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(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
Cincinnati, Ohio 45202 (US)

(72) Inventors:

- **Baillely, Gerard Marcel**
Gosforth, Newcastle upon Tyne NE3 5LS (GB)

- **Guedira, Nour-Eddine**

Jesmond, Newcastle upon Tyne NE2 2TA (GB)

- **Hall, Robin Gibson**

Newcastle upon Tyne NE1 4XB (GB)

(74) Representative: **Gibson, Tony Nicholas et al**
Procter & Gamble Limited,
Whitley Road
Longbenton,
Newcastle upon Tyne NE12 9TS (GB)

(54) **Bleaching compositions**

(57) There is provided a bleaching composition containing a clay mineral compound and an oxygen-releasing bleach system comprising a hydrogen peroxide source and a peroxyacid bleach precursor compound selected from the group consisting of

(i) a perbenzoic acid, or non-cationic substituted derivative thereof, precursor compound;

(ii) a cationic peroxyacid bleach precursor compound;

and any mixtures thereof wherein the weight ratio of clay mineral compound to peroxyacid bleach precursor compound is from 10:1 to 1:5. The composition preferably contains additionally a clay flocculating agent. The composition is useful in the bleaching of stains from stained coloured fabrics. The clay mineral compound acts to inhibit the fading of the colour of said fabrics during the stain bleaching process.

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Description

This invention relates to bleaching compositions containing a source of peroxyacid bleach, a clay mineral compound and preferably a clay flocculating agent.

The satisfactory removal of bleachable soils/stains such as tea, fruit juice and coloured vegetable soils from stained fabrics is a particular challenge to the formulator of a bleaching composition for use in a laundry washing method.

Traditionally, the removal of such bleachable stains has been enabled by the use of bleach components such as oxygen bleaches, including hydrogen peroxide and organic peroxyacids. The organic peroxyacids are often obtained by the in situ perhydrolysis reaction between hydrogen peroxide and an organic peroxyacid bleach precursor.

A problem which may be encountered with certain peroxyacid bleaches in laundry washing methods under certain wash conditions is the potential for these peroxyacid bleaches to induce fading of any coloured dyes on the fabrics. Perbenzoic acid, and substituted derivatives thereof, and cationic peroxyacids have been found to be particularly troublesome.

The detergent formulator thus faces the dual challenge of formulating a product which maximises bleachable soil/stain removal but minimises the occurrence of any unwelcome fabric colour fading effects of the bleach.

The Applicants have found that the problem of fabric colour fading can be reduced by the inclusion of a clay mineral compound into bleaching compositions containing an oxygen releasing bleaching system. Clays having a largest particle size dimension of from 0.01 mm to 800 nm have been found to be particularly effective in reducing the colour fading problem. The reduction in colour fading is particularly enhanced by the inclusion additionally of a clay flocculating agent into the composition.

The inclusion of the clay mineral compound and of any clay flocculating agent has been found not to significantly compromise the bleachable stain removal ability of the bleaching composition.

Laundry compositions including clay mineral compounds and clay flocculating agents for the purpose of providing fabric softening have previously been disclosed in European Patent Applications No.s EP-A-299,575 and EP-A-313,146. Whilst these documents disclose that the compositions may contain optional bleaching agents they contain no disclosure relating to any of perbenzoic acid, or non-cationic substituted derivatives thereof, or cationic peroxyacid precursor compounds. Furthermore, they provide no teaching of the use of clay mineral compounds, particularly in combination with clay flocculating agents to inhibit the fading of coloured fabrics.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

It is an object of the present invention to provide compositions suitable for use in laundry washing methods having good bleachable stain removal wherein the compositions have less propensity to cause fabric colour fading.

Summary of the Invention

According to the present invention there is provided a bleaching composition containing

(a) an oxygen-releasing bleach system comprising a hydrogen peroxide source and a peroxyacid bleach precursor compound selected from the group consisting of

(i) a perbenzoic and or non-cationic substituted derivative thereof, precursor compound;

(ii) a cationic peroxyacid bleach precursor compound;

and any mixtures of (i) to (ii); and

(b) a clay mineral compound;

wherein the weight ratio of clay mineral compound to peroxyacid bleach precursor compound is from 10:1 to 1:5.

Most preferably, the compositions contain a clay flocculating agent.

Preferably, the clay mineral compound is a smectite clay compound present at a level of from 0.05% to 40% by weight of the composition.

Preferably, the clay flocculating agent, where present, is an organic polymeric material having an average weight of from 100,000 to 10,000,000, preferably present at a level of from 0.005% to 10% by weight of the composition.

Preferably, the weight ratio of clay mineral compound to clay flocculating agent where present is from 300: 1 to 5:1.

According to another aspect of the present invention there is provided the use, in a method for washing stained coloured fabrics, of a bleaching composition containing an oxygen-releasing bleach system, preferably comprising a hydrogen peroxide source and a peroxyacid bleach precursor compound, wherein said composition contains a clay mineral compound and preferably a clay flocculating agent to inhibit the fading of the colour of said fabrics.

Oxygen-releasing bleaching system

An essential feature of the invention is an oxygen-releasing bleaching system containing a hydrogen peroxide source and a peroxyacid bleach precursor compound. The production of the peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches.

The peroxyacid bleach precursor is preferably selected from N-acylated lactam bleach precursors, perbenzoic acid precursors, perbenzoic acid derivative precursors and cationic peroxyacid precursors, or mixtures thereof.

Inorganic perhydrate bleaches

The compositions in accord with the invention include a hydrogen peroxide source. Suitable hydrogen peroxide sources include the inorganic perhydrate salts.

The inorganic perhydrate salts are normally incorporated in the form of the sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $\text{NaBO}_2\text{H}_2\text{O}_2$ or the tetrahydrate $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.

Sodium percarbonate, which is a preferred perhydrate for inclusion in compositions in accordance with the invention, is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in product stability.

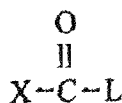
A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interlox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $\text{Na}_2\text{SO}_4 \cdot n \cdot \text{Na}_2\text{CO}_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Other coatings which contain silicate (alone or with borate salts or boric acids or other inorganics), waxes, oils, fatty soaps can also be used advantageously within the present invention.

