



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁷ : C11D 3/04, 3/395, 3/39</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/15744</p> <p>(43) International Publication Date: 23 March 2000 (23.03.00)</p>
<p>(21) International Application Number: PCT/US99/21588</p> <p>(22) International Filing Date: 16 September 1999 (16.09.99)</p> <p>(30) Priority Data: 98870196.7 16 September 1998 (16.09.98) EP</p> <p>(71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): BRIATORE, Andrea [IT/IT]; Viale Sacco e Vanzetti, 163, I-00155 Rome (IT). GRANDE, Giovanni [IT/IT]; Via Frigeri, 131, I-00136 Rome (IT). MOSS, Michael, Alan, John [GB/IT]; Largo Olgiata N15, Isola N 91C, I-00123 Rome (IT). TODINI, Oreste [IT/IT]; Via Garibaldi, 26a, Castelnuovo di Porto, I-00060 Rome (IT).</p> <p>(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).</p>		<p>(81) Designated States: CA, JP, NO, PL, RU, SK, SK (Utility model), US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: BLEACHING COMPOSITIONS</p>		
<p>(57) Abstract</p> <p>The present invention relates to the use of a borate and/or boric acid and a surfactant as a fabric protective system in a bleaching composition to treat fabrics whereby good fabric yellowing-prevention performance and/or good fabric safety is achieved.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakistan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

BLEACHING COMPOSITIONS

Field of the invention

The present invention relates to a fabric protective system for use in bleaching compositions, which can be used to bleach fabrics, e.g., clothes, carpets and the like.

Background of the invention

Bleach-containing compositions for bleaching fabrics, are well known in the art.

Amongst the different bleaching compositions available, those relying on bleaching by hypohalite bleach, such as hypochlorite, and those relying on peroxygen bleach, such as hydrogen peroxide, are often preferred, mainly for bleaching performance reasons.

However, a drawback associated with the use of bleach-containing compositions, e.g., hypochlorite-based compositions, is that said compositions may potentially damage and/or cause yellowing of the fabrics being bleached. During the bleaching operation, a liquid hypochlorite-containing composition for example, can be applied onto the fabric in neat or in diluted form. The hypochlorite bleach can be present in various forms, including hypochlorous acid and in the form of various molecule fragments resulting from its decomposition pathways. Hypochlorous acid and these molecules fragments are reactive with fabrics and may cause damage and/or yellowing of fabrics being bleached.

Therefore, bleaching compositions are often formulated comprising bleach and a fabric protective system. Compositions comprising bleach and one of various fabric protective systems are well-known in the art. An example is a bleaching

composition based on hypohalite bleach or peroxygen bleach comprising a polymer and a borate as a fabric protective system (EP-A-0 824 147), or bleaching compositions based on hypochlorite comprising a metaborate as a fabric protective system (EP-A-0 781 480).

However, there are some limitations to the convenience of said bleaches comprising a fabric protective system. In particular, it is well-known from consumer research that said compositions may still damage and/or yellow the fabrics which are being bleached, although said compositions comprise a fabric protective system.

It is therefore an object of the present invention to provide a bleach-containing composition, suitable for use in laundry applications, whereby the fabric yellowing-prevention is further improved.

It is a further object of the present invention to provide a bleaching composition, suitable for use in laundry application, whereby fabric safety is further improved.

Fabrics made of cotton and/or synthetic materials have free hydroxyl groups. It is believed that fabric damage and/or fabric yellowing occurs due to the oxidation of the hydroxyl groups by the bleach. The oxidation of the hydroxyl groups is believed to be further emphasised at lower pHs. Indeed, low pH shifts the chemical equilibrium between hypochlorite and hypochlorous acid in favor of the latter. Hypochlorous acid is a more aggressive bleach, which has been found to further contribute to fabric yellowing and fabric damage. Moreover, it is further believed that the hydroxyl groups of the fabric are more easily oxidised at lower pHs.

It has been found that fabric protection can be achieved using a combination of a borate and/or boric acid and a surfactant as a fabric protective system in

bleach-containing compositions. The use of a combination of a borate and/or boric acid and a surfactant in bleach-containing compositions provides further improved fabric yellowing-prevention and/or further improved fabric safety on fabrics bleached therewith, as compared to bleaching compositions comprising other fabric protective systems, e.g., a metaborate alone, or bleaching compositions comprising no fabric protective system. It is believed that the hydroxyl groups of a fabric are protected by the fabric protective system according to the present invention from oxidation by a bleach, especially a hypochlorite bleach, thus, providing fabric safety and/or fabric yellowing-prevention.

Advantageously, the bleaching composition as described herein are suitable for various laundry bleaching applications both when used in diluted conditions, e.g., as a detergent additive or a fully formulated laundry detergent composition, and when used in neat condition, e.g., as a liquid pretreater (spotter).

A further advantage of the bleaching compositions according to the present invention is that they are able to perform in a variety of conditions, i.e., in hard and soft water as well as when used neat or diluted.

Yet another advantage of the use of a borate and/or boric acid and a surfactant as a fabric protective system in a bleaching composition as described herein is that said bleaching compositions are suitable for the bleaching of different types of fabrics. More particularly, the compositions of the present invention are suitable for bleaching any type of fabrics including natural fabrics (e.g., fabrics made of cotton, viscose, linen, silk and wool), synthetic fabrics such as those made of polymeric fibers of synthetic origin as well as those made of both natural and synthetic fibers. Indeed, the compositions of the present invention may be used on synthetic fibers despite a standing prejudice against the use of hypohalite bleaches, especially hypochlorite bleaches, on synthetic fibers, as

evidenced by warning on labels of commercially available hypochlorite bleaches and clothes.

Background art

Bleach-containing compositions based on hypochlorite bleach or peroxygen bleach suitable for bleaching fabrics have been described in the art.

EP-A-622 451 discloses compositions comprising hypochlorite, sodium hydroxide, a bleach stable perfume and a buffering system whereby the pH of the diluted composition is buffered to a constant value throughout use, comprising carbonate and/or silicate. However, the use of a borate and/or boric acid and a surfactant, as described herein, is not disclosed.

EP-A-0 824 147 discloses liquid bleaching compositions comprising a hypohalite bleach and a polymer. The composition may further comprise a boron salt as pH buffering component. However, the use of a borate and/or boric acid and a surfactant, as described herein, is not disclosed.

EP-A-0 781 840 discloses composition comprising hypochlorite and a metaborate as a pH buffering means. However, the use of a combination of a borate and/or boric acid and a surfactant, as described herein, is not disclosed.

Summary of the invention

The present invention encompasses the use of a borate and/or boric acid and a surfactant as a fabric protective system in a bleaching composition to treat fabrics, whereby good fabric yellowing-prevention performance and/or good fabric safety is achieved.

In a preferred embodiment of the present invention the surfactant is selected from the group consisting of alkyl alkoxyated sulphate surfactants, alkyl alkoxyated sulphonate surfactants, alkyl alkoxyated carboxylate surfactants, alkoxyated nonionic surfactants, fatty acid surfactants, amineoxide surfactants, betaine surfactants and quaternary ammonium surfactants, or a mixture thereof.

Detailed description of the invention

The fabric protective system as described herein is used in a bleaching composition. Said fabric protective system may be added to said bleaching composition just prior to the use of said bleaching composition or at the time of manufacture of said bleaching composition.

The bleaching compositions may be formulated either as solids or liquids.

In the case where the bleaching compositions are formulated as solids, for example as granules, tablets or powders, they are preferably applied on the fabrics to be bleached according to the present invention in a liquid form, i.e., solid compositions are used in combination with an appropriate solvent, typically water.

In the case where the bleaching compositions are formulated as liquids including gel and paste form, the bleaching compositions are preferably but not necessarily formulated as aqueous compositions. Liquid bleaching compositions are preferred herein for convenience of use. Preferred liquid bleaching compositions of the present invention are aqueous and therefore, preferably comprise water in an amount of from 60% to 98%, more preferably of from 80% to 97% and most preferably 85% to 97% by weight of the total composition.

Bleach

The fabric protective system of the present invention is used in a composition comprising a bleach. Any bleach known to those skilled in the art may be suitable for use herein. Preferred bleaches include any hypohalite bleach, as well as any peroxygen bleach.

Suitable hypohalite bleaches may be provided by a variety of sources, including bleaches that lead to the formation of positive halide ions and/or hypohalite ions, as well as bleaches that are organic based sources of halides such as chloroisocyanurates.

Suitable hypohalite bleaches for use herein include the alkali metal and alkaline earth metal hypochlorites, hypobromites, hypoiodites, chlorinated trisodium phosphate dodecahydrates, potassium and sodium dichloroisocyanurates, potassium and sodium trichlorocyanurates, N-chloroimides, N-chloroamides, N-chloroamines and chlorohydantoins.

