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(54) **Title**: IMPROVEMENTS RELATING TO FABRIC FRESHNESS

(57) **Abstract**: A process for freshening cloth which comprises the sequential steps of: a) contacting the cloth with human skin to treat the cloth with sebum, b) washing the cloth in a surfactant solution (preferably at a temperature of below 30 Celsius) comprising a singlet oxygen photo-bleach (preferably a water-soluble phthalocyanine compound or a water soluble xanthene) to imperfectly remove the sebum and deposit photo-bleach on the cloth, c) exposing the cloth to light, preferably direct sunlight, whereby the deposited photo-bleach reacts with the residual sebum to produce an odiferous species, wherein a further catalytic agent which is not a photo-catalyst but which catalyses the conversion of hydroperoxides into odiferous species is present during at least step (b). Preferably, a blue or violet shading dye is present at least in step (b). Advantageously a further catalyst is present in step (c) to assist in the formation of odiferous species from intermediate hydroperoxides.

IMPROVEMENTS RELATING TO FABRIC FRESHNESS

Technical Field

The present invention concerns improvements relating to malodour and particularly to the in-situ generation of perfume components from sebum by laundry treatment compositions.

Background of the Invention

The major source of oily soil on textiles is human sebum. Sebum is a complex mixture of triglycerides (57%) with minor amounts of mono- and di-glycerides, wax esters (26%), squalene (12%), sterol esters (3%) and sterols (1.5%), (all figures being indicative only).

The transfer of sebum onto the skin surface from the sebaceous glands is a continuous process. Subsequent transfer onto the fabric is mainly through fabric contact with the sebum on the skin by mechanical contact. The amount of body sebum transferred to a shirt in the course of a single day varies between 2 to 8wt% (on cloth) for different individuals and generally is closer to 2%. The physio-chemical effects of sebum on textile yellowing and dinginess and the detergency of sebum have been thoroughly studied by Obendorf et al (JAOCS, 71(1), 17-30, 1994).

Sebum on fabrics undergoes chemical changes because of its ~ 50% unsaturated lipid content. The carbon-carbon double bonds of the unsaturated lipids in sebum are oxidised by the air producing hydroperoxides which can decompose into volatile odorous materials including aldehydes, ketones alcohols and hydrocarbons. This chemistry explains why the weight of sebum on fabrics decreases with age according to Obendorf et al.

This auto-oxidation of unsaturated oily soils is associated with, (1) undesirable odours on garments, (2) difficulty in removal of oily soils if larger molecules or polymers form in the auto-oxidation reactions, (3) hydroperoxides and some of their breakdown products cause polymerisation of protein soils in mixed soil systems leading to coloured insoluble complexes, and, as mentioned above, (4) changes in fabric appearance.

Another less known source of undesirable odorous originates from the action of bacteria on sebum, acting here as a malodour precursor. Poorly deterged sebum or built-up sebum acts as sink for malodours formed on the skin or in the wash and this can impact significantly on the intensity of ‘post-wash’ malodour build up.

It is desirable to control the malodour and mitigate the other problems caused by the decomposition of sebum.

US2010/0216687 discloses compositions comprising unsaturated fatty chains having reduced or eliminated base off-odour with the incorporation of a photobleach.

US2010/0216679 discloses fabric conditioner compositions comprising a photobleach, a quaternary ammonium fabric conditioner and a perfume. Freshness and perfume longevity of laundered articles are improved by use of the composition.

US 2007/0087953 discloses cleaning compositions comprising a photocatalytic material, a sensitiser which may be a photobleach, and a surfactant.

WO 2005/003277 discloses bleaching compositions comprising a photo-active red dye, a blue dye, bleaching species and further carriers and adjunct materials.

Brief Description of the Invention

We have now determined that sebum can be converted to volatile, pleasant-smelling species in the presence of a singlet-oxygen photo-bleach and upon exposure to light. Advantageously, the presence of a catalyst further improves this process by accelerating the decomposition of the hydroperoxides.

According to a first aspect of the present invention there is provided a process for refreshing cloth which comprises the steps of:

a) contacting the cloth with human skin to treat the cloth with sebum,

b) washing the cloth in a surfactant solution comprising a singlet-oxygen photo-bleach to imperfectly remove the sebum and deposit the photo-bleach on the cloth,

c) exposing the cloth to light, whereby the deposited photo-bleach reacts with the residual sebum to produce an odiferous species,

wherein a further catalytic agent which is not a photo-catalyst but which catalyses the conversion of hydroperoxides into odiferous species is present during at least step (b).

In the context of the present invention a “photo-bleach” is any chemical species which forms a reactive bleaching species on exposure to sunlight, and preferably is not permanently consumed in the reaction. Mixtures of photo-bleaches can be used.

Surprisingly, oxidation of sebum by photo-bleach appears to reduce the production of a rancid, oily “off” odour. For example, oleic acid oxidises in the presence of photo-bleach to produce nonanal (described as fruity), decanal (waxy orange) and 2tr-decenal (orange peel) and squalene oxidises to produce sweet smells resembling caramel and honey. The odour of several of the linear aldehydes is described in further detail below.

Ingredient	Odour
n-hexanal	Freshly cut grass, unripe fruit
n-heptanal	Fermented fruit
n-octanal	Refreshing orange-peel like
n-nonanal	floral-waxy, rosy, sweet, fresh
n-decanal	refreshing citrus-peel
n-undecenal	refreshing pleasant waxy floral
n-dodecanal	very fresh clean floral (lily-violet)
n-tridecanal	waxy fresh-citrus, grapefruit peel
n-tetradecanal	waxy-fruity

Nonanal and the other C_9 aldehydes are believed to produce a particularly strong impression of freshness which can be compared to that obtained by clean cotton which has been sun-dried. This marked benefit is not obtained when the sebum is removed completely. The preferred level of sebum left on the cloth at the end of the wash is between 0.004g sebum per g of fabric to 0.030g/g.

Levels of photo-bleach used in compositions for use in the method of the invention are typically in the range 0.001-0.2%wt.

Some of the photo-bleaches impart colour to the fabric. To give the clothes an appealing white hue, it is preferred if blue or violet shading dyes are used in combination with the photo-bleaches. Shading dyes and bleaches are quite distinct in their mode of operation to achieve whiteness. Bleaches function by destroying colour, dyes by adding colour which counters the perception of yellowness.

In the alternative, a combination of photo-bleaches of different colours can be used to generate a white hue.

The use of photo-bleach as envisaged in embodiments of the present invention, and in particular the combination with shading-dye enables the formulator to get a whiteness and freshness improvement which can enhance the overall performance of a laundry washing composition or which can be used, at relatively low cost, to restore the performance of a composition from which relatively expensive components, such as peroxide bleach, surfactant and builder have been removed in part or in total (such that sebum is not fully removed). A further advantage of using the photo-bleach and residual sebum to restore freshness instead of using other components to completely remove the sebum is that the photo-bleach based system is notably less bulky that the other components and an effective product can be made with a much lower mass. This brings benefits in terms of shelf-size, transportation and packaging.

The present invention is of particular benefit when the wash is carried out at a temperature of less that 30 Celsius as under these conditions sebum removal is particularly difficult. Moreover, while the benefit of the invention has been described in relation to obtaining fabrics which are fresh-smelling before they are worn, it is apparent that the photo-bleach will also remain active as regards any new sebum which become deposited on the cloth during further use.

According to a further aspect of the present invention there is provided a laundry treatment composition for fabrics which comprises:

a) a singlet-oxygen photo-bleach, to convert sebum into hydroperoxides, and

b) a catalyst other than the photo-bleach to decompose the hydroperoxides formed by the reaction of the singlet-oxygen photobleach with the sebum into odiferous species.

Whilst, the formation of the hydroperoxide intermediates is believed to be relatively rapid in the presence of a photo-bleach (which are generally catalytic in function as explained below), the hydroperoxide intermediates are believed to be relatively stable, and extended periods of time is required to break-down these intermediates to the odiferous decomposition products. This breakdown is advantageously accelerated by the further catalyst.

Transition metal bleach catalysts are suitable further catalytic agents for use in either the method or the composition of the present invention. The transition metal bleach catalyst typically comprises a transition metal ion, preferably selected from transition metal selected from the group consisting of Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cu(III), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(V), W(VI), Pd(II), Ru(II), Ru(III), and Ru(IV), more preferably Mn(II), Mn(III), Mn(IV), Fe(II), Fe(III), Cr(II), Cr(III), Cr(IV), Cr(V), and Cr(VI).

In the alternative, the further catalytic agent may be an enzyme.

Detailed Description of the Invention

In order that the present invention may be further understood it is described below with reference to various preferred features which may be applied either to the method aspect of the invention of the composition aspect.

Photo-Bleaches

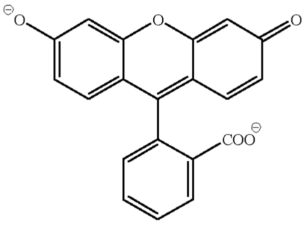
Singlet oxygen photo-bleaches (PB) function as follows:

$$PB + light \rightarrow PB^*$$
$$PB^* + {}^3O_2 \rightarrow PB + {}^1O_2$$

The photo-bleach molecule absorbs light and attains an excited state, PB*. This electronically excited state is quenched by triplet oxygen, ${}^3O_2$, in the surroundings to form singlet ${}^1O_2$. Singlet oxygen is a highly reactive bleach.

