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(54) Title: A DETERGENT COMPOSITION

(57) Abstract

The invention relates to a detergent composition comprising: a) a hydrophobic peroxyacid bleaching component, capable of providing a hydrophobic peroxyacid compound, with the proviso the component does not comprise the sodium salt of nonanoyloxybenzene sulfonate; b) a hydrophilic nonionic component, having a Hydrophilic/Lipophilic Balance of at least 10.8, as measured by the HLB-test; c) a cationic surfactant component, with the proviso that the cationic surfactant is not a cationic choline ester surfactant or a salt of the cationic C_{12}–C_{14} alkyl dimethyl ammonium ethanol surfactant.

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A Detergent Composition

Technical Field

The present invention relates to a detergent composition comprising cationic surfactants, hydrophobic peroxyacid bleaching components and a hydrophilic nonionic component.

Background to the Invention

Amongst consumers there is a need for detergents which provide improved cleaning and stain removal. Different stains can have different properties. Therefore, there is a need to provide detergent compositions which contain various components which together can ensure the removal of all the different stains. Thus, in the last few years detergents have been developed which contain various types of surfactants, such as anionic and cationic surfactants. Furthermore, since certain stains are bleachable, detergent manufacturers have developed bleaches, which can act on the bleachable stains selectively, thus removing the bleachable stains whilst not damaging the fabrics.
One type of bleach which is particularly useful therefor is a hydrophobic bleach.

However, the use of the variety of different surfactants, bleaches and other detergent ingredients has increased the complexity of the detergent formulations. The various components can interact with each other, thereby influencing each their respective properties.

The Applicants have found that a problem encountered with the more complex detergent formulations, can be a reduction of the performance of the individual detergent ingredients. It has been found that the introduction of an additional ingredient to a detergent composition, increasing the complexity of the detergent composition, does not always result in an increased cleaning performance of the final composition, as would be expected. In particular, it has been found that cationic and hydrophobic components, when comprised in a detergent composition, can diminish each others performance.

The Applicants have now found that this problem can be ameliorated or solved by the introduction of a hydrophilic nonionic component, especially certain nonionic surfactants, to the detergent composition comprising certain hydrophobic bleaching components and cationic surfactant components. It has been found that the incorporation of a hydrophilic nonionic component to a detergent composition comprising certain cationic surfactants and hydrophobic

bleaches, leads to an improved performance of these two latter components, in comparison to detergent compositions which do not comprise the hydrophilic nonionic component. Both the bleach performance and the cleaning performance are unexpectingly increased when a hydrophilic nonionic component is introduced to the composition. This leads to a much improved removal of both bleachable and non-bleachable stains. An additional benefit can be that the levels of the individual components can be reduced, if desired, because a more efficient performance by the individual components is achieved.

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

Summary of the Invention

According to the present invention there is provided a detergent composition comprising

a) a hydrophobic peroxyacid bleaching component, capable of providing a hydrophobic peroxyacid compound, with the proviso the component does not comprise the sodium salt of nonanoyloxybenzene sulfonate;

b) a hydrophilic nonionic component, having a Hydrophilic/ Lipophilic Balance of at least 10.8, as measured by the HLB-test;

c) a cationic surfactant component, with the proviso that the cationic surfactant is not a cationic choline ester surfactant or a salt of the cationic C_{12} - C_{14} alkyl dimethyl ammonium ethanol surfactant.

Detailed Description of the Invention

Hydrophilic nonionic component

According to the present invention a hydrophilic nonionic surface-active component is present, having a Hydrophilic/ Lipophilic Balance (HLB) of at least 10.8, as measured by the HLB test described herein.

To avoid confusion, by using the term 'having a Hydrophilic/ Lipophilic Balance (HLB)' or 'having a HLB' herein is meant that a hydrophilic nonionic surface-active component either has a HLB whereof the value is obtained by the calculation, described below, or has a HLB whereof the value is obtained by the comparison HLB- test, described below.

Preferably, the hydrophilic nonionic component has a HLB of at least 11, more preferably of at least 11.6, most preferably of at least 11.7.

The ratio of the cationic surfactant to the hydrophilic nonionic component is generally from 100:1 to 1:100, preferably from 20:1 to 1:30, more preferably from 5:1 to 1:20, most preferably from 1:1 to 1:10.

The ratio of the hydrophobic peroxyacid bleaching component to the hydrophilic nonionic component is generally from 150:1 to 1:100, preferably from 50:1 to 1:20, more preferably from 20:1 to 1:10, most preferably from 15:1 to 1:1.

Preferably, the hydrophilic nonionic component is present at a level of from 0.01% to 40%, more preferably from 0.5% to 20%, even more preferably from 1.0% to 14%, most preferably from 2.0% to 8% by weight of the composition.

Preferably, the nonionic component has an average molecular weight of from 200 to 2000, more preferably from 250 to 1000, most preferably from 250 to 600.

Preferably, the hydrophilic nonionic component is a nonionic surfactant as described below.

HLB-test

The HLB test serves to determine if a certain nonionic component has a Hydrophilic/ Lipophilic Balance or HLB of at least 10.8 and is therefore, according to the definition used for this invention, a hydrophilic nonionic component for use in the invention.

In the HLB-test nonionic components, whereof the HLB can not be calculated by the formula below, are compared to one or more standard nonionic components, whereof the HLB can be obtained by calculation, to thus determine the HLB of the former nonionic component. The procedure to compare the nonionic components with the standard-components is set out below.

Any linear nonionic component, consisting of y ethoxylate groups, x carbon atoms, 2x +1 hydrogen atoms and one hydroxy group, whereof the HLB can be calculated by the following formula, can be used as comparison standard nonionic components:

$$HLB = \frac{\text{weight \% of ethoxylate}}{5} = \frac{44\,y}{44\,y + 12\,x + 2\,x + 1 + 17} \times \frac{100}{5}$$

The comparison between the standard nonionic component and another nonionic component, to obtain its HLB, can be done by gas chromatography, as set out by G E Petrowski and J R Vanatta (Journal of American Oil Chemist's Society, August 1973, volume 50, pages 284-289).

With the above formulation the HLB's of linear standard nonionic components, with a purity of 95%, preferably 99%, with different x and y, are calculated.

For a good comparison of HLB values, several (preferably at least 6) standard nonionic components whereof the calculated HLB is less, than equal to, and more than 10.8 are to be used. The standard nonionic components and the nonionic component are each coated onto support material (chromosorb W-NAW 60/80 mesh, Jones Chromatography, Wales) and each at a time the coated support materials are packed into a 2 m copper columns (Jones Chromatography, Wales) of a gas chromatograph (Pye Unicam 204, with flame -ionisation detector, carrier gas nitrogen). A mixture of two solvents, one hydrophobic and one hydrophilic, preferably n-octane and butane-1-ol, is introduced into each column. The chromatography is conducted at a constant temperature, which is preferably selected such that the nonionic component is liquid.

Then the retention time of the two solvents of the mixture is determined, $\rho 1$ and $\rho 2$, and the ratio (R) of the retention times $\rho 1 / \rho 2$ is calculated. A graph is made of the ln R versus the calculated HLB values. An about linear relationship is found between these two values.

Then, the procedure above is repeated for each nonionic component, whereof the HLB needs to be determined, by coating it onto support material (chromosorb), using the same mixture of two solvents, and temperature.