For the bleaching compositions herein, the preferred hypohalite bleaches among those described above are the alkali metal or alkaline earth metal hypochlorites selected from the group consisting of sodium, potassium, magnesium, lithium and calcium hypochlorites, and mixtures thereof. Sodium hypochlorite is the most preferred hypohalite bleach.

Suitable peroxygen bleaches to be used herein are hydrogen peroxide, water soluble sources thereof, or mixtures thereof. A hydrogen peroxide source refers to any compound that produces perhydroxyl ions when said compound is in contact with water.

Suitable water-soluble sources of hydrogen peroxide for use herein include: percarbonates; persilicates; persulphates, such as monopersulfate; perborates;

peroxyacids, such as diperoxydodecandioic acid (DPDA), magnesium perphthalic acid, perlauric acid, perbenzoic and alkylperbenzoic acids, hydroperoxides, aliphatic and aromatic diacyl peroxides; and mixtures thereof. Preferred peroxygen bleaches herein are hydrogen peroxide, hydroperoxide and/or diacyl peroxide. Hydrogen peroxide is the most preferred peroxygen bleach herein.

Suitable hydroperoxides for use herein are tert-butyl hydroperoxide, cumyl hydroperoxide, 2,4,4-trimethylpentyl-2-hydroperoxide, di-isopropylbenzene-monohydroperoxide, tert-amyl hydroperoxide and 2,5-dimethyl-hexane-2,5-dihydroperoxide.

Suitable aliphatic diacyl peroxides for use herein are dilauroyl peroxide, didecanoyl peroxide, dimyristoyl peroxide, or mixtures thereof. Suitable aromatic diacyl peroxide for use herein is for example dibenzoyl peroxide.

Accordingly, the bleaching compositions according to the present invention may typically comprise from 0.01% to 20%, preferably from 0.25% to 15%, more preferably from 0.5% to 8% and most preferably from 1% to 6% by weight of the total composition of a bleach.

Borate and/or boric acid

The first essential ingredient of the fabric protective system of the present invention for use in a bleaching composition is a borate or boric acid or a mixture thereof.

Suitable borates include alkali metal salts of borates, and mixtures thereof. Suitable alkali metal salts of borates include alkali metal salts of metaborate, tetraborate, octoborate, pentaborate, dodecaborate, borontrifluoride and alkyl borates containing from 1 to 12, preferably from 1 to 4 carbon atoms. Preferred alkyl borate includes methyl borate, ethyl borate and propyl borate. Particularly

preferred herein are the alkali metal salts of metaborate, such as sodium metaborate, potassium metaborate, or mixtures thereof.

Borates like sodium metaborate and sodium tetraborate are commercially available from Borax and Societa Chimica Larderello under the name sodium metaborate and Borax®.

The bleaching compositions according to the present invention preferably comprise from 0.01% to 10%, more preferably from 0.1% to 5%, even more preferably from 0.5% to 3%, and most preferably from 0.5% to 1.5% by weight of the total composition of said borate or boric acid or a mixture thereof.

Surfactant

The second essential ingredient of the fabric protective system of the present invention for use in a bleaching composition is a surfactant.

Preferred surfactants are selected from the group consisting of alkyl alkoxyated sulphate surfactants, alkyl alkoxyated sulphonate surfactants, alkyl alkoxyated carboxylate surfactants, alkoxyated nonionic surfactants, fatty acid surfactants, amineoxide surfactants, betaine surfactants and quaternary ammonium surfactants, or a mixture thereof.

Suitable alkyl alkoxyated sulphate surfactants for use herein are according to the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C₆-C₂₀ alkyl or hydroxyalkyl group having a C₆-C₂₀ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₈ alkyl or hydroxyalkyl, A is an ethoxy or propoxy or butoxy unit, m is greater than zero, typically between 0.5 and 6, more preferably between 0.5 and 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl

ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate, C₁₂-C₁₈E(1.0)M, C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulfate, C₁₂-C₁₈E(2.25)M, C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulfate C₁₂-C₁₈E(3.0), and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate C₁₂-C₁₈E(4.0)M, wherein M is conveniently selected from sodium and potassium.

Suitable alkyl alkoxyated sulphonate surfactants for use herein are according to the formula R(A)_mSO₃M wherein R is an unsubstituted C₆-C₂₀ alkyl or hydroxyalkyl group having a C₆-C₂₀ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₈ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between 0.5 and 6, more preferably between 0.5 and 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulphonates as well as alkyl propoxylated sulphonates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulphonate, C₁₂-C₁₈E(1.0)M, C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulphonate, C₁₂-C₁₈E(2.25)M, C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulphonate C₁₂-C₁₈E(3.0), and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulphonate C₁₂-C₁₈E(4.0)M, wherein M is conveniently selected from sodium and potassium.

Suitable alkyl alkoxyated carboxylate surfactants for use herein are according to the formula $RO(A)_mCO_2M$ wherein R is an unsubstituted C_6 - C_{20} alkyl or hydroxyalkyl group having a C_6 - C_{20} alkyl component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy or butoxy unit, m is greater than zero, typically between 0.5 and 6, more preferably between 0.5 and 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated carboxylates as well as alkyl propoxylated carboxylates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12} - C_{18} alkyl polyethoxylate (1.0) carboxylate, C_{12} - $C_{18}E(1.0)M$, C_{12} - C_{18} alkyl polyethoxylate (2.25) carboxylate, C_{12} - $C_{18}E(2.25)M$, C_{12} - C_{18} alkyl polyethoxylate (3.0) carboxylate C_{12} - $C_{18}E(3.0)$, and C_{12} - C_{18} alkyl polyethoxylate (4.0) carboxylate C_{12} - $C_{18}E(4.0)M$, wherein M is conveniently selected from sodium and potassium.

Suitable alkoxyated nonionic surfactants for use herein include capped and non-capped alkoxyated nonionic surfactants. Suitable non-capped alkoxyated nonionic surfactants are non-capped ethoxylated nonionic surfactants according to the formula $RO-(C_2H_4O)_nH$, wherein R is a C_6 to C_{22} , preferably a C_8 to C_{22} alkyl chain or a C_6 to C_{28} alkyl benzene chain, and wherein n is from 0 to 20, preferably from 1 to 15 and, more preferably from 2 to 15 and most preferably from 2 to 12. The preferred R chains for use herein are the C_8 to C_{22} alkyl chains. Propoxylated, butoxylated, ethoxy/butoxylated,

ethoxy/propoxylated, butoxy/propoxylated and ethoxy/butoxy/propoxylated nonionic surfactants may also be used herein instead of the ethoxylated nonionic surfactants as defined herein above or together with said surfactants.

Accordingly suitable non-capped ethoxylated nonionic surfactants for use herein are Dobanol® 91-2.5 (HLB= 8.1; R is a mixture of C₉ and C₁₁ alkyl chains, n is 2.5), or Lutensol® TO3 (HLB=8; R is a C₁₃ alkyl chains, n is 3), or Lutensol® AO3 (HLB=8; R is a mixture of C₁₃ and C₁₅ alkyl chains, n is 3), or Tergitol® 25L3 (HLB= 7.7; R is in the range of C₁₂ to C₁₅ alkyl chain length, n is 3), or Dobanol® 23-3 (HLB=8.1; R is a mixture of C₁₂ and C₁₃ alkyl chains, n is 3), or Dobanol® 23-2 (HLB=6.2; R is a mixture of C₁₂ and C₁₃ alkyl chains, n is 2), or Dobanol® 45-7 (HLB=11.6; R is a mixture of C₁₄ and C₁₅ alkyl chains, n is 7) Dobanol® 23-6.5 (HLB=11.9; R is a mixture of C₁₂ and C₁₃ alkyl chains, n is 6.5), or Dobanol® 25-7 (HLB=12; R is a mixture of C₁₂ and C₁₅ alkyl chains, n is 7), or Dobanol® 91-5 (HLB=11.6; R is a mixture of C₉ and C₁₁ alkyl chains, n is 5), or Dobanol® 91-6 (HLB=12.5 ; R is a mixture of C₉ and C₁₁ alkyl chains, n is 6), or Dobanol® 91-8 (HLB=13.7 ; R is a mixture of C₉ and C₁₁ alkyl chains, n is 8), Dobanol® 91-10 (HLB=14.2 ; R is a mixture of C₉ to C₁₁ alkyl chains, n is 10), Dobanol® 91-12 (HLB=14.5 ; R is a mixture of C₉ to C₁₁ alkyl chains, n is 12), or mixtures thereof. Preferred herein are Lutensol® TO3, or Lutensol® AO3, or Tergitol® 25L3, or Dobanol® 23-3, or Dobanol® 23-6.5, or Dobanol® 45-7, Dobanol® 91-8, or Dobanol® 91-10, or Dobanol® 91-12, or mixtures thereof. These Dobanol® surfactants are commercially available from SHELL. These Lutensol® surfactants are commercially available from BASF and these Tergitol® surfactants are commercially available from UNION CARBIDE.

