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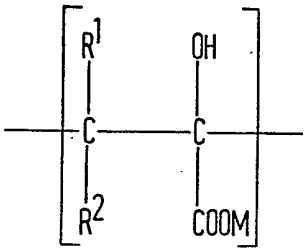
(54) **Stabilised bleaching and laundering composition**

(57) A particulate bleaching detergent composition is provided comprising (a) a bleaching agent comprising an inorganic peroxygen compound in combination with an activator therefore; (b) a polymer containing monomeric units of the formula



Wherein R^1 and R^2 each independently represent a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms, and M represents a hydrogen atom, or an alkali metal, an alkaline earth metal or ammonium cation; and (c) one or more surface active detergent compounds. The bleaching agent may be alkali metal perborate or peracetic acid.

GB 2 129 456 A

The chemical formulae appearing in the printed specification were submitted after the date of filing.

SPECIFICATION

Stabilized bleaching and laundering composition

The present invention relates, in general, to bleaching detergent compositions containing as a bleaching agent a peroxygen compound in combination with an organic activator therefore, and as a bleaching stabilizer a defined hydroxycarboxylic polymer, and the application of such compositions to laundering operations. More particularly, the present invention relates to particulate bleaching detergent compositions which provide enhanced bleaching performance concomitant with a significant improvement in the stability of the peroxyacid bleaching species in the wash solution owing to the presence of said hydroxycarboxylic polymer.

Bleaching compositions which release active oxygen in the wash solution are extensively described in the prior art and commonly used in laundering operations. In general, such bleaching compositions contain peroxygen compounds, such as, perborates, percarbonates, perphosphates and the like which promote the bleaching activity by forming hydrogen peroxide in aqueous solution. A major drawback attendant to the use of such peroxygen compounds is that they are not optimally effective at the relatively low washing temperatures employed in most household washing machines in the United States of America, i.e, temperatures in the range of 80°C to 130°F (27 to 54°C). By way of comparison, European wash temperatures are generally substantially higher extending over a range, typically from 90° to 200°F (32 to 93°C). However, even in Europe and those other countries which generally presently employ near boiling washing temperatures, there is a trend towards lower temperature laundering.

In an effort to enhance the bleaching activity of peroxygen bleaches, the prior art has employed materials called activators in combination with the peroxygen compounds, such activators usually consisting of carboxylic acid derivatives. It is generally believed that the interaction of the peroxygen compound and the activator results in the formation of a peroxyacid which is a more active bleaching species than hydrogen peroxide at lower temperatures. Numerous compounds have been proposed in the art as activators for peroxygen bleaches among which are included carboxylic acid anhydrides such as those disclosed in U.S. Patent Nos. 3,298,775; 3,338,839; and 3,532,634; carboxylic esters such as those disclosed in U.S. Patent No. 2,995,905; N-acyl compounds such as those described in U.S. Patent Nos. 3,912,648 and 3,919,102; cyanoamines such as described in U.S. Patent No. 4,199,466; and acyl sulphoamides such as disclosed in U.S. Patent No. 3,245,913.

The formation and stability of the peroxyacid bleaching species in bleach systems containing a peroxygen compound and an organic activator has been recognized as a problem in the prior art. U.S. Patent No. 4,255,452 to Leigh, for example, specifically address itself to the problem of avoiding the reaction of peroxyacid with peroxygen compound to form what the patent characterizes as "useless products, viz. the corresponding carboxylic acid, molecular oxygen and water". The patent states that such side-reaction is "doubly deleterious since peracid and percompound...are destroyed simultaneously". The patentee thereafter describes certain polyphosphonic acid compounds as chelating agents which are said to inhibit the above-described peroxyacid-consuming side reaction and provide an improved bleaching effect. In contrast with the use of these chelating agents, the patentee states that other more commonly known chelating agents, such as, ethylene diamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are substantially ineffective and do not provide improved bleaching effects. Accordingly, a disadvantage of the bleaching compositions of the Leigh patent is that they necessarily preclude the use of conventional sequestrants, many of which are less expensive and more readily available than the disclosed polyphosphonic acid compounds.

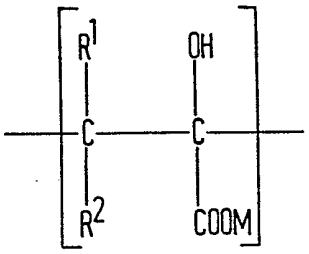
The influence of sodium silicate, a common ingredient in commercial detergent formulations, on the decomposition of peroxyacid in the wash and/or bleaching solution is disclosed in copending applications Serial Nos. 354,860 and 354,861, filed on March 4, 1982. The undesired loss of the peroxyacid bleaching species in the wash solution by reaction of peroxyacid with a peroxygen compound (or more specifically, hydrogen peroxide formed from such peroxygen compound) to form molecular oxygen is believed to be catalyzed by the presence of silicates in the wash solution. Conventional sequestrants are believed to be relatively ineffective in inhibiting the aforementioned silicate-catalyzed side reaction. Consequently, the compositions of the invention seek to provide a peroxyacid bleach species having substantially enhanced stability in the wash solution relative to that provided by conventional bleaching detergent compositions, particularly in the presence of silicates.