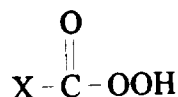
Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Peroxyacid bleach precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group, such that on perhydrolysis the structure of the peroxyacid produced is



The compositions of the invention contain a peroxyacid bleach precursor compound which on perhydrolysis provides a peroxyacid which is

(i) a perbenzoic acid, or non-cationic substituted derivative thereof; or

(ii) a cationic peroxyacid.

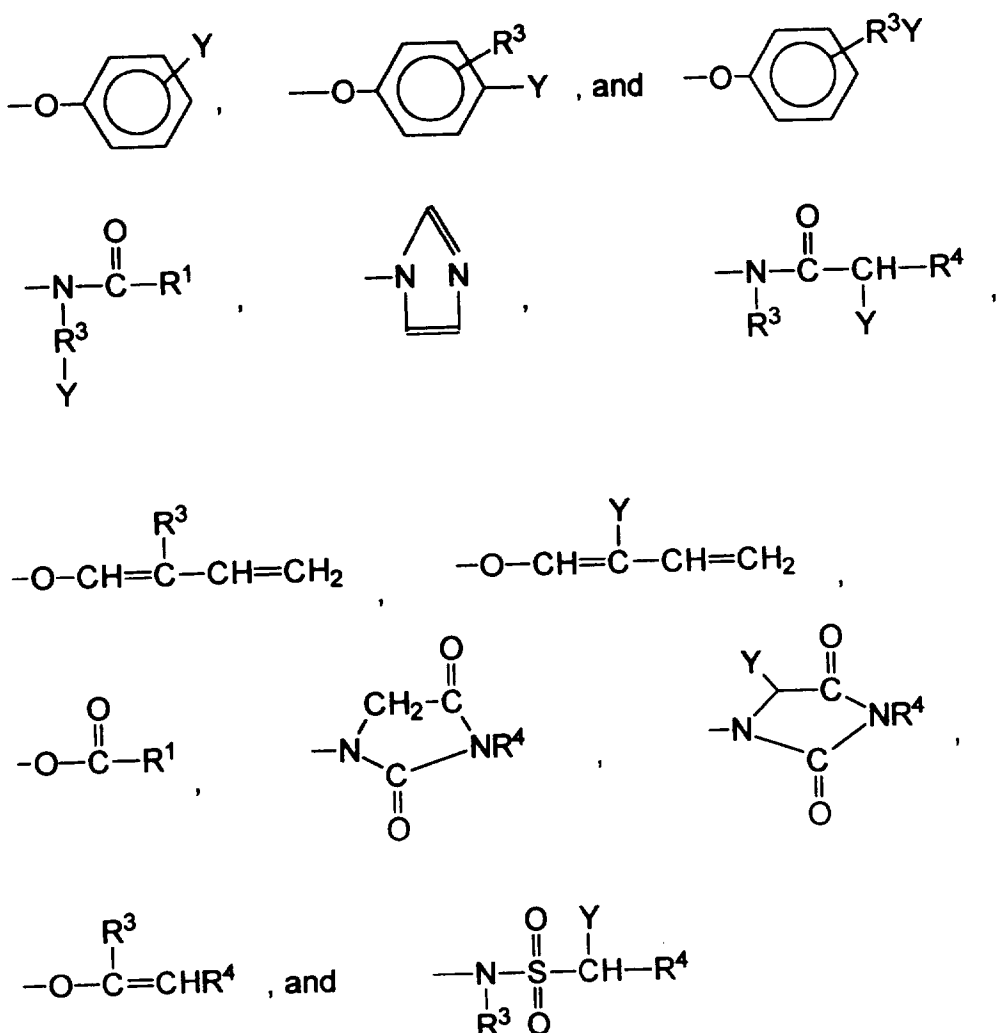
Such peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the compositions.

Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition. These characteristics are generally paralleled by the pKa of the conjugate acid of the leaving group, although exceptions to this convention are known. Ordinarily, leaving groups that exhibit such behaviour are those in which their conjugate acid has a pKa in the range of from 4 to 13, preferably from 6 to 11 and most preferably from 8 to 11.

Preferred L groups are selected from the group consisting of:



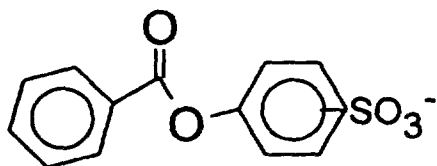
and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group.

The preferred solubilizing groups are $-\text{SO}_3^-\text{M}^+$, $-\text{CO}_2^-\text{M}^+$, $-\text{SO}_4^-\text{M}^+$, $-\text{N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O}=\text{N}(\text{R}^3)_3$ and most preferably $-\text{SO}_3^-\text{M}^+$ and $-\text{CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and anions which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

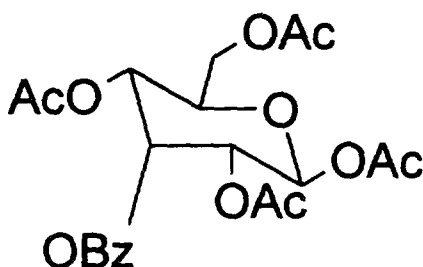
Perbenzoic acid precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis.

Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, including for example benzoyl oxybenzene sulfonate:



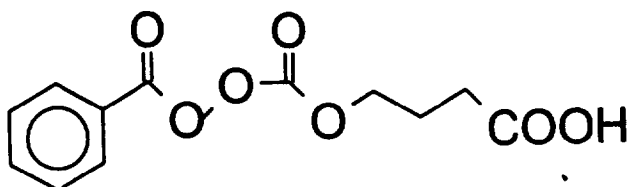
Also suitable are the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, including for example:



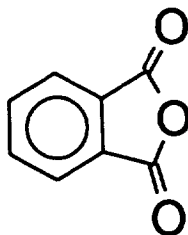
Ac = COCH₃; Bz = Benzoyl

Perbenzoic acid precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

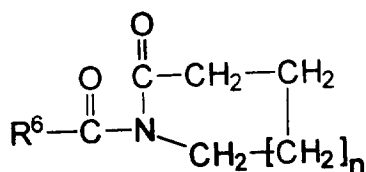
Other perbenzoic acid precursors include the benzoyl diacyl peroxides, the benzoyl tetraacyl peroxides, and the compound having the formula:



Phthalic anhydride is another suitable perbenzoic acid precursor compound herein:



Suitable N-acylated lactam perbenzoic acid precursors have the formula:



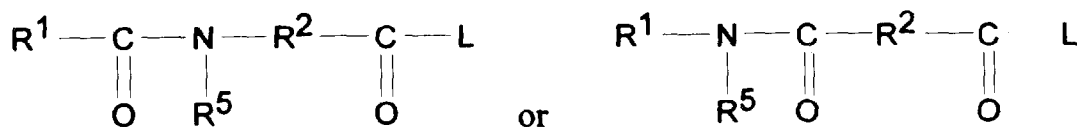
wherein n is from 0 to about 8, preferably from 0 to 2, and R⁶ is benzoyl group.

Perbenzoic acid derivative precursors

Suitable perbenzoic acid derivative precursors provide non-cationic, substituted perbenzoic acids on perhydrolysis.

Suitable substituted perbenzoic acid derivative precursors include any of the herein disclosed perbenzoic precursors in which the benzoyl group is substituted by essentially any non-positively charged (ie; non-cationic) functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl and amide groups.

A preferred class of substituted perbenzoic acid precursor compounds are the amide substituted compounds of the following general formulae:



wherein R¹ is an aryl or alkaryl group with from 1 to 14 carbon atoms, R² is an arylene, or alkarylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R¹ preferably contains from 6 to 12 carbon atoms. R² preferably contains from 4 to 8 carbon atoms. R¹ may be aryl, substituted aryl or alkaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

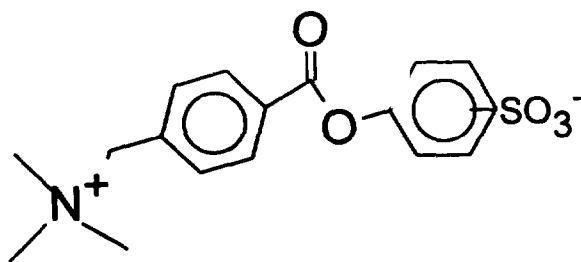
Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl fatty peroxyacid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

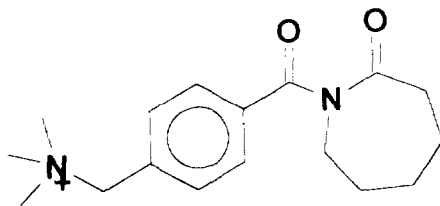
Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

A preferred cationically substituted benzoyl oxybenzene sulfonate is the 4-(trimethyl ammonium) methyl derivative of benzoyl oxybenzene sulfonate:



A preferred cationically substituted alkyl oxybenzene sulfonate is the methyl ammonium derivative of 2,3,3-trimethyl hexanoyloxybenzene sulfonate.

Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams, particularly trimethyl ammonium methylene benzoyl caprolactam:



Another preferred cationic peroxyacid precursor is 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride.

Additional peroxyacid bleach precursor

The compositions of the invention may optionally contain additional peroxyacid bleach precursor compounds which on perhydrolysis provide peroxyacids which are not any of the aforementioned perbenzoic acid, or non-cationic substituted derivatives thereof; or cationic peroxyacids. Examples of such compounds include the alkyl fatty peroxyacid precursor compounds and amide substituted alkyl peroxyacid precursors described in detail hereinafter.

Such additional peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the compositions.

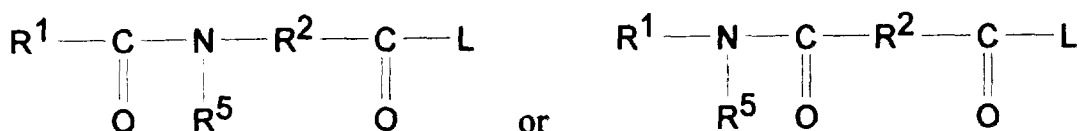
Alkyl fatty peroxyacid bleach precursors

Alkyl fatty peroxyacid bleach precursors form alkyl fatty peroxyacids on perhydrolysis. Preferred precursors of this type give rise to peracetic acid on perhydrolysis.

Preferred alkyl fatty peroxyacid precursor compounds of the imide type include the N-,N,N',N' tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Amide substituted alkyl peroxyacid precursors

A preferred class of additional peroxyacid bleach activator compounds are the amide substituted compounds of the following general formulae:



wherein R¹ is an alkyl group with from 1 to 14 carbon atoms, R² is an alkylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R¹ preferably contains from 6 to 12 carbon atoms. R² preferably contains from 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². The substitution can include alkyl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Clay mineral compound

The compositions of the invention contain a clay mineral compound, preferably present at a level of from 0.05% to 40%, more preferably from 0.5% to 30%, most preferably from 2% to 20% by weight of the composition. For clarity, it is noted that the term clay mineral compound, as used herein excludes sodium aluminosilicate zeolite builder compounds, which however, may be included in the compositions of the invention as optional components.

The weight ratio of clay mineral compound to peroxyacid bleach precursor compound is from 10:1 to 1:5, preferably from 5:1 to 1:2, most preferably from 3:1 to 1:1

The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents

No.s 3,862,058 3,948,790, 3,954,632 and 4,062,647 and European Patents No.s EP-A-299,575 and EP-A-313,146 all in the name of the Procter and Gamble Company.

The term smectite clays herein includes both the clays in which aluminium oxide is present in a silicate lattice and the clays in which magnesium oxide is present in a silicate lattice. Typical smectite clay compounds include the compounds having the general formula $Al_2(Si_2O_5)_2(OH)_2 \cdot nH_2O$ and the compounds having the general formula $Mg_3(Si_2O_5)_2(OH)_2 \cdot nH_2O$. Smectite clays tend to adopt an expandable three layer structure.