Suitable capped alkoxyated non-ionic surfactants, having the terminal hydroxyl group capped, are according to the formula : R(A)_n-O-R1 where R and R1 are

independently a C₆ to C₂₂, preferably a C₈ to C₂₂ alkyl chain or a C₆ to C₂₈ alkyl benzene chain; A is an ethoxy or propoxy or butoxy unit; and n is from 0 to 20, preferably from 1 to 15 and, more preferably from 2 to 15 and most preferably from 2 to 12.

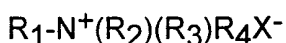
Suitable chemical processes for preparing the alkoxyated nonionic surfactants for use herein include condensation of corresponding alcohols with alkylene oxide, in the desired proportions. Such processes are well-known to the person skilled in the art and have been extensively described in the art.

Suitable fatty acid surfactants to be used herein are according to the formula : R-CH₂COOM; with R being a linear or branched C₁-C₃₀, preferably C₁₂-C₁₆ group; M being H or a metal ion, preferably an alkaline earth ion, more preferably Sodium or Potassium. An exemplary fatty acid surfactant is Prifac®, which is a C₁₂/C₁₄/C₁₆ fatty acid available from Unichema.

Suitable amine oxides to be used herein are according to the following formula R₁R₂R₃NO wherein each of R₁, R₂ and R₃ is independently a saturated substituted or unsubstituted, linear or branched hydrocarbon chains of from 1 to 30 carbon atoms. Preferred amine oxide surfactants to be used according to the present invention are amine oxides having the following formula : R₁R₂R₃NO wherein R₁ is an hydrocarbon chain comprising from 1 to 30 carbon atoms, preferably from 6 to 20, more preferably from 8 to 16, most preferably from 8 to 12; and wherein R₂ and R₃ are independently substituted or unsubstituted, linear or branched hydrocarbon chains comprising from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, and more preferably are methyl groups. R₁ may be a saturated substituted or unsubstituted linear or branched hydrocarbon chain. Suitable amine oxides for use herein are for instance natural blend C₈-

C₁₀ amine oxides as well as C₁₂-C₁₆ amine oxides commercially available from Hoechst.

A generic formula for betaine surfactants for use herein (i.e., betaine and/or sulfobetaine) is :



wherein R₁ is a hydrophobic group; R₂ is hydrogen, C₁-C₆ alkyl, hydroxy alkyl or other substituted C₁-C₆ alkyl group; R₃ is C₁-C₆ alkyl, hydroxy alkyl or other substituted C₁-C₆ alkyl group which can also be joined to R₂ to form ring structures with the N, or a C₁-C₆ carboxylic acid group or a C₁-C₆ sulfonate group; R₄ is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 10 carbon atoms; and X is the hydrophilic group which is a carboxylate or sulfonate group, preferably sulfonate group.

Preferred hydrophobic groups R₁ are aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chains that can contain linking groups such as amido groups, ester groups. More preferred R₁ is an alkyl group containing from 1 to 24 carbon atoms, preferably from 8 to 18, and more preferably from 10 to 16. These simple alkyl groups are preferred for cost and stability reasons. However, the hydrophobic group R₁ can also be an amido radical of the formula : R_a-C(O)-NR_b-(C(R_c)₂)_m, wherein R_a is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain containing from 8 up to 20 carbon atoms, preferably an alkyl group containing from 8 up to 20 carbon atoms, preferably up to 18, more preferably up to 16; R_b is either a hydrogen a short chain alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group

consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl or hydrogen; R_C is selected from the group consisting of hydrogen and hydroxy groups, and m is from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any $(C(R_C)_2)$ moiety.

Preferred R_2 is hydrogen, or an alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl. Preferred R_3 is a C_1 - C_4 carboxylic acid group, a C_1 - C_4 sulfonate group, or an alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably a group selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, more preferably methyl. Preferred R_4 is $(CH_2)_n$ wherein n is an integer from 1 to 10, preferably from 1 to 6, more preferably is from 1 to 3.

Some common examples of betaine/sulphobetaine are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082, incorporated herein by reference.

Examples of particularly suitable alkyldimethyl betaines include coconut-dimethyl betaine, lauryl dimethyl betaine, decyl dimethyl betaine, 2-(N-decyl-N, N-dimethyl-ammonia)acetate, 2-(N-coco N, N-dimethylammonio) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine. For example Coconut dimethyl betaine is commercially available from Seppic under the trade name of Amony 265®. Lauryl betaine is commercially available from Albright & Wilson under the trade name Empigen BB/L®.

A further example of betaine is Lauryl-immuno-dipropionate commercially available from Rhone-Poulenc under the trade name Mirataine H₂C-HA®.

Examples of particularly suitable sulfobetaine surfactants include tallow bis(hydroxyethyl) sulphobetaine, cocoamido propyl hydroxy sulfobetaines which are commercially available from Rhone Poulenc and Witco, under the trade name of Mirataine CBS® and Rewoteric AM CAS 15® respectively.

Further examples of amidobetaines/amidosulfobetaine include cocoamidoethylbetaine, cocoamidopropyl betaine or C₁₀-C₁₄ fatty acylamidopropylene(hydropropylene)sulfobetaine. For example C₁₀-C₁₄ fatty acylamidopropylene(hydropropylene)sulfobetaine is commercially available from Sherex Company under the trade name "Varion CAS® sulfobetaine".

Suitable quaternary ammonium surfactants for use herein are according to the formula : $R_1R_2R_3R_4N^+ X^-$, wherein X is a counteranion such as halogen, methyl sulphate, methyl sulphonate, or hydroxide; R₁ is a saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl group containing from 1 to 30 carbon atoms, preferably from 12 to 20, more preferably from 8 to 20; and R₂, R₃ and R₄ are independently hydrogen, or saturated or unsaturated, substituted or unsubstituted, linear or branched alkyl groups containing from 1 to 4 carbon atoms, preferably from 1 to 3 and more preferably methyl. In highly preferred quaternary ammonium surfactants herein R₁ is a C₁₀-C₁₈ hydrocarbon chain, most preferably C₁₂, C₁₄, or C₁₆; and R₂, R₃ and R₄ are all three methyl, and X is halogen, preferably bromide or chloride, most preferably bromide.

Examples of quaternary ammonium surfactants are myristyl trimethylammonium methyl sulphate, cetyl trimethylammonium methyl sulphate, lauryl trimethyl ammonium bromide, stearyl trimethyl ammonium bromide (STAB), cetyl trimethyl ammonium bromide (CTAB) and myristyl trimethyl ammonium bromide (MTAB).

Highly preferred herein are lauryl trimethyl ammonium salts. Such trimethyl quaternary ammonium surfactants may be commercially available from Hoechst, or from Albright & Wilson under the trade name Empigen CM®.

The bleaching compositions according to the present invention preferably comprise from 0.01% to 50%, more preferably from 0.03% to 40%, even more preferably from 0.07% to 20%, and most preferably from 0.1% to 10% by weight of the total composition of said surfactant.

Cotton fabrics contain cellulose (i.e., $(C_6H_{10}O_5)_n$). When a bleach-containing composition, e.g., a hypochlorite-containing composition, is used to bleach a cotton fabric, the bleach may react with the hydroxyl substituents of cellulose in position 6, 2, 3 and 5 of the cellulosic ring and thus may introduce new functional groups like carbonylic, aldehydic and/or carboxylic groups. Synthetic fabrics may be made of various synthetic materials like polyamide-elasthane that also comprise hydroxyl groups capable of being oxidized by bleach.

It has now been found that a borate and/or boric acid and a surfactant as described herein act together as a fabric protective agent for use in a bleaching composition. Compared to a bleach-containing composition comprising a fabric protective system other than that described by the present invention or no fabric protective system at all, the fabric yellowing-prevention performance and/or the fabric safety performance is further improved.

Whilst not wishing to be bound by theory, it is believed that the fabric protective system consisting of a borate and/or boric acid and a surfactant as described herein, for use in a bleaching composition is capable of protecting, i.e., esterifying and/or complexing, the hydroxyl groups present on the fibers of a treated fabric. Otherwise, said hydroxyl groups would be subject to oxidation by

the bleach, e.g., hypochlorite bleach, which leads to fabric yellowing and/or fabric damages.