Hydroxycarboxylic polymers have been disclosed in the art as additives to laundry compositions, principally as sequestrants or builders in detergent compositions, or alternatively as materials which improve the shelf life of certain relatively unstable peroxygen compounds. Thus, for example, U.S. Patent No. 3,920,570 describes a process for sequestering metal ions from aqueous solution using an alkali metal or ammonium salt of a poly-alpha-hydroxyacrylic acid as a replacement for sodium tripolyphosphate in the detergent composition. U.S. Patent No. 4,329,244 discloses improving the storage stability of particles of alkali metal percarbonate or perphosphate by incorporating into such particles polylactones derived from defined alpha-hydroxyacylic acid polymers. However, the use of hydroxycarboxylic polymers for improving the stability of peroxyacid bleaching species in an aqueous wash solution has heretofore not been appreciated or disclosed.

The present invention provides a particulate bleaching detergent composition comprising:

(a) a bleaching agent comprising an inorganic peroxygen compound in combination with an activator therefore;

(b) from about 0.1 to about 5%, by weight, of a polymer containing monomeric units of the formula



wherein R^1 and R^2 represent hydrogen or an alkyl group containing from 1 to 3 carbon atoms, and M represents a hydrogen atom, or an alkali metal, an alkaline earth metal or ammonium cation: and

(c) at least one surface active agent selected from the group consisting of anionic, cationic, nonionic, ampholytic and zwitterionic detergents.

In accordance with the process of the invention, bleaching of stained and/or soiled materials is effected by contacting such materials with an aqueous solution of the above-defined bleaching detergent composition.

The present invention is predicated on the discovery that the undesired loss of peroxyacid in the aqueous wash solution by the reaction of peroxyacid with a peroxygen compound (or more specifically, hydrogen peroxide formed from the peroxygen compound) to form molecular oxygen is significantly minimized in bleaching systems or wash solutions containing relatively minor amounts of a hydroxycarboxylic polymer in accordance with the invention. Although the applicants do not wish to be bound to any particular theory of operation, it is believed that the presence of silicates (particularly, water-soluble silicates such as sodium silicate) in peroxygen compound/activator bleach systems catalyzes the aforementioned reaction of peroxyacid with hydrogen peroxide which results in the loss of active oxygen from the wash solution which would otherwise be available for bleaching, and that such silicate-catalyzed side reaction is substantially minimized in the presence of hydroxycarboxylic polymers as herein described. It has been recognized in the art that metal ions, such as, for example, ions of iron and copper serve to catalyze the decomposition of hydrogen peroxide and also the peroxyacid reaction of hydrogen peroxide. However, with regard to such metal ion catalysis, it has been surprisingly discovered that conventional sequestrants, such, EDTA or NTA, which the prior art has deemed to be ineffective for inhibiting the aforementioned peroxyacid-consuming side reaction (see, for example, the statement in column 4, lines 30—45 of U.S. Patent 4,225,452) can be incorporated into the compositions of the present invention to stabilize the peroxyacid bleaching species in solution.

The polymers used in the present invention are comprised of monomeric units of the formula described above. R^1 and R^2 which can be identical or different, are preferably both hydrogen, and M is preferably an alkali metal or an ammonium group, most preferably, sodium. Accordingly, in a preferred embodiment of the invention the polymer employed is sodium poly-alpha-hydroxyacrylate. The degree of polymerization of the polymers is generally determined by the limit compatible with the solubility of the compound in water.

The polymers are employed in the compositions of the invention in sufficient amounts to provide the desired degree of stabilization of the peroxyacid bleaching species in the wash solution. Generally the concentration of polymer in the particulate composition is from about 0.1 to about 5%, by weight of the composition, preferably from about 0.5 to about 3%, and most preferably from about 0.5 to about 2%, by weight.

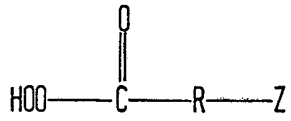
The hydroxycarboxylic polymers which are used in accordance with the present invention can be prepared by any of numerous processes described in the art. Thus, for example, salts of poly-alpha-hydroxy-acrylic acids of the type useful herein and their method of manufacture are extensively described in U.S. Patent Nos. 3,920,570; 3,994,969; 4,182,806; 4,005,136 and 4,107,411.

The peroxygen compounds useful in the present compositions include compounds that release hydrogen peroxide in aqueous media, such as, alkali metal perborates, e.g., sodium perborate and potassium perborate, alkali metal perphosphates and alkali metal percarbonates. The alkali metal perborates are usually preferred because of their commercial availability and relatively low cost.

Conventional activators such as those disclosed, for example, at column 4 of U.S. Patent 4,259,200 are suitable for use in conjunction with the aforementioned peroxygen compounds, such disclosure being incorporated herein by reference. The polyacylated amines are generally of special interest, tetraacetyl ethylene diamine (TAED) in particular, being a highly preferred activator. For purposes of storage stability, the TAED is preferably present in the compositions of the invention in the form of agglomerates, or coated granules which contain the TAED and a suitable carrier material such

as a mixture of sodium and potassium triphosphate. Such coated granules which contain the TAED granules are conveniently prepared by mixing finely divided particles of sodium triphosphate and TAED and then spraying on to such mixture an aqueous solution of potassium triphosphate using suitable granulation equipment such as a rotating pan granulator. A typical method of preparation for this type of coated TAED is described in U.S. Patent 4,283,302 to Foret, et al. granules of TAED have a preferred particle size distribution as follows: 0—20% greater than 150 micrometers; 10—100% greater than 100 microns but less than 150 microns; 0.50% less than 75 microns: and 0—20% less than 50 microns. Another particularly preferred particle size distribution is where the median particle size of TAED is 160 microns, i.e., 50% of the particles have a size greater than 160 microns. The aforementioned size distributions refer to the TAED present in the coated granules, and not to the coated granules themselves. The molar ratio of peroxygen compound to activator can vary widely depending upon the particular choice of peroxygen compound and activator. However, molar ratios of from about 0.5:1 to about 25:1 are generally suitable for providing satisfactory bleaching performance.

