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(54) **COMPOSITION DETERGENTE**
(54) **DETERGENT COMPOSITION**

(57) L'invention concerne des compositions détergentes ou leurs composants. Ces compositions renferment un ou plusieurs tensioactifs cationiques et un ou plusieurs composés cationiques qui sont des composés (poly)amine éthoxylés (partiellement) quaternisés ayant des propriétés d'élimination des taches d'argile et des propriétés d'antiredéposition.

(57) The present invention relates to detergent compositions or components thereof containing one or more cationic surfactants and one or more cationic compounds, which are cationic, (partially) quaternized ethoxylated (poly)amine compounds with clay-soil removal/antiredeposition properties.

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(54) Title: DETERGENT COMPOSITION

(57) Abstract

The present invention relates to detergent compositions or components thereof containing one or more cationic surfactants and one or more cationic compounds, which are cationic, (partially) quaternized ethoxylated (poly)amine compounds with clay-soil removal/antiredeposition properties.

Detergent Composition

Technical Field

The present invention relates to detergent compositions or components thereof containing cationic compounds with clay-soil removal/anti-redeposition properties and cationic surfactants for use in laundry processes.

Background to the Invention

A particularly important property of a detergent composition is its ability to remove particulate type soils from a variety of fabrics during laundering. Perhaps the most important particulate soils are the clay-type soils. Clay soil particles generally comprise negatively charged layers of aluminosilicates and positively charged cations (e.g. calcium) which are positioned between and hold together the negatively charged layers.

A variety of models can be proposed for compounds which would have clay soil removal properties. One model requires that the compound have two distinct characteristics. The first is the ability of the compound to adsorb onto the negatively charged layers of the clay particle. The second is the ability of the compound, once adsorbed, to push apart (swell) the negatively charged layers so that the clay particle loses its cohesive force and can be removed in the wash water.

In addition to clay soil removal, there is a need to keep the removed soil in suspension during the laundering cycle. Soil which is removed from the fabric and suspended in the wash water can redeposit on the surface of the fabric. This redeposited soil causes a dulling or "greying" effect which is especially noticeable on white fabrics. To minimise this problem, anti-redeposition agents can be included in the detergent composition.

For example EP-B-111 965 disclose the use in detergents of cationic compounds, which have both clay-soil removal and anti-redeposition properties.

A model proposed for the anti-redeposition action of the positively charged anti-redeposition compounds is as follows. Adsorption of the positively charged molecule on the surface of clay particles in the wash water gives the particles the dispersancy properties of the molecule. As more and more of these compounds adsorb onto the suspended clay soil particles, the latter become encased within a hydrophilic layer provided by the attached ethoxy units. As such the hydrophilically encased soil is prevented from redepositing on fabrics, in particular hydrophobic fabrics such as polyester, during the laundering cycle.

Other detergent components traditionally employed in detergents are surfactants, such as anionic and cationic surfactants.

US 4,659,802 and US 4,664,848 describe cationic (quaternized) amine compounds which have clay-soil removal and anti-redeposition properties, which have been found to be compatible with anionic surfactants. As mentioned therein, this finding was surprising, since anionic surfactants were found to interfere with certain other quaternized amines, known in the art, thereby diminishing the soil-removal capacity of these quaternized amines.

It has been found however that the soil-removal/ anti-redeposition capacity of the cationic (quaternized) amine compounds, as described in EP-B-111965 and above mentioned US patents, can be diminished as well by the use of particular anionic components, such as anionic surfactants, when used in certain levels and ratios.

The Applicants have found that this problem can be ameliorated by the use of cationic surfactants, in detergent compositions (or components thereof) containing (partially) quaternized ethoxylated (poly) amines which have clay-soil removal/anti-redeposition properties and anionic compounds such as anionic surfactants. Detergent compositions (or components thereof) employing both cationic quaternized ethoxylated (poly) amines and cationic surfactant have been shown to deliver a

surprisingly better cleaning performance than that of detergent compositions employing either of the two components individually.

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

Summary of the invention

The present invention relates to granular detergent compositions or components thereof, which comprise one or more cationic surfactants and one or more cationic compounds, which are cationic, (partially) quaternized ethoxylated (poly) amine compounds with particulate/ clay-soil removal / anti-redeposition properties.

