

(19)



(11)

EP 2 228 429 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

15.09.2010 Bulletin 2010/37

(51) Int Cl.:

C11D 3/39 (2006.01)

C11D 3/40 (2006.01)

(21) Application number: **09155165.5**

(22) Date of filing: **13.03.2009**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL
PT RO SE SI SK TR**

Designated Extension States:

AL BA RS

(71) Applicants:

• **Unilever PLC**

**100 Victoria Embankment
London, Greater London EC4Y 0DY (GB)**

Designated Contracting States:

CY GB IE MT

• **UNILEVER NV**

3013 AL Rotterdam (NL)

Designated Contracting States:

**AT BE BG CH LI CZ DE DK EE HU HR GR FR FI
ES IS IT LT LU LV MC MK NL NO PL PT RO SE SI
SK TR**

(72) Inventors:

• **Batchelor, Stephen Norman
Wirral,**

Merseyside CH63 3JW, (GB)

• **Dixon, Sarah**

Wirral,

Merseyside CH63 3JW, (GB)

• **Parry, Matthew Lloyd**

Wirral,

Merseyside CH63 3JW, (GB)

• **Whiteoak, Christopher John**

Loughborough,

Leicestershire LE12 7JZ, (GB)

(74) Representative: **Avila, David Victor et al**

Unilever Patent Group

Colworth House

Sharnbrook

Bedford

MK44 1LQ (GB)

(54) **Shading dye and catalyst combination**

(57) The present invention concerns the selection of appropriate conditions in order to permit bleaching of fabric stains whilst permitting fabric shading with a dye. The invention provides a laundry detergent composition com-

prising a peroxy species, a transition metal complex, a shading dye and a surfactant.

EP 2 228 429 A1

Description**FIELD OF INVENTION**

[0001] The present invention involves the balancing of levels of bleaching components and shading dye(s) in order to permit a shading dye effect whilst providing acceptable bleaching activity.

BACKGROUND

[0002] The use of shading dyes to provide a perception of whiteness is known as described in WO 05/003274. The use of transition metal catalysts together with a peroxy source is known as described in EP 0485397. Bleach systems that comprise a transition metal catalyst together with a peroxy source are capable of bleaching many different dyes in the wash solution as described in WO 02/088289 and US 6,800,775.

[0003] The presence of a shading dye and a catalyst/peroxide bleaching system in an aqueous medium results in the shading dye being bleached. The concentration of catalyst/peroxide bleaching system may be lowered to prevent dye bleaching, but then it would be expected the stain removal benefit would then not occur. Thus it appears not possible to obtain both benefits simultaneously.

SUMMARY OF INVENTION

[0004] Shading dyes are dyes added in low amounts to the laundry formulation which dissolve into the wash solution and then deposit onto the fabrics giving a pleasing white shade to garments. Peroxide activated metal catalyst bleaching systems and shading dyes therefore are not compatible as from the art it would be expected that the catalyst system will bleach the dye before it deposits onto the fabric.

[0005] We have found that the benefits of shading dyes and catalyst/peroxide may be enjoyed by selection of the appropriate conditions. An important aspect is that the laundry detergent provides, when dissolved in an aqueous solution, the correct ratio of dye to bleaching species; in particular, the level of hydrogen peroxide that is activated by the transition metal catalyst.

[0006] In one aspect the present invention provides a laundry detergent composition comprising:

- a peroxy species, for providing hydrogen peroxide in solution, in the range from 0.1% to 6 wt%;
- a transition metal complex, for catalytically bleaching a stain with hydrogen peroxide, in the range from 0.0001 to 0.1 wt%, the transition metal selected from Mn(II)-(III)-(IV)-(V), Fe(II)-(III)-(IV)-(V), and Co(I)-(II)-(III);
- a shading dye in the range from 0.00001 to 0.1 wt%; and,
- a surfactant in the range from 2 to 60 wt%.

[0007] The laundry detergent composition is most preferably a granular laundry detergent composition.

[0008] A more preferred aspect of the composition is one where the peroxy species is sodium percarbonate and is present in the range from 1 to 4 wt %;

the transition metal complex is present in the range from 0.005 wt% to 0.04; and,

the shading dye is present in the range from 0.0001 to 0.005 wt%.

[0009] In another aspect the present invention provides an aqueous fabric washing solution comprising:

- a) a transition metal catalyst in the range from 0.01 to 4 micromoles/L, preferably 0.5 to 2 micromoles/L;
- b) hydrogen peroxide in the range from 0.1 to 4 millimoles/L, preferably 0.5 to 2 millimoles/L;
- b) a shading dye in the range from 0.1 to 200ppb; and, a surfactant in the range from 0.1 to 4g/L.

[0010] The aqueous fabric washing solution preferably has a pH in the range from 9 to 11.

[0011] A unit dose as used herein is a particular amount of the bleaching composition used for a type of wash. The unit dose is added to the requisite amount of water. The unit dose may be in the form of a defined volume of powder, granules or tablet. The laundry detergent composition is preferably granular. The laundry granular detergent composition is preferably such that a unit dose is provided by an amount of the laundry detergent composition in the range from 1 to 10g/L.

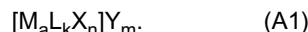
DETAILED DESCRIPTION OF THE INVENTION

[0012] There are a great number of transition metal catalysts that serve to bleach fabric stains in the presence of a peroxy species. The following are just some of the patents that deal with transition metal catalysts that are suitable for

use with the present invention: EP 0485397, WO 95/34628, WO 97/48787, WO 98/39098, WO 00/12667, WO 00/60045, WO 02/48301, WO 03/104234, EP1557457, US 6,696,403, US 6,432,900, US20050209120, and US20050181964.

[0013] Preferably the catalyst is formed from a ligand containing 3 to 6, nitrogens atoms that coordinate to the transition metal. Ligands containing pyridine substituents are especially preferred. Of the transition metals Fe and Mn are particularly preferred ions.

[0014] The ligand is preferably in the form of a complex of the general formula (A1) :



in which:

M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe(II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI), preferably selected from Fe(II)-(III)-(IV)-(V), Mn(II)-(III)-(IV)-(V) or Co(I)-(II)-(III), most preferably Fe(II)-(III)-(IV)-(V) or Mn(II)-(III)-(IV)-(V);

L represents a ligand as herein defined, or its protonated or deprotonated analogue;

X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner, preferably selected from O^{2-} , RBO_2^{2-} , $RCOO^-$, $RCONR^-$, OH^- , NO_3^- , NO , S^{2-} , RS^- , PO_4^{3-} , PO_3OR^{3-} , H_2O , CO_3^{2-} , HCO_3^- , ROH , $N(R)_3$, ROO^- , O_2^{2-} , O_2^- , RCN , Cl^- , Br^- , OCN^- , SCN^- , CN^- , N_3^- , F^- , I^- , RO^- , ClO_4^- , and $CF_3SO_3^-$, and more preferably selected from O^{2-} , RBO_2^{2-} , $RCOO^-$, OH^- , NO_3^- , S^{2-} , RS^- , PO_3^{4-} , H_2O , CO_3^{2-} , HCO_3^- , ROH , $N(R)_3$, Cl^- , Br^- , OCN^- , SCN^- , RCN , N_3^- , F^- , I^- , RO^- , ClO_4^- , and $CF_3SO_3^-$;

Y represents any non-coordinated counter ion, preferably selected from ClO_4^- , BR_4^- , $[MX_4]^-$, $[MX_4]^{2-}$, PF_6^- , $RCOO^-$, NO_3^- , RO^- , $N^+(R)_4$, ROO^- , O_2^{2-} , O_2^- , Cl^- , Br^- , F^- , I^- , $CF_3SO_3^-$, $S_2O_6^{2-}$, OCN^- , SCN^- , H_2O , RBO_2^{2-} , BF_4^- and BPh_4^- , and more preferably selected from ClO_4^- , BR_4^- , $[FeCl_4]^-$, PF_6^- , $RCOO^-$, NO_3^- , RO^- , $N^+(R)_4$, Cl^- , Br^- , F^- , I^- , $CF_3SO_3^-$, $S_2O_6^{2-}$, OCN^- , SCN^- , H_2O and BF_4^- ;

a represents an integer from 1 to 10, preferably from 1 to 4;

k represents an integer from 1 to 10;

n represents an integer from 1 to 10, preferably from 1 to 4;