The bleaching agent may optionally also contain a peroxyacid compound in combination with the peroxygen compound and activator. Useful peroxyacid compounds include water-soluble peroxyacids and their water soluble salts. The peroxyacids can be characterized by the following general formula:



wherein R represents an alkyl or alkylene group containing from 1 to about 20 carbon atoms, or a phenylene group, and Z is one or more groups selected from among hydrogen, halogen, alkyl, aryl and anionic groups.

The organic peroxyacids and the salts thereof can contain from about 1 to about 4, preferably one 1 or 2, peroxy groups and can be aliphatic or aromatic. The preferred aliphatic peroxyacids include diperoxyazelaic acid, diperoxydodecanedioic acid and monoperoxysuccinic acid. Among the aromatic peroxyacid compounds useful herein, monoperoxyphthalic acid (MPPA), particularly the magnesium salt thereof, and diperoxyterephthalic acid are especially preferred. A detailed description of the production of MPPA and its magnesium salt is set forth on pages 7—10, inclusive, of European Patent Publication 0,027,693, published April 29, 1981, the aforementioned pages 7—10 being incorporated herein by reference.

In a preferred embodiment of the invention, the bleaching compositions described herein additionally contain a non-polymeric sequestering agent to enhance the stability of the peroxyacid bleaching compound solution by inhibiting its reaction with peroxide in the presence of metal ions. The term "sequestering agent" as used herein refers to organic compounds which are able to form a complex with Cu^{2+} ions, such that the stability constant (pK) of the complexation is equal to or greater than 6, at 25°C, in water, at an ionic strength of 0.1 mole/litre, pK being conventionally defined by the formula: pK=—log K where K represents the equilibrium constant. Thus, for example, the pK values for complexation of copper ion with NTA and EDTA at the stated conditions are 12.7 and 18.8, respectively. The sequestering agents employed herein thus exclude inorganic compounds ordinarily used in detergent formulations as builder salts. Accordingly, suitable sequestering agents include the sodium salts of nitrilotriacetic acid (NTA): ethylene diamine tetraacetic acid (EDTA); diethylene triamine pentaacetic acid (DETPA); diethylene triamine pentamethylene phosphonic acid (DTPMP); and ethylene diamine tetramethylene phosphonic acid (EDITEMPA). EDTA is especially preferred for use in the present compositions.

The compositions of the present invention contain one or more surface active agents selected from the group of anionic, nonionic, cationic, ampholytic and zwitterionic detergents.

Among the anionic surface active agents useful in the present invention are those surface active compounds which contain an organic hydrophobic group containing from about 8 to 26 carbon atoms and preferably from about 10 to 18 carbon atoms in their molecular structure and at least one water-solubilizing group selected from the group consisting of sulphonate, sulphate, carboxylate, phosphonate and phosphate so as to form a water-soluble detergent.

Examples of suitable anionic detergents include soaps, such as the water-soluble salts (e.g., the sodium, potassium, ammonium and alkanolammonium salts) of higher fatty acids or resin salts containing from about 8 to 20 carbon atoms and preferably 10 to 18 carbon atoms. Suitable fatty acids can be obtained from oils and waxes of animal or vegetable origin, for example, tallow, grease, coconut oil and mixtures thereof. Particularly useful are the sodium and potassium salts of the fatty acid mixtures derived from coconut oil and tallow, for example, sodium coconut soap and potassium tallow soap.

The anionic class of detergents also includes the water-soluble sulphated and sulphonated detergents having an alkyl radical containing from about 8 to 26, and preferably from about 12 to 22 carbon atoms. (The term "alkyl" includes the higher acyl radicals). Examples of the sulphonated anionic detergents are the higher alkyl mononuclear aromatic sulphonates such as the higher alkyl benzene

sulphonates containing from about 10 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, such as, for example, the sodium, potassium and ammonium salts of higher alkyl benzene sulphonates, higher alkyl toluene sulphonates and higher alkyl phenol sulphonates.