By measuring the retention times, calculating the ln R, and comparing the obtained ln R with the graph of the standard nonionic components, it can be determined whether the HBL of this

nonionic component is above 10.8, being thus a hydrophilic ionic component in accord with the invention.

Nonionic surfactant

Highly preferred hydrophilic nonionic components for use in the inventions are nonionic surfactants, having a HLB of at least 10.8.

Alkoxylated nonionic surfactant

Highly preferred hydrophilic nonionic components are alkoxylated nonionic surfactants. Essentially any alkoxylated nonionic surfactants, having a HLB of at least 10.8 are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Other highly preferred alkoxylated surfactants are the nonionic ethoxylated alcohols and nonionic ethoxylated/propoxylated fatty alcohols.

Other preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic alkoxylated alcohol surfactant

In accord with the invention, highly preferred hydrophilic nonionic components can be the condensation products of aliphatic alcohols, which have a HLB of at least 10.8, and which have more than 6, preferably from 6 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene 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 6 to 16, more preferably from 12 to 16 carbon atoms with from 6 to 12 moles, more preferably 7 to 9 moles, of ethylene oxide per mole of alcohol.

Nonionic polyhydroxy fatty acid amide surfactant

In accord with the invention, preferred hydrophilic nonionic components can be the polyhydroxy fatty acid amides which have a HLB of at least 10.8. Polyhydroxy fatty acid amides suitable for use herein can be those having the structural formula R^2CONR^1Z wherein : R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C1-C4 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 alkoxylated 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 fatty acid amide surfactant

In accord with the invention, preferred hydrophilic nonionic components can be the fatty acid amide surfactant which have a HLB of at least 10.8

Suitable fatty acid amide surfactants can be those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and -$(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Nonionic alkylpolysaccharide surfactant

In accord with the invention, preferred hydrophilic nonionic components can be the alkylpolysaccharides which have a HLB of at least 10.8

Suitable alkylpolysaccharides for use herein can bethose, disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 8 to 10 carbon

atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Hydrophobic peroxyacid bleaching component

An essential feature of detergent compositions of the invention is a hydrophobic peroxyacid bleaching component, capable of providing a hydrophobic peroxyacid compound, with the proviso the component does not comprise the sodium salt of nonanoyloxybenzene sulfonate. Preferably, the hydrophobic peroxyacid compound
comprises at least one nitrogen atom. By hydrophobic organic peroxyacid compound it is meant herein an organic peroxyacid whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre and wherein said critical micelle concentration is measured in aqueous solution at 20°-50°C.

Preferably the hydrophobic peroxyacid bleaching component comprises a hydrogen peroxide source and a hydrophobic peroxyacid bleach precursor compound, with the proviso this precursor is not the sodium salt of nonanoyloxybenzene sulfonate. Preferably, the hydrophobic peroxyacid bleach precursor compound comprises at least one nitrogen atom. The production of the hydrophobic 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. In an alternative preferred execution the hydrophobic peroxyacid bleaching component comprises a preformed hydrophobic peroxyacid, comprising at least one nitrogen atom, which is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and hydrophobic peroxyacid precursor, in combination with a preformed hydrophobic peroxyacid are also envisaged.

Preferably, the hydrophobic peroxyacid contains at least 7 carbon atoms, more preferably at least 9 carbon atoms, most preferably at least 11 carbon atoms. In a preferred aspect the peroxyacid has an alkyl chain comprising at least 7 carbon atoms, more preferably at least 8 carbon atoms, most preferably at least 9 carbon atoms.

Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably 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. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

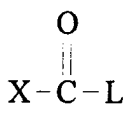
Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid.

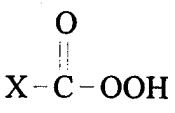
Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

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 and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



For the purposes of the present invention X will thus contain at least 6 carbon atoms, preferably from 9 to 25, more preferably from 9 to 15 carbon atoms.

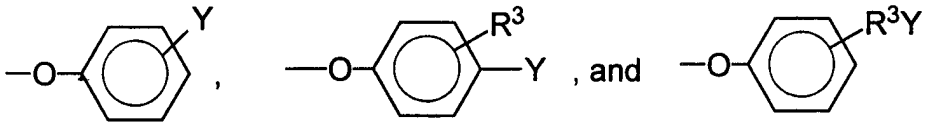
The hydrophobic peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.05% to 20% by weight, more preferably from 0.1% to 15% by weight, most preferably from 0.2% to 10% by weight of the detergent compositions.

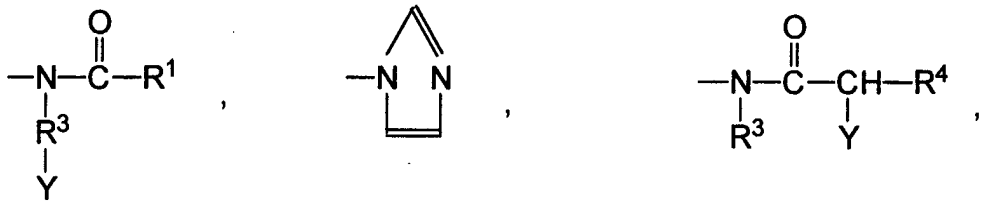
Suitable hydrophobic peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful 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.

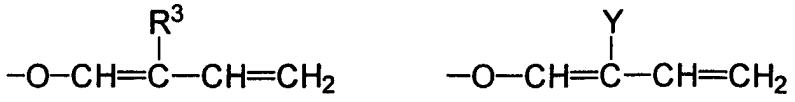
Leaving groups

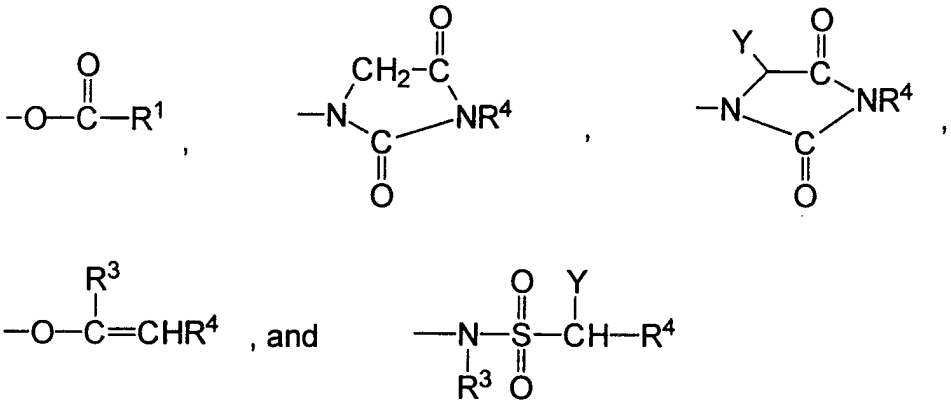
The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:







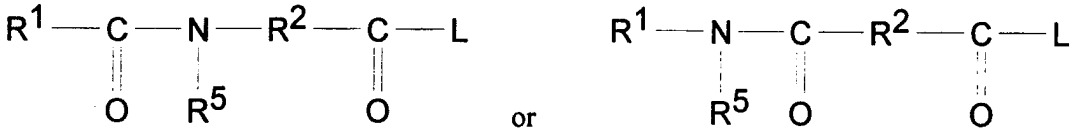


and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, and Y is H or a solubilizing group. Any of R^1, R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammmonium groups

The preferred solubilizing groups are, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<--N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$, most preferably - $SO_3^-M^+$, $-CO_2^-M^+$, 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 X is an anion 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.