Specific examples of suitable smectite clays include those selected from the classes of the montmorillonites, hectorites, volchonskoites, nontronites, saponites and sauconites, particularly those having an alkali or alkaline earth metal ion within the crystal lattice structure. Calcium montmorillonite is particularly preferred.

Suitable smectite clays, particularly montmorillonites, are sold by various suppliers including English China Clays, Laviosa, Georgia Kaolin and Colin Stewart Minerals.

Clays for use herein preferably have a largest particle dimension of from 0.01 μ m to 800 μ m, more preferably from 1mm to 400 μ m, most preferably from 5mm to 200 μ m.

Particles of the clay mineral compound, may be included as components of agglomerate particles containing other detergent compounds. Where present as such components, the term "largest particle dimension" of the clay mineral compound refers to the largest dimension of the clay mineral components as such and not of the agglomerated particle as a whole.

Substitution of small cations, such as protons, sodium ions, potassium ions, magnesium ions and calcium ions, and of certain organic molecules including those having positively charged functional groups can typically take place within the crystal lattice structure of the smectite clays. A clay may be chosen for its ability to preferentially absorb one cation type, such ability being assessed by measurements of relative ion exchange capacity. The smectite clays suitable herein typically have a cation exchange capacity of at least 50 meq/100g. U.S. Patent No. 3,954,632 describes a method for measurement of cation exchange capacity.

The crystal lattice structure of the clay mineral compounds may, in a preferred execution, be substituted by cationic fabric softening agents. Such substituted clays have been termed 'hydrophobically activated' clays. The cationic fabric softening agents are typically present at a weight ratio, cationic fabric softening agent to clay, of from 1:200 to 1:10, preferably from 1:100 to 1:20. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

A preferred example of a commercially available "hydrophobically activated" clay is a bentonite clay containing approximately 40% by weight of a dimethyl ditallow quaternary ammonium salt sold under the tradename Claytone EM by English China Clays International.

Clay flocculating agent

The compositions of the invention most preferably contain a clay flocculating agent, preferably present at a level of from 0.005% to 10%, more preferably from 0.05% to 5%, most preferably from 0.1% to 2% by weight of the composition.

The weight ratio of clay mineral compound to clay flocculating agent is preferably from 300:1 to 1:1, more preferably from 80:1 to 10:1, most preferably from 60:1 to 20:1.

The clay flocculating agent functions such as to bring together the particles of clay compound in the wash solution and hence to aid their deposition onto the surface of the fabrics in the wash. This functional requirement is hence different from that of clay dispersant compounds which are commonly added to laundry detergent compositions to aid the removal of clay soils from fabrics and enable their dispersion within the wash solution.

Preferred as clay flocculating agents herein are organic polymeric materials having an average weight of from 100,000 to 10,000,000, preferably from 150,000 to 5,000,000, more preferably from 200,000 to 2,000,000.

Suitable organic polymeric materials comprise homopolymers or copolymers containing monomeric units selected from alkylene oxide, particularly ethylene oxide, acrylamide, acrylic acid, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Homopolymers of ethylene oxide, acrylamide and acrylic acid are preferred.

European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe preferred organic polymeric clay flocculating agents for use herein.

Inorganic clay flocculating agents are also suitable herein, typical examples of which include lime and alum.

Additional detergent components

The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the laundering operation for which it is to be used.

The compositions of the invention may for example, be formulated as hand and machine laundry detergent com-

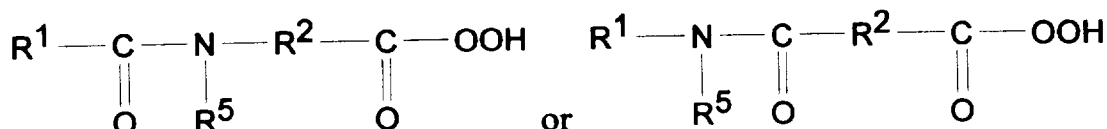
positions, including laundry additive compositions and compositions suitable for use in the pretreatment of stained fabrics.

The compositions of the invention preferably contain one or more additional detergent components selected from organic peroxyacids, surfactants, builders, organic polymeric compounds, additional enzymes, suds suppressors, lime soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

Organic peroxyacids

The compositions may also contain organic peroxyacids, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R¹ is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R¹ preferably contains from 6 to 12 carbon atoms. R² preferably contains from 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl, substituted aryl or alkaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms in total. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diperoxydodecanedioic acid, diperoxytetradecanedioic acid, diperoxyhexadecanedioic acid, mono- and diperazelaic acid, mono- and diperbrassylic acid, monoperoxy phthalic acid and its magnesium salt, perbenzoic acid, and their salts as disclosed in, for example, EP-A-0341 947.

Surfactant

The detergent compositions of the invention preferably contain as an additional detergent component a surfactant selected from anionic, cationic, nonionic ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation of surfactant are from 1% to 35% by weight, most preferably from 1% to 20% by weight.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic surfactant

Essentially any anionic surfactants useful for deterative purposes can be included in the compositions. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary alkyl sulfates, alkyl

ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpol-yglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₆-C₁₈ alkyl sulfates which have been ethoxylated with from about 0.5 to about 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₆-C₁₈ alkyl sulfate which has been ethoxylated with from about 0.5 to about 20, preferably from about 0.5 to about 5, moles of ethylene oxide per molecule.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Anionic carboxylate surfactants suitable for use herein include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Preferred alkyl ethoxy carboxylates for use herein include those with the formula RO(CH₂CH₂O)_xCH₂COO⁻M⁺ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20 %, and the amount of material where x is greater than 7, is less than about 25 %, the average x is from about 2 to 4 when the average R is C₁₃ or less, and the average x is from about 3 to 10 when the average R is greater than C₁₃, and M is a cation, preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C₁₂ to C₁₈ alkyl group.

Alkyl polyethoxy polycarboxylate surfactants suitable for use herein include those having the formula RO-(CHR₁-CHR₂-O)-R₃ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, wherein at least one R₁ or R₂ is a succinic acid radical or hydroxysuccinic acid radical, and R₃ is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Anionic secondary soap surfactant

Preferred soap surfactants are secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. The secondary carbon can be in a ring structure, e.g. as in p-octyl benzoic acid, or as in alkylsubstituted cyclohexyl carboxylates. The secondary soap surfactants should preferably contain no ether linkages, no ester linkages and no hydroxyl groups. There should preferably be no nitrogen atoms in the head-group (amphiphilic portion). The secondary soap surfactants usually contain 11-15 total carbon atoms, although slightly more (e.g., up to 16) can be tolerated, e.g. p-octyl benzoic acid.