Suitable singlet-oxygen photo-bleaches may be selected from, water soluble phthalocyanine compounds, particularly metallated phthalocyanine compounds where the metal is Zn or Al-Z1 where Z1 is a halide, sulphate, nitrate, carboxylate, alkanolate or hydroxyl ion. Preferably the phthalocyanin has 1-4 SO_3X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO2005/014769 (Ciba). Particularly preferred materials are Tinolux BMC (anionic 15%, a 20/80 Al/Zn sulphonated tetrabenzo tetraazaporphine - available from Ciba) and Tinolux LBS (anionic:15%, a 20/80 Al/Zn sulphonated tetrabenzo tetraazaporphine with 10% 6 Caprolactam, also ex. Ciba).

Xanthene type dyes are also preferred, particularly based on the structure:



where the dye may be substituted by halogens and other elements/groups. Particularly preferred examples are Food Red 14 (Acid Red 51), Rose Bengal, Phloxin B and Eosin Y.

Quantum yields for photosensitized formation of singlet oxygen may be found in J.Phys.Chem.Ref. Data 1993, vol 22, no1 pp113-262. It is preferred if the quantum yield for singlet oxygen formation measured in an organic solvent or D2O is greater than 0.05, more preferably greater than 0.1.

Preferably the photo-bleach exhibits a peak in its activity when illuminated with light of a wavelength less than 700 nm. Advantageously, this enables the benefit of the invention to be obtained when drying articles indoors under fluorescent light. While better results are obtained with direct sunlight, quite adequate benefits can be obtained under fluorescent lighting.

The singlet oxygen photo-bleaches generally impart some colour to the fabric. To give the clothes an appealing white hue, it is preferred if blue or violet shading dyes are used in combination with the shading dyes as described in WO2005/003274 (Unilever) and WO2005/003277 (Unilever). Particularly preferred shading dyes are bis azo direct dyes of the direct violet 9, 35 and 99 type and acid azine dyes such as acid violet 50 and acid blue 98.

<u>Shading Dyes</u>:

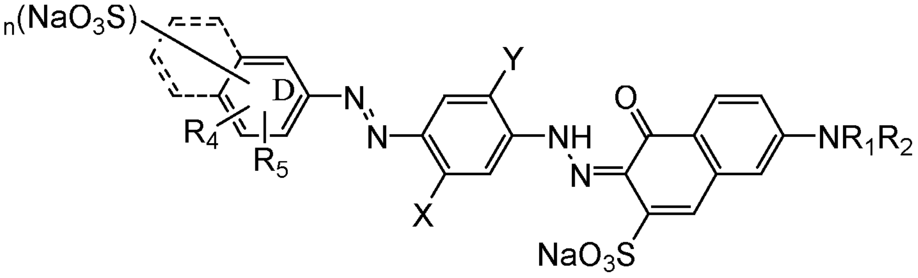
As noted above, an optional shading dye can be used to counteract the tendency of the photo-bleach to move the hue of fabrics away from white. Preferred dyes are violet or blue. Suitable and preferred classes of dyes are discussed below.

Direct Dyes:

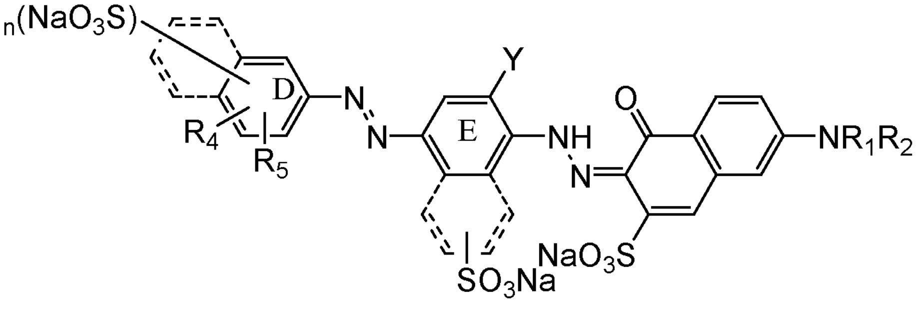
Direct dyes (otherwise known as substantive dyes) are the class of water soluble dyes which have a affinity for fibres and are taken up directly. Direct violet and direct blue dyes are preferred.

Preferably the dye are *bis*-azo or *tris*-azo dyes are used.

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.

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. Bis-azo copper containing dyes such as direct violet 66 may be used.

The benzidene based dyes are less preferred.

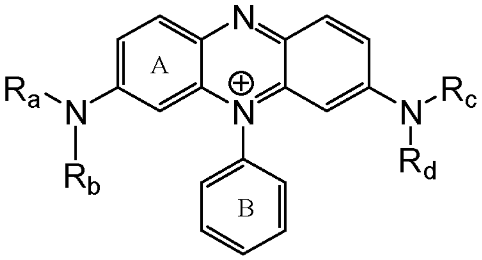
Preferably the direct dye is present at 0.00001 wt% to 0.0010 wt% of the formulation.

In another embodiment the direct dye may be covalently linked to the photo-bleach, for example as described in WO2006/024612.

Acid dyes:

Cotton substantive acid dyes give benefits to cotton containing garments. Preferred dyes and mixes of dyes are blue or violet. 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 $–COO^-$ 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, Cl, 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.

Other preferred non-azine acid dyes are acid violet 17, acid black 1 and acid blue 29.

Preferably the acid dye is present at 0.0005 wt% to 0.01 wt% of the formulation.

Hydrophobic dyes

The composition may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, napthalimides, pyrazole, napthoquinone, 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.

Preferred dyes include solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63 and disperse violet 77.

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

Basic dyes

Basic dyes are organic dyes which carry a net positive charge. They deposit onto cotton. They are of particular utility for used in composition that contain predominantly cationic surfactants. Dyes may be selected from the basic violet and basic blue dyes listed in the Colour Index International.

Preferred examples include triarylmethane basic dyes, methane 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.

Reactive dyes

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.

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 the link the dye to this species. Dyes may be selected from the reactive violet and reactive blue dyes listed in the Colour Index International.

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

Dye conjugates

Dye conjugates are formed by binding direct, acid or basic dyes to polymers or particles via physical forces.

Dependent on the choice of polymer or particle they deposit on cotton or synthetics. A description is given in WO2006/055787.

Particularly 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, direct violet 99, acid blue 98, acid violet 50, acid blue 59, acid violet 17, acid black 1, acid blue 29, solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63, disperse violet 77 and mixtures thereof.

In a particularly preferred embodiment, a composition for use in a method of the present invention comprises:

a) photo-bleach, preferably phthalocyanine or a xanthene, preferably at a level of 0.00001 to 1wt%, more preferably at a level of 0.001 to 0.2wt%, and,

b) a blue violet dye, preferably with an optical adsorption peak in the range 540-600nm, preferably a bis-azo direct dye, preferably at a level of 0.000001-1wt%

Fluorescent Agents:

In order to further improve whiteness, especially in the presence of both the photo-bleach and the shading dye, but also in the absence of the shading dye it is convenient and advantageous to employ a fluorescer in embodiments of the invention. The composition therefore preferably further comprises a fluorescent agent (optical brightener).

Fluorescent agents are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts.

The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.1 wt %.

Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]trazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfoslyryl)biphenyl.

It is preferred to use a shading dye in combination with a fluorescer in order to reduce yellowing due to chemical changes in adsorbed fluorescer.

Further Catalytic Agent:

The further catalytic agent is a complex. It is not, therefore, molecular titanium oxide. The catalytic agent is preferably a complex comprising a metal ion and at least one ligand.

The ligands may be organic or inorganic, preferably organic. In any case the complex preferably comprises at least one organic ligand.

Preferred organic ligands are nitrogen donating species. Preferred nitrogen donating ligands are bispidons, N4py type and TACN-Nx, most preferably bispidons.

Preferred inorganic ligands are H_2O, ROH, NR_3, RCN, OH, OOH, RS', $RCOO^-$ RO', OCN^-, SCN^-, N_3^-, CN^-, F^-, Cl^-, Br^-, I^-, O^{2-}, NO_3^-, NO_2^-, SO_4^{2-}, SO_3^{2-}, PO_4^{3-} or aromatic N donors such as pyridines, pyrazines, pyrazoles, imidazoles, benzimidazoles, pyrimidines, triazoles and thiazoles with R being H, optionally substituted alkyl or optionally substituted aryl.

The preferred transition metal catalyst or precursor thereof is formed from or provided by a tridentate, tetradentate, pentadentate or hexadentate nitrogen donor ligand.

The transition metal catalyst is preferably provided as a preformed transition metal catalyst. When provided as a precursor the ligand is added to sequester adventitious transition metals or transition metals salts are added. Where one particular transition metal is preferred to be part of the complex then the addition of a particular transition metal salt, with respect to the transition metal, is preferably employed. The tridentate, tetradentate, pentadentate or hexadentate nitrogen donor ligand may be built up within any organic structure which will support coordinating nitrogen atoms. For example one can take a basic tridentate ligand such as 1,4,7-triazacyclononane and have further nitrogen coordination groups, e.g., -CH2-CH2-NH2, -CH2-Py, covalently bound to one or more of the cyclic nitrogens or aliphatic groups .

Preferred metal ions include iron and manganese. Preferably the iron ion is selected from Fe(II) and Fe(III) and the manganese ion is selected from Mn(II), Mn(III), and Mn (IV).

Preferably the ligand is present in one or more of the forms: $[MnLCl_2]$; $[FeLCl_2]$; $[FeLCl]Cl$; $[FeL(H_2O)] (PF_6)_2$; $[FeL]Cl_2$, $[FeLCl]PF_6$ and $[FeL (H_2O)] (BF_4)_2$. However water soluble counter ions conferring increasing solubility, say over PF_6, are also preferred.