Other suitable anionic detergents are the olefin sulphonates including long chain alkene sulphonates, long chain hydroxyalkane sulphonates or mixtures of alkene sulphonates and hydroxyalkane sulphonates. The olefin sulphonate detergents may be prepared in a conventional manner by the reaction of sulphur trioxide with long chain olefins containing from about 8 to 25, and preferably from about 12 to 21 carbon atoms, such olefins having the formula $RCH{=}CHR^1$ wherein R is a higher alkyl group of from about 6 to 23 carbons and R^1 is an alkyl group containing from about 1 to 17 carbon atoms, or hydrogen to form a mixture of sultones and alkene sulphonic acids which is then treated to convert the sultones to sulphonates. Other examples of sulphate or sulphonate detergents are paraffin sulphonates containing from about 10 to 20 carbon atoms, and preferably from about 15 to 20 carbon atoms. The primary paraffin sulphonates are made by reacting long chain alpha olefins and bisulphites. Paraffin sulphonates having the sulphonate group distributed along the paraffin chain are shown in U.S. Nos. 2,503,280; 2,507,088; 3,260,741; 3,372,188 and German Patent No. 735,096. Other useful sulphate and sulphonate detergents include sodium and potassium sulphates of higher alcohols containing from about 8 to 18 carbon atoms, such as, for example, sodium lauryl sulphate and sodium and potassium salts of alpha-sulphofatty acid esters containing about 10 to 20 carbon atoms in the acyl group, for example, methyl alpha-sulphomyristate and methyl alpha-sulphotallowate, ammonium sulphates or mono- or di-glycerides of higher (C_{10}—C_{18}) fatty acids, for example, stearic monoglyceride monosulphate; sodium and alkylol ammonium salts of alkyl polyethenoxy ether sulphates produced by condensing 1 to 5 moles of ethylene oxide with 1 mole of higher (C_8—C_{18}) alcohol; sodium higher alkyl (C_{10}—C_{18}) glyceryl ether sulphonates; and sodium or potassium alkyl phenol polyethenoxy ether sulphates with about 1 to 6 oxyethylene groups per molecule and in which the alkyl radicals contain about 8 to 12 atoms.

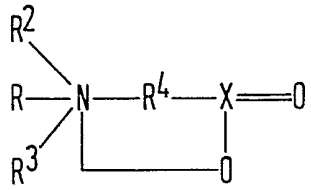
The most highly preferred water-soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono, di and tri-ethanolamine), alkali metal (such as, sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of the higher alkyl benzene sulphonates, olefin sulphonates and higher alkyl sulphates. Among the above-listed anionics, the most preferred are the sodium linear alkyl benzene sulphonates (LABS).

The nonionic synthetic organic detergents are characterized by the presence of an organic hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic or alkyl aromatic hydrophobic compound with ethylene oxide (hydrophilic in nature). Practically any hydrophobic compound having a carboxy, hydroxy, amido or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a nonionic detergent. The length of the hydrophilic or polyoxyethylene chain can be readily adjusted to achieve the desired balance between the hydrophobic and hydrophilic groups.

The nonionic detergents include the polyethylene oxide of 1 mole of alkylphenol containing from about 6 to 12 carbon atoms in a straight or branched chain configuration with about 5 to 30 moles of ethylene oxide. Examples of the aforementioned condensates include nonyl phenol condensed with 9 moles of ethylene oxide; dodecyl phenol condensed with 15 moles of ethylene oxide; and dinonyl phenol condensed with 15 moles of ethylene oxide. Condensation products of the corresponding alkyl thiophenols with 5 to 30 moles of ethylene oxide are also suitable.

Of the above-described types of nonionic surfactants, those of the ethoxylated alcohol type are preferred. Particularly preferred nonionic surfactants include the condensation product of coconut fatty alcohol, the condensation product of tallow fatty alcohol with about 11 moles of ethylene oxide per mole of tallow fatty alcohol, the condensation product of a secondary fatty alcohol containing about 11—15 carbon atoms with about 9 moles of ethylene oxide per mole of fatty alcohol and condensation products of more or less branched primary alcohols, whose branching is predominantly 2-methyl, with from about 4 to 12 moles of ethylene oxide.

Zwitterionic detergents such as the betaines and sulphobetaines having the following formula are also useful:



wherein R represents an alkyl group containing from about 8 to 18 carbon atoms, R^2 and R^3 are each an alkylene or hydroxyalkylene group containing about 1 to 4 carbon atoms, R^4 represents an alkylene or hydroxyalkylene group containing 1 to 4 carbon atoms, and X is C or S:O. The alkyl group can contain one or more intermediate linkages such as amido, ether, or polyether linkages or non-

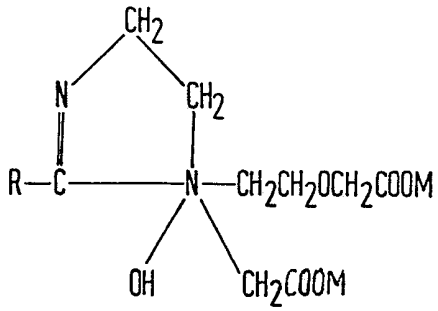
functional substituents such as hydroxyl or halogen which do not substantially affect the hydrophobic character of the group. When X represents a C atom, the detergent is called a betaine; and when X represents an S:O group, the detergent is called a sulphobetaine or sultaine.

Cationic surface active agents may also be employed. They comprise surface active detergent compounds which contain an organic hydrophobic group which forms part of a cation when the compound is dissolved in water, and an anionic group. Typical cationic surface active agents are amine and quaternary ammonium compounds.