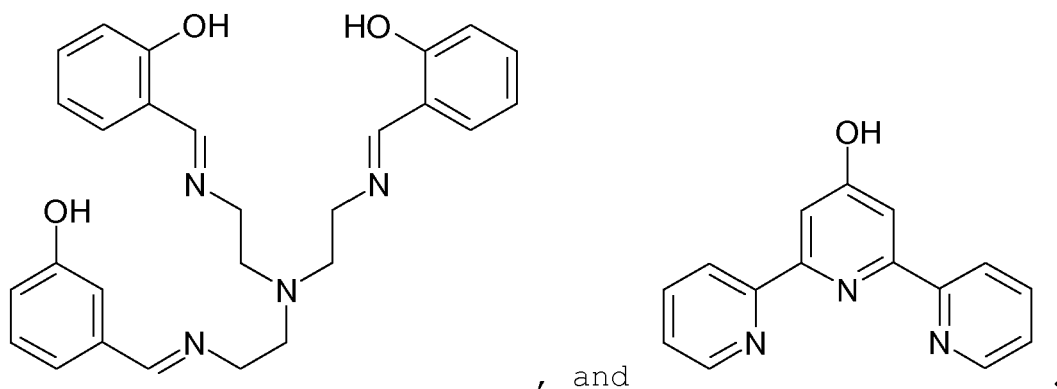
m represents zero or an integer from 1 to 20, preferably from 1 to 8; and

each R independently represents a group selected from hydrogen, hydroxyl, $-R'$ and $-OR'$, wherein R' = alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R' being optionally substituted by one or more functional groups E, wherein E independently represents a functional group selected from $-F$, $-Cl$, $-Br$, $-I$, $-OH$, $-OR'$, $-NH_2$, $-NHR'$, $-N(R')_2$, $-N(R')_3^+$, $-C(O)R'$, $-OC(O)R'$, $-COOH$, $-COO^-$ (Na^+ , K^+), $-COOR'$, $-C(O)NH_2$, $-C(O)NHR'$, $-C(O)N(R')_2$, heteroaryl, $-R'$, $-SR'$, $-SH$, $-P(R')_2$, $-P(O)(R')_2$, $-P(O)(OH)_2$, $-P(O)(OR')_2$, $-NO_2$, $-SO_3H$, $-SO_3^-(Na^+, K^+)$, $-S(O)_2R'$, $-NHC(O)R'$, and $-N(R')C(O)R'$, wherein R' represents cycloalkyl, aryl, arylalkyl, or alkyl optionally substituted by $-F$, $-Cl$, $-Br$, $-I$, $-NH_3^+$, $-SO_3H$, $-SO_3^-(Na^+, K^+)$, $-COOH$, $-COO^-$ (Na^+ , K^+), $-P(O)(OH)_2$, or $-P(O)(O^-(Na^+, K^+))_2$, and preferably each R independently represents hydrogen, optionally substituted alkyl or optionally substituted aryl, more preferably hydrogen or optionally substituted phenyl, naphthyl or C_{1-4} -alkyl.

[0015] The counter ions Y in formula (A1) balance the charge z on the complex formed by the ligand L, metal M and coordinating species X. Thus, if the charge z is positive, Y may be an anion such as $RCOO^-$, BPh_4^- , ClO_4^- , BF_4^- , PF_6^- , RSO_3^- , RSO_4^- , SO_4^{2-} , NO_3^- , F^- , Cl^- , Br^- , or I^- , with R being hydrogen, optionally substituted alkyl or optionally substituted aryl. If z is negative, Y may be a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation.

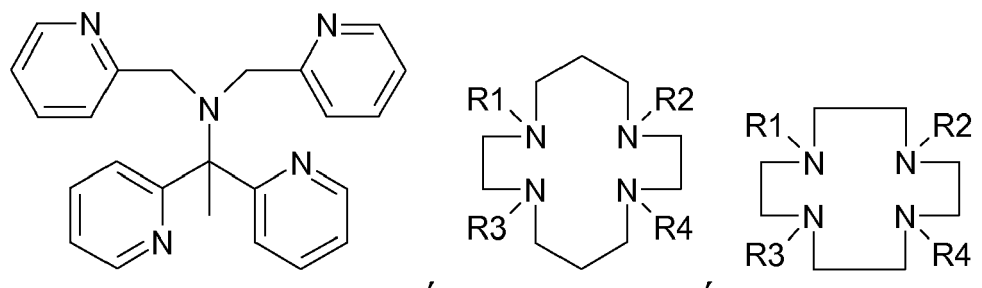
[0016] Suitable counter ions Y include those which give rise to the formation of storage-stable solids. Preferred counter ions for the preferred metal complexes are selected from R^7COO^- , ClO_4^- , BF_4^- , PF_6^- , RSO_3^- (in particular $CF_3SO_3^-$), RSO_4^- , SO_4^{2-} , NO_3^- , F^- , Cl^- , Br^- , and I^- , wherein R represents hydrogen or optionally substituted phenyl, naphthyl or C_{1-4} alkyl.

[0017] The following are preferred ligands. Ligands of the form:

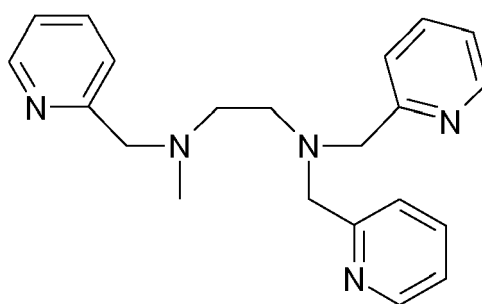


[0018] The above ligands and complexes thereof are described in WO 02/088289, US 6,800,775, and US 2005/0209920.

[0019] Ligands of the form:

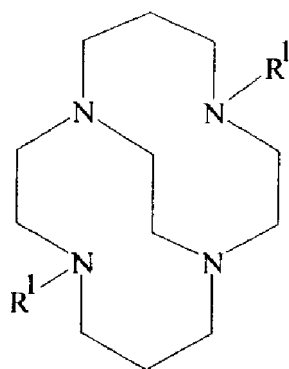


in the cyclic structures R1 to R4 may be the same or different and are H, and linear or branched, substituted or unsubstituted C1-C20 alkyl, alkylaryl, alkenyl or alkynyl. Alternatively, opposite R groups may together form a bridge, preferably an ethylene bridge, and



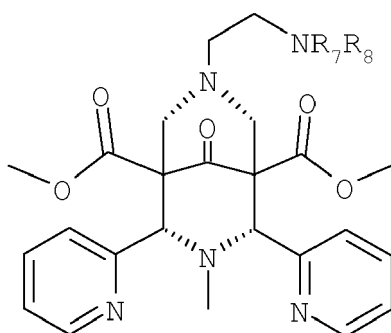
[0020] Ligands may be substituted as appropriate. For example they may be substituted by sulphonic and carboxylic acid groups; amines; quaternary amines; alkyl and alkoxy groups such as methyl, methoxy, ethyl and ethoxy; halogens; CN; and NO₂.

[0021] A preferred ligand is of the form:

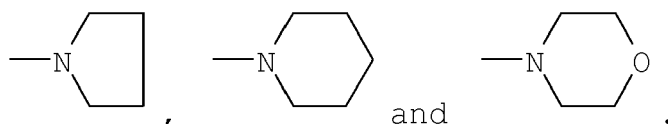


wherein R^1 is independently selected from H, and linear or branched, substituted or unsubstituted C1-C20 alkyl, alkylaryl, alkenyl or alkynyl. Preferably R^1 is methyl, most preferably ethyl.