The fabric yellowing-prevention and/or fabric safety performance benefit can be achieved when using the fabric protective system of the present invention in a liquid bleaching composition which is applied in a neat form, e.g., as a pretreater, as well as in a solid or liquid bleaching composition which is applied in a diluted form, e.g., typical dilution with water in conventional washing conditions.

Indeed, the yellowing-prevention effect and/or safety effect of the present invention can be evaluated by comparing the composition according to the present invention to a bleach-containing composition comprising a fabric protective system other than that claimed by the present invention.

By "further improved fabric yellowing-prevention", it is meant herein that the yellowing of fabrics, i.e., the appearance of a yellowish tone of said fabrics, that occurs by using the bleach-containing compositions of the present invention (e.g., those containing a hypohalite bleach, e.g., hypochlorite) is reduced, compared to the yellowing that occurs by using a bleach-containing composition comprising a fabric protective system other than that described by the present invention.

The degree of yellowing can be determined by both visual and instrumental grading. Visually, the difference in yellowing between items treated with different compositions can be determined by a team of expert panelists. Instrumentally, the assessment can be determined with the help of Colorimeters such as Ganz Griesser® instruments (e.g., Datacolor® Spectraflash® SF 500, Machbet White-eye® 500) or a ZEISS ELREPHO® or others which are available for instance from Hunterlab® or Gardner®.

By "further improved fabric safety", it is meant herein that the damage caused on fabric by using the bleach-containing compositions of the present invention (e.g., those containing a hypohalite bleach, e.g., hypochlorite) is reduced, compared to the damage caused by using a bleach-containing composition comprising a fabric protective system other than that described by the present invention.

Fabric safety may be evaluated by different test methods including the degree of polymerisation test method according to UNI (Ente Nazionale Italiano di Unificazione) official method UNI 8282-Determinazione della viscosità intrinseca in soluzione di cuprietilendiammina (CED).

pH

The fabric protective system as described herein may be used in liquid bleaching compositions, having a pH of from 0 to 14. The borate may also act as a pH buffering means.

In a preferred embodiment of the present invention wherein the bleaching composition herein is a composition comprising an alkali metal hypochlorite as the bleach, the boron salt provides a prolonged through-the-bleach buffering action, i.e., maintains the pH of the bleaching solution at a pH at least 8, preferably at least 8.5, more preferably at least 9.5 for a longer period of time, throughout the treatment, e.g., at a dilution level of 200:1 (water:composition), as compared to the buffering action obtained with the same composition without said boron salt.

It has been found that the buffering action of the boron salt also affects the hypochlorite/ hypochlorous acid such that the shift of hypochlorite into hypochlorous acid is reduced. It is believed that by controlling this equilibrium, fabric damage and/or fabric yellowing can be reduced.

In an embodiment, wherein the bleaching compositions herein are liquid and comprise a hypohalite bleach, typically an alkali metal hypochlorite, the recommended pH range of the bleaching composition is from 8 to 14, preferably from 8.5 to 14, more preferably from 9 to 13.5, and even more preferably from 9.5 to 13.5. It is in this alkaline pH range that the optimum stability and performance of the hypohalite bleach, e.g., hypochlorite, is obtained.

If appropriate, the compositions of the present invention may comprise an alkalinity source to adjust the pH of said composition. The bleaching compositions herein may comprise up to 10%, preferably of from 0.04% to 5% and more preferably of from 0.1% to 2% by weight of the total composition of said alkalinity source.

Suitable alkalinity sources for use herein are the caustic alkalis, such as sodium hydroxide, potassium hydroxide and/or lithium hydroxide, and/or the alkali metal oxides such, as sodium and/or potassium oxide or mixtures thereof. A preferred alkalinity source is a caustic alkali, more preferably sodium hydroxide and/or potassium hydroxide.

Other suitable alkalinity sources include ammonia, ammonium carbonate and hydrogen carbonate.

In an embodiment, wherein the bleaching compositions herein are liquid and comprise a peroxygen bleach, the recommended pH range of the bleaching composition to achieve good stability is from 1 to 9, preferably between pH 1 and 8, more preferably between pH 1 and 7 and most preferably between pH 1 and 6.

If appropriate, the bleaching compositions herein may further comprise an acid to adjust the pH of said composition. The bleaching compositions of the present invention may comprise up to 10%, preferably of from 0.04% to 5% and more preferably of from 0.1% to 2% by weight of the total composition of said acid.

Suitable acids for use herein may be organic acids, inorganic acids, or mixtures thereof. Preferred organic acids are citric, maleic, oxalic succinic, tartaric acids or mixtures thereof. A preferred inorganic acid is sulphuric acid.

Optional pH buffering components

The bleaching compositions according to the present invention may further comprise as an optional, but preferred ingredient, a pH buffering component in addition to the pH buffering action that the borate may have. Particularly useful are alkali metal salts of carbonates, polycarbonates, sesquicarbonates, silicates, polysilicates, phosphonates, stannates, alluminates or mixtures thereof. The preferred alkali metal salts to be used herein are sodium and potassium salts. Particularly preferred are alkali metal salts of carbonate. The preferred alkali metal salt of carbonate is sodium carbonate.

The bleaching compositions of the present invention may comprise up to 5%, preferably from 0.01% to 4% and more preferably from 0.02% to 3% by weight of the total composition of a pH buffering component.

Other optional ingredients

The bleaching compositions according to the present invention may further comprise other optional ingredients, such as bleach-stable surfactants, pigments, enzymes, dyes, optical brighteners, solvents, polymers, stabilizing agents, chelating agents, radical scavengers, bleach activators, hydrotropes and the like.

Bleach activators

In an embodiment of the present invention where the bleaching compositions herein comprise a peroxygen bleach, said compositions may comprise a bleach activator up to a level of 10% by weight of the total composition. Suitable bleach activators to be used herein include those belonging to the class of esters, amides, imides, or anhydrides. Examples of suitable compounds of this type are disclosed in British Patent GB 1 586 769 and GB 2 143 231 and a method for their formation into a prilled form is described in European Published Patent Application EP-A-62 523. Suitable examples of such compounds to be used herein are tetracetyl ethylene diamine (TAED), sodium 3,5,5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS). Also suitable are N-acyl caprolactams selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam pentanoyl caprolactam or mixtures thereof. A particular family of bleach activators of interest was disclosed in EP 624 154, and particularly preferred in that family is acetyl triethyl citrate (ATC). Acetyl triethyl citrate has the advantage that it is environmental friendly as it eventually degrades into citric acid and alcohol. Furthermore, acetyl triethyl citrate has a good hydrolytical stability in the product upon storage and it is an efficient bleach activator.

Stabilizing agents

The bleaching compositions of the present invention may further comprise a stabilizing agent, preferably a radical scavenger, a chelating agent or a mixture thereof. Naturally, for the purpose of the invention, the stabilizing agents have to be stable to the hypochlorite bleach. In an embodiment wherein the bleaching

compositions according to the present invention comprise a hypohalite bleach said stabilizing agents are highly preferred.

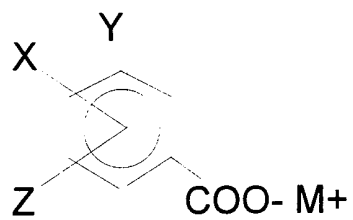
Highly preferred stabilizing agents are radical scavengers alone, or in combination with a chelating agent.

Suitable radical scavengers for use herein include aromatic radical scavengers comprising an unsaturated ring system of from 3 to 20, preferably of from 3 to 18 and more preferably of from 5 to 14 carbon atoms and having a double bond set comprising a total of $4n+2$ electrons, wherein n is an integer of from 0 to 4, preferably of from 1 to 3. Indeed said aromatic radical scavengers include benzene derivatives, naphthalene derivatives, annulene derivatives, cyclopentadiene derivatives, cyclopropene derivatives and the like, especially aryl carboxylates and/or aryl sulfonates.