Examples of suitable synthetic cationic detergents include: normal primary amines of the formula RNH_2 wherein R represents an alkyl group containing from about 12 to 15 atoms; diamines having the formula $RNHC_2H_4NH_2$ wherein R represents an alkyl group containing from about 12 to 22 carbon atoms, such as N-2-aminoethyl-stearyl amine and N-2-aminoethyl myristyl amine; amide-linked amines such as those having the formula $R^1CONHC_2H_4NH_2$ wherein R^1 represents an alkyl group containing about 8 to 20 carbon atoms, such as N-2-aminoethylstearyl amide and N-amino ethylmyristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom is an alkyl group containing about 8 to 22 carbon atoms and three of the groups linked to the nitrogen atom are alkyl groups which contain 1 to 3 carbon atoms, including alkyl groups bearing inert substituents, such as phenyl groups, and there is present an anion such as halogen, acetate, methosulphate, etc. The alkyl group may contain intermediate linkages such as amide which do not substantially affect the hydrophobic character of the group, for example, stearyl amido propyl quaternary ammonium chloride. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl-ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, trimethyl-stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, dimethyl-ethyl-lauryl ammonium chloride, dimethyl-propyl-myristyl ammonium chloride, and the corresponding methosulphates and acetates.

Ampholytic detergents are also suitable for use in the invention.

Ampholytic detergents are well known in the art and many operable detergents of this class are disclosed by A. M. Schwartz, J. W. Perry and J. Birch in "Surface Active Agents and Detergents", Interscience Publishers, New York, 1958, vol. 2. Examples of suitable amphoteric detergents include: alkyl betaiminodipropionates, $RN(C_2H_4COOM)_2$; alkyl beta-amino propionates, $RN(H)C_2H_4COOM$; and long chain imidazole derivatives having the general formula:



wherein in each of the above formulae R represents an acyclic hydrophobic group containing from about 8 to 18 carbon atoms and M is a cation to neutralize the charge of the anion. Specific operable amphoteric detergents include the disodium salt of undecylcycloimidinium-ethoxyethionic acid-2-ethionic acid, dodecyl beta alanine, and the inner salt of trimethylamine lauric acid.

The bleaching detergent compositions of the invention optionally contain a detergent builder of the type commonly used in detergent formulations. Useful builders include any of the conventional inorganic water-soluble builder salts, such as, for example, water-soluble salts of phosphates, pyrophosphates, orthophosphates, polyphosphates, silicates, carbonates, polyphosphonates, polyhydroxysulphonates, polyacetates, carboxylates, polycarboxylates, succinates and the like.

Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, pyrophosphates and hexametaphosphates. The organic polyphosphonates specifically include, for example, the sodium and potassium salts of ethane 1-hydroxy-1,1,2-triphosphonic acid. Examples of these and other phosphorous builder compounds are disclosed in U.S. Patent Nos. 3,213,030; 3,422,021; 3,422,137 and 3,400,176. Pentasodium tripolyphosphate and tetrasodium pyrophosphate are especially preferred water-soluble inorganic builders.

Specific examples of non-phosphorous inorganic builders include water-soluble inorganic carbonate, bicarbonate and silicate salts. The alkali metal, for example, sodium and potassium, carbonates, bicarbonates and silicates are particularly useful herein.

Water-soluble organic builders are also useful. For example, the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxysulphonates are useful builders for the compositions and processes of the invention. Specific examples of polyacetate and polycarboxylate builders include sodium, potassium, lithium, ammonium and substituted

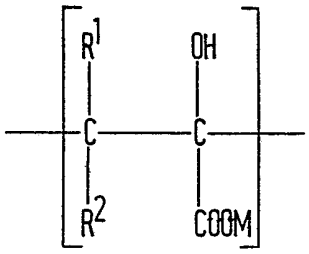
ammonium salts of ethylene diaminetetracetic acid, nitrilotriacetic acid, benzene polycarboxylic (i.e. penta-and tetra-) acids, carboxymethoxysuccinic acid and citric acid.

Water-insoluble builders may also be used, particularly, the complex silicates and more particularly, the complex sodium alumino silicates such as, zeolites, e.g., zeolite 4A, a type of zeolite molecule wherein the univalent cation is sodium and the pore size is about 4 Angstroms. The preparation of such type of zeolite is described in U.S. Patent 3,114,603. The zeolites may be amorphous or crystalline and have water of hydration as known in the art.

The use of inert, water-soluble filler salts is desirable in the compositions of the invention. A preferred filler salt is an alkali metal sulphate, such as, potassium or sodium sulphate, the latter being especially preferred.

Various adjuvants may be included in the bleaching detergent compositions of the invention. For example, colourants, e.g., pigments and dyes; antiredeposition agents, such as, carboxymethylcellulose; optical brighteners, such as, anionic, cationic and nonionic brighteners; foam stabilizers, such as alkanolamides; proteolytic enzymes; perfumes and the like are all well known in the fabric washing art for use in detergent compositions.

A preferred composition in accordance with the invention typically comprises (a) from about 2 to 50%, by weight, of a bleaching agent comprising a peroxygen compound in combination with an activator therefore: (B) from about 0.1 to about 5%, by weight, of a polymer containing monomeric units of the formula



wherein R^1 and R^2 represent a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms, and M represents a hydrogen atom, or an alkali metal, an alkaline earth metal or ammonium cation; (c) from about 3 to about 50%, by weight, of a detergent surface active agent; (d) from about 1 to about 60%, by weight, of a detergent builder salt; and (e) from about 0 to about 10% by weight, of a non-polymeric sequestering agent. The balance of the composition will predominantly comprise water, filler salts, such as sodium sulphate, and minor additives selected from among the various adjuvants described above.