[0022] A preferred ligand is of the form:



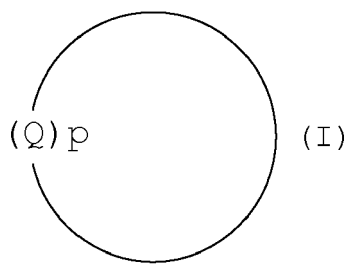
wherein $-NR_6R_7$ is selected from the group consisting of $-NMe_2$, NEt_2 , $-N(i-Pr)_2$,



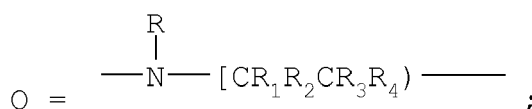
[0023] It is preferred that the ethylene bridge carrying the tertiary nitrogen is substituted by an alkyl group, preferably a methyl group. Most preferably the alkyl group is alpha to the bicyclo nitrogen carrying tertiary nitrogen.

[0024] A more preferred transition metal catalyst is as described in EP 0458397 and WO06/125517; both of these patents disclose the use of manganese 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me3-TACN) as related compounds as complexes. The PF_6^- ligand of Me3-TACN has been commercialised in laundry detergent powders and dish wash tablets. It is preferred that a preformed transition metal of Me3-TACN and related compounds is in the form of a salt such that it has a water solubility of at least 50 g/l at 20 °C. Preferred salts are those of chloride, acetate, sulphate, and nitrate. Most preferred are the acetate and sulphate salts.

[0025] The catalyst is most preferably a mononuclear or dinuclear complex of a Mn II-V transition metal catalyst, the ligand of the transition metal catalyst of formula (I):



wherein:



p is 3;

R is independently selected from: hydrogen, C1-C6-alkyl, C2OH, C1COOH, and pyridin-2-ylmethyl or one of R is linked to the N of another Q via an ethylene bridge;

R1, R2, R3, and R4 are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy.

R is preferably independently selected from: hydrogen, CH3, C2H5, CH2CH2OH and CH2COOH.

R, R1, R2, R3, and R4 are preferably independently selected from: H and Me.

1,4,7-Trimethyl-1,4,7-triazacyclononane (Me3-TACN) and 1,2-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me4-DTNE) are most preferred.

PEROXYL SPECIES

[0026] The laundry treatment composition comprises a source of hydrogen peroxide. A preferred peroxide is perborate or percarbonate, preferably percarbonate; the sodium salts are preferred. These peroxy species may be further enhanced by the use of an activator, for example, TAED or SNOBS. The laundry detergent composition comprises from 0.1% to 6 wt%, preferably 0.1 to 4 wt %, of a peroxy species.

SHADING DYE

[0027] The shading dyes used in the present invention are blue or violet. In this regard the dye gives a blue or violet colour to a white cloth with a hue angle of 240 to 345, more preferably 260 to 320, most preferably 270 to 300. The white cloth used is bleached non-mercerised woven cotton sheeting.

[0028] A detailed description of hue angle may be found on p57 of Color Chemistry 3rd edition by H. Zollinger published by Wiley-VCH.

[0029] For anionic dyes, all weights % refer to the Na salt of the dye. For cationic dyes all weight % refer to the Cl salt of the dye.

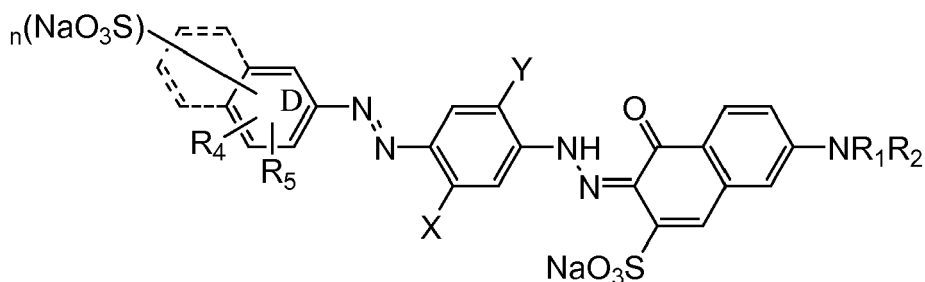
[0030] Most preferably the shading dye is selected from dyes with azo or azine chromophores.

[0031] Shading dyes are preferably selected from the following dyes:

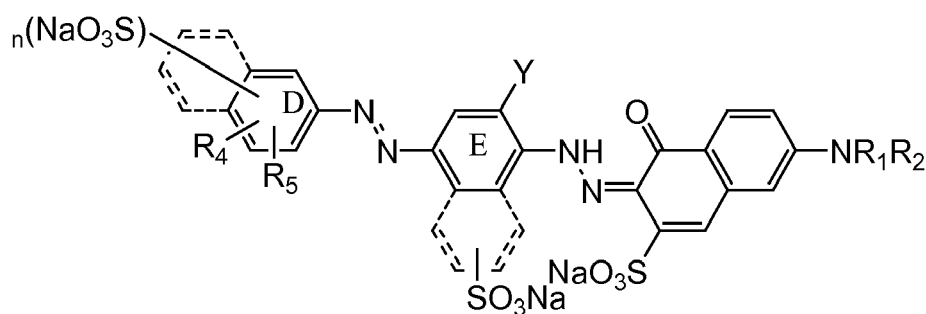
(1) Direct Dyes:

[0032] Direct blue and Direct violet dyes selected from triphenodioxazine dyes, bis-azo and *tris*-azo dyes.

[0033] Most preferably, the direct dye is a direct violet of the following structures:



or



wherein:

ring D and E may be independently naphthyl or phenyl as shown;

R_1 is selected from: hydrogen and C1-C4-alkyl, preferably hydrogen;

R_2 is selected from: hydrogen, C1-C4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl, preferably phenyl;

R_3 and R_4 are independently selected from: hydrogen and C1-C4-alkyl, preferably hydrogen or methyl;

X and Y are independently selected from: hydrogen, C1-C4-alkyl and C1-C4-alkoxy; preferably the dye has X = methyl; and, Y = methoxy and n is 0, 1 or 2, preferably 1 or 2.

[0034] Preferred dyes are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, and direct violet 99.

[0035] Bis-azo copper containing dyes such as direct violet 66 may be used. The benzidine based dyes are less preferred.

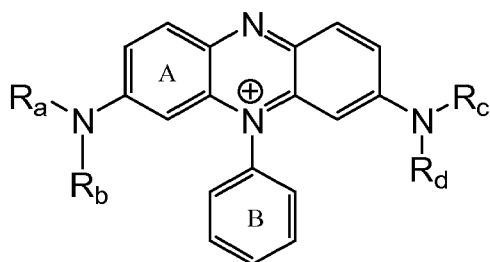
[0036] Preferably the direct dye is present at 0.00002 wt% to 0.005 wt% of the formulation.

[0037] In another embodiment the direct dye may be covalently linked to the photo-bleach, for example as described in W02006/024612.

(2) Acid dyes:

[0038] Preferred acid dyes are:

(i) azine dyes, wherein the dye is of the following core structure:



wherein R_a , R_b , R_c and R_d are selected from: H, an branched or linear C1 to C7-alkyl chain, benzyl a phenyl, and a naphthyl;

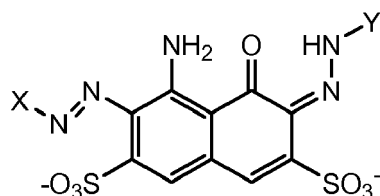
the dye is substituted with at least one SO_3^- or $-\text{COO}^-$ group;

the B ring does not carry a negatively charged group or salt thereof;

and the A ring may further substituted to form a naphthyl; the dye is optionally substituted by groups selected from: amine, methyl, ethyl, hydroxyl, methoxy, ethoxy, phenoxy, C1, Br, I, F, and NO_2 .