Amide substituted alkyl peroxyacid precursors

Preferred peroxyacid precursors are amide substituted alkyl peroxyacid precursor compounds, including those of the following general formulae:



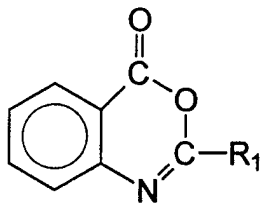
wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any

leaving group. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl 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 R^2. R^2 can include alkyl, aryl, wherein said R^2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386. It can be preferred that R^1 and R^5 forms together with the nitrogen and carbon atom a ring structure.

Preferred examples of bleach precursors of this type include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, and the highly preferred (6-nonanamidocaproyl)oxy benzene sulfonate, and mixtures thereof as described in EP-A-0170386.

Benzoxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

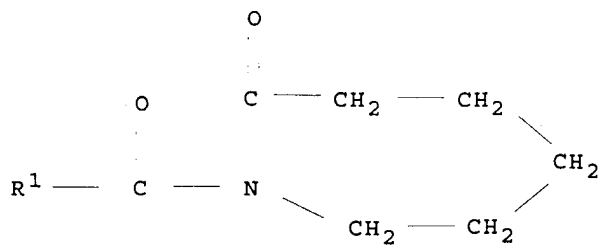


wherein R_1 is an alkyl, alkaryl, aryl, or arylalkyl containing at least 5 carbon atoms.

N-acylated lactam precursors

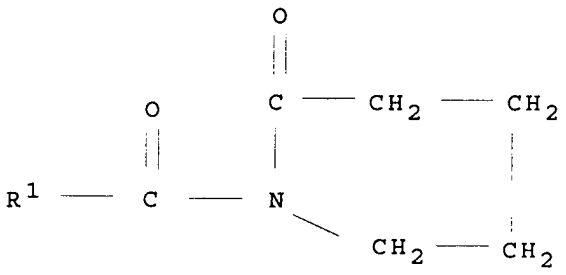
Still another class of hydrophobic bleach activators are the N-acylated precursor compounds of the lactam class disclosed generally in GB-A-955735. Preferred materials of this class comprise the caprolactams.

Suitable caprolactam bleach precursors are of the formula:



wherein R^1 is an alkyl, aryl, alkoxyaryl or alkaryl group containing from 6 to 12 carbon atoms. Preferred hydrophobic N-acyl caprolactam bleach precursor materials are selected from benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam and mixtures thereof. A most preferred is nonanoyl caprolactam.

Suitable valero lactams have the formula:



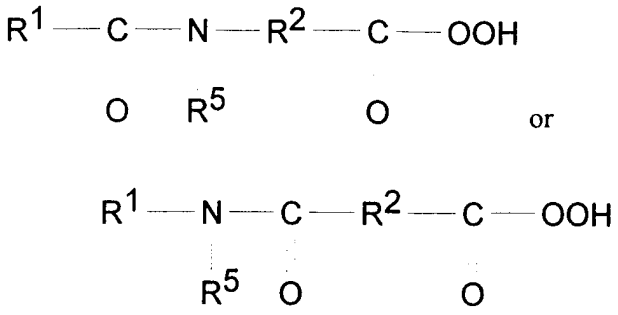
wherein R^1 is an alkyl, aryl, alkoxyaryl or alkaryl group containing from 6 to 12 carbon atoms. More preferably, R^1 is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

Mixtures of any of the peroxyacid bleach precursor, herein before described, may also be used.

Preformed organic peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed hydrophobic organic peroxyacid , typically at a level of from 0.05% to 20% by weight, more preferably from 1% to 10% by weight of the composition.

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

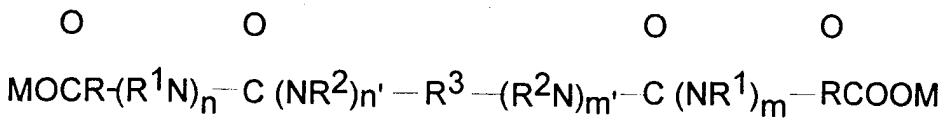


or

wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl 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 R^2. R^2 can include alkyl, aryl, wherein said R^2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386. Suitable examples of this class of agents include (6-octylamino)-6-oxo-caproic acid, (6-nonylamino)-6-oxo-caproic acid, (6-decylamino)-6-oxo-caproic acid, magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. 4,483,781, U.S. 4,634,551, EP 0,133,354, U.S. 4,412,934 and EP 0,170,386. A preferred hydrophobic preformed peroxyacid bleach compound for the purpose of the invention is mononononylamido peroxycarboxylic acid.

Other suitable organic peroxyacids include diperoxyalkanedioc acids having more than 7 carbon atoms, such as diperoxydodecanedioc acid (DPDA), diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid (PAP), nonanoylamido peroxo-adipic acid (NAPAA) and hexane sulphenoyl peroxypropionic acid and are also suitable herein.

Other suitable organic peroxyacids include diamino peroxyacids, which are disclosed in WO 95/ 03275, with the following general formula:



wherein:

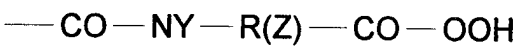
R is selected from the group consisting of C_1-C_{12} alkylene, C_5-C_{12} cycloalkylene, C_6-C_{12} arylene and radical combinations thereof;

R^1 and R^2 are independently selected from the group consisting of H, C_1-C_{16} alkyl and C_6-C_{12} aryl radicals and a radical that can form a C_3-C_{12} ring together with R^3 and both nitrogens; R^3 is selected from the group consisting of C_1-C_{12} alkylene, C_5-C_{12} cycloalkylene and C_6-C_{12} arylene radicals; n and n' each are an integer chosen such that the sum thereof is 1; m and m' each are an integer chosen such that the sum thereof is 1; and

M is selected from the group consisting of H, alkali metal, alkaline earth metal, ammonium, alkanolammonium cations and radicals and combinations thereof.

Other suitable organic peroxyacids are include the amido peroxyacids which are disclosed in WO 95/ 16673, with the following general structure:

in which X represents hydrogen or a compatible substituent, Ar is an aryl group, R represents $(CH_2)_n$ in which n = 2 or 3, and Y and Z each represent independently a substituent selected from hydrogen or an alkyl or aryl or alkaryl group or an aryl group substituted by a compatible substituent provided that at least one of Y and Z is not hydrogen if n = 3. The substituent X on the benzene nucleus is preferably a hydrogen or a meta or para substituent, selected from the group comprising halogen, typically chlorine atom, or some other non-released non-interfering species such as an alkyl group, conveniently up to C6 for example a methyl, ethyl or propyl group. Alternatively, X can represent a second amido-percarboxylic acid substituent of formula:-



in which R, Y, Z and n are as defined above.

MOOC-R^1CO-NR^2-R^3-NR^4-CO-R^5COOOM

wherein R^1 is selected from the group consisting of C_1-C_{12} alkylene, C_5-C_{12} cycloalkylene, C_6-C_{12} arylene and radical combinations thereof; R

It may be found to be particularly useful to mix the pre-formed peracid and cationic surfactant together prior to incorporation with any other components of the detergent composition.