The bleaching detergent compositions of the invention are particulate compositions which may be produced by spray-drying methods of manufacture as well as by methods of dry-blending or agglomeration of the individual components. The compositions are preferably prepared by spray drying an aqueous slurry of the non-heat-sensitive components to form the spray-dried particles, followed by admixing such particles with the heat-sensitive components, such as the bleaching agent (i.e., the peroxygen compound and organic activator) and adjuvants such as perfume and enzymes. Mixing is conveniently effected in apparatus such as a rotary drum. The particular poly-alpha-hydroxyacrylate to be used in the bleaching detergent compositions is conveniently formed by introducing a precurser thereof in the form of a polylactone into the crutcher slurry where it is hydrolyzed and then neutralized (generally with NaOH) to form the sodium poly-alpha-hydroxyacrylate as a component of the spray-dried detergent particles.

The bleaching detergent compositions of the invention are added to the wash solution in an amount sufficient to provide from about 3 to about 100 parts of active oxygen per million parts of solution, a concentration of from about 5 to about 40 ppm being generally preferred.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying Examples.

Example 1

A preferred bleaching detergent composition is prepared having the composition set out in Table 1 below:

Table 1

Component	*Weight percent*
Sodium linear C_{10}—C_{13} alkyl benzene sulphonate	5
Ethoxylated C_{11}—C_{18} primary alcohol (11 moles EO per mole alcohol)	3
Soap (sodium salt of C_{12}—C_{22} carboxylic acid)	5
Pentasodium tripolyphosphate (TPP)	40
EDTA	0.5
TAED	2.3
Sodium silicate	3
Sodium PLAC(1)	1
Sodium perborate tetrahydrate	13.2
Optical brightener and pigment	0.2
Perfume	0.3
Proteolytic enzymes	0.3
Sodium sulphate and water	balance

Note on Table 1

(1) A designation used herein for sodium poly-alpha-hydroxyacrylate.

The foregoing product is produced by spray drying an aqueous slurry containing 60%, by weight, of a mixture containing all of the above components except the enzyme, perfume, TAED and sodium perborate; the sodium PLAC is not introduced as such into the aqueous slurry, but rather, a precursor thereof, the polylactone corresponding to the product of poly-hydroxyacrylic acid is introduced into the crutcher where it hydrolyzes and is neutralized to form the sodium PLAC in the spray-dried powder. The resultant particulate spray dried product has a particle size in the range of 14 mesh to 270 mesh (US. Series which have openings 1410 microns and 53 microns across). The spray dried product is then mixed in a rotary drum with the appropriate amounts of sodium perborate of similar mesh size, TAED, enzyme and perfume to yield a particulate product of the foregoing composition having a moisture content of approximately 13%, by weight.

The above-described product is used to wash soiled fabrics by hand-washing as well as in a washing machine, and good laundering and bleaching performance is obtained for both methods of laundering.

Other satisfactory products can be obtained by varying the concentrations of the following principal components in the above-described composition as shown in Table 2 below.

Table 2

Composition	*Weight percent*
Alkyl benzene sulphonate	4—12
Ethoxylated alcohol	1—6
Soap	1—10
TPP	15—50
Enzymes	0.1—1
EDTA	0.1—2
TAED	1—10
Sodium perborate	5—20
Sodium PLAC	0.1—5

For highly concentrated heavy duty detergent powder, the alkyl benzene sulphonate and the soap components in the above-described composition may be deleted, and the ethoxylated alcohol content may be increased to an upper limit of 20%.

Examples 2 to 7

Bleaching tests are carried out as described below comparing the bleaching performance of bleaching detergent compositions which are similar except for the amount of sodium PLAC in the composition. The compositions are formulated by post-adding to a spray-dried detergent composition, granules of sodium perborate tetrahydrate and tetra acetyl ethylene diamine (TAED) to form the bleaching detergent compositions shown in Table 3 below. The numbers indicated in the Table 3 represent the percentage of each component, by weight, in the composition.

Table 3

Component	Example 2	3	4	5	6	7
	Composition					
Sodium linear C_{10}—C_{13} alkyl benzene sulphonate	6%	6%	6%	6%	6%	6%
Ethoxylated C_{11}—C_{18} primary alcohol (11 moles) EO per mole alcohol	3	3	3	3	3	3
Soap (Sodium salt of C_{12}—C_{22} carboxylic acid)	4	4	4	4	4	4
Sodium silicate ($1Na_2O:2SiO_2$)	4	4	4	4	4	4
Sodium PLAC	0.0	0.6	1.2	1.8	2.4	3.0
Pentasodium tripolyphosphate (TPP)	32	32	32	32	32	32
Optical brightener (stilbene)	0.2	0.2	0.2	0.2	0.2	0.2
Sodium perborate tetrahydrate	4.5	4.5	4.5	4.5	4.5	4.5
TAED	3.8	3.8	3.8	3.8	3.8	3.8
Sodium sulphate and water	balance					

Test procedure

Bleaching tests are carried out in an Ahiba apparatus at maximum temperatures of 60°C and 80°C, respectively, as hereinafter described. 600 ml of tap water having a water hardness of about 320 ppm, as calcium carbonate, are introduced into each of six buckets of the Ahiba. Six cotton swatches (8 cm×12 cm) soiled with immedial black are introduced into each bucket, the initial reflectance of each swatch being measured with a Gardner XL 20 reflectometer.

