)R_4$, wherein R_3 and R_4 are hydrogen; cyano or C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy or carboxy, and wherein the C_1 - C_8 alkyl group is uninterrupted or interrupted by $-O-$; unsubstituted or C_1 - C_4 alkyl-substituted cyclohexyl; or R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring, and

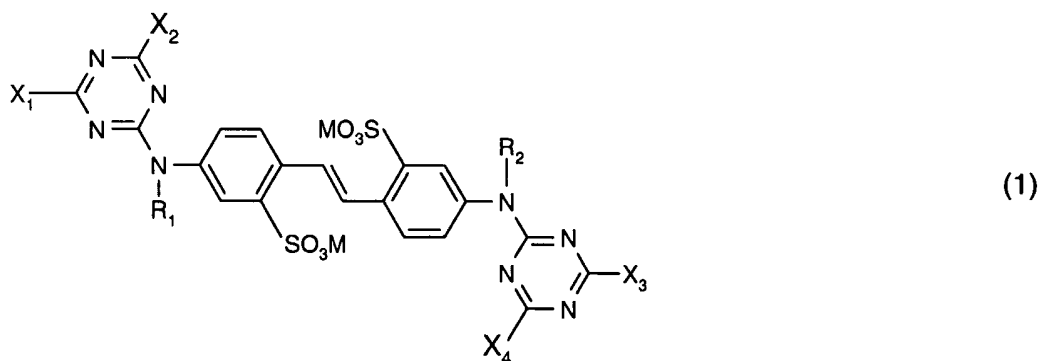
M is hydrogen, an alkaline- or alkaline earth-metal, or ammonium, preferably sodium.

22. A process according to claim 21, wherein

R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring, preferably a morpholino ring.

23. A process according to any of claims 19 to 22, wherein the textile fibre materials are treated with 0.05 to 3.0% by weight, based on the weight of the textile fibre material, of the compound of formula (1a).

24. A mixture of compounds comprising at least one compound of formula



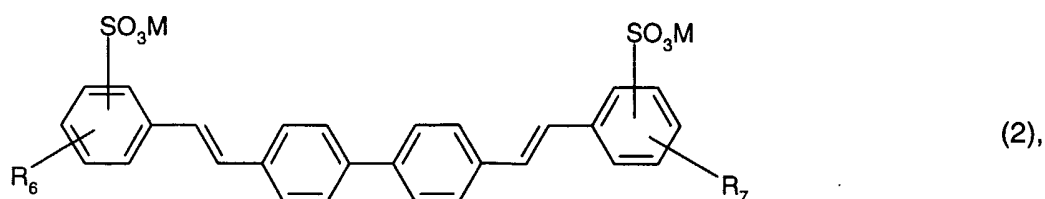
wherein

R_1 and R_2 are, independently of each other, hydrogen or unsubstituted or substituted C_1 - C_8 alkyl,

X_1 , X_2 , X_3 and X_4 are, independently of each other, $-N(R_3)R_4$ or $-OR_5$, wherein R_3 and R_4 are hydrogen, cyano, unsubstituted or substituted C_1 - C_8 alkyl or C_5 - C_7 cycloalkyl, or R_3 and R_4 , together with the nitrogen atom linking them, form a heterocyclic ring, and R_5 is unsubstituted or substituted C_1 - C_8 alkyl, and

M is hydrogen or a cation,

together with at least one compound of formula



wherein

R_6 and R_7 , independently of each other, are hydrogen, C_1 - C_8 alkyl, C_1 - C_8 alkoxy or halogen, and M is as defined above under formula (1).

25. A mixture of compounds according to claim 24, wherein

R_1 and R_2 are hydrogen or C_1 - C_4 alkyl,

R_3 and R_4 are hydrogen; cyano; C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, $-CONH_2$ or phenyl and wherein the C_1 - C_8 alkyl group is uninterrupted or interrupted by $-O-$; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_7 cycloalkyl; or R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring; and

R_5 is C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy.

26. A mixture of compounds according to any of claims 24 and 25, wherein

X_1 , X_2 , X_3 and X_4 are a radical of formula $-N(R_3)R_4$.

27. A mixture of compounds according to any of claims 24 to 26, wherein

X_1 and X_3 are amino, and

X_2 and X_4 are a radical of formula $-N(R_3)R_4$, wherein R_3 and R_4 are hydrogen; cyano or C_1 - C_8 alkyl which is unsubstituted or substituted by hydroxy or carboxy, and wherein the C_1 - C_8 alkyl group is uninterrupted or interrupted by $-O-$; unsubstituted or C_1 - C_4 alkyl-substituted cyclohexyl; or R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring.

28. A mixture of compounds according to claim 27, wherein

R_3 and R_4 , together with the nitrogen atom linking them, form an unsubstituted or C_1 - C_4 alkyl-substituted morpholino, piperidine or pyrrolidine ring, preferably a morpholino ring.

29. A mixture of compounds according to any of claims 24 to 28, wherein

R₆ and R₇ are hydrogen and each of the sulfo groups indicated in formula (2) are bonded in ortho position.

30. A mixture of compounds according to any of claims 24 to 29, wherein M is hydrogen, an alkaline- or alkaline earth-metal, or ammonium, preferably sodium.

31. A process for the fluorescent whitening of textile materials comprising contacting the textile materials with a mixture of compounds of formulae (1) and (2) as defined in claim 1.

32. A process according to claim 31 in which the textile materials are polyamides, wool or cotton.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 03/01618

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/42 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 728 749 A (CIBA GEIGY AG) 28 August 1996 (1996-08-28) page 2, line 48 -page 4, line 40 page 2, line 45-47; examples page 4, line 42 -page 5, line 39 page 6, line 46-54 page 7, line 39,40 page 6, line 43-45 --- -/--	1-32



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

13 May 2003

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/01618

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 850 934 A (CIBA GEIGY AG) 1 July 1998 (1998-07-01) page 6, line 25, 26 page 3, line 1 -page 4, line 29; claims 1-11; examples 1-10 -----	1-32

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