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(54) Title: BLEACHING COMPOSITION

(57) Abstract: A stabilised bleaching composition is provided. The bleaching composition provided comprises a transition metal catalyst together with a UV screen.

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BLEACHING COMPOSITION

FIELD OF INVENTION

This invention relates to the enhancement of bleaching
5 compositions.

BACKGROUND OF INVENTION

The use of bleaching catalysts for stain removal has been
developed over recent years.

10

EP0458397(triazacyclononanes), EP 0966323 (X-bridged
macrocycles), EP 909 809 and WO 02/48301 (bispidons)
disclose classes of widely divergent ligands complexed to a
transition metal for use as bleaching catalysts in laundry
15 with an oxygen bleaching agent.

20

A problem with the prior art is the instability of the
transition metal catalyst in the bleaching compositions upon
exposure to incident UV irradiation. Another problem with
the prior art is that bleaching may be ascribed to
mechanisms other than the action of the bleaching catalyst
with peroxy species, for example singlet oxygen, acting
upon a stain upon exposure to incident UV irradiation.

25

SUMMARY OF INVENTION

Transition metal complexes when used in laundry compositions
are particularly susceptible to degradation by UV light.

30

The present invention provides a bleaching composition
comprising: (a) a transition metal catalyst for
catalytically bleaching with a peroxygen bleach; (b)

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between 2 to 35 wt% of a peroxygen bleach or source thereof;
(c) between 0.0005 to 0.5 wt% of a photostable organic
sunscreen having a C Log P value of at least 1.9 and having
an extinction coefficient of greater than $2000 \text{ mol}^{-1} \text{ cm}^{-1}$ at
5 300 nm and an extinction coefficient of less than 100 mol^{-1}
 cm^{-1} at any single wavelength in the range from 400 nm at 750
nm; (d) an antioxidant selected from: (i) a phenolic
antioxidant, the phenolic antioxidant present in the range
0.0001 to 3 % wt %; and, (ii) an amine antioxidant, the
10 hindered amine antioxidant in the range from 0.0001 to 20%;
and, (e) the balance carriers and adjunct ingredients to 100
wt/wt % of the total bleaching composition.

The role sunscreen and the antioxidant may be performed by a
15 single entity but it is preferred the sunscreen and the
antioxidant are separate entities such that the sunscreen is
other than an antioxidant.

The present invention extends to a method of bleaching a
20 substrate/textile with a composition of the present
invention. The method comprising the steps of treating a
substrate with the bleaching composition in an aqueous
environment, rinsing the substrate and drying the substrate.

25 The present invention also extends to a commercial package
together with instructions for its use.

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Detailed Description of the Invention

The Sunscreen

A Sunscreen in the context of the present invention is an
5 organic compound that absorbs all or part of the UV
radiation of the sun (290 to 400 nm) and converts it to heat
with a high quantum yield and hence do not undergo
photochemical reactions. The photochemical inert nature of
the sunscreen results in incident irradiation being reduced
10 upon those moieties that do undergo photochemical reactions.

The use of a sunscreen is applicable to the reduction in
incident radiation from the sun and incandescent light.

15 A sunscreen may function both as an antioxidant and a
sunscreen but within the scope the present application the
sunscreen is preferably other than an antioxidant.
Antioxidants are organic chemicals that chemically quench
autoxidation chain reactions. This may occur by a number of
20 chemical routes, for example by termination of reactive
radical intermediates, or by decomposition of peroxides and
hydroperoxide intermediates.

Protection against solar radiation can be achieved with UVA
25 and UVB absorbing materials with high extinction
coefficients. These compounds are commonly called
sunscreens. However, the use of such materials is preferably
limited for protection against UV radiation with a
wavelength of 400nm or below as compounds with the whole or
30 part of their spectra above 400nm will be coloured.

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It is preferred that the sunscreen has a C Log P value of at least 1.9, more preferably of at least 2.5, most preferably greater than 3.5. If solid the sunscreen should be dispersed in a liquid, the liquid having a C Log P value of at least
5 1.9, more preferably of at least 2.5, most preferably greater than 3.5. It is preferred that the sunscreen has an upper limit C Log P value of 8.5. It is also beneficial if the liquid in which the solid sunscreen is to be dissolved is immiscible in water or only sparingly soluble. By
10 sparingly soluble a solubility of no more than 0.04 moles/litre is meant.