The following are preferred classes of catalyst that are iron or manganese complexes of tetradentate, pentadentate or hexadentate nitrogen donor ligands.

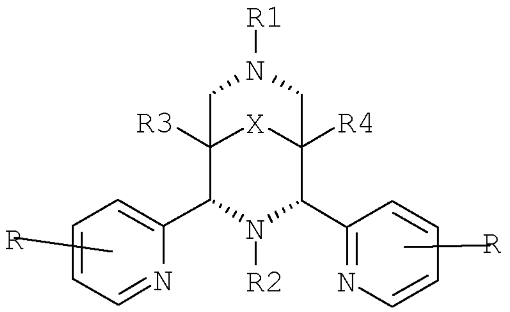
These include, bispions, N4py types, TACN-Nx types, cyclam and cross-bridged ligands, tridentate ligands with managanese, tetradentate ligands with managanese or iron, trispicen types, Collin's type catalysts and ME3-TACN and related compounds.

If unspecified the length of any alkyl chain is preferably Cl to C8-alkyl chain and preferably linear. If unspecified the aryl group is a phenyl group.

Bispidons

The bispidon class are preferably in the form of an iron transition metal catalyst.

The bispidon ligand is preferably of the form:



(I)

wherein each R is independently selected from: hydrogen, F, Cl, Br, hydroxyl, C1-C4-alkylO-, -NH-CO-H, -NH-CO-C1-C4-alkyl, -NH2, -NH-C1-C4-alkyl, and C1-C4-alkyl;

R1 and R2 are independently selected from:
C1-C24-alkyl,
C6-C10-aryl, and,
a group containing a heteroatom capable of coordinating to a transition metal;

R3 and R4 are independently selected from hydrogen, C1-C8 alkyl, C1-C8-alkyl-O-C1-C8-alkyl, C1-C8-alkyl-O-C6-C10-aryl, C6-C10-aryl, C1-C8-hydroxyalkyl, and -(CH2)nC(O)OR5
wherein R5 is independently selected from: hydrogen, C1-C4-alkyl, n is from 0 to 4, and mixtures thereof; and,
X is selected from C=O, -[C(R6)2]y- wherein Y is from 0 to 3 each R6 is independently selected from hydrogen, hydroxyl, C1-C4-alkoxy and C1-C4-alkyl.

Preferably R3 = R4 and selected from -C(O)-O-CH3, -C(O)-O-CH2CH3, -C(O)-O-CH2C6H5 and CH2OH.

Preferably the heteroatom capable of coordinating to a transition metal is pyridin-2-ylmethyl optionally substituted by –C0-C4-alkyl.

Preferably X is C=O or C(OH)2.

Preferred groups for R1 and R2 are CH3, -C2H5, -C3H7, benzyl, -C4H9, -C6H13, -C8H17, -C12H25, and -C18H37 and pyridin-2-yl. A preferred class of bispidon is one in which at least one of R1 or R2 is pyridin-2-ylmethyl or benzyl, preferably pyridin-2-ylmethyl.

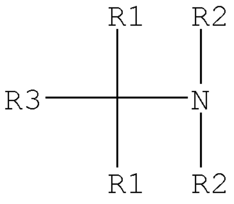
A preferred bispidon is dimethyl 2,4-di-(2-pyridyl) -3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (N2py3o-C1) and the iron complex thereof FeN2py3o-C1 which was prepared as described in W002/48301. Other preferred bispidons are one in which instead of having a methyl group (C1) at the 3 position have longer alkyl chains, namely isobutyl, (n-hexyl) C6, (n-octyl) C8, (n-dodecyl) C12, (n-tetradecyl) C14, (n-octadecyl) C18, which were prepared in an analogous manner.

Preferred tetradentate bispidons are also illustrated in WO00/60045 and preferred pentadentate bispidons are illustrated in WO02/48301 and WO03/104379.

N4py type

The N4py are preferably in the form of an iron transition metal catalyst.

The N4py type ligands are preferably of the form:



$$R3-C(R1)_2-N(R2)_2$$

(II)

Wherein:

each R1, R2 independently represents -R4-R5,
R3 represents hydrogen, optionally substituted alkyl, aryl or arylalkyl, or -R4-R5,
each R4 independently represents a single bond or optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene, alkylene ether, carboxylic ester or carboxylic amide, and
each R5 independently represents an optionally N-substituted aminoalkyl group or an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl.

Preferably R1 represents pyridin-2-yl or R2 represents pyridin-2-yl-methyl. Preferably R2 or R1 represents 2-amino-ethyl, 2-(N-(m)ethyl)amino-ethyl or

2-(N,N-di(m)ethyl)amino-ethyl. If substituted, R5 preferably represents 3-methyl pyridin-2-yl. R3 preferably represents hydrogen, benzyl or methyl.

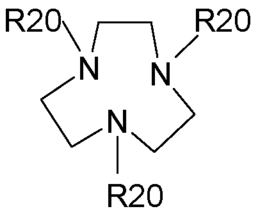
The preferred ligands are N4Py (i.e. N, N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine) which is disclosed in WO95/34628 and MeN4py (i.e. N,N-bis(pyridin-2-yl-methyl-1,1-bis(pyridin-2-yl)- 1- aminoethane, as disclosed in EP0909809.

TACN-Nx

The TACN-Nx are preferably in the form of an iron transition metal catalyst.

The ligands possess the basic 1,4,7-triazacyclononane structure but have one or more pendent nitrogen groups that complex with the transition metal to provide a tetradentate, pentadentate or hexadentate ligand. Preferably, the basic 1,4,7-triazacyclononane structure has two pendent nitrogen groups that complex with the transition metal (TACN-N2).

The TACN-Nx is preferably of the form:



(III)

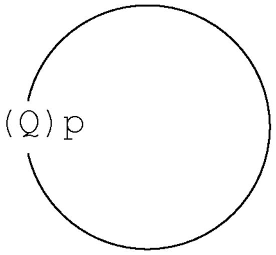
wherein each R20 is selected from: an alkyl, cycloalkyl, heterocycloalkyl, heteroaryl, aryl and arylalkyl groups optionally substituted with a substituent selected from hydroxy, alkoxy, phenoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and N+(R21)3 , wherein R21 is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether, alkenyl ether, and –CY2-R22, in which Y is independently selected from H, CH3, C2H5, C3H7 and R22 is independently selected from an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl; and wherein at least one of R20 is a –CY2-R22.

Preferably R22 is selected from optionally substituted pyridin-2-yl, imidazol-4-yl, pyrazol-1-yl, quinolin-2-yl groups. Most preferably R22 is either a pyridin-2-yl or a quinolin-2-yl.

Cyclam and cross bridged

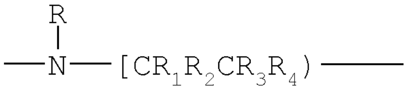
The cyclam and cross bridged ligands are preferably in the form of a manganese transition metal catalyst.

The cyclam ligand is preferably of the form:



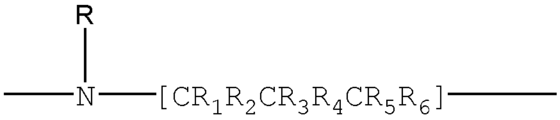
(IV)

wherein: Q is independently selected from:



$-N(R)-[CR_1R_2CR_3R_4)-$

and



$-N(R)-[CR_1R_2CR_3R_4CR_5R_6]-$;

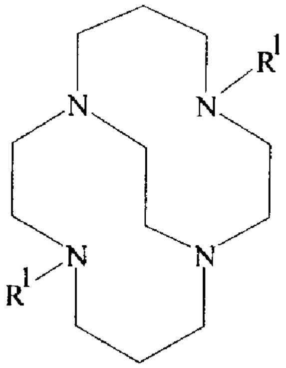
p is 4;

R is independently selected from: hydrogen, C1-C6-alkyl, CH2CH2OH, pyridin-2-ylmethyl, and CH2COOH, or one of R is linked to the N of another Q via an ethylene bridge;

R1, R2, R3, R4, R5 and R6 are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy.

Preferred non-cross-bridged ligands are 1,4,8,11-tetraazacyclotetradecane (cyclam), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me4cyclam), 1,4,7,10-tetraazacyclododecane (cyclen), 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (Me4cyclen), and 1,4,7,10-tetrakis(pyridine-2ylmethyl)-1,4,7,10-tetraazacyclododecane (Py4cyclen). With Py4cyclen the iron complex is preferred.

A preferred cross-bridged ligand is of the form:



(V)

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

Preferably R1 = Me, which is the ligand 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane of which the complex [Mn(Bcyclam)Cl2] may be synthesised according to WO98/39098.