Cationic surfactant

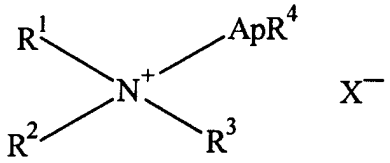
Another essential component of the detergent composition of the invention is a cationic surfactant, with the proviso that the cationic surfactant is not a cationic choline ester surfactant or a salt of the cationic C_{12} - C_{14} alkyl dimethyl ammonium ethanol surfactant.

Preferably, the cationic surfactant is selected from the group consisting of cationic mono-alkoxylated amine surfactants (not being the sodium salt of the cationic C_{12} - C_{14} alkyl dimethyl ammonium ethanol surfactant), cationic bis-alkoxylated amine surfactants and mixtures thereof.

The cationic surfactant is preferably present at a level of from 0.1% to 20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3% by weight of the detergent composition.

Cationic mono-alkoxylated amine surfactants

The cationic surfactant of the present invention can be a cationic mono-alkoxylated amine surfactant, which has the general formula I:



(I)

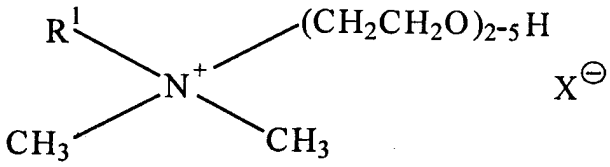
wherein R^1 is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about 6 to about 14 carbon atoms; R^2 and R^3 are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl, most preferably both R^2 and R^3 are methyl groups; R^4 is selected from hydrogen (preferred), methyl and ethyl; X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is a alkoxy group, especially

a ethoxy, propoxy or butoxy group; and p is from 0 to about 30, preferably 2 to about 15, most preferably 2 to about 8, with the proviso that if A is ethoxy and R_4 is hydrogen and p is 1, R_1 is not a C_{12}-C_{14} alkyl group.

Preferably the ApR^4 group in formula I has p=1 and is a hydroxyalkyl group, having no greater than 6 carbon atoms whereby the —OH group is separated from the quaternary ammonium nitrogen atom by no more than 3 carbon atoms. Particularly preferred ApR^4 groups are —CH_2-CH_2OH, —$CH_2CH_2CH_2OH$, —$CH_2CH(CH_3)OH$ and —$CH(CH_3)CH_2OH$, with —CH_2CH_2OH being particularly preferred. Preferred R^1 groups have have no greater than 10 carbon atoms, or even no greater than 8 or 9 carbon atoms. Preferred R^1 groups are linear alkyl groups. Linear R^1 groups having from 8 to 11 carbon atoms, or from 8 to 10 carbon atoms are preferred. Such a cationic surfactant which is highly preferred has a formula wherein R_1 is a C_8-C_{10} alkyl group, p is 1, A is ethoxy and R_2 and R_3 are methyl groups.

It has been found that mixtures of the cationic surfactants of formula I may be particularly effective, for example, surfactant mixtures in which R^1 may be a combination of C_8 and C_{10} linear alkyl groups, or C_9 and C_{11} alkyl groups.

Another highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula



wherein R^1 is C_{10}-C_{18} hydrocarbyl and mixtures thereof, especially C_{10}-C_{14} alkyl, preferably C_{10} and C_{12} alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

As noted, compounds of the foregoing type include those wherein the ethoxy (CH_2CH_2O) units (EO) are replaced by butoxy, isopropoxy [$CH(CH_3)CH_2O$] and [$CH_2CH(CH_3O$] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

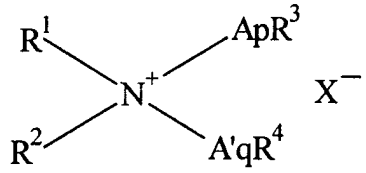
When used in granular detergent compositions cationic mono-alkoxylated amine surfactants wherein the hydrocarbyl substituent R^1 is C_8-C_{11}, especially C_{10}, are preferred, because they

enhance the rate of dissolution of laundry granules, especially under cold water conditions, as compared with the higher chain length materials.

The levels of the cationic mono-alkoxylated amine surfactants used in detergent compositions of the invention is preferably from 0.1% to 20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3.0% by weight of the composition.

Cationic bis-alkoxylated amine surfactant

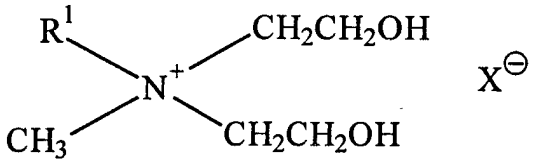
The cationic surfactant of the invention can be a cationic bis-alkoxylated amine surfactant, which has the general formula II:



(II)

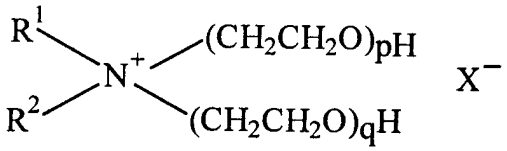
wherein R^1 is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R^2 is an alkyl group containing from one to three carbon atoms, preferably methyl; R^3 and R^4 can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C_1-C_4 alkoxy, especially ethoxy, (i.e., $-CH_2CH_2O-$), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

Highly preferred cationic bis-alkoxylated amine surfactants for use herein are of the formula



wherein R^1 is C_{10}-C_{18} hydrocarbyl and mixtures thereof, preferably C_{10}, C_{12}, C_{14} alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in a preferred compound R^1 is derived from (coconut) C_{12}-C_{14} alkyl fraction fatty acids, R^2 is methyl and ApR^3 and $A'qR^4$ are each monoethoxy.

Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:



wherein R^1 is C_{10}-C_{18} hydrocarbyl, preferably C_{10}-C_{14} alkyl, independently p is 1 to about 3 and q is 1 to about 3, R^2 is C_1-C_3 alkyl, preferably methyl, and X is an anion, especially chloride or bromide.

Other compounds of the foregoing type include those wherein the ethoxy (CH_2CH_2O) units (EO) are replaced by butoxy (Bu) isopropoxy [$CH(CH_3)CH_2O$] and [$CH_2CH(CH_3O$] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid (PAP), nonanoylamido peroxo-adipic acid (NAPAA) and hexane sulphenoyl peroxypropionic acid and are also suitable herein.

When used in granular detergent compositions in accord with the invention, cationic bis alkoxylated amine surfactants wherein the hydrocarbyl substituent R^1 is C_8-C_{11}, especially C_{10}, are preferred cationic surfactants, because they enhance the rate of dissolution of laundry granules, especially under cold water conditions, as compared with the higher chain length materials.

The levels of the cationic bis-alkoxylated amine surfactants used in detergent compositions of the invention can range from 0.1% to 20%, preferably from 0.4% to 7%, most preferably from 0.5% to about 3.0%, by weight of the detergent composition.

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 washing operation for which it is to be used.

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

Additional Detergent Surfactants

Optionally, additional surfactants, selected from the group consisting of anionic zwitterionic, ampholytic and amphoteric surfactants can be present.

The total amount of surfactants is preferably of from 1% to 95%, preferably 3% to 70%, more preferably 5% to 40%, even more preferably 10% to 30%, most preferably 12% to 25% by weight of the detergent composition.