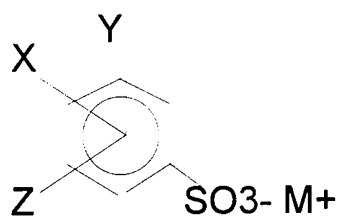
Particularly suitable radical scavengers (aryl carboxylates, aryl sulphonate and derivatives thereof) for use in the present invention have one of the following formulas:

23

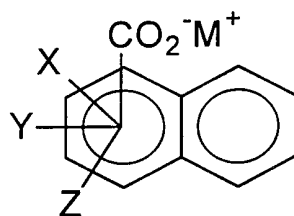
(a)



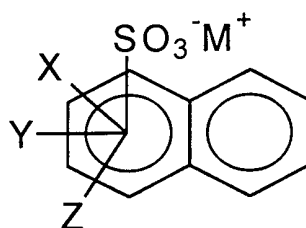
(b)



(c)



(d)



wherein each X, Y, and Z are -H, -COO-M⁺, -Cl, -Br, -SO₃-M⁺, -NO₂, -OCH₃, or a C₁ to C₁₀ primary and secondary alkyl groups and M is H or an alkali metal, or mixtures thereof. Examples of these components include pyromellitic acid, i.e. where X, Y and Z are -COO-H⁺; hemimellitic acid, trimellitic acid, i.e. where X and Y are -COO-H⁺ and Z is H. Preferred to be used in the present invention as radical scavengers are phthalic acid; sulfophthalic acid; other mono-substituted phthalic acids; di-substituted benzoic acids; alkyl-, chloro-, bromo-, sulfo-, nitro- and alkoxy- benzoic acids, i.e. where Y and Z are -H and X is a C₁ to C₁₀ primary and secondary alkyl groups, -Cl, -Br, -SO₃-H⁺, -NO₂ or -OCH₃ (anisic acid) respectively and substituted sulfonic acids. Highly preferred examples of the radical scavengers useful in the present invention are benzoic acid, toluic acid, 4-toluene sulfonic acid, 3-nitro benzoic acid, 2 n-octyl benzoic acid, 2 n-octyl sulfonic acid, anisic acid or mixtures thereof. Most preferred herein are n-anisic acid, benzoic acid, methoxy benzoic acid and/or 3-nitrobenzoic acid.

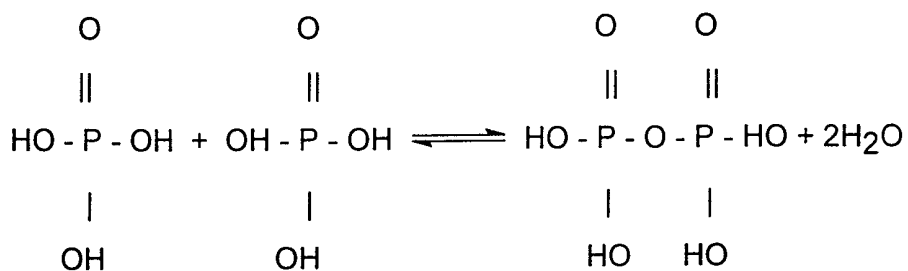
The radical scavengers described above are the acidic form of these species, i.e., M is H. It is intended that the present invention also covers the salt derivatives of these species, i.e., M is an alkali metal, preferably sodium or potassium. In fact, where the pH of the bleaching compositions of the present invention is in the alkaline range, the radical scavengers of the present invention exist primarily as the ionized salt in the aqueous composition herein. The anhydrous derivatives of certain species described herein above can also be

used in the present invention, e.g., pyromellitic dianhydride, phthalic anhydride, sulphthalic anhydride and the like.

Suitable chelating agents for use herein may be any of those known to those skilled in the art such as the ones selected from the group comprising phosphonate chelating agents, phosphate chelating agents, polyfunctionally-substituted aromatic chelating agents, ethylenediamine N,N'- disuccinic acids, or mixtures thereof.

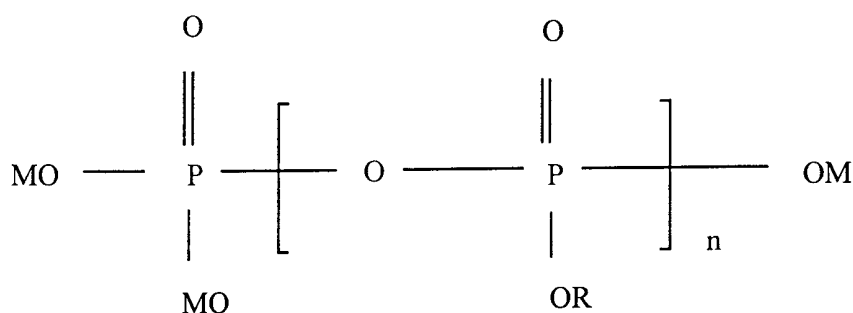
Suitable phosphonate chelating agents to be used herein may include alkali metal ethane 1-hydroxy diphosphonates (HEDP), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino aminotri(methylene phosphonic acid) (ATMP), nitrilo trimethylene phosphonates (NTP), ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates (DTPMP). The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonate (DTPMP) and ethane 1-hydroxy diphosphonate (HEDP). Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST®.

Suitable phosphate chelating agents are as follows: Phosphonic acid can be condensed in the reaction

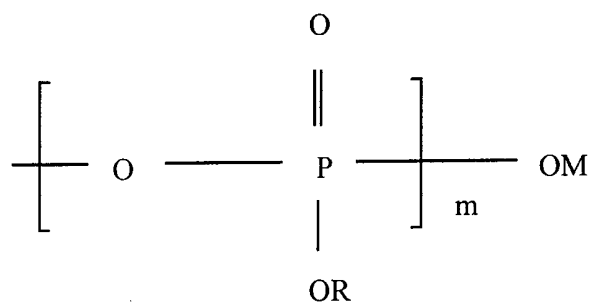


The reaction can be repeated with any of the reactive OH groups, and phosphate ingredients are obtained which can be

- linear or branched polyphosphates of structure



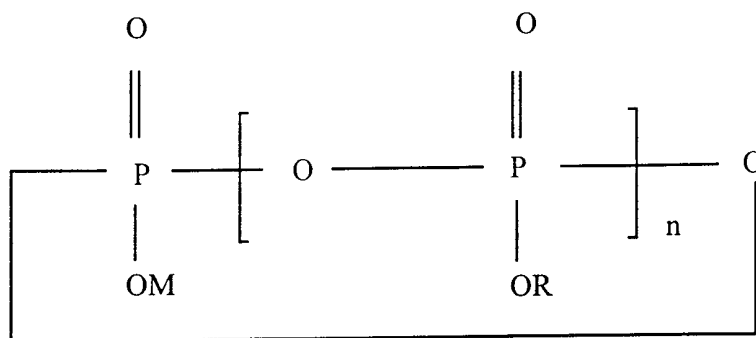
-when R is M or



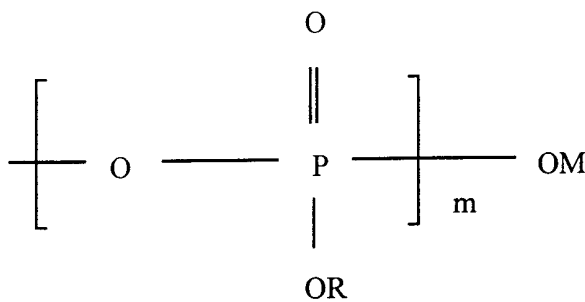
- when M is a counterion, preferably alkali metal;

- when $0 \leq n+m < 500$ (if $n+m = 0$ then the compound is phosphonic acid)

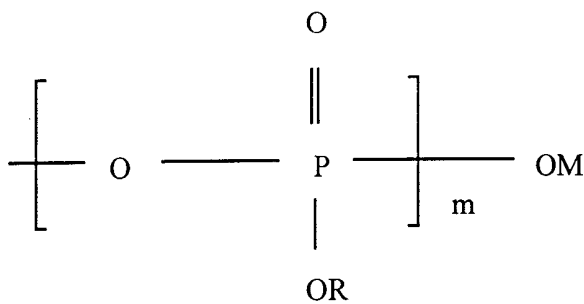
- cyclic polyphosphates (also referred to as metaphosphates), of structure



-when R is M or



-if R is



the phosphate compound contains both cycles and branched chain, and can be referred to as an ultraphosphate.)

- where M is a counterion, preferably an alkali metal

- where $0 \leq n+m < 500$

All such phosphate ingredients are suitable for use herein, and preferred are linear phosphate ingredients (i.e., R_n is M) where n is 1 (pyrophosphate) and n is 2 (tripolyphosphate (STPP)), most preferably where n is 2. The most commonly available form of this phosphate is where M is Sodium.

Phytic acid, which is a chelating agent particularly suitable for use herein, is a hexa-phosphoric acid that occurs naturally in the seeds of many cereal grains, generally in the form of the insoluble calcium-magnesium salt. It may also be derived from corn steep liquor. Commercial grade phytic acid is commercially available from J.T.Baker Co., e.g., as a 40% aqueous solution. It is intended that the present invention covers the acidic form of phytic acid as well as alkali metal salt derivatives thereof, particularly sodium or potassium salts thereof. Sodium phytate is available from Jonas Chemical Co (Brooklyn, N.Y.). In fact since the typical pH of the compositions of the present invention are in the alkaline pH range, the phytic acid component exists primarily as the ionized salt in the liquid compositions herein even if it is added in its acidic form. Mixtures of such salts of phytic acid are also covered.

Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelating agent for use herein is ethylene diamine N,N' -disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N' -disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4,704,233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N' -disuccinic acids is, for instance, commercially available under the tradename ssEDDS[®] from Palmer Research Laboratories.

Particularly preferred chelating agents for use herein are phosphate chelating agents like sodium tripolyphosphate, sodium pyrophosphate, phytic acid, and mixtures thereof.

Typically, the bleaching compositions according to the present invention may comprise from 0.01% to 10%, preferably from 0.01% to 8% by weight, more preferably from 0.1% to 5%, and most preferably from 0.2% to 3% by weight of the total composition of a stabilising agent.

Optional surfactants

The bleaching compositions of the present invention may further comprise another surfactant in addition to the surfactants which are part of the fabric protective system. Said surfactant may be present in the bleaching compositions according to the present invention in amounts up to 30%, preferably of from 0.1% to 20% and more preferably of from 0.1% to 10% by weight of the total composition.

Surfactants for use herein include other anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof. Naturally, for the purpose of the invention, the additional surfactants have to be stable to the used bleach.

Optional polymers

An optional component of the bleaching compositions herein is a polymer. Naturally, for the purpose of the invention, the polymer has to be stable in the presence of the used bleach.

Suitable polymers for use are polymers comprising monomeric units selected from the group consisting of unsaturated carboxylic acids, polycarboxylic acids,

sulphonic acids, phosphonic acids and mixtures thereof. Co-polymerisation of the above monomeric units among them or with other co-monomers such as styrenesulphonic acid is also suitable.

Preferred examples of such polymers are the polymers and co-polymers of monomeric units selected from the group consisting of acrylic acid, maleic acid, vinylsulphonic acid and mixtures thereof. Also suitable for use herein are the above mentioned polymers and co-polymers which are modified in order to contain other functional groups such as aminophosphonic and/or phosphonic units. More preferred polymers are selected from the group consisting of polyacrylate polymers, co-polymers of acrylic and maleic acid, co-polymers of styrene sulphonic acid and maleic acid, and mixtures thereof, preferably modified with aminophosphonic and/or phosphonic groups.

The molecular weight for these polymers and co-polymers is preferably below 100,000, most preferably between 500 and 50,000. In an embodiment of the present invention where the bleaching compositions herein comprise a hypochlorite bleach, the most suitable polymers and co-polymers for use herein will be soluble in an amount up to 0.1% by weight, in an aqueous composition comprising 5% by weight of sodium hypochlorite with its pH adjusted to 13 with sodium hydroxide.

Commercially available polymers, suitable for use herein, are the polyacrylate polymers sold under the tradename Good-Rite® from BF Goodrich, Acrysol® from Rohm & Haas, Sokalan® from BASF, Norasol® from Norso Haas. Also suitable for use herein are the co-polymers of styrene sulphonic acid and maleic acid, commercially available under the tradename Versaflex® from National Starch such as Versaflex 157, as well as Acumer® terpolymers from Rohm and Haas, in particular Acumer® 3100. Preferred commercially available polymers are the polyacrylate polymers, especially the Norasol® polyacrylate polymers

and more preferred are the polyacrylate polymer Norasol® 410N (MW 10,000) and the polyacrylate polymer modified with phosphonic groups Norasol® 440N (MW 4000) and its corresponding acid form Norasol® QR 784 (MW 4000).

A preferred polymer for use herein is a polyacrylate polymer modified with phosphonic groups commercially available under the tradename Norasol® 440N (MW 4000) and its corresponding acid form Norasol® QR 784 (MW 4000) from Norso-Haas.

Mixtures of the polymers described herein may also be used in the present invention.

Polymers herein are preferably present in low amounts, i.e., in amounts of up to 10% by weight, preferably up to 1%, more preferably from 0.001% to 0.5% by weight, most preferably from 0.005% to 0.2% by weight of the liquid composition.

Optional brighteners

The bleaching compositions according to the present invention may also comprise a brightener or a mixture thereof as an optional ingredient. Naturally, for the purpose of the invention, the brightener has to be stable in the presence of the bleach used. The brighteners may be desired herein to further enhance the whiteness performance of the bleaching compositions herein.

Brighteners are compounds which have the ability to fluoresce by absorbing ultraviolet wave-lengths of light and re-emitting visible light. Brighteners, also referred to as fluorescent whitening agent (FWA), have been extensively described in the art, see for instance EP-A-0 265 041, EP-A-0 322 564, EP-A-0 317 979 or "Fluorescent whitening agents" by A.K. Sarkar, published by MERROW, especially page 71-72.

Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982). Further optical brighteners which may also be used in the present invention include naphthlimide, benzoxazole, benzofuran, benzimidazole and any mixtures thereof.

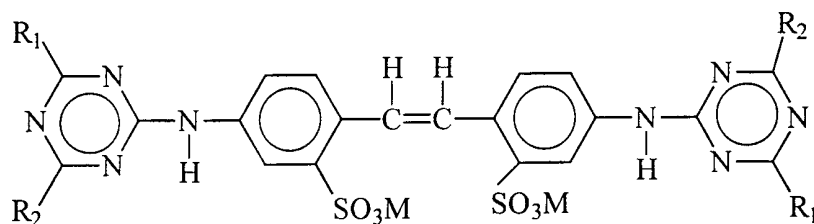
Examples of optical brighteners which are useful in the present bleaching compositions are those identified in U.S. Patent 4,790,856. These brighteners include the PHORWHITE® series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal-UNPA®, Tinopal CBS® and Tinopal 5BM® available from Ciba-Geigy; Artic White CC® and Artic White CWD®; the 2-(4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins.

Specific examples of brighteners useful herein include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphtho-[1,2-d]oxazole; 2-(stilbene-4-yl)-2H-naphtho[1,2-d]triazole, 3-phenyl-7-(isoindolinyl) coumarin; 3-methyl-7-(isoindolinyl) coumarin; 3-chloro-7-(isoindolinyl) coumarin; 4-(isoindolinyl)-4'-methylstilbene; 4-(isoindolinyl)-4'-methoxystilbene; sodium 4-(isoindolinyl)-4'-stilbenesulfonate; 4-(isoindolinyl)-4'-phenylstilbene; 4-(isoindolinyl)-3-methoxy-4'-methylstilbene; 4-(2-chloroisoindolinyl)-4'-(2-methylisoindolinyl)-2,2'-stilbenedisulfonic acid; disodium 4,4'-diisoindolinyl-2,2'-stilbene disulfonate; 4,4'-diisoindolinyl-2,2'-stilbenedisulfonamide; disodium 4,4'-(7,8-dichloro-1-

isoindolinyl)2,2-stilbenedisulfonate; disodium 4,4'-(7-chloro-1-isoindolinyl)2,2-
 stilbenedisulfonate; disodium 4,4'-(6-isopropoxy-1-isoindolinyl)2,2-
 stilbenedisulfonate; disodium 4,4'-(7,8-diisopropyl-1-isoindolinyl)2,2-
 stilbenedisulfonate; disodium 4,4'-(7-butoxy-1-isoindolinyl)2,2-
 stilbenedisulfonate; disodium 4,4'-(6-trifluoromethyl-1-isoindolinyl)2,2-
 stilbenedisulfonate; disodium 4,4'-[6-(1,4,7-trioxanonyl)-1-isoindolinyl]2,2-
 stilbenedisulfonate; disodium 4,4'-(7-methoxymethyl-1-isoindolinyl)2,2-
 stilbenedisulfonate; disodium 4,4'-(6-phenyl-1-isoindolinyl)2,2-
 stilbenedisulfonate; disodium 4,4'-(6-naphthyl-1-isoindolinyl)2,2-
 stilbenedisulfonate; disodium 4,4'-(6-methylsulfonyl-1-isoindolinyl)2,2-
 stilbenedisulfonate; disodium 4,4'-(7-cyano-1-isoindolinyl)2,2-stilbenedisulfonate;
 and disodium 4,4'-[7-(1,2,3-trihydroxypropyl)-1-isoindolinyl]2,2-
 stilbenedisulfonate; disodium 4-isoindolinyl-4'-ethoxy-2,2'-stilbenedisulfonate;
 disodium 4-isoindolinyl-4'-methoxy-2,2'-stilbenedisulfonate; disodium 4-
 isoindolinyl-4'-ethoxy-2,2'-stilbenedisulfonamide; disodium 4-isoindolinyl-4'-
 methyl-2,2'-stilbenedisulfonamide; 4,4'-bis(4-phenyl-2H-1,2,3-triazol-2-yl)-2,2'-
 stilbenedisulfonic acid and mixture thereof. See also U.S. Patent 3,646,015,
 U.S. Patent 3,346,502 and U.S. Patent 3,393,153 for further examples of
 brighteners useful herein.