Suitable transition metal bleach catalysts include:
Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II);

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Hexa-fluorophosphate;

Aquo-hydroxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III) Hexafluorophosphate;

Diaquo-4,10-dimethyl-1,4,7,10-tetraazabicyclo [5.5.2] tetradecane Manganese(II) Hexafluorophosphate;

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Tetrafluoroborate;

Diaquo-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II)Tetrafluoroborate;

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III);Hexafluorophosphate;

Dichloro-5,12-di-n-butyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-5,12-dibenzyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-5-n-octyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecaneIron(II);

Dichloro-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Iron(II);

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Copper(II);

Dichloro-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Copper(II);

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Cobalt(II);

Dichloro-4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Cobalt(II);

Dichloro 5,12-dimethyl-4-phenyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-4,10-dimethyl-3-phenyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II);

Dichloro-5,12-dimethyl-4,9-diphenyl-1,5,8,12-tetraazabicyclo [6.6.2] hexadecane Manganese(II);

Dichloro-4,10-dimethyl-3,8-diphenyl-1,4,7,10-tetraazabicyclo [5.5.2]tetradecane Manganese(II);

Dichloro-5,12-dimethyl-2,11-diphenyl-1,5,8,12-tetraazabicyclo [6.6.2] hexadecane Manganese(II);

Dichloro-4,10-dimethyl-4,9-diphenyl-1,4,7,10-tetraazabicyclo [5.5.2]tetradecane Manganese(II);

Dichloro-2,4,5,9,11,12-hexamethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-2,3,5,9,10,12-hexamethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-2,2,4,5,9,9,11,12-octamethyl-1,5,8,12-tetraazabicyclo [6.6.2] hexadecane Manganese(II);

Dichloro-2,2,4,5,9,11,11,12-octamethyl-1,5,8,12-tetraazabicyclo [6.6.2] hexadecane Manganese(II);

Dichloro-3,3,5,10,10,12-hexamethyl-1,5,8,12-tetraazabicyclo [6.6.2] hexadecane Manganese(II);

Dichloro-3,5,10,12-tetramethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-3-butyl-5,10,12-trimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II);

Dichloro-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Manganese(II);

Dichloro-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Iron(II);

Dichloro-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane Iron(II);

Aquo-chloro-2-(2-hydroxyphenyl)-5,12-dimethyl,5,8,12-tetraaz abicyclo[6.6.2]hexadecane Manganese(II);

Aquo-chloro-10-(2-hydroxybenzyl)-4,10-dimethyl-1,4,7,10-tetraaza bicyclo[5.5.2]tetradecane Manganese(II);

Chloro-2-(2-hydroxybenzyl)-5-methy1,5,8,12-tetraazabicyclo [6.6.2] hexadecane Manganese(II);

Chloro-10-(2-hydroxybenzyl)-4-methyl-1,4,7,10-tetraazabicyclo [5.5.2] tetradecane Manganese(II);

Chloro-5-methyl-12-(2-picolyl)-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Chloride;

Chloro-4-methyl-10-(2-picolyl)-1,4,7,10-tetraazabicyclo [5.5.2] tetradecane Manganese(II) Chloride;

Dichloro-5-(2-sulfato)dodecyl-12-methyl-1,5,8,12-tetraazabicyclo [6.6.2]hexadecane Manganese(III);

Aquo-Chloro-5-(2-sulfato)dodecyl-12-methyl-1,5,8,12-tetraazabicycle [6.6.2]hexadecane Manganese(II);

Aquo-Chloro-5-(3-sulfonopropyl)-12-methyl-1,5,8,12-tetraazabicyclo [6.6.2]hexadecane Manganese(II);

Dichloro-5-(Trimethylammoniopropyl)dodecyl-12-methyl-1,5,8,1,2-tetraazabicyclo [6.6.2] hexadecane Manganese(III) Chloride;

Dichloro-5,12-dimethyl-1,4,7,10,13-pentaazabicyclo[8.5.2]heptadecane Manganese(II);

Dichloro-14,20-dimethyl-1,10,14,20-tetraazatriyclo[8.6.6]docosa-3(8),4,6-triene Manganese(II);

Dichloro-4,11-dimethyl-1,4,7,11-tetraazabicyclo[6.5.2]pentadecane Manganese(II);

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[7.6.2]heptadecane Manganese(II);

Dichloro-5,13-dimethyl-1,5,9,13-tetraazabicyclo[7.7.2]heptadecane Manganese(II);

Dichloro-3,10-bis(butylcarboxy)-5,12-dimethyl-1,5,8,12-tetraazabicyclo [6.6.2] hexadecane Manganese(II);

Diaquo-3,10-dicarboxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo [6.6.2] hexadecane Manganese(II);

Chloro-20-methyl-1,9,20,24,25-pentaaza-tetracyclo [7.7.7.1.3,7.1,11,15] pentacosa-3,5,7 (24),11,13,15(25)-hexaene manganese(II) Hexafluorophosphate;

Trifluoromethanesulfono-20-methyl-1,9,20,24,25-pentaaza-tetracyclo[7.7.7.1, 3,7,1,11,15] pentacosa-3,5,7(24),11,13,15(25)-hexaene Manganese(II) Trifluoromethanesulfonate;

Trifluoromethanesulfono-20-methyl-1,9,20,24,25-pentaaza-tetr acyclo[7.7.7.1, 3,7,1,11,15] pentacosa-3,5,7(24),11,13,15(25)-hexaene Iron(II) Trifluoromethanesulfonate;

Chloro-5,12,17-trimethyl-1,5,8,12,17-pentaazabicyclo[6.6.5]nonadecane Manganese(II) Hexafluorophosphate;

Chloro-4,10,15-trimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane Manganese(II) Hexafluorophosphate;

Chloro-5,12,17-trimethyl-1,5,8,12,17-pentaazabicyclo[6.6.5]nonadecane Manganese(II) Chloride;

Chloro-4,10,15-trimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane Manganese(II) Chloride;

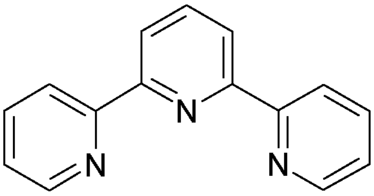
Dichloro-5,12-diethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane manganese; dichloro-4,11 diethyl-1,4,8,11 tetraazabicyclo (6.6.2) hexadecane manganese (II);

and any mixture thereof.

Other suitable transition metal bleach catalysts are described in U.S. Pat. No. 5,580,485, U.S. Pat. No. 4,430,243; U.S. Pat. No. 4,728,455; U.S. Pat. No. 5,246,621; U.S. Pat. No. 5,244,594; U.S. Pat. No. 5,284,944; U.S. Pat. No. 5,194,416; U.S. Pat. No. 5,246,612; U.S. Pat. No. 5,256,779; U.S. Pat. No. 5,280,117; U.S. Pat. No. 5,274,147; U.S. Pat. No. 5,153,161; U.S. Pat. No. 5,227,084; U.S. Pat. No. 5,114,606; U.S. Pat. No. 5,114,611, EP 549,271 A1; EP 544,490 A1; EP 549,272 A1; and EP 544,440 A2.

<u>Tridentate ligands with manganese</u>:

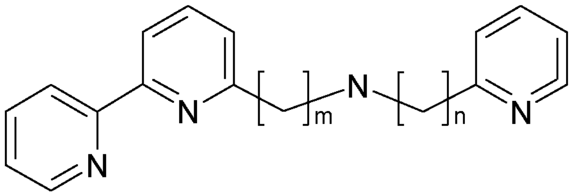
A suitable class of tridentate ligands is based on terpyridine-type ligands, depicted below.



Also terpyridine derivatives could be employed, such as bispyridylpyrimidine or bispyridyltriazine. Preferred classes include the ones disclosed in WO2002088289; WO2004007657; WO2004039933; WO2004039934; WO2005068075; and WO2005068074; WO2005105303.

Tetradentate ligands with manganese or iron:

Another suitable class of molecules contains a substituted bipyridine-alkylamine-alkylpyridine unit, depicted below with m, n =1 or 2 as disclosed in WO07/090461.



Trispicen-type:

The trispicens are preferably in the form of an iron transition metal catalyst.

The trispicen type ligands are preferably of the form:

R17R17N-X-NR17R17 (VI),

wherein:
X is selected from -CH¬¬2CH2-, -CH¬¬2CH¬¬2CH2-, -CH2C(OH)HCH2-; and,
R17 independently represents a group selected from: R17 and alkyl, cycloalkyl, heterocycloalkyl, heteroaryl, aryl and arylalkyl groups optionally substituted with a substituent selected from hydroxy, alkoxy, phenoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and N+(R19)3 , wherein R19 is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether, alkenyl ether, and –CY2-R18, in which Y is independently selected from H, CH3, C2H5, C3H7 and R18 is

independently selected from an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl;
and wherein at least two of R17 are –CY2-R18.

The heteroatom donor group is preferably pyridinyl optionally substituted by –C0-C4-alkyl.

Other preferred heteroatom donor groups are imidazol-2-yl, 1-methyl-imidazol-2-yl, 4-methyl-imidazol-2-yl, imidazol-4-yl, 2-methyl-imidazol-4-yl, 1-methyl-imidazol-4-yl, benzimidazol-2-yl and 1-methyl-benzimidazol-2-yl.

Preferably three of R17 are CY2-R18.

The ligand Tpen (i.e. N, N, N', N'-tetra(pyridin-2-yl-methyl)ethylenediamine) is disclosed in WO97/48787.

Other suitable, and preferred, trispicens are found in WO02/077145 and WO08/003652.

<u>Collins</u>:

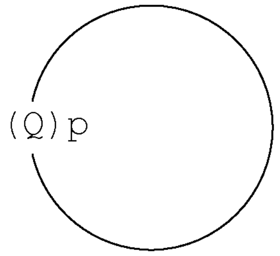
A class of oxidatively stable iron (III) complexes with dianionic tetradentate nitrogen donor ligands have been disclosed by Collins and co-workers.

References are made to WO1999058634; WO A 9803625 1996; Acc. Chem. Res. 2002, 35, 782; J. Am. Chem. Soc. 1990, 112, 5637; J. Am. Chem. Soc. 1989, 111, 4511; J. Am. Chem. Soc. 1990, 112, 899; Inorg Chem. 1992, 31, 1550; J. Am. Chem. Soc. 1998, 120, 11540; J. Am. Chem. Soc. 1998, 120, 4867; J. Am. Chem. Soc. 2003, 125, 12379; J. Am. Chem. Soc. 2005, 127, 2505.