The C Log P values were calculated using daylight software (PCModels version 4.8) available from Daylight Chemical
15 Information Systems, Inc. Sheraton House - Castle Park - Cambridge, UK CB3 0AX.

The presence of an alkyl chain(s) substituent on the sunscreen serves to increase Log P of the sunscreen and
20 serves to aid deposition and adhesion to a relatively apolar substrate/textile.

It is preferred that the sunscreen or sunscreen mixture is present at levels from 0.0005 wt% to 10 wt% of the total
25 weight of the composition. The more preferred level of sunscreen is from 0.001 wt% to 2.5 wt %, and the most preferably 0.005 wt% to 0.5 wt %.

In the context of this invention a sunscreen is described as
30 any material which absorbs UVA or UVB radiation. It is preferred that the sunscreens have a molar extinction

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coefficient (ϵ) of greater than $2000 \text{ mol}^{-1} \text{ cm}^{-1}$ at 300 nm,
most preferably $5000 \text{ mol}^{-1} \text{ cm}^{-1}$ at 300 nm. Further it is
preferred that the extinction coefficient of the sunscreen
is less than $100 \text{ mol}^{-1} \text{ cm}^{-1}$ at any single wavelength in the
5 range from 400 nm at 750 nm.

The International Commission on Illumination (CIE) in 1970
defined the UV wavelength subdivisions as:-

10	UVA	315-400nm
	UVB	280-315nm
	UVC	100-280nm

Preferably the sunscreen absorbs light at a wavelength from
15 about 280-400nm.

Suitable sunscreens are described in:

N.A. Saath, Cosmetics and Toiletries Vol. 102 March 1987
20 page 21-39 Classifications given as table 2 on page 22,;
N.A. Saath, Evolution of modern sunscreen chemicals pages 3-
35; Cosmetics and Toiletries Vol. 107 March 1992. Sunscreen
use in cosmetic formulas, pages 45-47; Ultra violet
absorbers by S.B. Miller, G.R. Lappin, and C.E. Tholstrup in
25 1968-1969 Modern Plastics Encyclopedia, pages 442-447 and;
G.R. Lappin, Encyclopedia of polymer science and technology,
vol. 14, pages 125-148, Ultra violet radiation absorbers.

Typical examples of sunscreens that may be employed in the
30 present invention are: cinnamates, hydroxybenzophenones,

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alpha-cyanoacrylates, oxanilides, phenylsalicylates, and 2-hydroxyphenylbenzotriazoles.

5 Examples of typical sunscreens but not meant to be exclusive are:

UVA absorbers

Oxybenzone

Suisobenzzone

10 Dioxybenzone

tinuvin 329

tinuvin 327

tinuvin 328

15 **UVB absorber**

aminobenzoic acid

amyl dimethyl (PABA)

2-Ethoxyethyl-p-methoxycinnamate

amyl dimethyl PABA (padimate A)

20 2-Ethylhexyl salicylate (Sunarome WMO)

Ethyl 4-bis(hydroxypropyl)aminobenzoate

2-Ethylhexyl-2-cyano-3,3-diphenylacrylate

Ethylhexyl-p-methoxycinnate

2-Ethylhexyl salicylate (Sunarome WMO)

25 Glyceryl aminobenzoate (Glyceryl PABA)

Homomenthyl salicylate

Lawsone with dihydroxyacetate

Octyldimethyl PABA (Padimate O)

2-Phenylbenzimidazole-5-sulphonic acid

30 Thethanolamine salicylate

Cyasorb UV 2908

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Cyasorb UV 24

Chimassorb 81

ANTIOXIDANT

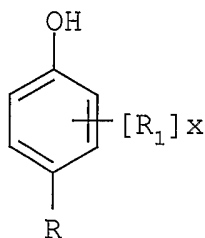
- 5 The bleaching compositions of the present invention comprise an effective amount of an antioxidant. In contrast to the sunscreens, the antioxidant is

10 An effective amount of an antioxidant is in the range 0.001 to 20 wt/wt % depending upon the nature of the antioxidant and subsidiary purpose of the antioxidant, for example as a carrier or solvent. Preferably the antioxidant is present in the range from 0.001 to 2 wt/wt %. When a phenolic antioxidant is present it is preferred that the phenolic
15 antioxidant present in the range from 0.0001 to 3 % wt % of the composition. When an amine antioxidant it is present it is preferred that the phenolic antioxidant present in the range from 0.0001 to 20 % wt % of the composition.