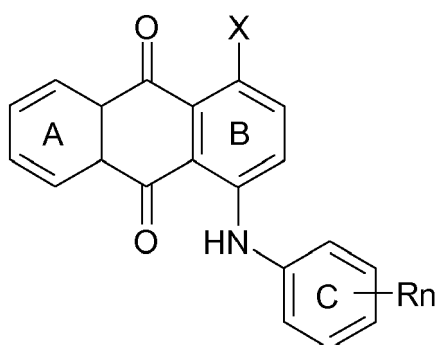
Preferred azine dyes are: acid blue 98, acid violet 50, and acid blue 59, more preferably acid violet 50 and acid blue 98.

(ii) Bis-azo acid dyes Blue and violet acid dyes of the structure



where at least one of X and Y must be an aromatic group, preferably both, the aromatic groups may be a substituted phenyl or naphthyl group, which may be substituted with non water solubilising groups such as CN, NO_2 , ester, acid amide, F, Cl, Br, alkyl or alkyloxy or aryloxy groups, X and Y may not be substituted with water solubilising groups such as sulphonates or carboxylates, most preferred is where X and Y are substituted phenyl groups.

(iii) anthraquinone dyes of the structure:



wherein:

X is selected from the group consisting of $-\text{OH}$ and $-\text{NH}_2$;

R is selected from the group consisting of $-\text{CH}_3$ and $-\text{OCH}_3$;

n is an integer selected from 0, 1 2 and 3; and

one of the rings A, B and C is substituted by one sulphonate group.

(iv) triphenylmethane acid dyes, such as acid violet 17.

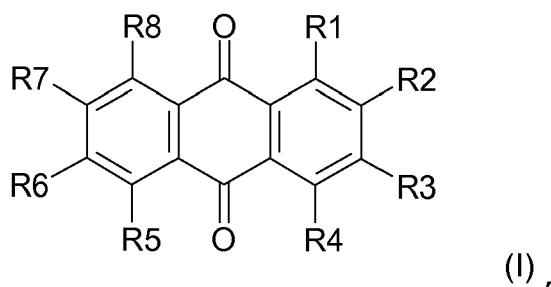
[0039] Preferably the acid dye is present at 0.0003 wt% to 0.01 wt% of the formulation.

(3) Hydrophobic dyes

[0040] The composition may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, naphthalimides, pyrazole, naphthoquinone, anthraquinone and mono-azo or di-azo dye chromophores. Hydrophobic dyes are dyes which do not contain any charged water solubilising group. Hydrophobic dyes may be selected from the groups of disperse and solvent dyes. Blue and violet anthraquinone and mono-azo dye are preferred.

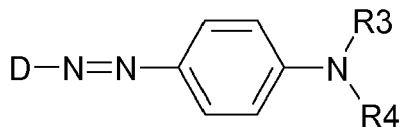
[0041] Most preferred dyes are:

(i) solvent violet 13 and disperse violet 27 and an anthraquinone structure of the following anthraquinone structure (I):



wherein R1, R4, R5, and R8 are independently selected from the groups consisting of -H, -OH, -NH₂, NHCOCH₃ and -NO₂, such that a maximum of only one -NO₂ group and a maximum of two -H are present as R1, R4, R5, and R8 substituents; and R2, R3, R6, and R7 is selected from -H, F, Br, Cl or -NO₂, and -Oaryl.

(ii) mono-azo dye selected from a compound of the following formula:

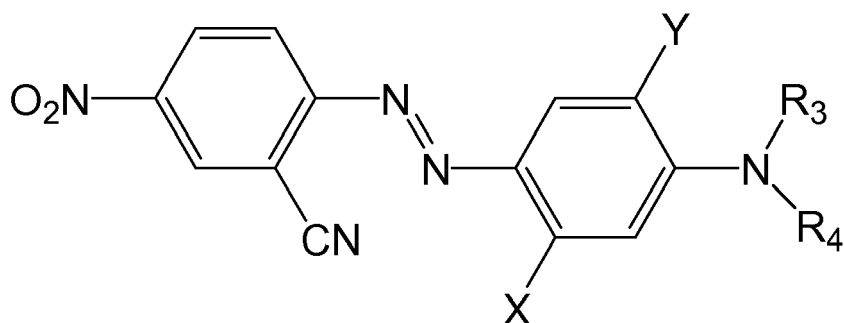


wherein R3 and R4 are selected from optionally substituted polyether groups, C2 to C12 alkyl chains having optionally therein ether (-O-) or ester links, the chain being optionally substituted with -Cl, -Br, -CN, -NO₂, and -SO₂CH₃; and, D denotes an aromatic or heteroaromatic group.

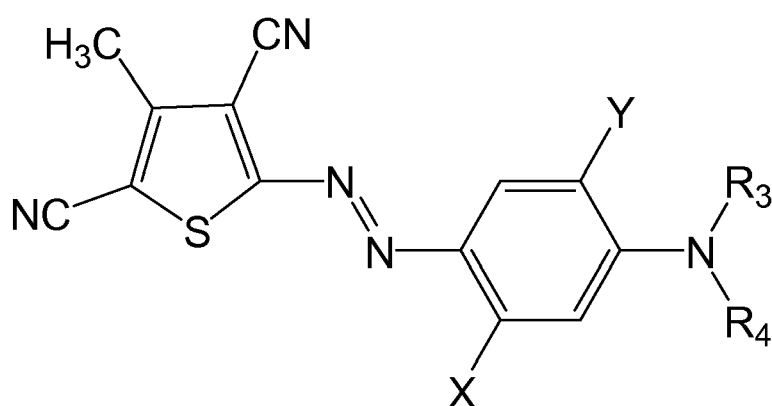
[0042] The aromatic rings may be further substituted by preferably -Cl, -Br, -CN, -NO₂, -SO₂CH₃ and -NHCOR and R is selected from CH₃, C₂H₅, and CH₂Cl.

[0043] Polyether groups for shading dyes are discussed in W02008/087497 (Procter & Rambling).

[0044] Most preferred mono-azo dyes are of the form:



and



[0045] Where X and Y are selected from -Cl, -Br, -CN, -NO₂, -SO₂CH₃ and -NHCOR and R is selected from CH₃, C₂H₅, and CH₂Cl. Preferably X is NHCOCH₃ or NHCOCH₂Cl.

[0046] Preferred dyes include solvent violet 13, disperse violet 27, disperse violet 28, disperse violet 63 and disperse violet 77.

[0047] Preferably the hydrophobic dye is present at 0.0001 wt% to 0.005 wt% of the formulation.

(4) Basic dyes

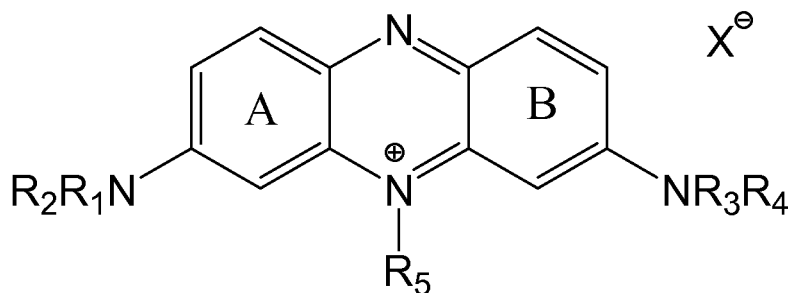
[0048] Basic dyes are organic dyes which carry a net positive charge. They deposit onto cotton. Dyes may be selected from the basic violet and basic blue dyes listed in the Colour Index International.

[0049] Preferably the dye is not covalently bound to a negatively charged substituent. Preferably the basic dye is present at 0.0001 wt% to 0.005 wt% of the formulation.