Me3-TACN and related compounds

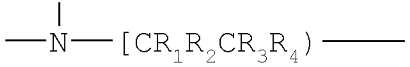
A more preferred transition metal catalyst for the method is as described in EP 0458397 and WO06/125517; both of these patents disclose the use of manganese 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me3-TACN) as related compounds as complexes. The PF6- ligand of MnMe3-TACN has been commercialised in laundry 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.

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):



(I)

,

wherein: Q = 

$-\overset{R}{\overset{|}{N}}-[CR_1R_2CR_3R_4)-$;

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.

When a preformed transition metal of complex Me3-TACN is used it is preferred that it is used in a carbonate buffer.

Polymers

The embodiments of the invention may utilize one or more polymers. Examples are carboxymethylcellulose, poly(vinylpyrrolidone), poly (ethylene glycol), poly(vinyl alcohol), poly(vinylpyridine-N-oxide), poly(vinylimidazole), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

Modern detergent compositions typically employ polymers as so-called ‘dye-transfer inhibitors’. These prevent migration of dyes, especially during long soak times. Any suitable dye-transfer inhibition agents may be used in accordance with the present invention. Generally, such dye-transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese pthalocyanine, peroxidases, and mixtures thereof.

Nitrogen-containing, dye binding, DTI polymers are preferred. Of these polymers and co-polymers of cyclic amines such as vinyl pyrrolidone, and/or vinyl imidazole are preferred.

Polyamine N-oxide polymers suitable for use herein contain units having the following structural formula: R-A_X-P; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is an aliphatic, ethoxylated aliphatic, aromatic, heterocyclic or alicyclic group or combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups, or the N-O group can be attached to both units.

Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures: $N(O)(R')_{0-3}$, or $=N(O)(R')_{0-1}$, wherein each R′ independently represents an aliphatic, aromatic, heterocyclic or alicylic group or combination thereof; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a<10$, preferably $pK_a<7$, more preferably $pK_a< 6$.

Any polymer backbone can be used provided the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamides, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferably 1,000 to 500,000; most preferably 5,000 to 100,000. This preferred class of materials is referred to herein as "PVNO". A preferred polyamine N-oxide is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (as a class, referred to as "PVPVI") are also preferred. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000, as determined by light scattering as described in Barth, et al., Chemical Analysis, Vol. 113. "Modern Methods of Polymer Characterization". The preferred PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched. Suitable PVPVI polymers include Sokalan$^{(TM)}$ HP56, available commercially from BASF, Ludwigshafen, Germany.

Also preferred as dye transfer inhibition agents are polyvinylpyrrolidone polymers ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 2000,000, and more preferably from about 5,000 to about 50,000. PVP's are disclosed for example in EP-A-262,897 and EP-A-256,696. Suitable PVP polymers include Sokalan$^{(TM)}$ HP50, available commercially from BASF. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

Also suitable as dye transfer inhibiting agents are those from the class of modified polyethyleneimine polymers, as disclosed for example in WO-A-0005334. These modified polyethyleneimine polymers are water-soluble or dispersible, modified polyamines. Modified polyamines are further disclosed in US-A-4,548,744; US-A-4,597,898; US-A- 4,877,896; US-A- 4,891, 160; US-A-4,976,879; US-A-5,415,807; GB-A-1,537,288; GB-A-1,498,520; DE-A-28 29022; and JP-A-06313271.

Preferably the composition according to the present invention comprises a dye transfer inhibition agent selected from polyvinylpyrridine N-oxide (PVNO), polyvinyl pyrrolidone (PVP), polyvinyl imidazole, N-vinylpyrrolidone and N-vinylimidazole copolymers (PVPVI), copolymers thereof, and mixtures thereof.

The amount of dye transfer inhibition agent in the composition according to the present invention will be from 0.01 to 10 %, preferably from 0.02 to 5 %, more preferably from 0.03 to 2 %, by weight of the composition. It will be appreciated that the dye transfer inhibition agents will assist in the preservation of whiteness by preventing the migration of dyes from coloured articles to white ones.

Other polymers used in laundry compositions include soil-release, anti-ashing and anti-redeposition polymers as well as polymers which improve powder properties.

Polymeric dispersing agents can advantageously be utilized in the compositions herein, especially in the presence of layered silicate builders. Suitable polymeric dispersing agents include polycarboxylates and polyethylene glycols, although others known in the art can also be used.

It is also believed that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release, peptization, and anti-redeposition.

Polycarboxylate materials, which can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, are preferably admixed in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight of the polymer.

Particularly suitable polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Pat. No. 3,308,067, issued Mar. 7, 1967. In the present invention, the preferred polycarboxylate is sodium polyacrylate.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1: 1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published Dec. 15, 1982, as well as in EP 193,360, published Sep. 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Polyethylene glycol (PEG) can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 3,000 to about 10,000. Polyaspartate and polyglutamate dispersing agents may also be used. Dispersing agents such as polyaspartate preferably have an average molecular weight of about 10,000.

Any polymeric soil release agent known to those skilled in the art can optionally be employed in compositions according to the invention. Polymeric soil release agents are characterised by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

Generally the soil release polymers will comprise polymers of aromatic dicarboxylic acids and alkylene glycols (including polymers containing polyalkylene glycols).

The polymeric soil release agents useful herein especially include those soil release agents having:

(a) one or more nonionic hydrophilic components consisting essentially of:

  (i) polyoxyethylene segments with a degree of polymerization of at least 2,
  or

  (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or

  (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or

(b) one or more hydrophobe components comprising:

(i) C_3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C_3 oxyalkylene terephthalate units is about 2:1 or lower,

(ii) C_4 -C_6 alkylene or oxy C_4 -C_6 alkylene segments, or mixtures therein,

(iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or (iv) C_1 -C_4 alkyl ether or C_4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C_1 -C_4 alkyl ether or C_4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C_1 -C_4 alkyl ether and/or C_4 hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C_4-C_6 alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as $MO_3S(CH_2)_nOCH_2 CH_2 O$-, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to Gosselink.

Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C_1 -C_4 alkyl and C_4 hydroxyalkyl cellulose; see U.S. Pat. No. 4,000,093, issued Dec. 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C_1 -C_6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published Apr. 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Pat. No. 3,959,230 to Hays, issued May 25, 1976 and U.S. Pat. No. 3,893,929 to Basadur issued Jul. 8, 1975.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from DuPont) and MILEASE T (from ICI). See also U.S. Pat. No. 4,702,857, issued Oct. 27, 1987 to Gosselink.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Pat. No. 4,968,451, issued Nov. 6, 1990 to J.J. Scheibel and E. P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Pat. No. 4,711,730, issued Dec. 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Pat. No. 4,702,857, issued Oct. 27, 1987 to Gosselink.

Preferred polymeric soil release agents also include the soil release agents of U.S. Pat. No. 4,877,896, issued Oct. 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoarolyl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

It is believed that those polymers which deposit on cloth as a part of their activity may assist in the retention of perfume components generated in the presence of the photo-bleach and/or other perfume components present.

Other types of polymeric deposition aid may also be used. These include cationic polymeric deposition aids. Suitable cationic polymeric deposition aids include cationic guar polymers such as Jaguar (ex Rhone Poulenc), cationic cellulose derivatives such as Celquats (ex National Starch), Flocaid (ex National Starch), cationic potato starch such as SoftGel (ex Aralose), cationic polyacrylamides such as PCG (ex Allied Colloids). Cationic polymeric aids are particularly preferred in the absence of any other cationic material in the composition.

Polymers having amine groups are preferred, especially polyamine polymers as it is believed that these may reversibly react with odoriferous aldehydes and retain them on the fabric for longer.

Other Components

Compositions for use in the methods of the present invention may be formulated as additives to be used with a separate detergent product. However, in a preferred embodiment a composition for use in the method of the present invention also contains one or more surfactants and/or optionally other ingredients such that the composition is fully functional as a laundry cleaning and/or care composition. A composition of the invention may be in dry solid or liquid form. The composition may be a concentrate to be diluted, rehydrated and/or dissolved in a solvent, including water, before use. The composition may also be a ready-to-use (in-use) composition.

The present invention is suitable for use in industrial or domestic fabric wash compositions, fabric conditioning compositions and compositions for both washing and conditioning fabrics (so-called through the wash conditioner compositions). The present invention can also be applied to industrial or domestic non-detergent based fabric care compositions, for example spray-on compositions.

Fabric wash compositions according to the present invention may be in any suitable form, for example powdered, tableted powders, liquid or solid detergent bars.

Other contemplated ingredients including surfactants, hydrotropes, preservatives, fillers, builders, complexing agents, stabilizers, perfumes per se, other conventional detergent ingredients, or combinations of one or more thereof are discussed below. The composition may also contain other conventional detergent ingredients such as e.g. fabric conditioners including clays, foam boosters, suds suppressors (anti-foams), anti-corrosion agents, anti-microbials or tarnish inhibitors.

Surfactants

Embodiments of the invention preferably utilize a fabric wash detergent material selected from non-soap anionic surfactant, nonionic surfactants, soap, amphoteric surfactants, zwitterionic surfactants and mixtures thereof.

Detergent compositions suitable for use in domestic or industrial automatic fabric washing machines generally contain anionic non-soap surfactant or nonionic surfactant, or combinations of the two in suitable ratio, as will be known to the person skilled in the art, optionally together with soap.