Indeed one of the functionally equivalent derivative salts of 4,4'-bis(4-phenyl-2H-
 1,2,3-triazol-2-yl)-2,2'-stilbenedisulfonic acid, namely its sodium salt is available
 from Mobay Chemical Corporation, a subsidiary of Bayer AG under the name
 Phorwite® CAN. The amine salt is available from Molay under the name
 Phorwite® CL solution. The potassium salt is available under the name
 Phorwite® BHC 766.

Other specific examples of optical brighteners useful in the present invention are
 those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener

species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Other substituted stilbene 2,2'-disulfonic acid derivatives also include 4-4'-bis (2-2' styryl sulfonate) biphenyl, commercially available from Ciba-Geigy under the trade name Brightener 49® or other hydrophilic brighteners like for example Brightener 3® or Brightener 47®, also commercially available from Ciba-Geigy.

Further specific examples of brighteners useful in the present invention include the polycyclic oxazole derivatives such as benzo-oxazole derivatives, or mixtures thereof and particularly preferred herein the benzo-oxazole derivatives. An example of such a brightener is benzoxazole,2,2'-(thiophenaldyl)bis having the following formula C₁₈H₁₀N₂O₂S, commercially available from Ciba-Geigy under the trade name Tinopal SOP®. This brightener is almost insoluble in water, i.e. it has a solubility being lower than 1 gram per liter. Another example of such a brightener is bis(sulfobenzofuranyl)biphenyl, commercially available from Ciba-Geigy under the trade name Tinopal PLC®.

Typically the bleaching compositions according to the present invention may comprise up to 1.0% by weight of the total composition of a brightener or a mixture thereof, preferably from 0.005% to 0.5%, more preferably from 0.005% to 0.3% and most preferably from 0.008% to 0.1%.

Process of bleaching fabrics:

In the present invention, the bleaching composition of the present invention is used by applying the composition to the fabric to be treated. The compositions according to the present invention are preferably used in liquid form.

By "in liquid form" it is meant that liquid compositions can be used per se in neat or in diluted form, and solid compositions, for example granules, tablets or

powders, are dissolved in an appropriate solvent, typically water, before use, i.e., before being contacted to said fabrics.

By "in diluted form", it is meant herein that the compositions for the bleaching of fabrics according to the present invention may be diluted with a solvent by the user, the preferred solvent is water. Such dilution may occur for instance in hand laundry applications as well as by other means such as in a washing machine. Said compositions can be used at a dilution level of up to 500:1 (solvent:composition), preferably from 5:1 to 200:1 and more preferably from 10:1 to 80:1 (solvent:composition).

Fabrics to be treated herein include, but are not limited to, clothes, curtains, drapes, bed linens, bath linens, table cloths, sleeping bags, tents, upholstered furniture and the like, and/or carpets.

By "treating a fabric", it is meant herein bleaching and/or disinfecting said fabric as the compositions of the present invention comprise a bleach.

In the process of treating (e.g., bleaching) a fabric, a bleaching composition according to the present invention is contacted with the fabrics to be treated.

This can be done either in a so-called "pretreatment mode", where a liquid bleaching composition, as defined herein, is applied neat onto said fabrics before the fabrics are rinsed, or washed then rinsed, or in a "soaking mode" where a bleaching composition, as defined herein, is first diluted in an aqueous bath and the fabrics are immersed and soaked in the bath, before they are rinsed, or in a "through the wash mode", where a bleaching composition, as defined herein, is added on top of a wash liquor formed by dissolution or dispersion of a typical laundry detergent. It is also essential in both cases, that

the fabrics be rinsed after they have been contacted with said composition, before said composition has completely dried off.

The compositions according to the present invention are preferably used on fabrics in a liquid form. More specifically, the process of bleaching fabrics according to the present invention comprises the steps of first contacting said fabrics with a bleaching composition according to the present invention, in its diluted form, then allowing said fabrics to remain in contact with said composition, for a period of time sufficient to bleach said fabrics, typically 1 to 60 minutes, preferably 5 to 30 minutes, then rinsing said fabrics with water. If said fabrics are to be washed, i.e., with a conventional composition comprising at least one surface active agent, said washing may be conducted by contacting said fabrics at the same time with a bleaching composition according to the present invention and said detergent composition, or said washing may be conducted before or after said fabrics have been bleached. Accordingly, said process allows the bleaching of fabrics and optionally the washing of fabrics with a detergent composition comprising at least one surface active agent before the step of contacting said fabrics with said bleaching composition and/or in the step where said fabrics are contacted with said bleaching composition and/or after the step where said fabrics are contacted with the bleaching composition and before the rinsing step and/or after the rinsing step.

In another embodiment of the present invention the process of bleaching fabrics comprises the step of contacting fabrics with a liquid bleaching composition according to the present invention, in its neat form, of allowing said fabrics to remain in contact with said bleaching composition for a period of time sufficient to bleach said fabrics, typically 5 seconds to 30 minutes, preferably 1 minute to 10 minutes and then rinsing said fabrics with water. If said fabrics are to be washed, i.e., with a conventional composition comprising at least one surface active agent, said washing may be conducted before or after that said fabrics

have been bleached. In an embodiment of the present invention wherein the liquid bleaching composition of the present invention, is contacted to the fabrics in its neat form, it is preferred that the level of hypohalite bleach, is from 0.01% to 5%, preferably from 0.1% to 3.5%, more preferably from 0.2% to 2% and most preferably from 0.2% to 1%. Advantageously, the present invention provides liquid hypohalite bleach-containing compositions that may be applied neat onto a fabric to bleach, despite a standing prejudice against using hypochlorite-containing compositions neat on fabrics.

It is preferred to perform the bleaching process herein before said fabrics are washed. Indeed, it has been observed that bleaching said fabrics with the compositions according to the present invention (diluted and/or neat bleaching processes) prior to washing them with a detergent composition provides superior whiteness and stain removal with less energy and detergent than if said fabrics are washed first, then bleached.

Alternatively instead of following the neat bleaching process as described above (pretreatment application) with a rinsing step and/or a conventional washing step with a liquid or powder conventional detergent, the bleaching pre-treatment operation may also be followed by the diluted bleaching process as described above either in bucket (hand operation) or in a washing machine.

Examples

The following bleaching compositions which further illustrate the present invention were made by mixing the listed ingredients in the listed proportions:

Compositions (weight %)	I	II	III	IV	V	VI	VII
Sodium hypochlorite	5.0	5.0	5.0	2.5	2.5	5.0	5.0
Sodium hydroxide	1.3	1.3	1.3	0.7	1.4	0.7	1.4
Sodium carbonate	1.2	1.2	1.2	1.0	1.2	1.2	1.2
Sodium silicate	--	--	--	--	--	0.2	--
Sodium metaborate	1.0	--	0.75	1.0	0.75	0.5	--
Sodium tetraborate	--	--	1.0	--	--	--	--
Sodium borate	--	1.0	--	--	--	--	1.0
C12E3S	1.0	3.0	5.0	--	10.0	2.0	--
C10E2S	--	--	--	5.0	--	--	2.0
Minors and water	-----balance up to 100%-----						

Compositions (weight %)	VIII	IX	X	XI	XII	XIII	XIV
Sodium hypochlorite	5.0	5.0	5.0	2.5	2.5	5.0	5.0
Sodium hydroxide	1.3	1.3	1.3	0.7	1.4	0.7	1.4
Sodium carbonate	1.2	1.2	1.2	1.0	1.2	1.2	1.2
Sodium silicate	--	--	--	--	--	0.2	--
Sodium metaborate	1.0	--	0.75	1.0	0.75	0.5	--
Sodium tetraborate	--	--	1.0	--	--	--	--
Sodium borate	--	1.0	--	--	--	--	1.0
Plurafac LF231®	1.0	--	2.0	1.0	--	5.0	--

C12/14E7C	--	1.0	--	--	0.5	--	0.5
Minors and water	-----balance up to 100%-----						

C12E3S is an alkyl C₁₂ (ethoxy)₃ sulphate commercially available from Albright & Wilson or Rhone Poulenc.

C10E2S is an alkyl C₁₀ (ethoxy)₂ sulphate commercially available from Albright & Wilson.

Plurafac LF231® is a capped alkoxyated non-ionic surfactant commercially available from BASF.

C12/14E7C is an alkyl ethoxy carboxylate commercially available from Clariant.

All the above bleaching compositions provide excellent fabric safety and/or excellent fabric yellowing-prevention to fabrics when used to treat fabrics.