A preferred aspect of the present invention is a granular detergent composition. One or more of the surfactants can be comprised in a base composition, containing optionally hydrophobic peroxyacid bleaching component and/or hydrophilic nonionic surface-active component. The base composition may be prepared by spray-drying and dry-mixing/agglomeration. Alternatively, the hydrophobic peroxyacid bleaching component and/or hydrophilic nonionic surface-active component may be added as separate components to the detergent base composition, preferably combined with other additional detegrent components, as described herein, in a granular form.

Anionic surfactant

The detergent composition of the present invention can comprise one or more anionic surfactants. Any anionic surfactant useful for detersive purposes is suitable. Examples 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. Anionic sulfate surfactants are preferred.

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 C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} 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.

The anionic surfactant is preferably present at a level of 0.5% to 60%, preferably at a level of from 3% to 50%, more preferably of from 5% to 35%, most preferably from 6% to 20% by weight of the composition.

The ratio of the anionic surfactant to the cationic surfactant is preferably from 25:1 to 1:3, more preferably from 15:1 to 1:1. most preferably from 10:1 to 1:1.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C_9-C_{22} alkyl sulfates, more preferably the C_{11}-C_{15} branched chain alkyl sulfates and the C_{12}-C_{14} linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10}-C_{18} alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_{11}-C_{18}, most preferably C_{11}-C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_20)_x\ CH_2C00^-$ M^+ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO\text{-}(CHR_1\text{-}CHR_2\text{-}O)X\text{-}R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. 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. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula $R\text{-}CON\ (R^1)\ CH_2$ COOM, wherein R is a $C_5\text{-}C_{17}$ linear or branched alkyl or alkenyl group, R^1 is a $C_1\text{-}C_4$ 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.

Amphoteric surfactant

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

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

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

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions or components thereof in accord with the invention. 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.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, each R^1 is typically C_1-C_3 alkyl, and R^2 is a C_1-C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

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 that two carbon atoms, borates, phosphates, 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. Polycarboxylates 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. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Suitable 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.

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 largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula $Na_z[(AlO_2)_z(SiO_2)y]. xH_2O$ 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 HS and mixtures thereof. Zeolite A has the formula

$Na_{12}[AlO_2)_{12}(SiO_2)_{12}]. xH_2O$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]. 276 H_2O$.

Preferred crystalline layered silicates for use herein have the general formula

$$NaMSi_xO_{2x+1}.yH_2O$$

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. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is preferably 2. The most preferred material is δ-$Na_2Si_2O_5$, available from Hoechst AG as NaSKS-6.

Bleach catalyst

The compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach

catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include Mn^{IV}_2(u-O)$_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(PF_6)_2$, Mn^{III}_2(u-O)$_1$(u-OAc)$_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_2$, Mn^{IV}_4(u-O)$_6$(1,4,7-triazacyclononane)$_4$-$(ClO_4)_2$, $Mn^{III}Mn^{IV}_4$(u-O)$_1$(u-OAc)$_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)$(OCH_3)_3$-(PF_6). Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including N_4Mn^{III}(u-O)$_2Mn^{IV}N_4)^+$and [$Bipy_2Mn^{III}$(u-O)$_2Mn^{IV}bipy_2$]-$(ClO_4)_3$.

Further suitable bleach catalysts are described, for example, in European patent application No. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Acid Source

An acid source can be present in the detergent composition of the inevntion such that it is capable of reacting with a source of alkali, preferably a carbonate or bicarbonate salt, in the presence of water to produce a gas.

The acid source is preferably present at a level of from 0.1% to 50%, more preferably from 0.5% to 25%, even more preferably from 1% to 12%, even more preferably from 1% to 7%, most preferably from 2% to 5% by weight of the composition. In a preferred embodiment of the present invention the source of acidity is present in the range of about 1% to about 3%, most preferably about 3% by weight of the composition.

The acid source may be any suitable organic, mineral or inorganic acid, or a derivative thereof, or a mixture thereof. The acid source may be a mono-, bi- or tri-protonic acid. Preferred derivatives include a salt or ester of the acid. The source of acidity is preferably non-hygroscopic, which can improve storage stability. However, a monohydrate acidic source can be useful herein. Organic acids and their derivatives are preferred. The acid is preferably water-soluble. Suitable acids include citric, glutaric, tartaric acid, succinic or adipic acid, monosodium phosphate, sodium hydrogen sulfate, boric acid, or a salt or an ester thereof. Citric acid is especially preferred.

Heavy metal ion sequestrant

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

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 hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic 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.

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 alos suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are 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, cutinases, 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 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 Pseudomas 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, Huge-Jensen et al, issued March 7, 1989.

Organic polymeric compound

Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. 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, including 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.

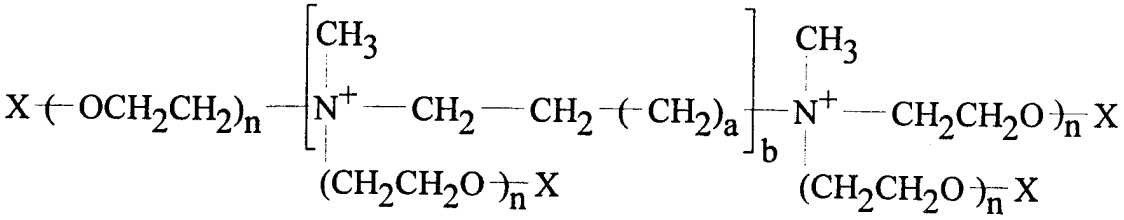
The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

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, hydroxypropylmethylcellulose 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.

Another organic compound, which is a preferred clay dispersant/ anti-redeposition agent, for use herein, can be the ethoxylated cationic monoamines and diamines of the formula:



wherein X is a nonionic group selected from the group consisting of H, C_1-C_4 alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic monoamines (b=0), n is at least 16, with a typical range of from 20 to 35; for cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

Other dispersants/ anti-redeposition agents for use herein are described in EP-B-011965 and US 4,659,802 and US 4,664,848.

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 and 2-alkyl alcanol 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 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 C_{18}-C_{40} ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine 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.

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 C_{16}-C_{18} 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 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.

Clay softening system

The detergent compositions may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent.

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

Polymeric dye transfer inhibiting agents

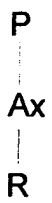
The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

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

a) Polyamine N-oxide polymers

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

(I)



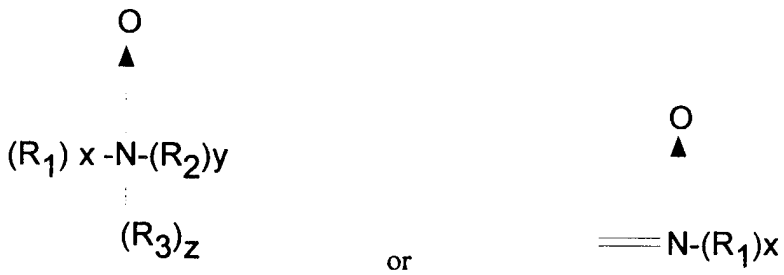
wherein P is a polymerisable unit, and

O O O

A is NC, CO, C, -O-, -S-, -N-; x is O or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto 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 pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises 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 pyrridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-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.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Suitable herein are coploymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. 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.

d) Polyvinyloxazolidone

The detergent compositions herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000.