Many suitable detergent-active compounds are available and fully described in the literature, for example in “Surface-Active Agents and Detergents”, Volumes I and II, by Schwartz, Perry & Berch.

The surfactants may be present in the composition at a level of from 0.1% to 60% by weight.

Suitable anionic surfactants are well known to the person skilled in the art and include alkyl benzene sulphonate, primary and secondary alkyl sulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates, dialkyl sulphosuccinates; ether carboxylates; isethionates; sarcosinates; fatty acid ester sulphonates and mixtures thereof. The sodium salts are generally preferred. When included therein the composition usually contains from about 1% to about 50%, preferably 10 wt%-40 wt% based on the fabric treatment composition of an anionic surfactant such as linear alkylbenzenesulfonate, alpha-olefinsulfonate, alkyl sulfate (fatty alcohol sulfate), alcohol ethoxysulfate, secondary alkanesulfonate, alpha-sulfo fatty acid methyl ester, alkyl- or alkenylsuccinic acid or soap. Preferred surfactants are alkyl ether sulphates and blends of alkoxylated alkyl nonionic surfactants with either alkyl sulphonates or alkyl ether sulphates.

Preferred alkyl ether sulphates are C_8-C_{15} alkyl and have 2-10 moles of ethoxylation. Preferred alkyl sulphates are alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}. The counter ion for anionic surfactants is typically sodium, although other counter-ions such as TEA or ammonium can be used. Suitable anionic surfactant materials are available in the marketplace as the ‘Genapol’™ range from Clariant.

Nonionic surfactants are also well known to the person skilled in the art and include primary and secondary alcohol ethoxylates, especially C_8-C_{20} aliphatic alcohol 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 alkyl polyglycosides, glycerol monoethers and polyhydroxy amides (glucamide). Mixtures of nonionic surfactant may be used. When included therein the composition usually contains from about 0.2% to about 40%, preferably 1 to 20 wt%, more preferably 5 to 15 wt% of a non-ionic surfactant such as alcohol ethoxylate, nonylphenol ethoxylate, alkylpolyglycoside, alkyldimethylamineoxide, ethoxylated fatty acid monoethanolamide, fatty acid monoethanolamide, polyhydroxy alkyl fatty acid amide, or N-acyl N-alkyl derivatives of glucosamine (“glucamides”).

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 35 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.

Higher levels of surfactant may be employed (up to almost 100%) but this can leave little space in the formulation for builders and other components and may lead to a sticky product which requires special processing.

Hydrotropes

The term "hydrotrope" generally means a compound with the ability to increase the solubilities, preferably aqueous solubilities, of certain slightly soluble organic compounds, which may include dyes, photo-bleaches, fluorescer and or phobleaches. Hyprotropes are preferably present in embodiments of the invention.

Examples of hydrotropes include sodium xylene sulfonate, SCM.

Solvents

Compositions for use in the inventive method may comprise a solvent such as water or an organic solvent such as isopropyl alcohol or glycol ethers. Solvents are typically present in liquid or gel compositions.

Metal chelation agents

Compositions for use in the inventive method or which otherwise embody the invention may contain a metal chelating agent such as carbonates, bicarbonates, and sesquicarbonates. The metal chelating agent can be a bleach stabiliser (i.e. heavy metal sequestrant). Suitable metal chelation agents include ethylenediamine tetraacetate (EDTA), diethylenetriamine pentaacetate (DTPA), ethylenediamine disuccinate (EDDS), and the polyphosphonates such as the Dequests (Trade Mark), ethylenediamine tetramethylene phosphonate (EDTMP) and diethylenetriamine pentamethylene phosphate (DETPMP).

Builders or Complexing agents

Suitable builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

The composition may also contain 0-65 % of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below. Many builders are also bleach-stabilising agents by virtue of their ability to complex metal ions.

Where builder is present, the compositions may suitably contain less than 20%wt, preferably less than 10% by weight, and most preferably less than 10%wt of detergency builder.

The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 15%w. Aluminosilicates are materials having the general formula:

$$0.8\text{-}1.5\ M_2O.\ \ Al_2O_3.\ \ 0.8\text{-}6\ \ SiO_2$$

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. The ratio of surfactants to alumuminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term 'phosphate' embraces diphosphate, triphosphate, and phosphonate species. Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).

For low cost formulations carbonate (including bicarbonate and sesquicarbonate) and/or citrate may be employed as builders. Precipitating and ion-exchange builders are generally absent from liquid compositions.

Enzymes

One or more enzymes may be present in a composition when practicing a method of the invention, or present in combinations according to the invention. As noted above an enzyme can be the means by which the hydroperoxide is converted into the odiferous species. However the same or different enzymes may also be present to assist in cleaning.

Especially contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.

Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens*, *Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

Other examples are lipase variants such as those described in WO 92/05249, WO 94/01541, EP 407 225, EP 260 105, WO 95/35381, WO 96/00292, WO 95/30744, WO 94/25578, WO 95/14783, WO 95/22615, WO 97/04079 and WO 97/07202.

Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ (Novozymes A/S).

The method of the invention may be carried out in the presence of phospholipase classified as EC 3.1.1.4 and/or EC 3.1.1.32. As used herein, the term phospholipase is an enzyme which has activity towards phospholipids. Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several types of phospholipase activity can be distinguished, including phospholipases A_1 and A_2 which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D (phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.

The enzyme and the pro-fragance may show some interaction and should be chosen such that this interaction is not negative. Some negative interactions may be avoided by encapsulation of one or other of enzyme and pro-fragrance and/or other segregation within the product.

Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and FN3™ (Genencor International Inc.).

The method of the invention may be carried out in the presence of cutinase. classified in EC 3.1.1.74. The cutinase used according to the invention may be of any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus*, e.g. a special strain of *B. licheniformis*, described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, e.g. the fungal cellulases produced from *Humicola insolens*, *Thielavia terrestris*, *Myceliophthora thermophila,* and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).

Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from *Coprinus*, e.g. from *C. cinereus*, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

Enzyme Stabilizers

Any enzyme present in the composition or when practicing the method may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

It should be noted that the enzymes mentioned above may be present to assist in cleaning as well as in the role of the catalyst for the decomposition of the hydroperoxide.

Perfumes per se

Embodiment of the present invention will preferably also comprise some perfume per se or have additional perfume present during the method steps. Useful components of the perfume include materials of both natural and synthetic origin. They include single compounds and mixtures. Specific examples of such components may be found in the current literature, e.g., in Fenaroli's Handbook of Flavor Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M. B. Jacobs, edited by Van Nostrand; or Perfume and Flavor Chemicals by S. Arctander 1969, Montclair, N.J. (USA). These substances are well known to the person skilled in the art of perfuming, flavouring, and/or aromatizing consumer products, i.e., of imparting an odour and/or a flavour or taste to a consumer product traditionally perfumed or flavoured, or of modifying the odour and/or taste of said consumer product.

By perfume in this context is not only meant a fully formulated product fragrance, but also selected components of that fragrance, particularly those which are prone to loss, such as the so-called ‘top notes’.

Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Examples of well known top-notes include citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol. Top notes typically comprise 15-25%wt of a perfume composition and in those embodiments of the invention which contain an increased level of top-notes it is envisaged at that least 20%wt would be present within the encapsulate.

Some or all of the perfume or pro-fragrance may be encapsulated, typical perfume components which it is advantageous to encapsulate, include those with a relatively low boiling point, preferably those with a boiling point of less than 300, preferably 100-250 Celsius and pro-fragrances which can produce such components.

It is also advantageous to encapsulate perfume components which have a low Log P (ie. those which will be partitioned into water), preferably with a Log P of less than 3.0. These materials, of relatively low boiling point and relatively low Log P have been called the “delayed blooming” perfume ingredients and include the following materials:

Allyl Caproate, Amyl Acetate, Amyl Propionate, Anisic Aldehyde, Anisole, Benzaldehyde, Benzyl Acetate, Benzyl Acetone, Benzyl Alcohol, Benzyl Formate, Benzyl Iso Valerate, Benzyl Propionate, Beta Gamma Hexenol, Camphor Gum, Laevo-Carvone, d-Carvone, Cinnamic Alcohol, Cinamyl Formate, Cis-Jasmone, cis-3-Hexenyl Acetate, Cuminic Alcohol, Cyclal C, Dimethyl Benzyl Carbinol, Dimethyl Benzyl Carbinol Acetate, Ethyl Acetate, Ethyl Aceto Acetate, Ethyl Amyl Ketone, Ethyl Benzoate, Ethyl Butyrate, Ethyl Hexyl Ketone, Ethyl Phenyl Acetate, Eucalyptol, Eugenol, Fenchyl Acetate, Flor Acetate (tricyclo Decenyl Acetate), Frutene (tricyclco Decenyl Propionate), Geraniol, Hexenol, Hexenyl Acetate, Hexyl Acetate, Hexyl Formate, Hydratropic Alcohol, Hydroxycitronellal, Indone, Isoamyl Alcohol, Iso Menthone, Isopulegyl Acetate, Isoquinolone, Ligustral, Linalool, Linalool Oxide, Linalyl Formate, Menthone, Menthyl Acetphenone, Methyl Amyl Ketone, Methyl Anthranilate, Methyl Benzoate, Methyl Benyl Acetate, Methyl Eugenol, Methyl Heptenone, Methyl Heptine Carbonate, Methyl Heptyl Ketone, Methyl Hexyl Ketone, Methyl Phenyl Carbinyl Acetate, Methyl Salicylate, Methyl-N-Methyl Anthranilate, Nerol, Octalactone, Octyl Alcohol, p-Cresol, p-Cresol Methyl Ether, p-Methoxy Acetophenone, p-Methyl Acetophenone, Phenoxy Ethanol, Phenyl Acetaldehyde, Phenyl Ethyl Acetate, Phenyl Ethyl Alcohol, Phenyl Ethyl Dimethyl Carbinol, Prenyl Acetate, Propyl Bornate, Pulegone, Rose Oxide, Safrole, 4-Terpinenol, Alpha-Terpinenol, and /or Viridine.