The following general structures further illustrate some of the preferred secondary soap surfactants:

A. A highly preferred class of secondary soaps comprises the secondary carboxyl materials of the formula R³CH(R⁴)COOM, wherein R³ is CH₃(CH₂)_x and R⁴ is CH₃(CH₂)_y, wherein y can be 0 or an integer from 1 to 4, x is an integer from 4 to 10 and the sum of (x + y) is 6-10, preferably 7-9, most preferably 8.

B. Another preferred class of secondary soaps comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbyl unit, i.e., secondary soaps of the formula R⁵-R⁶-COOM, wherein R⁵ is C⁷-C¹⁰ preferably C⁸-C⁹, alkyl or alkenyl and R⁶ is a ring structure, such as benzene, cyclopentane and cyclohexane. (Note: R⁵ can be in the ortho, meta or para position relative to the carboxyl on the ring.)

C. Still another preferred class of secondary soaps comprises secondary carboxyl compounds of the formula CH₃(CHR)_k-(CH₂)_m-(CHR)_n-CH(COOM)-(CHR)_o-(CH₂)_p-(CHR)_q-CH₃, wherein each R is C₁-C₄ alkyl, wherein k, n, o, q are integers in the range of 0-8, provided that the total number of carbon atoms (including the carboxylate) is in the range of 10 to 18.

In each of the above formulas A, B and C, the species M can be any suitable, especially water-solubilizing, counterion.

Especially preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R-CON(R^1)CH_2COOM$, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Nonionic surfactant

Essentially any anionic surfactants useful for detergative purposes can be included in the compositions. Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein : R^1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferable C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_5-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain $C_{11}-C_{17}$ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Nonionic condensates of alkyl phenols

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 18 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

The ethoxylated C_6-C_{18} fatty alcohols and C_6-C_{18} mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the $C_{10}-C_{18}$ ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the $C_{12}-C_{18}$ ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available PluronicTM surfactants, marketed by BASF.

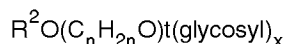
Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula



wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3; t is from 0 to 10, preferably 0, and X is from 1.3 to 8, preferably from 1.3 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose.

Nonionic fatty acid amide surfactant

Fatty acid amide surfactants suitable for use herein are those having the formula: R⁶CON(R⁷)₂ wherein R⁶ is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R⁷ is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and-(C₂H₄O)_xH, where x is in the range of from 1 to 3.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

A suitable example of an alkyl aphodicarboxylic acid for use herein is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Amine Oxide surfactant

Amine oxides useful herein include those compounds having the formula R³(OR⁴)_xN⁰(R⁵)₂ wherein R³ is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 18 carbon atoms; R⁴ is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, preferably 2 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from 1 to 3, preferably from 1 to 2 carbon atoms, or a polyethylene oxide group containing from 1 to 3, preferable 1, ethylene oxide groups. The R⁵ groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₈ alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include dimethyloctylamine oxide, diethyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyltetradecylamine oxide, methylethylhexadecylamine oxide, dodecylamidopropyl dimethylamine oxide, cetyl dimethylamine oxide, stearyl dimethylamine oxide, tallow dimethylamine oxide and dimethyl-2-hydroxyoctadecylamine oxide. Preferred are C₁₀-C₁₈ alkyl dimethylamine oxide, and C₁₀₋₁₈ acylamido alkyl dimethylamine oxide.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Betaine surfactant

The betaines useful herein are those compounds having the formula $R(R^1)_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, preferably a C₁₀-C₁₆ alkyl group or C₁₀₋₁₆ acylamido alkyl group, each R¹ is typically C₁-C₃ alkyl, preferably methyl, and R² is a C₁-C₅ hydrocarbyl group, preferably a C₁-C₃ alkylene group, more preferably a C₁-C₂ alkylene group. Examples of suitable betaines include coconut acylamidopropyl dimethyl betaine; hexadecyl dimethyl betaine; C₁₂₋₁₄ acylamidopropyl betaine; C₈₋₁₄ acylamido hexyldiethyl betaine; 4[C₁₄₋₁₆ acylmethylamidodiethyl-ammonio]-1-carboxybutane; C₁₆₋₁₈ acylamidodimethyl betaine; C₁₂₋₁₆ acylamidopentanedithyl betaine; [C₁₂₋₁₆ acylmethylamidodimethyl betaine. Preferred betaines are C₁₂₋₁₈ dimethyl-ammonio hexanoate and the C₁₀₋₁₈ acylamido-propane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Sultaine surfactant

The sultaines useful herein are those compounds having the formula $(R(R^1)_2N^+R^2SO_3^-)$ wherein R is a C₆-C₁₈ hydrocarbyl group, preferably a C₁₀-C₁₆ alkyl group, more preferably a C₁₂-C₁₃ alkyl group, each R¹ is typically C₁-C₃ alkyl, preferably methyl, and R² is a C₁-C₆ hydrocarbyl group, preferably a C₁-C₃ alkylene or, preferably, hydroxy-alkylene group.

Ampholytic surfactant

Ampholytic surfactants can be incorporated into the detergent compositions herein. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched.

Cationic surfactants

Cationic surfactants can also be used in the detergent compositions herein. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Water-soluble builder compound

The detergent compositions of the present invention preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, silicates and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycar-

boxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis-dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less than about 50°C, especially less than about 40°C.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Suitable silicates include the water soluble sodium silicates with an SiO_2 : Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.4 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2 : Na_2O ratio of 2.0 is the most preferred silicate.

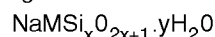
Silicates are preferably present in the detergent compositions in accord with the invention at a level of from 5% to 50% by weight of the composition, more preferably from 10% to 40% by weight.