What is claimed is:

1. The use of a borate or boric acid or a mixture thereof and a surfactant as a fabric protective system in a bleaching composition to treat fabrics whereby good fabric yellowing-prevention performance and/or good fabric safety is achieved.
2. The use according to claim 1 wherein the bleach of said bleaching composition is a hypohalite bleach or a peroxygen bleach.
3. The use according to any of the preceding claims wherein the bleach is an alkali metal or an alkaline earth metal hypochlorite.
4. The use according to any of the preceding claims wherein the bleach is hydrogen peroxide and/or a water soluble source of hydrogen peroxide.
5. The use according to any of the preceding claims wherein said bleach is present at a level of from 0.01% to 20% by weight of the total composition.
6. The use according to any of the preceding claims wherein said borate is an alkali metal salt of borate, or an alkyl borate, or a mixture thereof.
7. The use according to claim 1 wherein said borate or boric acid or a mixture thereof is present at a level of from 0.01% to 10% by weight of the total composition.
8. The use according to any of the preceding claims wherein said surfactant is selected from the group consisting of alkyl alkoxyated sulphate surfactants, alkyl alkoxyated sulphonate surfactants, alkyl alkoxyated carboxylate surfactants, alkoxyated nonionic surfactants, fatty acid surfactants,

amineoxide surfactants, betaine surfactants and quaternary ammonium salt surfactants, or a mixture thereof.

9. The use according to any of the preceding claims wherein said surfactant is present at a level of from 0.01% to 50% by weight of the total composition of said surfactant.
10. The use according to any of the preceding claims wherein said bleaching composition is liquid.
11. The use according to any of the preceding claims wherein said fabrics are clothes, curtains, drapes, bed linens, bath linens, table cloths, sleeping bags, tents, upholstered furniture and the like and/or carpets.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/21588

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C11D3/04 C11D3/395 C11D3/39

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 D06L

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 825 250 A (PROCTER & GAMBLE) 25 February 1998 (1998-02-25) examples XV-XIX claims 1-16	1-11
X	WO 96 33258 A (ALBRIGHT & WILSON UK LTD ;NICHOLSON WILLIAM JOHN (GB); HASLOP WILL) 24 October 1996 (1996-10-24) page 1, line 1 - line 29 examples 3,4 claims 1-12	1,2,4-11
X	US 4 568 477 A (OAKES JOHN) 4 February 1986 (1986-02-04) example II claim 1	1,2,4-11
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "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

21 December 1999

Date of mailing of the international search report

11/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 851 epo nl,
 Fax: (+31-70) 340-3018

Authorized officer

Richards, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/21588

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 431 747 A (CLOROX CO) 12 June 1991 (1991-06-12) page 2, line 1 - line 9 claims 1-10	1,2,4-11
X	WO 91 12309 A (UNILEVER PLC ; UNILEVER NV (NL)) 22 August 1991 (1991-08-22) example III claims 1-8	1,2,4-11
X	US 4 686 063 A (BURNS MICHAEL E) 11 August 1987 (1987-08-11) column 1, line 65 - column 2, line 5 column 3, line 49 - column 6, line 17 claims 1-17	1,2,4,5, 7-9,11
X	US 4 083 795 A (JOUBERT DANIEL) 11 April 1978 (1978-04-11) * Abstract * claims 1-6	1,2,5-9
P,X	EP 0 937 772 A (PROCTER & GAMBLE) 25 August 1999 (1999-08-25) page 7, line 18 - line 34 example XXII claims 1-17	1-3,5-7, 10,11
A	EP 0 396 341 A (PROCTER & GAMBLE) 7 November 1990 (1990-11-07) page 3, line 25 - line 30 example 2 claims 1-3	1,2,4,7, 9
A	DATABASE WPI Section Ch, Week 8621 Derwent Publications Ltd., London, GB; Class D25, AN 86-136703 XP002092499 & SU 1 189 877 A (CAUCASUS CHEM IND), 7 November 1985 (1985-11-07) abstract	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/21588

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0825250 A	25-02-1998	AU 3915997 A	06-03-1998
		CZ 9900561 A	13-10-1999
		NO 990801 A	08-04-1999
		PL 331712 A	02-08-1999
		WO 9807654 A	26-02-1998
WO 9633258 A	24-10-1996	AU 5690296 A	07-11-1996
US 4568477 A	04-02-1986	AT 30739 T	15-11-1987
		AU 559720 B	19-03-1987
		AU 3622384 A	13-06-1985
		BR 8406209 A	01-10-1985
		CA 1226783 A	15-09-1987
		DE 3467373 A	17-12-1987
		DK 580384 A	07-06-1985
		EP 0145091 A	19-06-1985
		FI 844747 A	07-06-1985
		GB 2150952 A,B	10-07-1985
		GB 2189267 A,B	21-10-1987
		GR 81175 A	13-03-1985
		IN 160861 A	08-08-1987
		JP 60139796 A	24-07-1985
		NO 844832 A,B,	07-06-1985
		NZ 210397 A	12-11-1986
		PH 21224 A	21-08-1987
		PT 79625 A,B	01-01-1985
		TR 21985 A	23-12-1985
		ZA 8409477 A	27-08-1986
EP 0431747 A	12-06-1991	AT 145424 T	15-12-1996
		CA 2030772 A	31-05-1991
		DE 69029190 D	02-01-1997
		DE 69029190 T	20-03-1997
		ES 2095240 T	16-02-1997
		JP 2866193 B	08-03-1999
		JP 3182600 A	08-08-1991
		US 5464552 A	07-11-1995
		WO 9112309 A	22-08-1991
AU 652736 B	08-09-1994		
AU 7187391 A	03-09-1991		
AU 643503 B	18-11-1993		
AU 7187491 A	03-09-1991		
CA 2073432 A	09-08-1991		
CA 2073563 A,C	09-08-1991		
DE 69003683 D	04-11-1993		
DE 69014207 D	22-12-1994		
DE 69014207 T	23-03-1995		
DE 69102059 D	23-06-1994		
DE 69102059 T	01-09-1994		
DE 69126203 D	26-06-1997		
WO 9104314 A	04-04-1991		
WO 9112308 A	22-08-1991		
EP 0491723 A	01-07-1992		
EP 0513136 A	19-11-1992		
EP 0514434 A	25-11-1992		
ES 2066216 T	01-03-1995		
ES 2053321 T	16-07-1994		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/21588

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9112309 A		JP 7072280 B	02-08-1995
		JP 5502907 T	20-05-1993
		JP 5502471 T	28-04-1993
		JP 7068549 B	26-07-1995
		JP 4506535 T	12-11-1992
		JP 7074360 B	09-08-1995
		JP 5500075 T	14-01-1993
		KR 9513224 B	26-10-1995
		KR 9508566 B	03-08-1995
		TR 27315 A	12-01-1995
		AU 636629 B	06-05-1993
		AU 5954190 A	06-02-1991
		AU 6177990 A	18-04-1991
		AU 646018 B	03-02-1994
		AU 7210991 A	03-09-1991
		CA 2062781 A,C	14-01-1991
		CA 2064900 A,C	14-03-1991
		CA 2073445 A	09-08-1991
		DE 69109273 D	01-06-1995
		DE 69109273 T	24-08-1995
		WO 9100902 A	24-01-1991
		WO 9112307 A	22-08-1991
		EP 0514422 A	25-11-1992
		ES 2072601 T	16-07-1995
		JP 7068542 B	26-07-1995
		JP 5502908 T	20-05-1993
		KR 9604489 B	06-04-1996
		KR 9513223 B	26-10-1995
TR 25827 A	01-09-1993		
US 4686063 A	11-08-1987	CA 1283255 A	23-04-1991
		EP 0260134 A	16-03-1988
		JP 2608898 B	14-05-1997
		JP 63132999 A	04-06-1988
		MX 165371 B	06-11-1992
US 4083795 A	11-04-1978	FR 2298599 A	20-08-1976
		FR 2360662 A	03-03-1978
		BE 837874 A	23-07-1976
		CA 1079602 A	17-06-1980
		CH 608829 A	31-01-1979
		DE 2602357 A	29-07-1976
		DK 28376 A	25-07-1976
		ES 444532 A	16-06-1978
		GB 1524301 A	13-09-1978
		GB 1524302 A	13-09-1978
		JP 51097608 A	27-08-1976
		LU 74226 A	31-12-1976
		NL 7600705 A	27-07-1976
		NO 760201 A	27-07-1976
		PT 64736 A,B	01-02-1976
SE 7600646 A	26-07-1976		
EP 0937772 A	25-08-1999	WO 9942552 A	26-08-1999
EP 0396341 A	07-11-1990	AU 643206 B	11-11-1993
		AU 5454990 A	01-11-1990
		CA 2015490 A	01-11-1990

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/21588

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0396341 A		CN 1046932 A JP 3000800 A MX 173060 B	14-11-1990 07-01-1991 31-01-1994
SU 1189877 A	07-11-1985	NONE	