It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components from the list given of delayed blooming perfumes given above present in the perfume.

Another group of perfumes with which the present invention can be applied are the so-called ‘aromatherapy’ materials. These include many components also used in perfumery, including components of essential oils such as Clary Sage, Eucalyptus, Geranium, Lavender, Mace Extract, Neroli, Nutmeg, Spearmint, Sweet Violet Leaf and Valerian. By means of the present invention these materials can be transferred to textile articles that will be worn or otherwise come into contact with the human body (such as handkerchiefs and bed-linen).

In order that the invention will be further understood it is described below with reference to the following examples:

EXAMPLES

Sebum monitors

Artificially soiled test fabrics are used to determine the cleaning performance of detergents and washing processes.

The following examples used standard cotton sebum monitors from Centre for Testmaterials B.V. The sebum monitors were CS-32-033 (sebum Bey with carbon black) and CS-30-002 (sebum Bey). These monitors were 15x15 cm and weighed about 3.60g impregnated with 0.168g of the sebum model; hence 0.047g/g of fabric or about 4.7% sebum. Table 1 gives the composition of Bey sebum.

Table 1

The composition of Bey sebum according to Centre for Testmaterials B.V (Netherlands)

Component	Weight %
Beef tallow	32.8
Free fatty acids	18.0
Lanoline	13.8
Hydrocarbon mixture (Squalene)	12.0
Cutina	11.6
Cholesterol	3.7
Fatty acid triglycerides	3.6

The sebum monitors were made fresh for the purpose of these experiments and vacuum packed in aluminium foils. They were kept in a refrigerator during the length of these experiments to ensure freshness. The monitors were evaluated for odours before every experiment to ensure a lack of oily/fatty rancid malodour originating from the untreated monitors. All monitors used in the experiments were initially odour free.

Wash procedure

The washing was simulated in a Linitest™ machine. The Linitest is a laboratory scale washing machine (Ex. Heraeus). The equipment is designed and built to comply with the requirements for international standard test specifications. It is used for small scale detergency testing particularly when low liquor to cloth ratio is involved.

The Linitest model used in the examples had a single rotation speed of 40 rpm. The carrier is capable of accommodating twelve steel containers and can be operated at temperatures up to 100°C. Its 20 litre tank and thermostatically controlled heating elements ensure the bath liquor reaches the required temperature. The stainless steel construction throughout ensures efficient heat transfer to the specimen containers that are mounted on a rotating horizontal carrier driven by a geared motor. The rotating movement of the carrier ‘throws’ the liquid from one end of the container to the other in a continuous action. This movement simulates the mechanical washing process.

The washing process involved the following steps;

1. Linitester pots filled with 100 ml tap water (Wirral Water),
2. 0.4g detergent powder (if used) weighed in the pot,
3. The photobleach solution weighed in the pot (as the amounts specified in the following tables).
4. Two monitor pieces (pre-wetted under running water) added to the pots.
5. Pots replaced in the Linitester and the wash process started for 45 minutes at the required wash temperature.
6. After this wash stage the monitors were removed, hand wrung and then dried on line inside (in a laboratory lit with fluorescent tubes) or dried in the Weather-o-meter. If detergent used the monitors were returned to the pots which were washed and filled with 100 ml of fresh water and replaced in the Linitest for a 10 minutes rinse. This rinse stage was repeated twice. Then monitors hand-wrong and line dried or dried in the Weather-o-meter.

The detergent used was Indian Rin Advanced powder with and without perfume which contains 15 wt% LAS, 30% carbonate, 40% NaCl ± 0.4% perfume and the remainder including minors and calcite (no dyes).

The Photobleaches evaluated included:

- Acid Red 51 (Erythrosin B, ex Aldrich),
- Tinolux BMC (anionic 15%, Tetrabenzo tetraazaporphine, ex Ciba), and,
- Tinolux LBS (anionic:15%, Tetrabenzo tetraazaporphine with 10% 6-Caprolactam, ex Ciba)

Drying procedure

The two monitors from the same pot (same treatment) are dried one on line inside under fluorescent light (for at least 12 hours) and the second one in a Weather-o-meter™ (WOM) for 30 minutes. WOM produces artificial sunlight and was set up at a lamp power of 0.33 W/m^2 at a wavelength of 340nm. The relative humidity remained around 20%.

The monitors after the drying stage were stored in 60 ml clear class bottles and stored in daylight out of direct sunlight. Storage of the monitors in a glass bottle enhanced their odours and made it easier for the panellists to describe the smells.

Odour description

The monitors in the bottles were evaluated by an expert panel and the smell described according to perfumery practices.

Example 1

In this example CS-32-033 (sebum Bey with carbon black) monitors were washed in water (Wirral water) at 40 °C without detergent and treated with AR51 (Acid Red 51), and Tinolux MBC. Table 2 summarises the resulting overall smells as assessed by an expert panel.

Table 2. The odour of sebum monitors washed in water with and without photobleach and dried on line (under fluorescent light) or died under artificial sunlight.

Treatment	Drying method	Odours (same day)
Auto-oxidation (comparative)	Line	Light oily/fatty smell, unclean.
	w-o-m	Stronger oily; frying oil, rancid, unclean
Photo-oxidation (comparative - without surfactant being present)		
0.001%AR51	Line	Clean, no fat smell.
	w-o-m	Caramel, sweet aldehydic , no oil or fat.
0.002%AR51	Line	Clean, no fat, oil smell.
	w-o-m	Relatively strong caramel, waxy.
0.0005%BMC	Line	No smell of oil or fat, not clean either
	w-o-m	Rich nutty, frying oil.
0.001%BMC	Line	No smell
	w-o-m	Slight fatty/oily smell, not clean
0.002%BMC	Line	No fatty /oily or rancid smell, clean.
	w-o-m	Slight sweet caramel smell,

In this example (without surfactant being present) most of the sebum has remained on the monitor after this water wash. The olfactory benefit can be readily perceived by the panel. Surprisingly the oxidation in presence of the photo-bleach has, for those examples in which high levels of photo-bleach strong simulated sunlight were used, changed the odour profile of the monitors to that of a clean pleasant smell in spite of the presence of most of the sebum on the monitor and lack of any perfume. Better results are obtained with higher levels of photo-bleach.

Example 2

Whilst, the formation of the hydroperoxide intermediates is relatively quick in the presence of a photo-bleach (for example Rose Bengal) the hydroperoxide intermediates are relatively stable, and extended periods of time was required to break-down these intermediates to the odiferous decomposition products. This breakdown can be accelerated with a calatyst.

In order to show the stability of the typical hydroperoxides formed when squalene (SQ, a constituent of sebum) was firstly irradiated in d^6-acetone with Rose-Bengal at 25 C. $SQ(OOH)_6$ was synthesized from SQ as follows: SQ (1.64 g, 0.1 M) was weighed, dissolved in 40mL of acetone (containing $1x10^{-5}$ M of Rose Bengal as a photosensitizer), and exposed to a Na lamp and oxygen bubbling at 5 °C. The treatment was stopped after 6 hours, and the only species remaining, according to the TLC monitoring, was the $SQ(OOH)_6$.

After the photo-oxidation step, the medium was evaporated to leave the $SQ(OOH)_6$ material, which was then re-dissolved in 10 mL of diethyl ether. This solution was then loaded onto a Discovery® SPE DSC-Si silica tube (Supelco, Bellefonte, PA). The tube was eluted with an additional 5mL of diethyl ether, and the elutant containing $SQ(OOH)_6$ was collected. During this procedure, the rose Bengal was retained on the silica phase. Finally, the elutant was evaporated and $SQ(OOH)_6$ was then stored at -18°C until further use.

In order to indicate the stability of the the $SQ(OOH)_6$ at relatively high temperature, a solution containing $SQ(OOH)_6$ (0.1 M) in Acetone-d6 was prepared. 500 µL of this solution was then added in a NMR tube and allowed to age in a thermostatic bath at 60 °C over a 10 hour period. At time periods of 1, 3, 5, 10 hours a spectrum was taken and the hydroperoxide area (4.2-6.0 p.p.m.) was monitored for change along with any appearance of peaks at 7.6-8 p.p.m. typical of aldehyde species.

The NMR spectrometer consisted of a Bruker Avance 300 MHz Ultrashield and the software used was TopSpin. The ^1H experiments were performed with a pulse at 30° and 32 scans.

Table 3 illustrates the results.

Table 3

Transformation of SQ(OOH)$_6$ at 60 ^{0}C in d^6-Acetone Monitored by ^{1}H NMR.

Time/h.	Peak p.p.m.	Change in Area	Time/h.	Peak p.p.m.	Appearance of peak at 7.7 p.p.m.
0	4.2-6.0	None	0	7.7	No
1	4.2-6.0	None	1	7.7	No
3	4.2-6.0	Reduction	3	7.7	No
5	4.2-6.0	Reduction	5	7.7	Yes
10	4.2-6.0	Reduction[a]	10	7.7	Yes[b]

[a]Relative reduction of the peak here from that at t=0 was about 75 %; [b]relative increase of the peak from that at t=5 h was about 200 %.