- 20 Anti-oxidants are substances as described in Kirk-Othmers (Vol. 3, pg 424) and in Uhlmans Encyclopedia (Vol 3, pg 91).

One class of anti-oxidants suitable for use in the present invention is alkylated phenols having the general formula:

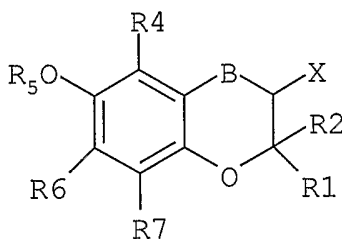
25.



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wherein R is C1-C22 linear or branched alkyl, preferably methyl or branched C3-C6 alkyl; C3-C6 alkoxy, preferably methoxy; R1 is a C3-C6 branched alkyl, preferably tert-butyl; x is 1 or 2. Hindered phenolic compounds are preferred as antioxidant.

Another class of anti-oxidants suitable for use in the present invention is a benzofuran or benzopyran derivative having the formula:



wherein R1 and R2 are each independently alkyl or R1 and R2 can be taken together to form a C5-C6 cyclic hydrocarbonyl moiety; B is absent or CH2; R4 is C1-C6 alkyl; R5 is hydrogen or -C(O)R3 wherein R3 is hydrogen or C1-C19 alkyl; R6 is C1-C6 alkyl; R7 is hydrogen or C1-C6 alkyl; X is -CH2OH, or -CH2A wherein A is a nitrogen comprising unit, phenyl, or substituted phenyl. Preferred nitrogen comprising A units include amino, pyrrolidino, piperidino, morpholino, piperazino, and mixtures thereof.

Other suitable antioxidants are found as follows. A derivative of α -tocopherol, beta-tocopherol, gamma-tocopherol, delta-tocopherol, and alkyl esters of gallic acid, especially octyl gallate and dodecyl gallate.

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Another example of suitable antioxidants are the class of hindered amine light stabilisers (HALS), particularly those based 2,2,6,6-tetramethylpiperidines.

- 5 Non-limiting examples of anti-oxidants suitable for use in the present invention include phenols *inter alia* 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-methylphenol, mixtures of 2 and 3- tert-butyl-4-methoxyphenol.
- 10 Mixtures of antioxidants may be use and in particular mixtures that have synergic antioxidant effects as found in, for example, WO02/072746.

Hydroperoxide Decomposing Antioxidants

- 15 Hydroperoxide Decomposing Antioxidants (HADs) are compounds that cause the degradation of hydroperoxides. Examples of HADs are found in the organic compounds of sulphur and trivalent phosphorous which are commercialised for stabilising compositions and are widely used in combination
- 20 with phenolic antioxidants. Zinc Dialkyl Dithio phosphate (ZDDP) is an example of a HAD that is used widely in the automotive oil industry. Generally phosphites decompose hydroperoxides at substantially lower temperatures than sulphides. Triphenylphosphine, a HAD, is a widely recognised
- 25 reductant for hydroperoxides and functions well at ambient temperatures. Hindered amine light stabilisers (HALS) also function as HADs and is an example of a class of preferred HADs for use with the present invention. A review of HADs are found in: J. Pospíšil, P. P. Klemchuk (Eds) Oxidation
- 30 inhibition in organic materials, Vol. I. CRC Press 1990, pp. 38 to 47. It is preferred that the bleaching composition of

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the present invention comprises one or more HADs and most preferably in conjunction with a non-HAD antioxidant.