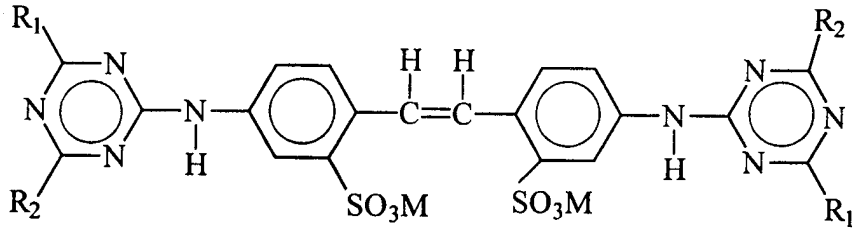
e) Polyvinylimidazole

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.

Optical brightener

The detergent compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include 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.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. 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.

pH of the compositions

The present compositions preferably have a pH measured as a 1% solution in distilled water of at least 10.0, preferably from 10.0 to 12.5, most preferably from 10.5 to 12.0.

Form of the compositions

The detergent composition of the invention can be made via a variety of methods, including dry-mixing and agglomerating of the various compounds comprised in the detergent composition. The acid source of the invention is preferably dry-added as a separate component.

The compositions in accordance with the invention can take a variety of physical forms including granular, tablet, bar and liquid forms. The compositions are particularly the so-called concentrated granular detergent compositions adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

The mean particle size of the base composition of granular compositions in accordance with the invention can be from 0.1 mm to 5.0 mm, but it should preferably be such that no more that 5%

of particles are greater than 1.7mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 600 g/litre, more preferably from 650 g/litre to 1200 g/litre. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

Surfactant agglomerate particles

The surfactant system herein is preferably present in granular compositions in the form of surfactant agglomerate particles, which may take the form of flakes, prills, marumes, noodles, ribbons, but preferably take the form of granules. The most preferred way to process the particles is by agglomerating powders (e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-

4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name).

A high active surfactant paste comprising from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of surfactant is typically used. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used. An operating temperature of the paste of 50°C to 80°C is typical.

In an especially preferred embodiment of the present invention, the detergent composition has a density of greater than about 600 g/l and is in the form of powder or a granulate containing more than about 5% by weight of the alkali, preferably (bi-) carbonate or percarbonate. The carbonate material is either dry-added or delivered via agglomerates. The acid, preferably citric acid, (preferably up to 10%) may be introduced into the product as a dry-add as a separate compound, or as a part of the agglomerate mix.

Laundry washing method

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. 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 use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. 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 contact with 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 with the composition of 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 know as the "granulette". Another preferred dispensing device for use with the compositions of this invention is disclosed in PCT Patent Application No. WO94/11562.

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.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published

Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

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 European Application No. 94921505.7.

Abbreviations used in Examples

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

LAS	:	Sodium linear C_{12} alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C45AS	:	Sodium C_{14}-C_{15} linear alkyl sulfate
CxyEzS	:	Sodium C_{1x}-C_{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
C45E7	:	A C_{14-15} predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
CxyEz	:	A C_{1x-1y} branched primary alcohol condensed with an average of z moles of ethylene oxide
QAS I		$R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_8$
QAS II	:	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with R_2 = 50%-60% C_9; 40%-50% C_{11}
QAS III	:	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with R_2 = 30%-70% C_{10}; 30%-70% C_8
QAS IV	:	$R_1.N^+(CH_3)(C_2H_4OH)_2$ with $R_1 = C_{12}$-C_{14}
QAS V	:	$R^2O(C_2H_4O)_x$(glycosyl)$_2$, wherein R^2 is a C_8-C_{10} alkyl group ; t is from 2 to 8
Soap	:	Sodium linear alkyl carboxylate derived from an

80/20 mixture of tallow and coconut oils.

TFAA : C_{16}-C_{18} alkyl N-methyl glucamide

TPKFA : C12-C14 topped whole cut fatty acids

STPP : Anhydrous sodium tripolyphosphate

Zeolite A : Hydrated Sodium Aluminosilicate of formula $Na_{12}(AlO_2SiO_2)_{12}.27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers

NaSKS-6 : Crystalline layered silicate of formula δ-$Na_2Si_2O_5$

Citric acid : Anhydrous citric acid

Carbonate : Anhydrous sodium carbonate with a particle size between 200μm and 900μm

Bicarbonate : Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm

Silicate : Amorphous Sodium Silicate (SiO_2:Na_2O; 2.0 ratio)

Sodium sulfate : Anhydrous sodium sulfate

Citrate : Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and q 850μm

MA/AA : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.

CMC : Sodium carboxymethyl cellulose

Protease : Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase

Alcalase : Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S

Cellulase : Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme

Amylase : Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T

Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase	:	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4	:	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
Percarbonate	:	Sodium Percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
NAC-OBS	:	(Nonanamido caproyl) oxybenzene sulfonate in the form of the sodium salt.
DPDA	:	Diperoxydodecanedioic acid
PAP	:	N-phthaloylamidoperoxicaproic acid
NAPAA	:	Nonanoylamido peroxo-adipic acid
NACA	:	6 nonylamino - 6 oxo - capronic acid.
TAED	:	Tetraacetylethylenediamine
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
Photoactivated dextrin soluble polymer	:	Sulfonated Zinc Phthlocyanine encapsulated in bleach
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
HEDP	:	1,1-hydroxyethane diphosphonic acid
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrolidone and vinylimidazole
QEA	:	bis $((C_2H_5O)(C_2H_4O)_n)(CH_3)-N^+-C_6H_{12}-N^+-(CH_3)$ bis $((C_2H_5O)-(C_2H_4O)_n)$, wherein n=from 20 to 30
SRP 1	:	Sulfobenzoyl end capped esters with oxyethylene oxy and terephtaloyl backbone
SRP 2	:	Diethoxylated poly (1, 2 propylene terephtalate) short block polymer

Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

In the following Examples all levels are quoted as parts per weight of the composition or % by weight of the composition, as indicated:

Example 1

The following high density granular laundry detergent compositions A to F of particular utility under European machine wash conditions were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E9	3.4	-	-	3.4	5.4	2.4
C25E7	-	3.0	4.5	-	-	-
C46AS	1.0	2.0	2.5	-	3.0	4.0
C24AS	3.0	2.0	5.0	7.0	1.0	0.5
QAS I	0.8	2.0	-	1.5	0.5	-
QAS II	-	-	0.8	-	-	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Citric acid	2.0	1.0	-	-	-	-
Silicate	1.4	1.4	1.4	3.0	3.0	3.0

Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
PB4	9.0	9.0	9.0	-	-	-
Percarbonate	-	-	-	18.0	15.0	20.0
TAED	-	-	1.0	1.5	-	-
NAC-OBS	4.0	2.5	0.5	1.0	2.0	5.0
DTPMP	0.25	0.25	0.25	0.25	0.25	0.25
EDDS	-	-	0.25	0.4	-	-
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
QEA	0.5	1.0	-	-	0.5	-
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions G to I of bulk density 750 g/litre are compositions according to the invention:

	G	H	I
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
QAS I	0.8	2.0	-
QAS II	0.4	1.0	2.5
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Sodium sulfate	39.8	-	7.0

PB4	5.0	12.7	-
TAED	0.5	0.2	-
DPDA	-	-	9.0
NAC OBS	1.0	2.2	-
DTPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Protease	0.26	0.85	0.85
Lipase	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28
Amylase	0.1	0.1	0.1
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
PVP	-	-	0.8
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04
Perfume	0.3	0.3	0.3

Silicone antifoam	0.5	2.4	2.4
Minors/misc to 100%	n.a.	n.a.	