Six grams of each of the compositions of Examples 2 to 7 (described in Table 3) are introduced separately into the six buckets of the Ahiba, a different composition being introduced into each bucket. The bleaching detergent compositions are thoroughly mixed in each bucket with a blender-type apparatus and the wash cycle thereafter initiated. The bath temperature, initially at 30°C, is allowed to rise about 1° Centigrade per minute until the maximum test temperature (60° or 80°C) is reached, such maximum temperature being then maintained for about 15 minutes. The buckets are then removed and each swatch washed twice with cold water and dried.

The final reflectance of the swatches are measured and the difference (ΔRd) between the final and initial reflectance values is determined. An average value of ΔRd for the six swatches in each bucket is then calculated. The results of the bleaching tests are set forth below in Table 4, the values of ΔRd being provided as an average value for the particular composition and test indicated.

Table 4
ΔRd (Average)

Soil: Immedial black

Example	2	3	4	5	6	7
	0%	0.6%	1.2%	1.8%	2.4%	3.0%
Test temperature	Sodium PLAC	Sodium PLAC	Sodium PLAC	Sodium PLAC	Sodium PLAC	Sodium PLAC
60°C	6.2	6.3	6.7	6.9	7.3	7.2
80°C	10.5	10.9	11.2	11.8	12.4	12.8

As indicated in Table 4, the greater the amount of sodium PLAC in the detergent composition, the better the resulting bleaching performance.

Examples 8—10

The concentration of peroxyacid (peracetic acid) in solution and the total active oxygen concentration are determined as a function of time for wash solutions containing each of compositions 8, 9 and 10 described in Table 5 below. The test procedure is as follows:

One litre of tap water is introduced into a two litre beaker and then heated to a constant temperature of 60°C in a water bath. Ten grams of the particular composition being tested are added to the beaker (time=0) with thorough mixing to form a uniform wash solution. After given periods of time (3, 7, 13, 20 and 30 minutes), two 50 ml aliquots are withdrawn from the wash solution and the total active oxygen concentration and the peracetic acid concentration are determined by the procedure set forth below.

Determination of total active O_2 concentration

One of the aforementioned 50 ml aliquots is poured into a 300 ml Erlenmeyer flask fitted with a ground stopper and containing 15 ml of a sulphuric/molybdate mixture, the latter mixture having been prepared in large-scale amounts by dissolving 0.18 grams of ammonium molybdate in 750 ml of deionized water and then adding thereto 320 ml of sulphuric acid (about 36N) with stirring. The solution in the Erlenmeyer flask is thoroughly mixed and 5 ml of a 10% potassium iodide solution in deionized water is then added thereto. The Erlenmeyer flask is sealed with a stopper, agitated and then allowed to stand in a dark place for seven minutes. The solution in the flask is then titrated with a

solution of 0.1N sodium thiosulphate in deionized water. The volume of thiosulphate required, in ml, is equal to the total active oxygen concentration, in millimole/litre, in the wash solution. The test results for the three compositions tested are shown in Table 6 below.

Determination of peracetic acid concentration

A 50 ml aliquot is poured into a 400 ml beaker containing about 100 grams of crushed ice while stirring, followed by the addition of 10 ml of acetic acid (analytical grade) and 5 ml of the aforementioned 10% aqueous potassium iodide solution, the mixture being thoroughly stirred after each such addition. The resulting solution is then immediately titrated with the aforementioned 0.1N thiosulphate solution until the yellow-brown colour disappears. The volume of thiosulphate required, in ml, is equal to the concentration of peroxyacid in millimole/litre, in the wash solution. The test results are shown in Table 7.

Table 5

	Example		
	8	*9*	*10*
Component	*Composition*		
Sodium linear C_{10}—C_{13} alkyl benzene sulphonate	6.0%	6.0%	6.0%
Ethoxylated C_{11}—C_{18} primary alcohol (11 mole EO per mole alcohol)	3.0	3.0	3.0
Soap (sodium salt of C_{12}—C_{22} carboxylic acid)	4.0	4.0	4.0
Pentasodium tripolyphosphate (TPP)	32.0	32.0	32.0
Sodium disilicate	4.0	4.0	4.0
Sodium PLAC	0.0	1.0	3.0
EDTA	0.0	0.50	0.0
TAED	5.0	5.0	5.0
Sodium perborate tetrahydrate	6.0	6.0	6.0
Optical brighteners	0.2	0.2	0.2
Sodium sulphate and water		balance	

The numbers indicated above in the Table represent the percentage of each component, by weight, in the composition.

Table 6

Total active oxygen in wash solution (mmol/litre)

	Example		
	8	*9*	*10*
	Without sodium	*With 1% sodium*	*With 3% sodium*
Time (min)	*PLAC*	*PLAC*	*PLAC*
3	2.75	3.2	3.4
7	2.0	2.8	3.3
13	1.45	2.2	3.15
20	1.0	1.8	2.9
30	0.5	1.3	2.3

Table 7

Peracetic acid concentration in wash solution (mmol/litre)

	Example		
Time (min)	*8*	*9*	*10*
3	2.4	2.8	2.9
7	1.9	2.5	2.7
13	1.30	2.0	2.3
20	0.9	1.5	1.8
30	0.40	1.0	1.1

As is evident from Table 6 and 7, the compositions containing sodium PLAC are substantially more stable and are characterized by a far slower loss of the peroxyacid bleaching species from solution, as well as a greater availability of total active oxygen relative to the corresponding PLAC-free composition of Example 8.