Partially soluble or insoluble builder compound

The detergent compositions of the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of partially water soluble builders include the crystalline layered silicates. Examples of largely water insoluble builders include the sodium aluminosilicates.

Crystalline layered sodium silicates have the general formula

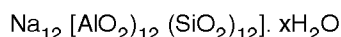


wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purpose of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. The most preferred material is $\delta\text{-Na}_2\text{Si}_2\text{O}_5$, available from Hoechst AG as NaSKS-6.

The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof.

Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_2[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite MAP, Zeolite HS and mixtures thereof. Zeolite A has the formula



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86} [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

Heavy metal ion sequestrant

The detergent compositions of the invention preferably contain as an optional component a heavy metal ion se-

questrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxyethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Examples of such preferred sodium salts of EDDS include Na₂EDDS and Na₃EDDS. Examples of such preferred magnesium complexes of EDDS include MgEDDS and Mg₂EDDS.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133.

The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS) is also suitable.

Enzyme

Another preferred ingredient useful in the detergent compositions is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α-amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme (lipase) may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of *Humicola* sp., *Thermomyces* sp. or *Pseudomonas* sp. including *Pseudomonas pseudoalcaligenes* or *Pseudomonas fluorescens*. Lipase from chemically or genetically modified mutants of these strains are also useful herein.

A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from *Humicola lanuginosa* and expressing the

gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

5 Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, but excluding any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000.

Other suitable organic polymeric compounds include the copolymers of acrylamide and acrylate having a molecular weight of from 3,000 to 100,000, and the acrylate/fumarate copolymers having a molecular weight of from 2,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

30 Suds suppressing system

The detergent compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl and alkanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

Copolymers of ethylene oxide and propylene oxide, particularly the mixed ethoxylated/propoxylated fatty alcohols with an alkyl chain length of from 10 to 16 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of

propoxylation of from 1 to 10, are also suitable antifoam compounds for use herein.

Suitable 2-alkyl-alkanols antifoam compounds for use herein have been described in DE 40 21 265. The 2-alkyl-alkanols suitable for use herein consist of a C₆ to C₁₆ alkyl chain carrying a terminal hydroxy group, and said alkyl chain is substituted in the a position by a C₁ to C₁₀ alkyl chain. Mixtures of 2-alkyl-alkanols can be used in the compositions according to the present invention.

A preferred suds suppressing system comprises

(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A preferred particulate suds suppressor system useful herein comprises a mixture of an alkylated siloxane of the type hereinabove disclosed and solid silica.

The solid silica can be a fumed silica, a precipitated silica or a silica, made by the gel formation technique. The silica particles suitable have an average particle size of from 0.1 to 50 micrometers, preferably from 1 to 20 micrometers and a surface area of at least 50m²/g. These silica particles can be rendered hydrophobic by treating them with dialkylsilyl groups and/or trialkylsilyl groups either bonded directly onto the silica or by means of a silicone resin. It is preferred to employ a silica the particles of which have been rendered hydrophobic with dimethyl and/or trimethyl silyl groups. A preferred particulate antifoam compound for inclusion in the detergent compositions in accordance with the invention suitably contain an amount of silica such that the weight ratio of silica to silicone lies in the range from 1:100 to 3:10, preferably from 1:50 to 1:7.

Another suitable particulate suds suppressing system is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50m²/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Other highly preferred particulate suds suppressing systems are described in copending European Application 91870007.1 in the name of the Procter and Gamble Company which systems comprise silicone antifoam compound, a carrier material, an organic coating material and glycerol at a weight ratio of glycerol : silicone antifoam compound of 1:2 to 3:1. Copending European Application 91201342.0 also discloses highly preferred particulate suds suppressing systems comprising silicone antifoam compound, a carrier material, an organic coating material and crystalline or amorphous aluminosilicate at a weight ratio of aluminosilicate : silicone antifoam compound of 1:3 to 3:1. The preferred carrier material in both of the above described highly preferred granular suds controlling agents is starch.

An exemplary particulate suds suppressing system for use herein is a particulate agglomerate component, made by an agglomeration process, comprising in combination

(i) from 5% to 30%, preferably from 8% to 15% by weight of the component of silicone antifoam compound, preferably comprising in combination polydimethyl siloxane and silica;

(ii) from 50% to 90%, preferably from 60% to 80% by weight of the component, of carrier material, preferably starch;

(iii) from 5% to 30%, preferably from 10% to 20% by weight of the component of agglomerate binder compound, where herein such compound can be any compound, or mixtures thereof typically employed as binders for agglomerates, most preferably said agglomerate binder compound comprises a C₁₆-C₁₈ ethoxylated alcohol with a degree of ethoxylation of from 50 to 100; and

(iv) from 2% to 15%, preferably from 3% to 10%, by weight of C₁₂-C₂₂ hydrogenated fatty acid.

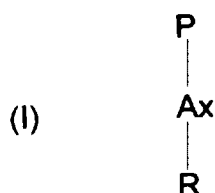
Polymeric dye transfer inhibiting agents

The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

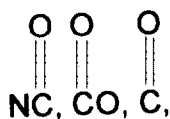
The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

a) Polyamine N-oxide polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



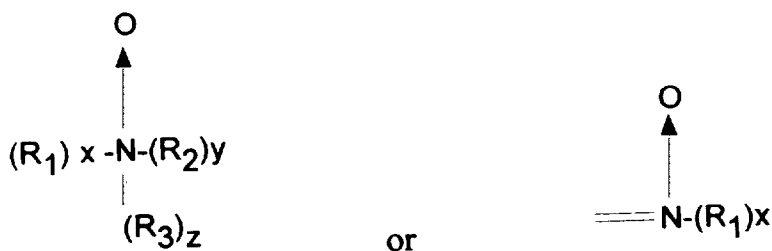
wherein P is a polymerisable unit, whereto the R-N-O group can be attached to, or wherein the R-N-O group forms part of the polymerisable unit or a combination of both. A is



-O-, -S-, -N-; x is 0 or 1;

Rare aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof where the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the

N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides wherein the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a $\text{PKa} < 10$, preferably $\text{PKa} < 7$, more preferred $\text{PKa} < 6$.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Preferred polymers for use herein may comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000. The preferred N-vinylimidazole N-vinylpyrrolidone copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4.