Example 3

The following are detergent formulations, according to the present invention where J is a phosphorus-containing detergent composition, K is a zeolite-containing detergent composition and L is a compact detergent composition:

	J	K	L	M
Blown Powder				
STPP	24.0	-	24.0	-
Zeolite A	-	24.0	-	24.0
C45AS	9.0	6.0	13.0	5.0
QAS I	-	2.0	-	-
QAS II	-	-	2.0	-
QAS III	2.0	-	-	-
QAS IV	-	-	-	1.0
MA/AA	2.0	4.0	2.0	4.0
LAS	6.0	8.0	11.0	8.0
TAS	2.0	-	-	-
Silicate	7.0	3.0	3.0	3.0
CMC	1.0	1.0	0.5	1.0
Brightener 2	0.2	0.2	0.2	0.2
Soap	1.0	1.0	1.0	1.0
DTPMP	0.4	0.4	0.2	0.4
Spray On				
C25E9	-	-	2.0	-
C45E7	2.5	2.5	-	2.5
C25E3	2.5	2.5	2.0	2.5
Silicone antifoam	0.3	0.3	0.3	0.3
Perfume	0.3	0.3	0.3	0.3
Dry additives				
QEA	-	0.5	1.0	-
Carbonate	6.0	13.0	15.0	13.0
PB4	18.0	18.0	10.0	18.0
PB1	4.0	4.0	-	4.0
NAC-OBS	3.0	4.2	1.0	3.0
Photoactivated bleach	0.02	0.02	0.02	0.02
Protease	1.0	1.0	1.0	1.0
Lipase	0.4	0.4	0.4	0.4
Amylase	0.25	0.30	0.15	0.3

Dry mixed sodium sulfate	3.0	3.0	5.0	3.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0	100.0
Density (g/litre)	630	670	670	670

Example 4

The following are detergent formulations according to the present invention:

	N	O	P	Q
LAS	20.0	14.0	24.0	22.0
QAS I	0.7	1.0	-	0.7
QAS II	0.4	-	1.0	-
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	6.5
C45E9	2.5	2.5	1.0	-
STPP	30.0	18.0	30.0	22.0
Silicate	9.0	5.0	10.0	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DTPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Protease	0.8	1.0	0.5	0.5
Amylase	0.8	0.4	-	0.25
Lipase	0.2	0.1	0.2	0.1
Cellulase	0.15	0.05	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NACA	-	-	-	3.0
NAC OBS	2.0	1.0	0.9	3.1
Balance (Moisture and Miscellaneous)	100	100	100	100

Example 5

The following are detergent formulations according to the present invention:

	R	S	T
Blown Powder			
QAS I	1.5	1.5	1.5

QAS III	-	0.4	1.5
Zeolite A	30.0	22.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	3.0	3.0	6.0
LAS	14.0	12.0	22.0
C45AS	8.0	7.0	7.0
Silicate	-	1.0	5.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
Carbonate	8.0	16.0	20.0
Spray On			
C45E11	1.0	-	2.5
C45E7	1.0	1.0	-
Dry additives			
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NACA	-	6.1	-
NAC OBS	3.4	-	4.5
Sodium sulfate	-	6.0	-
Balance (Moisture and Miscellaneous)	100	100	100

Example 6

The following are high density and bleach-containing detergent formulations according to the present invention:

	U	V	W
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodium sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS V	-	-	0.5
QAS I	0.9	-	-
QAS II	-	1.5	1.5
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0

Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
C25E9	-	0.5	1.5
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
QEA	-	-	0.5
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
NAC OBS	6.0	2.0	5.0
NACA	2.0	-	-
PB1	14.0	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Citric acid	-	-	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 7

The following are high density detergent formulations according to the present invention:

	X	Y
Agglomerate		
C45AS	11.0	14.0
QAS I	1.8	2.2
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DTPMP	0.4	0.4
Spray On		
C45E11	-	4.0
C25E7	5.0	1.0

Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	-	1.0
Citric acid	2.0	-
NAC OBS	4.1	6.2
TAED	0.8	1.0
Percarbonate	20.0	20.0
SRP 1	0.3	0.3
Protease	1.4	1.4
Lipase	0.4	0.4
Cellulase	0.6	0.6
Amylase	0.6	0.6
QEA	1.0	-
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Density (g/litre)	850	850

Example 8

The following are liquid detergent formulations according to the present invention:

	Z	AA	AB	AC	AD	AE	AF	AG
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E9	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
QAS I	-	-	-	-	3.0	1.0	1.0	-
QAS II	0.6	1.2	-	-	3.5	-	-	-
QAS III	-	-	0.8	-	-	3.5	-	-
QAS V	-	-	-	1.0	-		-	2.0
TPKFA	2.0	-	13.0	2.0	-	15.0	7.0	7.0
Rapeseed fatty acids	-	-	-	5.0	-	-	4.0	4.0
Citric acid	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl/tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Oleic acid	4.0	2.0	1.0	-	1.0	-	-	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.-
Mono Ethanol Amine	-	-	-	5.0	-	-	9.0	9.0
Tri Ethanol Amine	-	-	8	-	-	-	-	-
NaOH up to pH	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2

Ethoxylated tetraethylene pentamine	0.5	-	0.5	0.2	-	-	0.4	0.3
NAC OBS	1.0	1.0	0.5	1.0	2.0	1.2	1.0	1.6
NACA	-	1.1	1.8	-	1.9	-	1.4	1.0
PB_4	2.0	2.6	3.1	3.0	3.1	3.5	2.9	2.5
SRP 2	0.3	-	0.3	0.1	-	-	0.2	0.1
PVNO	-	-	-	-	-	-	-	0.10
Protease	0.5	0.5	0.4	0.25	-	0.5	0.3	0.6
Alcalase	-	-	-	-	1.5	-	-	-
Lipase	-	0.10	-	0.01	-	-	0.15	0.15
Amylase	0.25	0.25	0.6	0.5	0.25	0.9	0.6	0.6
Cellulase	-	-	-	0.05	-	-	0.15	0.15
Endolase	-	-	-	0.10	-	-	0.07	-
Boric acid	0.1	0.2	-	2.0	1.0	1.5	2.5	2.5
Na formate	-	-	1.0	-	-	-	-	-
Ca chloride	-	0.015	-	0.01	-	-	-	-
Bentonite clay	-	-	-	-	4.0	4.0	-	-
Suspending clay SD3	-	-	-	-	0.6	0.3	-	-
Balance (Moisture and Miscellaneous)	100	100	100	100	100	100	100	100

Example 9

The following granular detergent formulations are examples of the present invention.