[0050] Preferred examples include triarylmethane basic dyes, methine basic dye, anthraquinone basic dyes, basic blue 16, basic blue 65, basic blue 66, basic blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48; basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141. Other thiazolium dyes besides basic blue 66 may also be used.

[0051] Most preferably basic dyes are selected from:

(i) a cationic azine dye of the following form:

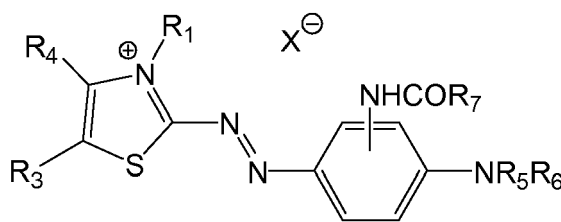


wherein X⁻ is a negative anion;

no more than three of the groups R₁, R₂, R₃ and R₄ are H and are independently selected from: a polyether chain, benzyl, phenyl, amine substituted benzyl, amine substituted phenyl, COCH₃, H, a linear or branched alkyl chains; a linear or branched alkyl chains which is substituted by one or more groups selected from: ester groups; Cl; F; CN; OH; CH₃O⁻; C₂H₅O⁻; and, phenyl;

R₅ is selected from the group consisting of: a branched or linear C₁ to C₁₀ alkyl; a branched or linear C₁ to C₁₀ alkyl group substituted by a phenyl group; and, an aromatic group; one or more of rings A or B may be further substituted to form a naphthyl ring; and,

(ii) a cationic thiazolium dye, preferably of the form:



wherein R₁ is a branched or linear C₁-C₄ alkyl group;

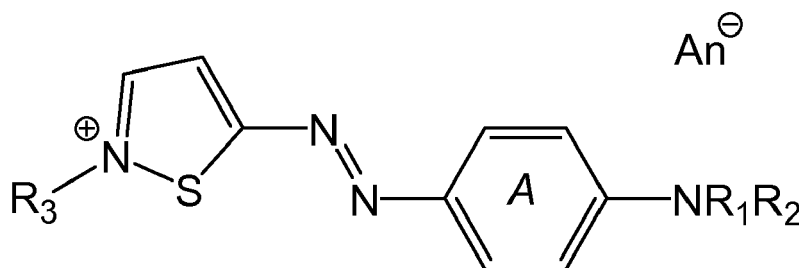
R₃ and R₄ are independently selected from H, CH₃, and C₂H₅ or R₃ and R₄ are joined to form a benzene ring;

R₅ and R₆ are independently selected from: H, a branched or linear C₁-C₄ alkyl group, wherein the alkyl group chain may be substituted by OH groups, phenyl, COR₇, CH₂Ph, (C₂H₄O)_nH wherein n is 2 to 5;

R₇ is a branched or linear C₁-C₄ alkyl group; and,

X is a negative anion.

(iii) a cationic isothiazolium dye of the following structure:



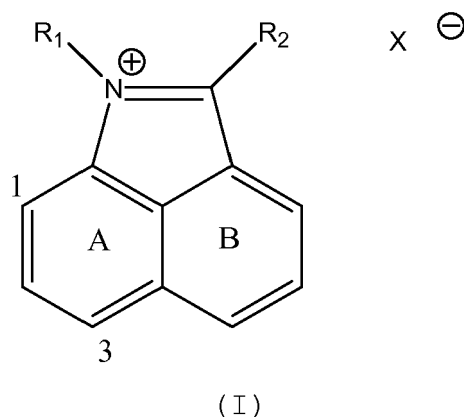
Wherein:

R₁ and R₂ are independently selected from H, alkyl, aryl; alkylaryl; alkylesters; polyethers; and R₁ and R₂ may be joined to form a five or six member aliphatic ring which may comprise a further heteroatom selected from oxygen and nitrogen;

R₃ is selected from: H; alkyl; alkylaryl; and, aryl; and, the isothiazolium ring may be further condensed to a

benzene ring.

(iv) a cationic naphtholactams dye of the following structure:



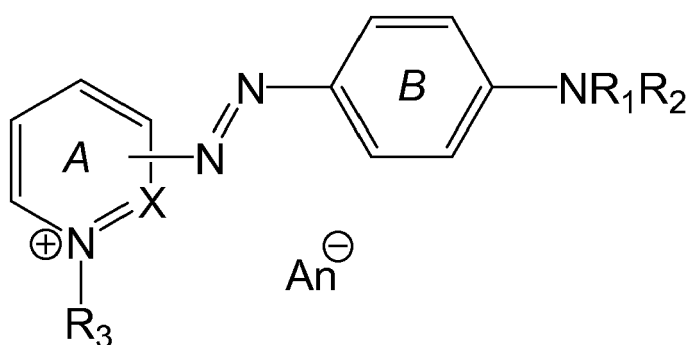
wherein:

X⁻ is a counter ion;

R₁ is an optionally substituted alkyl which may form an alkylene bridge at the 1 position;

R₂ is a group having at least one benzene moiety directly bound to a nitrogen atom, wherein the benzene moiety is between 1 and 4 bonds removed from the naphtholactam and in conjugation with the naphtholactam and rings A and B are optionally substituted.

(v) a cationic pyridine/pyridazine dye of the following structure:



wherein

X is selected from: N; CH; and, C-N=N-phenyl(B)-para-NR₁R₂;

R₁ and R₂ are independently selected from H, alkyl, aryl; alkylaryl; alkylesters; polyethers; and R₁ and R₂ may be joined to form a five or six member aliphatic ring which may comprise a further heteroatom selected from oxygen and nitrogen;

R₃ is selected from: H; alkyl; alkylaryl; and, aryl; and, Ring A may be further condensed to a benzene ring.

(5) Reactive dyes

[0052] Reactive dyes are dyes which contain an organic group capable of reacting with cellulose and linking the dye to cellulose with a covalent bond. They deposit onto cotton.

[0053] Preferably the reactive group is hydrolysed or reactive group of the dyes has been reacted with an organic

species such as a polymer, so as to link the dye to this species. Dyes may be selected from the reactive violet and reactive blue dyes listed in the Colour Index International.

[0054] Preferred examples include reactive blue 19, reactive blue 163, reactive blue 182 and reactive blue, reactive blue 96.

[0055] The following table illustrates various shading dyes.

10		
15		
20		
25		
30		
35		
40		
45		
50		

[0056] Shading dyes may be included into granular laundry detergent products via addition to the surfactant slurry before granulation of the product, or via post-dosing to the granulated product. Preferably the shading dye is post-dosed to the granulated product via a dye granule.

[0057] Suitable dye granules are discussed in W02005/003274 (Unilever), W02006/053598 (Unilever), W02007/006357 (Unilever), W02007/039042 (Unilever), W02007/096052, and W02008/056324 (Proctor & Gamble).

[0058] The shading granules are preferably formed by drying a liquid slurry or solution of the shading dye, for example

by vacuum drying, freeze drying, drying in drum dryers, Spin Flash® (Anhydro), but most preferably by spray drying. Most preferably the liquid is water and other ingredients maybe present, most preferably a dispersant and/or an acidic polymer.

[0059] Most preferably the dye granule comprises:

- (i) 20 to 60 wt% of a shading dye;
- (ii) 40 to 80 wt% of a dispersant selected from:

ligninsulphonates; alkali metal salts of the condensation products of naphthalenesulphonic acids and formaldehyde;

polyvinylsulphonates; and, ethoxylated novolacs;

- (iii) 0 to 10 of wt% auxillary agents selected from: anionic surfactants; non-ionic surfactants; acidic polymers; and dust proofing oil;

[0060] The shading dye and dispersant are preferably ground before or during the making of the slurry. This grinding is preferably accomplished in mills, such as for example ball, swing, bead or sand mills, or in kneaders.

[0061] The production of such granules is discussed in W02006/131530. Such granules are suitably made immediately after synthesis of the dye.