THE BLEACH CATALYST

- 5 The bleach catalysts may be used to bleach with added peroxy species. In contrast, we have recently found that oily stains are bleached in the presence of selected transition metal catalysts in the absence of an added peroxy source. The bleaching of an oily stain in the
10 absence of an added peroxy source has been attributed to oxygen derived from the air. Whilst it is true that bleaching is effected by oxygen sourced from the air the route in which oxygen plays a part is becoming understood.
- 15 We have concluded from our research that bleaching of a chromophore in an oily stain is effected by products formed by adventitious oxidation of components in the oily stain. These products, alkyl hydroperoxides, are generated naturally by autoxidation of the oily stain and the alkyl
20 hydroperoxides together with a transition metal catalyst serve to bleach chromophores in the oily stain. Alkyl hydroperoxides (ROOH) are generally less reactive than other peroxy species, for example, peracids (RC(O)OOH), hydrogen peroxide (H₂O₂), percarbonates and perborates. In this
25 regard, the phrase "for bleaching a substrate with atmospheric oxygen" is synonymous with "for bleaching a substrate via atmospheric oxygen" because it is the oxygen in the air that provides the bleaching species used by catalyst to bleach the substrate stain.

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The bleach catalyst per se may be selected from a wide range of transition metal complexes of organic molecules (ligands). In typical washing compositions the level of the organic substance is such that the in-use level is from 0.05
5 μM to 50 mM, with preferred in-use levels for domestic laundry operations falling in the range 1 to 100 μM . Higher levels may be desired and applied in industrial textile bleaching processes. A mixture of different catalysts may be employed in the bleaching composition. The bleaching
10 composition comprises at least 1 ppb (0.0000001 wt%) of the ligand or complex thereof, more preferably 100 ppb (0.00001 wt%), yet more preferably 500 ppb (0.00005 wt%), still more preferably about 1 ppm (0.0001 wt%) to about 5 %, still more preferably 500 ppm (0.05 wt%).

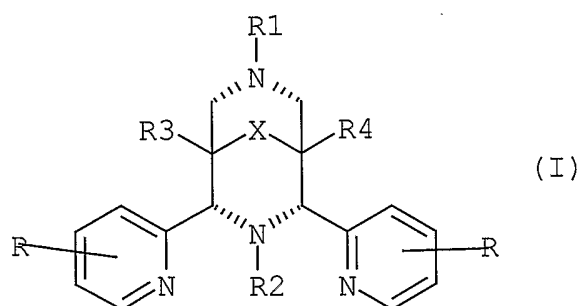
15 Suitable organic molecules (ligands) for forming complexes and complexes thereof are found, for example in:
GB 9906474.3; GB 9907714.1; GB 98309168.7, GB 98309169.5;
GB 9027415.0 and GB 9907713.3; DE 19755493; EP 999050;
20 WO9534628; EP-A-458379; EP 0909809; United States Patent 4,728,455; WO9839098; WO9839406, WO9748787, WO0029537; WO0052124, and WO0060045 the complexes and organic molecule (ligand) precursors of which are herein incorporated by reference. An example of a preferred catalyst is a
25 transition metal complex of MeN4Py ligand (N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane).

The ligand forms a complex with one or more transition metals, in the latter case for example as a dinuclear
30 complex. Suitable transition metals include for example: manganese in oxidation states II-V, iron II-V, copper I-III,

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cobalt I-III, titanium II-IV, tungsten IV-VI, vanadium II-V and molybdenum II-VI. Preferred transition metals are iron and manganese, in particular iron.

- 5 An example of a preferred catalyst is a monomer ligand or transition metal catalyst thereof of a ligand having the formula (I):



10

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

R1 and R2 are independently selected from:

15 C1-C4-alkyl,

C6-C10-aryl, and,

a group containing a heteroatom capable of coordinating to a transition metal, wherein at least one of R1 and R2 is the group containing the heteroatom;

20 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

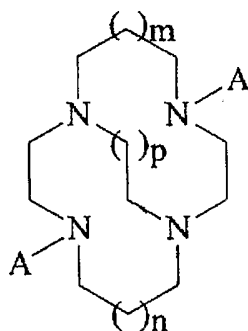
wherein R₅ is independently selected from: hydrogen, C1-C4-alkyl, n is from 0 to 4, and mixtures thereof; and,

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X is selected from $C=O$, $-[C(R_6)_2]_Y-$ wherein Y is from 0 to 3 each R_6 is independently selected from hydrogen, hydroxyl, C1-C4-alkoxy and C1-C4-alkyl.