	AH	AI	AJ
Blown powder			
LAS	5.0	9.0	8.0
C45AS	7.0	-	-
C46AS	4.0	-	-
C45E35	3.0	8.0	5.0
QAS II	-	-	3.0
QAS III	0.5	2.0	-
Zeolite A	16.0	19.0	16.0
MA/AA	3.0	-	-
AA	3.0	2.0	3.0
Sodium sulfate	3.3	24.0	13.3
Silicate	1.0	2.0	1.0
Carbonate	9.0	25.7	8.0
QEA	0.4	-	0.5
PEG 4000	-	1.0	1.5
Brightener	0.3	0.3	0.3
Spray on			
C25E5	-	-	-
C45E7	2.0	0.5	2.0
Perfume	0.3	1.0	0.3
Agglomerates			

C45AS	5.0	-	5.0
LAS	2.0	-	2.0
Zeolite A	7.5	-	7.5
HEDP	1.0	-	2.0
Carbonate	4.0	-	4.0
PEG 4000	0.5	-	0.5
Misc (water etc)	2.0	-	2.0
Dry additives			
NAPAA	8.0	-	4.0
PAP	-	1.0	1.0
TAED	-	-	1.0
PB4	-	-	2.0
Carbonate	5.3	-	2.5
Cumeme sulfonic acid	2.0	-	2.0
Lipase	0.4	0.1	0.05
Cellulase	0.2	-	0.2
Amylase	0.3	-	-
Protease	1.6	-	1.6
PVPVI	0.5	-	-
PVNO	0.5	-	-
SRP1	0.5	-	-
Silicone antifoam	0.2	-	0.2

What is claimed is:

1. A detergent composition comprising

a) a hydrophobic peroxyacid bleaching component, capable of providing a hydrophobic peroxyacid compound, with the proviso the component does not comprise the sodium salt of nonanoyloxybenzene sulfonate;

b) a hydrophilic nonionic component, having a Hydrophilic/ Lipophilic Balance of at least 10.8, as measured by the HLB-test;

c) a cationic surfactant component, with the proviso that the cationic surfactant is not a cationic choline ester surfactant or a salt of the cationic C_{12} - C_{14} alkyl dimethyl ammonium ethanol surfactant.

2. A detergent composition according to claim 1 wherein the hydrophilic nonionic component is a nonionic surfactant.

3. A detergent composition according to claim 2 wherein the nonionic surfactant is a C_6-C_{16} alkyl with from 6 to 12 moles of alkylene oxide.

4. A detergent composition according to claim 2 or 3 wherein the nonionic surfactant is a C_{12}-C_{16} alkyl with from 7 to 9 moles of ethylene oxide.

5. A detergent composition according to claim 2 wherein the nonionic surfactant is a alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl group contains from 8 to 10 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8 and the glycosyl is derived from glucose.

6. A detergent composition according to any preceding claim wherein the hydrophilic nonionic component is present at a level of from 0.5% to 20% by weight of the detergent composition.

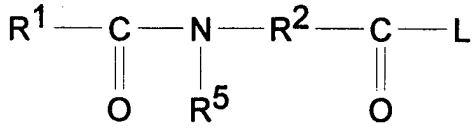
7. A detergent composition according to any preceding claim wherein the hydrophilic nonionic component has a Hydrophilic/ Lipophilic Balance of at least 11.6, as measured by the HLB-test

8. A detergent composition according to any preceding claim wherein said hydrophobic peroxyacid bleaching component comprises a hydrogen peroxide source and a hydrophobic organic peroxyacid precursor.

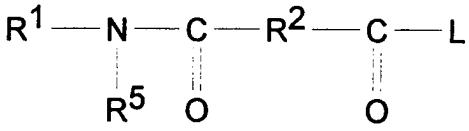
9. A detergent composition according to claim 8 wherein said hydrophobic organic peroxyacid precursor comprises at least one nitrogen atom.

10. A detergent composition according to claim 8 wherein said hydrophobic organic peroxyacid precursor is present at a level of from 0.05% to 20% by weight of the detergent composition.

11. A detergent composition according to any of claims 8 to 10 wherein the organic peroxyacid precursor compound is an amide substituted alkyl peroxyacid precursor compound selected from the group consisting of



and



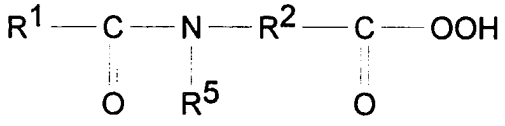
wherein L can be essentially any leaving group, R^1 is an aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms such that R^1 and R^5 in total not contain more than 18 carbon.

12. A detergent composition according to any of claims 1 to 7 wherein

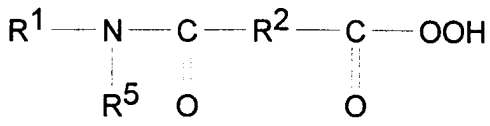
said hydrophobic peroxyacid bleaching component comprises a preformed organic peroxyacid.

13. A detergent composition according to claim 12 wherein said preformed organic peroxyacid is present at a level of from 0.05% to 20% by weight of the detergent composition.

14. A detergent composition according to either of claims 12 or 13 wherein the preformed organic peroxyacid is selected from the group consisting of:



and



wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms such that R^1 and R^5 not contain more than 18 carbon atoms total.

15. A detergent composition according to any preceding claim wherein said cationic surfactant is present at a level of from 0.1% to 20% by weight of the composition.

16. A detergent composition according to any preceding claim wherein the cationic surfactant is selected from the group consisting of mono-alkoxylated amine and bis-alkoxylated amine.

17. A detergent composition according to claim 16 wherein said cationic mono-alkoxylated amine contains a positively charged amine group, which is substituted with two methyl groups, a C_6-C_{18} alkyl group and an alkoxy group.

18. A detergent composition according to claim 17 wherein said positively charged amine group is substituted with a C_8-C_{11} alkyl group and a hydroxyalkyl group having no greater than 6 carbon atoms.

19. A detergent composition or component thereof according claim 16 wherein said cationic bis-ethoxylated amine surfactant contains a positively charged amine group, which is substited with a methyl group, a C_8-C_{18} alkyl group and two (poly) alkoxy groups.

20. A detergent composition or component thereof according to any preceding claim wherein the ratio of the cationic surfactant to the hydrophilic nonionic component is from 20:1 to 1:30.

21. A detergent composition or component thereof according to any preceding claim wherein the ratio of the hydrophobic peroxyacid bleaching component to the hydrophilic nonionic component is from 50:1 to 1:20.

22. A method of washing laundry in a domestic washing machine comprising,

introducing into a dispensing device which is placed in the drum of the washing machine, or introducing into the dispensing drawer of a washing machine, an effective amount of a detergent composition of any one of claims 1 to 21.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/17817

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C11D 1/72, 1/835, 3/39, 3/395
US CL :510/302, 303, 310, 341, 349, 350, 356, 372, 375, 378, 470
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/302, 303, 310, 341, 349, 350, 356, 372, 375, 378, 470

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

NONE

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

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,503,639 A (WILLEY ET AL) 02 April 1996, see Abstract; column 2, lines 20-35; column 3, lines 45-69; column 5, line 10 to column 7, line 10; column 11, line 40 to column 12, line 30.	1-5
X	US 5,458,809 A (FREDJ ET AL) 17 October 1995, see Abstract; column 4, line 20 to column 9, line 60; column 12, line 20 to column 13, line 15.	1-5
X	US 5,259,982 A (CHAPPLE) 09 November 1993, see Abstract; column 2, lines 10-69; column 4, line 50 to column 5, line 35.	1-5

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search
20 NOVEMBER 1997

Date of mailing of the international search report
29 JAN 1998

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/17817

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 6-22
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/17817

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS
search terms: perborate, percarbonate, TAED, tetraacetyl ethylene diamine, cationic, alkyl polyglycoside, valerolactam, caprolactam, ethoxy, ethoxylated