[0062] Acidic polymer are described in W02007/039042. In a 1wt% solution in demineralised water they provide a pH of less than 6.

[0063] Preferably, the dye granules have an average particle size, APS, from 0.1 to 300 microns, preferably 10 to 150 microns. Preferably this is as measured by a laser diffraction particle size analyser, preferably a Malvern HP with 100mm lens.

[0064] Use of such granules prevents decomposition of the dye in the product during storage. The dye granules are preferably post-dosed into the powder in a 0.1 to 1 wt% dry mix with an alkali metal salt, preferably Na₂SO₄ or NaCl.

SURFACTANT

[0065] The laundry treatment composition comprises between 2 to 60 wt % of a surfactant, most preferably 2 to 30 wt %, more preferably 10 to 30 wt %. In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

[0066] Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C₆ to C₂₂ alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C₈ to C₁₈ primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

[0067] Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₈ to C₁₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₉ to C₂₀ benzene sulphonates, particularly sodium linear secondary alkyl C₁₀ to C₁₅ benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C₁₁ to C₁₅ alkyl benzene sulphonates and sodium C₁₂ to C₁₈ alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

[0068] Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C₁₆ to C₁₈ primary alcohol sulphate together with a C₁₂ to C₁₅ primary alcohol 3 to 7 EO ethoxylate.

[0069] The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25 to 90 wt % of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 5% to about 40 wt % of the surfactant system.

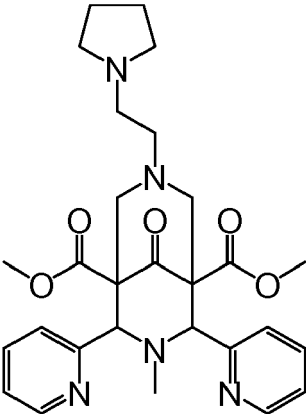
Examples

Catalyst structures:

[0070]

Code	Metal	Ligand structure
AC	Fe (II)	
BC	Fe (II)	
CC	Fe (II)	
DC	Mn(II)	

(continued)

Code	Metal	Ligand structure
EC	Fe (II)	

[0071] Catalyst AC, BC, CC and EC were prepared as described in WO 03/104379 or by analogous procedures.

[0072] The DC ligand was purchased from Aldrich, complexed with Mn(II) in aqueous solution and used.

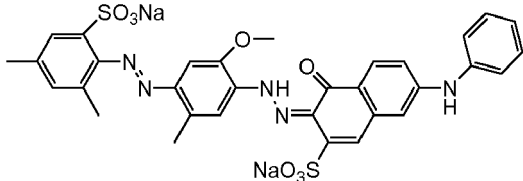
Example 1

[0073] A selection of shading dyes, which deposit onto cotton from wash solutions and have varying structures, was made. Solution of these dyes were made in pH=10 buffer such that the optical density at 1 cm was approximately 1. To this solution the catalyst AC was added alongside hydrogen peroxide such that the concentrations were:

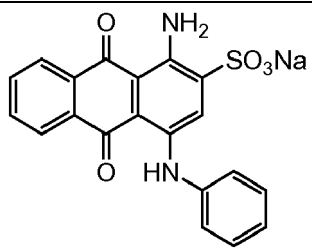
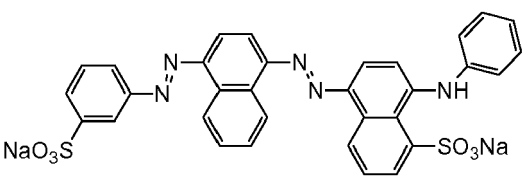
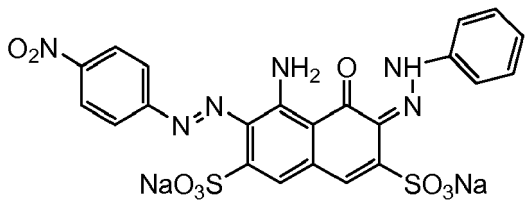
(a) 1 micromolar AC, 1 millimolar hydrogen peroxide

(b) 4 micromolar AC, 4 millimolar hydrogen peroxide The optical density of the dye was measured at the beginning of the experiment and after 30 minutes at 20 °C. From these measurements the % of dye bleaching was calculated using the equation

$$\% \text{ bleaching} = 100 \times (\text{OD}_{\text{initial}} - \text{OD}_{30 \text{ minutes}}) / \text{OD}_{\text{initial}}$$

Dye	% bleaching	
	(a)	(b)
Direct violet 51 	1	29
Acid blue 25	66	96

(continued)

Dye	% bleaching	
	(a)	(b)
		
Acid blue 113 	79	99
Acid black 1 	27	53

[0074] From the results all the dyes are bleached by the catalyst peroxide system in 30 minutes, a typical domestic wash time. Acid blue 113 was the most susceptible to bleaching. Of the 3 azo dyes, acid blue 113 is the only dye not to have 1 azo group in the hydrazone form. Hence azo shading dyes containing sulphonates should preferably have at least one of the azo groups in the hydrazone form. Hydrazones are formed when an OH groups is adjacent to the azo group on the aromatic ring.

[0075] The bleaching of the dye is much smaller at lower catalyst and peroxide concentrations.

Example 2

[0076] Various amounts of catalyst AC and DC were separately added to Persil Colour (TM) washing powder, such that when the powder was dosed at 2.5g/L a 1, 2, 4 and 8 micromolar solution of the catalysts were obtained. Persil Colour is a commercial washing powder containing 5-15% anionic surfactant and non-ionic surfactant, 15-30% zeolite and less than 5% soap, polycarboxylate and phosphate. It also contains enzymes. 0.3% of the dye acid blue 25 was also added to the powder. The so-created powders were used to wash bleach non-mercerised woven cotton at 30°C, for 30 minutes with a liquor to the cloth-ration of 30:1 and 2.5g/L powder. Various amounts of hydrogen peroxide was added to activate the catalyst. Following the wash the clothes were rinsed dried and the shading on the cloth measured using a reflectometer and expressed as the delta E values relative to cloth washed with Persil Colour without added dye or bleach system.

[0077] The results are displayed below:

[catalyst]/ micromolar	[H ₂ O ₂]/ millimolar	Catalyst	Delta E
0	0	-	12.4
1	1	AC	5.1
2	2	AC	2.0
4	4	AC	0.4

EP 2 228 429 A1

(continued)

[catalyst]/ micromolar	[H ₂ O ₂] / millimolar	Catalyst	Delta E
8	8	AC	0.3
1	1	DC	12.3
2	2	DC	12.2
4	4	DC	12.0
8	8	DC	11.7

[0078] Bleaching of the dye is seen for both AC and DC, evidenced by lower Delta E on the cloth. Notably less dye bleaching is found at lower catalyst concentrations.

Example 3

[0079] BC1 (fixed tea stain) bleachable stain test monitor cloth was washed in a bicarbonate buffer (pH=10) with 0.5g/L LAS surfactant, a Liquor to Cloth ratio of 60:1, a temperature of 30°C and a wash time of 30 minutes. The experiment was repeated with various levels of catalyst AC and hydrogen peroxide. The final colour of the cloth was measured and expressed as the delta E relative to a clean piece of cotton. Lower values indicate effective bleaching of the stain.

[AC]/ micromolar	[H ₂ O ₂] / millimolar	Delta E
0	0	19.6
0	1	18.5
0	2	18.1
1	1	17.0
1	2	16.2
2	1	15.9
2	2	14.6

[0080] Effective bleaching of the stain is seen at these levels of AC and hydrogen peroxide.

Example 4

[0081] Black tea beverage was created by placing 1 PG Tips pyramid tea bag in 400ml of boiled ultrapure water for 5 minutes. The tea bag was then removed and the beverage cooled to room temperature. Non-mercerised non-fluorescent white cotton sheeting was dipped in the cold tea and removed. The cloth was left to dry for 1 day in the dark, then used for experiments.