- 5 With regard to the above formula (I) it is also particularly preferred that R_1 and R_2 may also be independently selected from: C1 to C22-optionally substituted alkyl, and an optionally substituted tertiary amine of the form -C2-C4-alkyl-NR₇R₈, in which R_7 and R_8 are independently selected
 10 from the group consisting of straight chain, branched or cyclo C1-C12 alkyl, benzyl, the -C2-C4-alkyl- of the -C2-C4-alkyl-NR₇R₈ may be substituted by 1 to 4 C1-C2-alkyl, or may form part of a C3 to C6 alkyl ring, and in which R_7 and R_8 may together form a saturated ring containing one or more
 15 other heteroatoms.

Another preferred class of ligands are macropolycyclic rigid ligands of the formula:



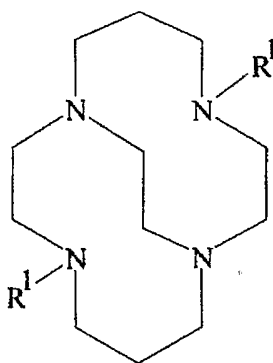
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- wherein m and n are 0 or integers from 1 to 2, p is an integer from 1 to 6, preferably m and n are both 0 or both 1 (preferably both 1), or m is 0 and n is at least 1; and p
 25 is 1; and A is a nonhydrogen moiety preferably having no

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aromatic content; more particularly each A can vary independently and is preferably selected from methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, C5-C20 alkyl, and one, but not both, of the A moieties is benzyl, and combinations thereof.

Preferably, the macropolycyclic ligand is of the formula:



10

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

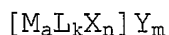
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Of the macropolycyclic ligands 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane is preferred. This ligand is most preferred as its manganese complex [Mn(Bcyclam)Cl₂] and may be synthesised according to W09839098.

20

The transition metal complex preferably is of the general formula (AI):

25



- 15 -

in which:

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

L represents the ligand, preferably N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, or its protonated or deprotonated analogue;

10 X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;

15 a represents an integer from 1 to 10;

k represents an integer from 1 to 10;

n represents zero or an integer from 1 to 10;

m represents zero or an integer from 1 to 20.

20 THE PEROXY SPECIES OR PRECURSOR THEREOF

In a "peroxyl mode" the composition of the present invention uses an added peroxyl species to bleach a substrate. The peroxyl bleaching species may be a compound which is capable of yielding hydrogen peroxide in aqueous solution. Hydrogen
25 peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates persilicates and persulphates. Mixtures of two or more such compounds may
30 also be suitable.

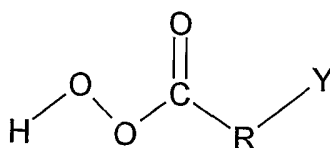
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Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons. The amount thereof in the composition of the invention usually will be within the range of about 2 to 35% by weight, preferably from 5 to 25% by weight. One skilled in the art will appreciate that these amounts may be reduced in the presence of a bleach precursor e.g., N,N,N'N'-tetraacetyl ethylene diamine (TAED).

Another suitable hydrogen peroxide generating system is a combination of a C1-C4 alkanol oxidase and a C1-C4 alkanol, especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in International Application PCT/EP 94/03003 (Unilever), which is incorporated herein by reference.

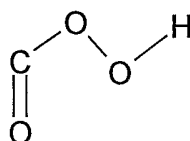
Alkylhydroxy peroxides are another class of peroxy bleaching compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

Organic peroxyacids may also be suitable as the peroxy bleaching compound. Such materials normally have the general formula:



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wherein R is an alkylene or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen,
5 alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or



group or a quaternary ammonium group.

10

Typical monoperoxy acids useful herein include, for example:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-.alpha.-naphthoic acid;

15

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxy lauric acid, peroxy stearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and

20 (iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

Typical diperoxyacids useful herein include, for example:

(iv) 1,12-diperoxydodecanedioic acid (DPDA);

25

(v) 1,9-diperoxyazelaic acid;

(vi) diperoxybrassicilic acid; diperoxysebacic acid and diperoxyisophthalic acid;

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(vii) 2-decyldiperoxybutane-1,4-dioic acid; and

(viii) 4,4'-sulphonylbisperoxybenzoic acid.