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP" having an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

Polyvinylpyrrolidone may be incorporated in the detergent compositions herein at a level of from 0.01% to 5% by weight of the detergent, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylpyrrolidone delivered in the wash solution is preferably from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

d) Polyvinylloxazolidone

The detergent compositions herein may also utilize polyvinylloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinylloxazolidones have an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinylloxazolidone incorporated in the detergent compositions may be from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylloxazolidone delivered in the wash solution is typically from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

e) Polyvinylimidazole

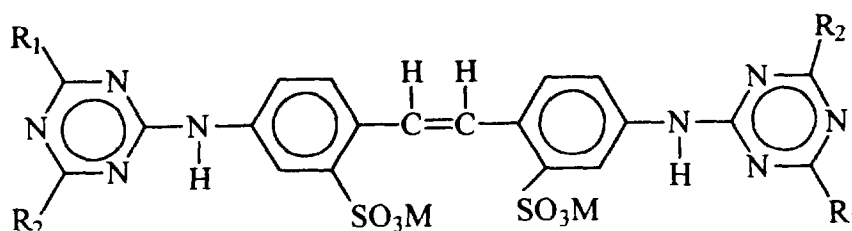
The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinylimidazole incorporated in the detergent compositions may be from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylimidazole delivered in the wash solution is from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

Optical brightener

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

Suitable hydrophilic optical brighteners herein 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.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. These may be present as distinct components or as components of, the hereinbefore described, hydrophobically activated clay materials. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

Form of the compositions

The detergent compositions of the invention can be formulated in any desirable form such as powders, granulates, pastes and tablets.

Solid compositions

The detergent compositions of the invention are preferably in the form of solids, such as powders and granules.

The particle size of the components of granular compositions in accordance with the invention should preferably be such that no more than 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 450 g/litre, more usually at least 600 g/litre and more preferably from 650 g/litre to 1200 g/litre.

Making processes - granular compositions

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

Laundry washing methods

The compositions of the invention may be used in essentially any washing or cleaning method, including machine laundry washing methods.

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. The detergent can be added to the wash solution either via the dispenser drawer of the washing machine or by a dispensing device. By an effective amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred washing method herein a dispensing device containing an effective amount of detergent product is introduced into the drum of a front-loading washing machine before the commencement of the wash cycle.

The dispensing device is a container for the detergent product which is used to deliver the product directly into the drum of the washing machine. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its immersion in the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle. Especially preferred dispensing devices for use in accord with the invention have been described in the following patents; GB-B-2, 157, 717, GB-B-2, 157, 718, EP-A-0201376, EP-A-0288345 and EP-A-0288346. An article by J.Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry products which are of a type commonly known as the "granulette".

Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

Packaging for the compositions

Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in copending European Application No. 93970141.4.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

XYAS :	Sodium C _{1X} -C _{1Y} alkyl sulfate
25EY :	A C ₁₂₋₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
XYEZ :	A C _{1X} -C _{1Y} predominantly linear primary alcohol condensed with an average of Z moles of ethylene oxide
XYEZX :	C _{1X} - C _{1Y} sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole
TFAA :	C ₁₆ -C ₁₈ alkyl N-methyl glucamide.
Silicate :	Amorphous Sodium Silicate (SiO ₂ :Na ₂ O ratio = 2.0)
NaSKS-6 :	Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
Carbonate :	Anhydrous sodium carbonate
Polycarboxylate :	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000
Zeolite A :	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ .27H ₂ O having a primary particle size in the range from 1 to 10 micrometers
Citrate :	Tri-sodium citrate dihydrate
Percarbonate :	Anhydrous sodium percarbonate bleach coated with a coating of sodium silicate (Si ₂ O:Na ₂ O ratio = 2:1) at a weight ratio of percarbonate to sodium silicate of 39:1
TAED :	Tetraacetylenediamine particle formed by agglomerating TAED with citric acid and polyethylene glycol (PEG) of Mw=4,000 with a weight ratio of components of TAED: citric acid: PEG of 75:10:15, coated with an external coating of citric acid at a weight ratio of agglomerate: citric acid coating of 95:5.

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5	Benzoyl Caprolactam :	Benzoyl caprolactam particle formed by agglomerating benzoyl caprolactam (BzCl) with citric acid and polyethylene glycol (PEG) of Mw=4,000, with a weight ratio of components of BzCl: citric acid: PEG of 63:21:16, coated with an external coating of citric acid at a weight ratio of agglomerate: citric acid coating of 95:5
	Cationic Caprolactam	p-(N,N, N triethylammoniummethyl) benzoyl caprolactam chloride salt
10	Protease :	Proteolytic enzyme sold under the tradename Savinase by Novo Industries A/S with an activity of 4 KNU/g.
	Amylase :	Amylolytic enzyme sold under the tradename Termamyl 60T by Novo Industries A/S with an activity of 300 KNU/g
15	Cellulase :	Cellulosic enzyme sold by Novo Industries A/S with an activity of 1000 CEVU/g
	Lipase :	Lipolytic enzyme sold under the tradename Lipolase by Novo Industries A/S with an activity of 165 KLU/g
20	CMC :	Sodium carboxymethyl cellulose
	HEDP :	1,1-hydroxyethane diphosphonic acid
	EDDS :	Ethylenediamine -N, N'-disuccinic acid, [S,S] isomer in the form of the sodium salt.
25	PVNO :	Poly (4-vinylpyridine)-N-oxide copolymer of vinylimidazole and vinylpyrrolidone having an average molecular weight of 10,000.
	DETPMP :	Diethylene triamine penta (menthylene) phosphonic acid.
30	Flocculant	Homopolymer of ethylene oxide having an average molecular weight of 1,000,000
	Clay	Calcium montmorillonite
35	DTMAC	Ditallow methyl ammonium chloride
	Granular Suds Suppressor :	12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form