[0082] When washed in a pH=10 solution containing 2 micromolar DC and 2 millimolar peroxide bleaching of the tea stain was observed significantly above that of a control solution containing 2 micromolar Mn(II) and 2 millimolar peroxide.

Example 5

[0083] Catalyst BC and CC effectively bleached Direct violet 51 and Acid blue 25 in solution at pH=10 when used at concentration of 10 micromolar with 10 millimolar peroxide. Bleaching was much slower with 2 micromolar with 2 millimolar peroxide. Direct violet 51 was much less susceptible to bleaching.

Example 6

[0084] White knitted polyester was washed for 30 minutes at 20°C in 1.8g/L of Brihlante™ washing powder (ex Brasil) with a liquor to cloth ration of 100:1. This is a phosphate/anionic surfactant based powder. Various levels of catalyst BC and hydrogen peroxide was added to the wash liquor alongside 0.2ppm of the hydrophobic shading dyes disperse blue 79:1 (azo dye) and solvent violet 13 (anthraquinone dye). The take up of the hydrophobic shading by the polyester was

EP 2 228 429 A1

measured as the delta E relative to white cotton and the results shown below.

[AC] / micromolar	[H ₂ O ₂] / millimolar	Dye	Delta E
0	0	Blue 79:1	2.8
1	1	Blue 79:1	2.8
10	10	Blue 79:1	2.3
0	0	Violet 13	4.0
1	1	Violet 13	1.6
10	10	Violet 13	0.2

[0085] Both dyes are bleached by the catalyst/peroxide, as seen by the lower Delta E on the cloth. This is much less at the lower concentration. The azo dye, Disperse Blue 79:1 is much less susceptible to bleaching than the anthraquinone, solvent violet 13.

Example 7

[0086] White non-mercerised cotton sheeting was washed at 40°C in 5g/L Persil Colour for 30 minutes with a liquor to cloth ratio of 60:1. Persil Colour is a zeolite/anionic/non-ionic surfactant based washing powder. Direct Violet 51 was added to the powder such that 100 ppb of direct violet 51 was in the wash liquor.

[0087] The experiment was repeated with the addition of 10 micromolar catalyst with 10 millimolar peroxide and 2 micromolar catalyst with 2 millimolar peroxide. Following rinsing and drying the colour of the cloth was measured relative to a white cotton control cloth washed without addition of direct violet 51.

[0088] The experiment was then repeated using a BC1 model tea bleach monitor and a liquor to cloth ratio of 120:1. For clarity no direct violet 51 was added to the Persil Colour in this case. The results are given below in the table below.

Bleach system	White cotton	BC1
2 millimolar H ₂ O ₂	1.5	19.3
10 millimolar H ₂ O ₂	1.4	18.9
2 micromolar AC 2 millimolar H ₂ O ₂	1.5	16.5
10 micromolar AC 10 millimolar H ₂ O ₂	0.5	10.9
2 micromolar EC 2 millimolar H ₂ O ₂	1.5	17.5
10 micromolar EC 10 millimolar H ₂ O ₂	0.7	13.1

[0089] From the table it can be seen that at the high catalyst concentration approximately 2/3 of the direct violet dye is bleached in solution reducing the transfer of shading colour to the cloth. At the low catalyst concentration no dye is lost. At both high and low catalyst concentration effective bleaching of the BC1 cloth is found, compared to control without catalyst addition.

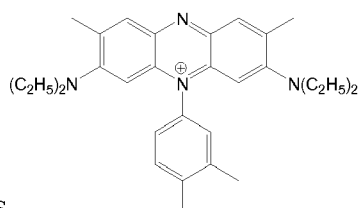
Exemplary Base Powder Formulations A, B, C and D

[0090]

Formulation	A	B	C	D
NaLAS	10	20	12	14
NI(7E0)	-	-	-	10
NaPAS	5	-	2	-
Na tripolyphosphate	-	10	-	-
Soap	-	-	-	2

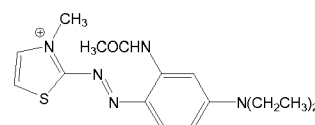
(continued)

Formulation	A	B	C	D
Zeolite A24	7	-	-	17
Sodium silicate	5	4	5	1
Sodium carbonate	25	20	30	20
Sodium sulphate	40	33	40	22
Carboxymethylcellulose	0.2	0.3	-	0.5
Sodium chloride	-	-	-	5
Lipase (Lipex™)	0.005	0.01	-	0.005
Protease	0.005	0.01	-	0.005
Amylase	0.001	0.003	-	-
Cellulase	-	0.003	-	-
Acid Violet 50	0.0015	0.002	-	0.001
Direct violet 9	0.0001	-	-	0.0002
Dye 1	-	0.002	-	0.001
Dye 2	-	-	0.002	-
Fluorescer	0.1	0.15	0.05	0.3
Catalyst	0.01 Me3-TACN	0.05 Me3-TACN	0.025 Me3-TACN	0.025 Me4-DTNE
percarbonate	2	2	2	2
Water/impurities/minors	Remainder	remainder	remainder	Remainder



Dye 1 is

and dye 2 is



[0091] Enzyme dye and catalyst levels refer to pure compounds. The catalyst was used as both the PF_6^- and sulphate salt in the exemplified formulations.

Claims

1. A laundry detergent composition comprising:

- a peroxy species, for providing hydrogen peroxide in solution, in the range from 0.1% to 6 wt%;
- a transition metal complex, for catalytically bleaching a stain with hydrogen peroxide, in the range from 0.0001 to 0.1 wt%, the transition metal selected from Mn(II)-(III)-(IV)-(V), Fe(II)-(III)-(IV)-(V), and Co(I)-(II)-(III);
- a shading dye in the range from 0.00001 to 0.1 wt%;
- and,
- a surfactant in the range from 2 to 60 wt%.

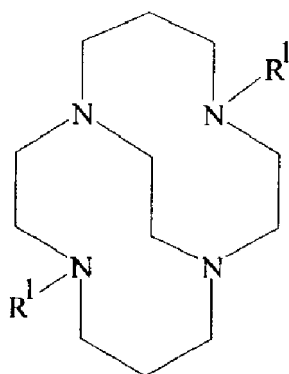
2. A laundry detergent composition according to claim 1, wherein the peroxy species is percarbonate and is present

in the range from 1 to 4 wt %;

the transition metal complex is present in the range from 0.005 wt% to 0.04;

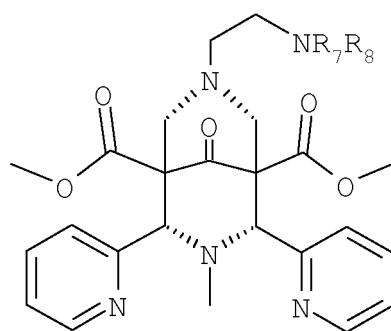
and the shading dye is present in the range from 0.0001 to 0.005 wt% dye.

3. A laundry detergent composition according to claim 1 or 2, wherein the molar ratio of the transition metal catalyst to the peroxide is in the range from 1:2000 to 1:10.
4. A laundry detergent composition according to any one of claim 1 to 3, wherein the ligand of the transition metal catalyst coordinates to the transition metal with 3 to 6 nitrogen atoms.
5. A laundry detergent composition according to claim 4, wherein the ligand of the transition metal complex is a macropolycyclic ligand of the formula:



wherein "R¹" is independently selected from H, and linear or branched, substituted or unsubstituted C1-C20 alkyl, alkylaryl, alkenyl or alkynyl; and all nitrogen atoms in the macropolycyclic rings are coordinated with the transition metal.