5 Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS). If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10% by weight, preferably from 4-8% by weight.

10

Peroxyacid bleach precursors are known and amply described in literature, such as in the British Patents 836988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and
15 U.S. Pat. Nos. 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

20

Another useful class of peroxyacid bleach precursors is that of the cationic i.e. quaternary ammonium substituted peroxyacid precursors as disclosed in US Pat. Nos. 4,751,015 and 4,397,757, in EP-A0284292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are:

25

2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphonphenyl carbonate chloride (SPCC);

N-octyl-N,N-dimethyl-N10-carbophenoxy decyl ammonium chloride (ODC);

30

3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and

- 19 -

N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520 and in
5 European Patent Specification No.'s 458,396 and 464,880.

Any one of these peroxyacid bleach precursors can be used in the present invention, though some may be more preferred than others.

10

Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors
15 including the cationic nitriles.

15

Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N'-tetraacetyl ethylene diamine (TAED);
20 sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; SPCC; trimethyl ammonium toluyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyloxybenzene sulphonate (STHOBS); and the substituted cationic
25 nitriles.

25

Other classes of bleach precursors for use with the present invention are found in WO0015750, for example 6-(nonanamidocaproyl)oxybenzene sulphonate.

30

- 20 -

The precursors may be used in an amount of up to 12%, preferably from 2-10% by weight, of the composition.

BALANCE CARRIERS AND ADJUNCT INGREDIENTS

5 These are generally surfactants, builders, foam agents, anti-foam agents, solvents, and enzymes. The use and amounts of these components are such that the bleaching composition performs depending upon economics, environmental factors and use of the bleaching composition.

10

The composition may comprise a surfactant and optionally other conventional detergent ingredients. The composition may also comprise an enzymatic detergent composition which comprises from 0.1 - 50 % by weight, based on the total
15 detergent composition, of one or more surfactants. This surfactant system may in turn comprise 0 - 95 % by weight of one or more anionic surfactants and 5 to 100 % by weight of one or more nonionic surfactants. The surfactant system may additionally contain amphoteric or zwitterionic detergent
20 compounds, but this is not normally desired owing to their relatively high cost. The enzymatic detergent composition according to the invention will generally be used as a dilution in water of about 0.05 to 2%.

25 In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's
30 Emulsifiers and Detergents" published by Manufacturing

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Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.

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

15
Suitable anionic detergent compounds which may be used are
usually water-soluble alkali metal salts of organic
sulphates and sulphonates having alkyl radicals containing
from about 8 to about 22 carbon atoms, the term alkyl being
20 used to include the alkyl portion of higher acyl radicals.
Examples of suitable synthetic anionic detergent compounds
are sodium and potassium alkyl sulphates, especially those
obtained by sulphating higher C₈-C₁₈ alcohols, produced for
example from tallow or coconut oil, sodium and potassium
25 alkyl C₉-C₂₀ benzene sulphonates, particularly sodium linear
secondary alkyl C₁₀-C₁₅ benzene sulphonates; and sodium alkyl
glyceryl ether sulphates, especially those ethers of the
higher alcohols derived from tallow or coconut oil and
synthetic alcohols derived from petroleum. The preferred
30 anionic detergent compounds are sodium C₁₁-C₁₅ alkyl benzene

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5 sulphonates and sodium C₁₂-C₁₈ alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

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

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

20

One skilled in the art will appreciate that some adventitious peroxy species may be in the composition nevertheless it is most preferred that the bleaching composition of the present invention has less than 1%, preferably less than 0.1%, most preferably less than 0.01%,
25 of a peroxy species present. These adventitious peroxy are predominantly alkyl hydroperoxides formed by autoxidation of the surfactants.

- 23 -

The composition may contain additional enzymes as found in WO 01/00768 A1 page 15, line 25 to page 19, line 29, the contents of which are herein incorporated by reference.

- 5 Builders, polymers and other enzymes as optional ingredients may also be present as found in WO0060045.

Suitable detergency builders as optional ingredients may also be present as found in WO0034427.