Example 1

40 The following laundry detergent compositions A to D were prepared in accord with the invention:

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	A	B	C	D
5				
45AS/25AS (3:1)	9.1	9.1	9.1	9.1
10				
35AE3S	2.3	2.3	2.3	2.3
24E5	4.5	4.5	4.5	4.5
15				
TFAA	2.0	2.0	2.0	2.0
Zeolite A	10.2	10.2	10.2	7.2
20				
Na SKS-6/citric acid (79:21)	10.6	10.6	10.6	10.6
25				
Carbonate	7.6	7.6	7.6	7.6
2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride	6.3	-	-	2.3
30				
Benzoyl Caprolactam	-	5.0	5.0	2.7
35				
Percarbonate	22.5	22.5	22.5	22.5
40				
Clay	12.0	12.0	12.0	9.0
45				
DTMAC	-	-	-	3.0
50				
Flocculant	0.3	0.4	0.2	0.5

DETPMP	0.5	0.8	-	-
EDDS	-	-	0.3	0.75
Protease	0.55	1.27	0.55	1.27
Lipase	0.15	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28	0.28
Amylase	0.27	0.27	0.27	0.27
Polycarboxylate	3.1	3.1	3.1	3.1
CMC	0.4	0.4	0.4	0.4
PVNO	0.03	0.03	0.03	0.03
Granular suds suppressor	1.5	1.5	1.5	1.5
Minors/misc to 100%				

Example 2 - Comparative Performance Testing

The following laundry detergent compositions E to H were prepared, E and G are comparative compositions and F and H are in accord with the invention:

	E	F	G	H
45AS/25AS (3:1)	9.1	9.1	9.1	9.1
35AE3S	2.3	2.3	2.3	2.3
24E5	4.5	4.5	4.5	4.5
TFAA	2.0	2.0	2.0	2.0
Zeolite A	10.2	10.2	10.2	7.2
Na SKS-6/citric acid (79:21)	10.6	10.6	10.6	10.6
Carbonate	7.6	7.6	7.6	7.6
Cationic caprolactam	-	-	3.0	3.0
TAED	3.0	3.0	-	-
Benzoyl Caprolactam	3.0	3.0	-	-
Percarbonate	22.5	22.5	22.5	22.5
Clay	-	12.0	-	12.0
Flocculant	-	0.3	-	0.3

DETPMP	0.5	0.8	-	-
EDDS	-	-	0.3	0.75
Protease	0.55	0.55	0.55	0.55
Lipase	0.15	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28	0.28
Amylase	0.27	0.27	0.27	0.27
Polycarboxylate	3.1	3.1	3.1	3.1
CMC	0.4	0.4	0.4	0.4
PVNO	0.03	0.03	0.03	0.03
Granular suds suppressor	1.5	1.5	1.5	1.5
Minors/misc to 100%				

The colour fading observed with Compositions F and H, in accord with the invention, was less than that observed with Compositions E and G when washed using a representative laundry washing method.

Claims

1. A bleaching composition containing

(a) an oxygen-releasing bleach system comprising a hydrogen peroxide source and a peroxyacid bleach precursor compound selected from the group consisting of

(i) a perbenzoic acid, or non-cationic substituted derivative thereof, precursor compound;

(ii) a cationic peroxyacid bleach precursor compound;

and any mixtures of (i) to (ii); and

(b) a clay mineral compound;

wherein the weight ratio of clay mineral compound to peroxyacid bleach precursor compound is from 10:1 to 1:5.

2. A bleaching composition according to Claim 1 containing an additional peroxyacid bleach precursor compound which is not a perbenzoic acid, or non-cationic substituted derivative thereof, precursor compound or a cationic peroxyacid bleach precursor compound.

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3. A bleaching composition according to either of Claims 1 or 2 additionally containing a clay flocculating agent.
4. A bleaching composition according to any of Claims 1 to 3 wherein the clay mineral compound is a smectite clay compound present at a level of from 0.05% to 40% by weight of the composition.
5. A bleaching composition according to Claim 4 wherein the smectite clay compound is selected from either of sodium or calcium montmorillonite.
6. A bleaching composition according to any of Claims 1 to 5 wherein the clay mineral component has a largest particle dimension of from 0.01mm to 800mm.
7. A bleaching composition according to any of Claims 1 to 6 wherein the crystal lattice structure of the clay mineral compound has a cationic fabric softening agent substituted therein.
8. A bleaching composition according to any of Claims 3 to 7 wherein the clay flocculating agent is an organic polymeric material having an average molecular weight of from 100,000 to 10,000,000 present at a level of from 0.005% to 10% by weight of the composition.
9. A bleaching composition according to Claim 8 wherein said organic polymeric material is selected from the homopolymers of ethylene oxide, acrylamide, and acrylic acid.
10. A bleaching composition according to any of Claims 3 to 9 wherein the weight ratio of clay mineral compound to clay flocculating agent is from 300: 1 to 1:1.
11. A bleaching composition according to any of Claims 1 to 10 wherein the hydrogen peroxide source is an inorganic perhydrate salt.
12. The use, in a method for washing stained coloured fabrics, of a bleaching composition containing an oxygen-releasing bleach system wherein said composition contains a clay mineral compound to inhibit the fading of the colour of said fabrics.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 7285

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Section Ch, Week 9413 Derwent Publications Ltd., London, GB; Class C09, AN 94-107094 MIYAJI NOBUO ET AL. 'fading controlling agent for oxygen-type bleachers used to bleach colour patterned clothes...' & JP-A-06 057 297 (NIPPON CORN STARCH K.K.) , 1 March 1994 * abstract *	1,11,12	C11D3/12 C11D3/39 C11D3/37
X	--- EP-A-0 299 575 (THE PROCTER & GAMBLE CO.) * page 5, line 9 - line 12; claims 1-8; examples COMP. II, VII *	1-11	
X,P	--- WO-A-94 27970 (THE PROCTER & GAMBLE CO.) * examples *	1	
X	--- EP-A-0 297 673 (THE PROCTER & GAMBLE) * examples *	1,2	
X	--- EP-A-0 051 987 (THE PROCTER & GAMBLE CO.) * examples II, V,VIII *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
X	--- GB-A-2 249 104 (BP CHEMICALS LTD) * claims 1,2,8 * -----	1,6	C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 February 1996	Examiner Loiselet-Taisne, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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