The results illustrated above indicate that the hydroperoxides formed from squalene were relatively stable at 60 ^{0}C for extended periods of time.

Example 3

In this example a preferred metal-ion centred catalyst, based on an iron centre such as iron(II), in particular, N,N-bis(pyridine-2-yl-methyl)-1,1-bis(pyridine-2-yl)-1-amino-ethane dichloride (IronMeN4py) was employed to increase the rate of hydroperoxide transformation to the end products consisting of fragrance aldehydes along with other odourous materials.

To a 25 ml round bottomed three necked flask equipped with magnetic stirrer, air inlet, and outlet, and water bath maintained at 10 ^{0}C was added 260 mg of squalene (ex. Aldrich), 10 ml of acetone and 200 µl of Rose Bengal solution (2 mg/ml). Rose Bengal (4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein) is a singlet-oxygen photobleach.

Air was bubbled through the solution over the whole of the 3 hour monitoring period without the metal ion catalyst, under irradiation by a xenon lamp to simulate day-light.

In a second experiment the metal ion catalyst (5 mg) was added after 90 minutes.

The reaction monitored by HPLC using via UV. detection at 230 nm and 260 nm and actonitrile was the mobile phase. The first HPLC measurement taken was at t=0 (before addition of Rose Bengal). Typically the squalene peak was eluted at 15 minutes, and the hydroperoxides eluted at times between 2-10 minutes. For the purpose of the experiment the hydroperoxide peaks at 3 and 5.7 minutes after starting the column were monitored for any change in relative peak height.

To check that hydroperoxides had been produced, a third experiment as described above but without the metal ion catalyst present was run and 1 ml aliquots taken at 0, 1.5, 3 hr added to 2 ml of glacial acetic acid followed by 0.2 g of potassium iodide. At t=0 no colour change was observed, whereas at t=1.5, and 3 hrs the solution turned pale-yellow to brown indicating the oxidation of the iodide to iodine.

Table 4 shows results of photolysis with rose Bengal followed by decomposition of the formed hydroperoxides in the presence of the metal ion catalyst.

Table 4

Production and Decomposition of Squalene Hydroperoxides in the Presence of Rose-Bengal and Metal ion Catalyst.

Time/h	Catalyst Present	Relative Peak Height at t=3 minutes[c]	Relative Peak Height at t=5.7 minutes[c]
0	RB[a] None IronMeN4py[b] None	0	0
1.0	RB[a] Yes IronMeN4py[b] None	600	2100
3.0	RB[a] Yes IronMeN4py[b] None	2000	2100
1.5	RB[a] None IronMeN4py[b] Yes	0	300

[a] RB = Rose Bengal photo-bleach;

[b] IronMe4py = iron(II) N,N-bis(pyridine-2-yl-methyl)-1,1-bis(pyridine-2-yl)-1-amino-ethane dichloride;

[c] Squalene hydroperoxide species ($SQ(OOH)_n$ where n is between 1-6).

The results show that in the absence of the metal ion catalyst the hydroperoxide species were stable up to the 3 hours over which the experiment was conducted. However, upon addition of the metal ion catalyst within half an hour there was a large decrease in the hydroperoxide species at t=3 and 5.7 minutes.

CLAIMS

1. A process for freshening cloth which comprises the sequential steps of:

   a) contacting the cloth with human skin to treat the cloth with sebum,

   b) washing the cloth in a surfactant solution comprising a singlet oxygen photo-bleach to imperfectly remove the sebum, preferably to a level of from 0.004g sebum per g of fabric to 0.030g/g. and deposit photo-bleach on the cloth,

   c) exposing the cloth to light, whereby the deposited photo-bleach reacts with the residual sebum to produce an odiferous species,

   wherein a further catalytic agent which is not a photo-catalyst but which catalyses the conversion of hydroperoxides into odiferous species is present during at least step (b).

2. A process according to claim 1, wherein the further catalytic agent is a complex comprising a metal ion and at least one ligand.

3. A process according to claim 3, wherein the organic ligand is selected from the group consisting of bispidons, N4py type and TACN-Nx.

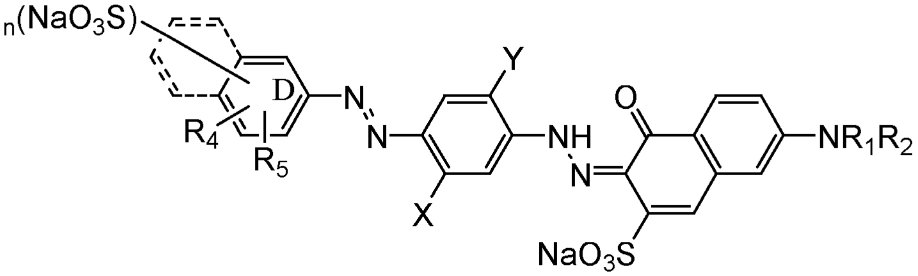
4. A process according to claim 2, wherein the metal ion is selected from iron and manganese.

5. A process according to any preceding claim , wherein the photo-bleach comprises a water-soluble phthalocyanine compound or a water soluble xanthene compound.

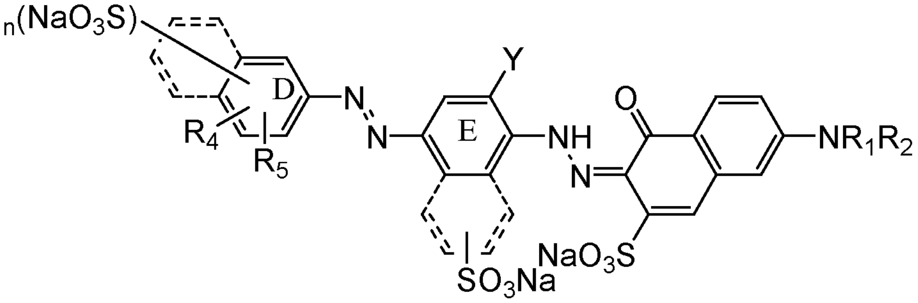
6. A process according to any preceding claim, wherein a blue or violet shading dye is present at least in step (b).

7. A process according to claim 6, wherein the shading dye is a *bis*-azo or *tris*-azo dye.

8. A process according to claim 7, wherein the shading dye is a Direct Violet dye comprising the following structures:



and/or

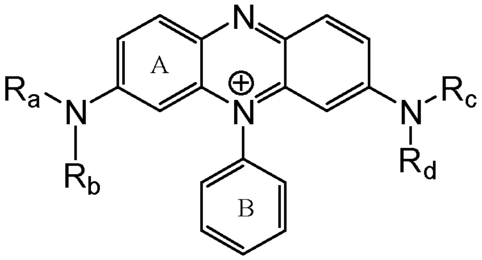


wherein: ring D and E may be independently naphthyl or phenyl as shown; R$_1$ is selected from: hydrogen and C1-C4-alkyl; R$_2$ is selected from: hydrogen, C1-C4-alkyl, substituted or unsubstituted phenyl and substituted or unsubstituted naphthyl; R$_4$ and R$_5$ are independently selected from:

hydrogen and C1-C4-alkyl; X and Y are independently selected from: hydrogen, C1-C4-alkyl and C1-C4-alkoxy and n is 0, 1 or 2.

9. A process according to claim 6, wherein the dye is selected from 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, direct violet 99, acid blue 98, acid violet 50, acid blue 59, acid violet 17, acid black 1, acid blue 29, solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63, disperse violet 77, 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, reactive blue 19, reactive blue 163, reactive blue 182, reactive blue 96 and mixtures thereof.

10. A process according to claim 6, wherein the shading dye is an azine dye comprising the following 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 $-COO^-$ group; the B ring does not carry a negatively charged group or salt thereof; the A ring is optionally substituted to form a naphthyl; and the structure is optionally substituted by groups selected from: amine, methyl, ethyl, hydroxyl, methoxy, ethoxy, phenoxy, Cl, Br, I, F, NO_2 and mixtures thereof.

11. A process according to any preceding claim, wherein a fluorescer is present at least in step (b).

12. A process according to any preceding claim, wherein a fabric-substantive polymer as a deposition aid is present during at least step (b)

13. A laundry treatment composition for fabrics which comprises:

    a) a singlet-oxygen photo-bleach, to convert sebum into hydroperoxides,

    and

    b) a catalyst other than the photo-bleach to decompose the hydroperoxides formed by the reaction of the singlet-oxygen photo-bleach with the sebum into odiferous species.

14. A composition according to claim 13 which further comprises a fluorescer

15. A composition according to any of claims 13-14 which further comprises a blue or violet shading dye.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/058232

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/00 C11D3/16 C11D3/39 C11D3/40 C11D3/42
ADD.

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)
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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/003277 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]) 13 January 2005 (2005-01-13) cited in the application page 4, line 30 - page 5, line 6 page 15, lines 17-18 page 16, lines 1-8 claims; examples -----	1-15
X	US 2010/216687 A1 (HUNTER ROBERT ALLAN [GB] ET AL) 26 August 2010 (2010-08-26) paragraphs [0011], [0016], [0020], [0022], [0078] - [0110], [0136], [0137]; claims; examples ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 6 June 2013	Date of mailing of the international search report 14/06/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Péntek, Eric

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International application No
PCT/EP2013/058232

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/216679 A1 (BATCHELOR STEPHEN NORMAN [GB] ET AL) 26 August 2010 (2010-08-26) paragraphs [0012], [0029], [0202] - [0251]; claims; examples -----	1-15
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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