10

The composition of the present invention may be used for laundry cleaning, hard surface cleaning (including cleaning of lavatories, kitchen work surfaces, floors, mechanical ware washing etc.). As is generally known in the art, 15 bleaching compositions are also employed in waste-water treatment, pulp bleaching during the manufacture of paper, leather manufacture, dye transfer inhibition, food processing, starch bleaching, sterilisation, whitening in oral hygiene preparations and/or contact lens disinfection.

20

In the context of the present invention, bleaching should be understood as relating generally to the decolourisation of stains or of other materials attached to or associated with a substrate. However, it is envisaged that the present 25 invention can be applied where a requirement is the removal and/or neutralisation by an oxidative bleaching reaction of malodours or other undesirable components attached to or otherwise associated with a substrate. Furthermore, in the context of the present invention bleaching is to be

30

understood as being restricted to any bleaching mechanism or

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process that does not require the presence of light or activation by light.

It is preferred that the composition does not comprise an ester of 2-cyano-3,3-diphenylacrylic acid, in particular C6- to C18-alkyl ester or C5 to C8-cycloalkyl esters of 2-cyano-3,3-diphenylacrylic acid. If the ester of 2-cyano-3,3-diphenylacrylic acid is present the level must be less than 10 wt% of the total of the photostable organic sunscreen, most preferably less than 5 wt%, most preferably less than 1 wt%.

Experimental

The transition metal catalyst present in the liquid formulation was the iron chloride complex of 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 $[\text{FeCl}(\text{N}_2\text{Py}_3\text{o})]\text{Cl}$ which was prepared as described in WO0248301.

The activities of the liquid bleaching compositions were determined at 40 °C in a H_2O_2 containing $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ pH7 buffer and Acid Blue 45 (CAS No. 2861-02-1) as substrate using the following protocol.

Samples of 70 mg liquid were diluted in 10.00 ml MilliQ water. We added 45 μl of this solution to an assay of 230 μL containing 20 mM H_2O_2 , 75 μM Acid blue 45 and 54 mM $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ pH7 buffer.

- 25 -

The solutions were mixed and pre incubated for 1 min at 40 °C. The changes in absorbance at 600 nm were measured for 8 min at 40 °C using a spectrophotometer.

- 5 The absolute changes in absorbance were correlated to activities obtained with freshly prepared calibration samples. The measured activities were expressed as $\mu\text{Mol/l}$.

Polyethylene teraphthalate = PET

- 10 High density polyethylene = PEHD

The liquid bleaching composition were irradiated on a sun bed having the following measured properties: UV A= 2.7 mW/cm³ and UV B= 0.05 mW/cm³. UV-A is irradiation in the
15 range 320-400 nm and UV-B is irradiation in the range 280 to 320 nm.

Table 1: The concentration bleach catalyst ($\mu\text{Mol/l}$) in liquid A after irradiation in different types of bottles.

20

Irradiation (MJ/m ²)	Bottle A	Bottle A + UV absorber	Bottle B	Bottle B + UV absorber	Bottle C	Bottle C + UV absorber
0	2.48	2.44	2.26	2.32	2.37	2.29
0.6	2.28	2.32	2.34	2.3	2.27	2.12
2.4	2.34	2.26	2.13	2.16	2.25	2.26
3.6	2.29	2.13	2.09	2.16	2.24	2.22
8.4	1.96	2.22	1.87	2.32	2.19	2.23
12	1.81	2.29	1.73	2.29	2.12	2.31
16.8	1.55	2.27	1.37	2.13	1.81	2.23

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25.2	1.49	2.27	1.24	2.19	1.59	2.3
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Bottle A: PEHD +/- Clariant Sarmastab UV 9M-B@ 2% UV absorber (ex Alpla)

Bottle B: PET 8 fl.Oz Resin 7352 +/- UV absorber 117880 (ex Owens Illinois)

Bottle C: PET 20 fl.Oz +/- UV absorber Clearshield UV 400M (5% T@390 nm) (ex Milliken)

Liquid A:

10 6 % LAS

6 % sLES 3 EO

6 % Nonionic 7 EO

0.016 % Proxel GXL

3.35 % sorbitol

15 2.30 % Borax.10 H₂O

4.75 % MPG

0.75 % NaOH

0.4 % Relase 16.0L EXI

Table 2: The concentration bleach catalyst ($\mu\text{Mol/l}$) in liquid B after irradiation in different types of bottles.