Example 11

This example compares the stabilizing properties of EDTA and sodium PLAC with regard to the active oxygen measured in the wash solution. The test procedure followed is the same as that described in Example 3. The tested compositions include the composition of Example 9 containing sodium PLAC and EDTA and the composition of Example 11 containing EDTA but no sodium PLAC,

both of said compositions being set forth below in Table 8. A comparison of the compositions of Examples 9 and 11 with the composition of Example 8 (described in Table 5) which contains no sodium PLAC or other sequestrant is shown in Table 9.

Table 8

Component	*Example 11* Composition	*9*
Sodium linear C_{10}—C_{13} benzene sulphonate	6.0%	6.0%
Ethoxylated C_{11}—C_{18} primary alcohol (11 mole EO per mole alcohol)	3.0	3.0
Soap (Sodium salt of C_{12}—C_{22} carboxylic acid)	4.0	4.0
Pentasodium tripolyphosphate (TPP)	32.0	32.0
Sodium disilicate	4.0	4.0
EDTA	1.0	0.5
TAED	5.0	5.0
Sodium perborate tetrahydrate	6.0	6.0
Optical brighteners	0.2	0.2
Sodium sulphate and water	balance	

Table 9

Total active oxygen in wash solution (mmol/litre)

Example	*8*	*11*	*9*
Time (min.)	*No sequestrant*	*With 1% EDTA*	*With 1% PLAC and 0.5% EDTA*
3	2.8	2.9	3.2
7	2.0	2.3	2.8
13	1.5	1.7	2.2
20	1.0	1.3	1.8

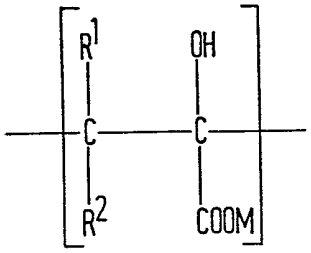
As shown in Table 9, the presence of sodium PLAC in the composition of Example 9 produced a significant improvement in the stability of the bleaching species (i.e. active oxygen), particularly after longer periods of time, relative to the compositions of Examples 8 and 11.

Claims

1. A particulate bleaching detergent composition comprising:

(a) a bleaching agent comprising an inorganic peroxygen compound in combination with an activator therefore:

(b) from about 0.1 to about 5%, by weight based on the weight of the said detergent composition of a polymer containing monomeric units of the formula



wherein R^1 and R^2 each independently represent a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms, and M represents a hydrogen atom, or an alkali metal, an alkaline earth metal or ammonium cation; and

(c) at least one surface active agent selected from the group consisting of anionic, cationic, nonionic, ampholytic and zwitterionic detergents.

2. A composition as claimed in Claim 1 in which the said bleaching agent also contains a peroxyacid compound.

3. A composition as claimed in Claim 1 or Claim 2 in which the polymer is an alkali metal poly-alpha-hydroxyacrylate.

4. A composition as claimed in Claim 3 in which the concentration of polymer is from about 0.5 to about 3%, by weight.

5. A composition as claimed in anyone of Claims 1 to 4 also containing a detergent builder salt.

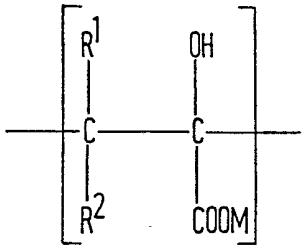
6. A composition as claimed in any one of Claims 1 to 5 in which the said surface active agent comprises an anionic detergent.

7. A composition as claimed in Claim 6 in which the said anionic detergent is a linear alkyl benzene sulphonate.

8. A particulate bleaching detergent composition comprising:

(a) from about 2 to about 50% by weight of a bleaching agent comprising an inorganic peroxygen compound in combination with an activator therefore;

(b) from about 0.1 to about 5%, by weight, of a polymer containing monomer units of the formula



wherein R^1 and R^2 each independently represent a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms, and M represents a hydrogen atom or an alkali metal, an alkaline earth metal or ammonium cation;

(c) from about 3 to 50% by weight, of at least one detergent surface active agent selected from the group consisting of anionic, cationic, nonionic, ampholytic and zwitterionic detergents.

9. A composition as claimed in any one of Claims 1 to 8 in which the said bleaching agent comprises an alkali metal perborate in combination with tetraacetyl ethylene diamine (TAED).

10. A composition as claimed in Claim 9 in which the said TAED is contained in granules in combination with a mixture of sodium and potassium triphosphate.

11. A composition as claimed in any one of Claims 1 to 10 in which the said TAED has the following particle size distribution; 0—20% greater than 150 micrometers; 10—100% greater than 100 microns but less than 150 microns; 0—50% less than 75 microns and 0—20% less than 50 microns.

12. A composition as claimed in any one of Claims 1 to 11 in which about 50% of the particles of TAED have a size greater than 160 microns.

13. A composition as claimed in any one of Claims 1 to 12 also containing a non-polymeric sequestering agent.

14. A composition as claimed in Claim 13 in which the said sequestering agent comprises ethylene diamine tetraacetic acid (EDTA).

15. A composition as claimed in Claim 1 substantially as specifically described herein with reference to Examples 1 to 7, 9 and 10.

16. A process for bleaching which comprises contacting the stained and/or soiled material to be bleached with an aqueous solution of a particulate bleaching detergent composition as claimed in any one of Claims 1 to 15.

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