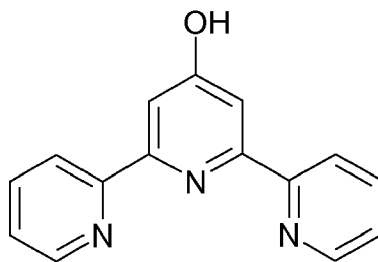
6. A laundry detergent composition according to claim 4, wherein the ligand of the transition metal complex of



wherein -NR₆R₇ is selected from the group consisting of -NMe₂, NEt₂, -N(*i*-Pr)₂,

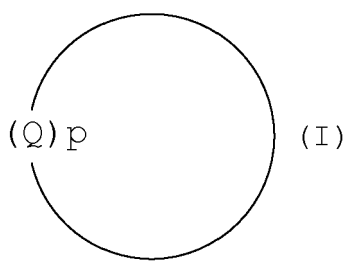


7. A laundry detergent composition according to claim 4, wherein the ligand of the transition metal complex is of the form:

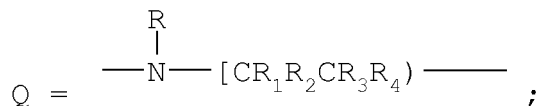


and may be optionally substituted.

8. A method according to claim 4, wherein the transition metal catalyst or precursor thereof transition metal catalyst is a mononuclear or dinuclear complex of a Mn(III) or Mn(IV) transition metal catalyst wherein the ligand of the transition metal catalyst is of formula (I):



wherein:



p is 3;

R is independently selected from: hydrogen, C1-C6-alkyl, CH₂CH₂OH, and CH₂COOH, or one of R is linked to the N of another Q via an ethylene bridge;

R₁, R₂, R₃, and R₄ are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy.

9. A method according to claim 8, wherein R₁, R₂, R₃, and R₄ are independently selected from: H and Me.
10. A method according to claim 8, wherein the catalyst is derived from a ligand selected from the group consisting of 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) and 1,2-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me₄-DTNE).
11. A method according to any one of claims 8 to 10, wherein the preformed transition metal catalyst salt is a dinuclear Mn(III) or Mn(IV) complex with at least one O² bridge.
12. A laundry detergent composition according to any one of the preceding claims, wherein the shading dye is selected from the groups of dyes having chromophores selected from: azo and azine.
13. A laundry detergent composition according to claim 12, wherein the shading dye is selected from: Acid Violet 50; Acid Blue 59, Acid Blue 98; Direct Violet 9; Direct Violet 35; Direct violet 51; and, Direct Violet 99.
14. A laundry detergent composition according to any preceding claim, wherein a unit dose dissolved in a requisite volume of water provides an aqueous fabric washing solution comprising:

- a) a transition metal catalyst in the range from 0.01 to 4 micromoles/L;
- b) hydrogen peroxide in the range from 0.1 to 4 millimoles/L;
- c) a dye in the range from 0.1 to 200 ppb; and,
- a surfactant in the range from 0.1 to 4g/L.

5

15. The aqueous fabric washing solution as defined in claim 13.

16. The aqueous fabric washing solution as defined in claim 14 wherein the pH of the solution is in the range from 9 to 11.

10 **17.** An aqueous solution according to claim 14 or 15, wherein the transition metal catalyst is in the range from 0.5 to 2 micromoles/L, hydrogen peroxide is in the range from 0.5 to 2 millimoles/L, dye is in the range from 1 to 50ppb, and a surfactant concentration of 0.4 to 2g/L.

15

20

25

30

35

40

45

50

55



EUROPEAN SEARCH REPORT

Application Number
EP 09 15 5165

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,X	US 6 800 775 B1 (BACHMANN FRANK [DE] ET AL) 5 October 2004 (2004-10-05) * column 1, lines 22-35 * * column 8, lines 42-53 * * column 10, lines 23-33 * * examples 14-21 * * claims 1,10 *	1-17	INV. C11D3/39 C11D3/40
A	WO 2005/003277 A (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]) 13 January 2005 (2005-01-13) * page 2, lines 7-15 * * page 7, lines 18-25 * * claims *	1-17	
D,A	WO 02/088289 A (CIBA SC HOLDING AG [CH]) 7 November 2002 (2002-11-07) * page 2 * * page 12, paragraph 5 * * page 25, paragraph 3 * * page 54; example 8 *	1-17	
D,A	WO 03/104379 A (UNILEVER NV [NL]; UNILEVER PLC [GB]; LEVER HINDUSTAN LTD [IN]) 18 December 2003 (2003-12-18) * claims *	1-17	
			TECHNICAL FIELDS SEARCHED (IPC)
			C11D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		18 August 2009	Bertran Nadal, Josep
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 2
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 09 15 5165

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-08-2009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6800775 B1	05-10-2004	AT 315627 T	15-02-2006
		AU 6156200 A	05-02-2001
		BR 0012390 A	19-03-2002
		CA 2377279 A1	25-01-2001
		CN 1361816 A	31-07-2002
		DE 60025492 T2	27-07-2006
		WO 0105925 A1	25-01-2001
		EP 1194514 A1	10-04-2002
		ES 2255503 T3	01-07-2006
		JP 2003505349 T	12-02-2003
		MX PA01013297 A	02-07-2002
WO 2005003277 A	13-01-2005	AT 391166 T	15-04-2008
		BR PI0411581 A	08-08-2006
		DE 602004012854 T2	14-05-2009
		EP 1633844 A1	15-03-2006
		ES 2303076 T3	01-08-2008
WO 02088289 A	07-11-2002	AT 328057 T	15-06-2006
		BR 0209292 A	13-07-2004
		CN 1646672 A	27-07-2005
		DE 60211884 T2	23-11-2006
		EP 1383857 A2	28-01-2004
		ES 2265041 T3	01-02-2007
		JP 2004533918 T	11-11-2004
		MX PA03009905 A	29-01-2004
		US 2008262225 A1	23-10-2008
		US 2009068282 A1	12-03-2009
		US 2004142843 A1	22-07-2004
		US 2006264633 A1	23-11-2006
WO 03104379 A	18-12-2003	AU 2003232796 A1	22-12-2003
		BR 0307977 A	21-12-2004
		CA 2476599 A1	18-12-2003
		CN 1659266 A	24-08-2005
		EP 1509592 A1	02-03-2005
		US 2003232732 A1	18-12-2003

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 05003274 A [0002]
- EP 0485397 A [0002] [0012]
- WO 02088289 A [0002] [0018]
- US 6800775 B [0002] [0018]
- WO 9534628 A [0012]
- WO 9748787 A [0012]
- WO 9839098 A [0012]
- WO 0012667 A [0012]
- WO 0060045 A [0012]
- WO 0248301 A [0012]
- WO 03104234 A [0012]
- EP 1557457 A [0012]
- US 6696403 B [0012]
- US 6432900 B [0012]
- US 20050209120 A [0012]
- US 20050181964 A [0012]
- US 20050209920 A [0018]
- EP 0458397 A [0024]
- WO 06125517 A [0024]
- WO 2006024612 A [0037]
- WO 2008087497 A [0043]
- WO 2005003274 A [0057]
- WO 2006053598 A [0057]
- WO 2007006357 A [0057]
- WO 2007039042 A [0057] [0062]
- WO 2007096052 A [0057]
- WO 2008056324 A [0057]
- WO 2006131530 A [0061]
- EP 328177 A [0067]
- EP 070074 A [0067]
- EP 346995 A [0068]
- WO 03104379 A [0071]

Non-patent literature cited in the description

- Color Chemistry. Wiley-VCH, 57 [0028]
- **Schwartz ; Perry.** Surface Active Agents. Interscience, 1949, vol. 1 [0065]
- **Schwartz ; Perry ; Berch.** SURFACE ACTIVE AGENTS. Interscience, 1958, vol. 2 [0065]
- McCutcheon's Emulsifiers and Detergents. Manufacturing Confectioners Company [0065]
- **H. Stache.** Tenside-Taschenbuch. Carl Hauser Verlag, 1981 [0065]