Irradiation (MJ/m ²)	Bottle A	Bottle A + UV absorber	Bottle B	Bottle B + UV absorber	Bottle C	Bottle C + UV absorber
0	2	1.87	1.86	1.86	1.86	1.95
0.6	1.94	1.83	1.82	1.8	1.76	1.82
2.4	1.92	1.82	1.86	1.85	1.79	1.72
3.6	1.66	1.74	1.73	1.73	1.71	1.66
8.4	1.61	1.74	1.52	1.76	1.67	1.68

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12	1.41	1.88	1.31	1.91	1.45	1.77
16.8	1.16	1.77	1.05	1.8	1.34	1.75
25.2	0.77	1.81	0.62	1.61	1.2	1.64

Bottle A: PEHD +/- Clariant Sarmastab UV 9M-B@ 2% UV
absorber (ex Alpla)

Bottle B: PET 8 fl.Oz Resin 7352 +/- UV absorber 117880 (ex
5 Owens Illinois)

Bottle C: PET 20 fl.Oz +/- UV absorber Clearshield UV 400M
(5% T@390 nm) (ex Milliken)

Liquid B:

10 6 % LAS
6 % sLES 3 EO
6 % Nonionic 7 EO
0.016 % Proxel GXL
3.35 % sorbitol
15 2.30 % Borax.10 H2O
4.75 % MPG
0.75 % NaOH
0.5 % Prifac 7908
0.4 % Relase 16.0L EXI

20

The above demonstrates the UV instability of the bleach
catalyst.

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CLAIMS

1. A bleaching composition comprising:

5 (a) a transition metal catalyst for catalytically bleaching with a peroxygen bleach;

(b) between 2 to 35 wt% of a peroxygen bleach or source thereof;

10

(c) between 0.0005 to 0.5 wt% of a photostable organic sunscreen having a C Log P value of at least 1.9 and having an extinction coefficient of greater than 2000 mol⁻¹ cm⁻¹ at 300 nm and an extinction coefficient of less than 100 mol⁻¹ cm⁻¹ at any single wavelength in the range from 400 nm at 750 nm;

15

(d) an antioxidant selected from:

(i) a phenolic antioxidant, the phenolic antioxidant present in the range 0.0001 to 3 % wt %; and,

20

(ii) an amine antioxidant, the hindered amine antioxidant in the range from 0.0001 to 20%; and,

(e) the balance carriers and adjunct ingredients to 100 wt/wt % of the total bleaching composition.

25

2. A bleaching composition according claim 1, wherein the extinction coefficient of the organic sunscreen is greater than 5000 mol⁻¹ cm⁻¹ at 300 nm.

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3. A bleaching composition according to claims 1 or 2,
wherein the antioxidant is selected from the group
consisting of: 2, 6-di-tert-butyl hydroxy toluene,
octylgallate, and dodecylgallate.
- 5
4. A bleaching composition according to claim 3, wherein
the antioxidant is 2, 6-di-tert-butyl hydroxy toluene.
- 10
5. A bleaching composition according to any preceding
claim, wherein the antioxidant is present in the
bleaching composition in the range from 0.001 to 2 wt %.
- 15
6. A bleaching composition according to any one of claims 1
to 5, wherein the a peroxygen bleach or source thereof
is selected from: sodium percarbonate and sodium
perborate.
- 20
7. A bleaching composition according to any preceding
claim, wherein the transition metal is iron.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/005487A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/16 C11D3/42 C11D3/395

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 03/006593 A (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN; SUNDER, MATTHIAS; BAYERSDOERF) 23 January 2003 (2003-01-23) page 68, line 5 - page 71, line 4; claims 20-23 page 37, lines 22-28 page 38, lines 4-11	1-7
Y	US 2003/119698 A1 (BUSCH DARYLE HADLEY ET AL) 26 June 2003 (2003-06-26) paragraphs '0007!, '0401!; claims 1-49; examples 1-27 ----- -/--	1-7

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/005487

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97/44422 A (UNILEVER PLC; UNILEVER N.V) 27 November 1997 (1997-11-27) page 1, lines 5-8; claims 1-10; tables 1-8 page 3, lines 32-36 page 4, line 26 - page 14, line 35 page 22, lines 5-9 -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/005487

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