In more detail, the present invention relates to a detergent composition or component thereof which comprise

(a) a cationic surfactant selected from the group consisting of:

(1) cationic ester surfactants;

(2) cationic mono-alkoxylated amine surfactants; and

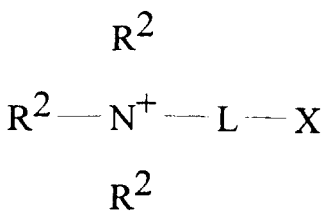
(3) cationic bis-alkoxylated amine surfactants;

(4) mixtures thereof;

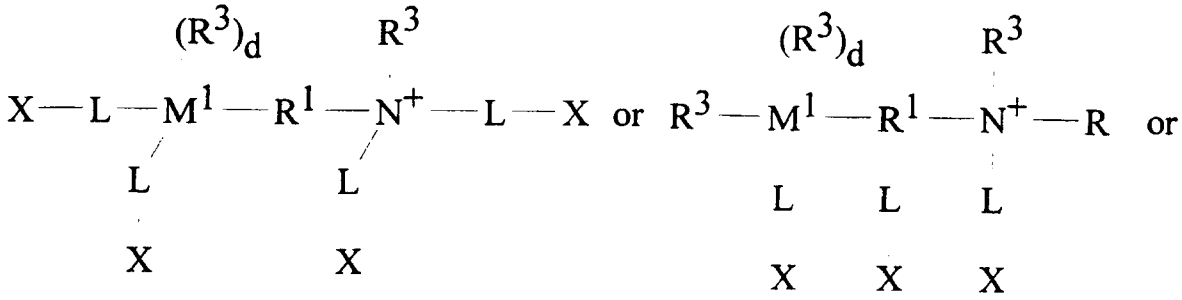
and

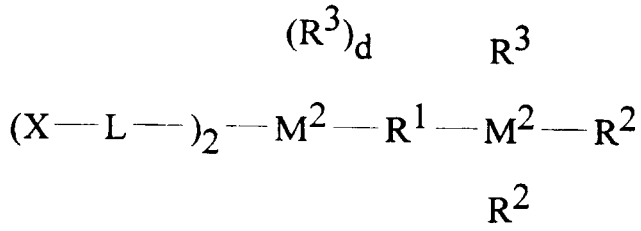
(b) a water-soluble cationic compound
having clay soil removal/anti-redeposition properties, which is selected from the group consisting of:

1) ethoxylated cationic monoamines having the formula:



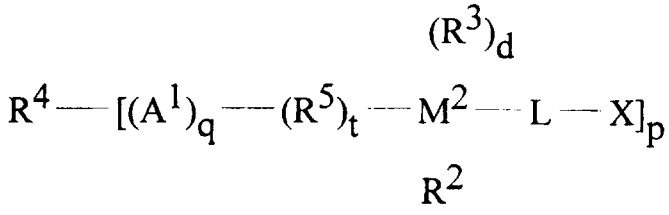
2) ethoxylated cationic diamines having the formula:



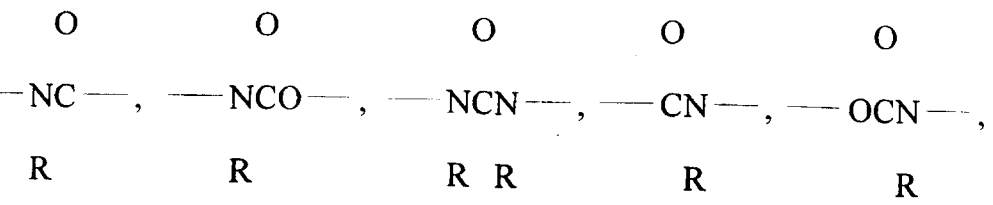


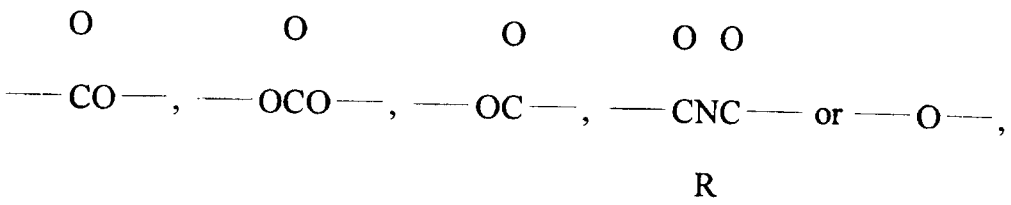
wherein M^1 is an N+ or N group; each M^2 is an N+ or N group, and at least one M^2 is an N+ group;

3) ethoxylated cationic polyamines having the formula:



4) mixtures thereof;

wherein A^1 is 



R is H or C_1-C_4 alkyl or hydroxyalkyl, R^1 is C_2-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R^2 is C_1-C_4 alkyl or hydroxyalkyl, the moiety -L-X, or two R^2 together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$, wherein A^2 is -O- or $-CH_2-$, r is 1 or 2, s is 1 or 2 and r + s is 3 or 4; each R^3 is C_1-C_8 alkyl or hydroxyalkyl, benzyl, the moiety L-X, or two R^3 or one R^2 and one R^3 together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$; R^4 is a substituted C_3-C_{12} alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl group having p substitution sites; R^5 is C_1-C_{12} alkenyl, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; 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; L is a hydrophilic chain which contains the polyoxyalkylene moiety $-[(R^6O)_m(CH_2CH_2O)_n]-$; wherein R^6 is C_3-C_4 alkylene or hydroxyalkylene and m and n are numbers such that the moiety $-(CH_2CH_2O)_n-$ comprises at least about 50% by weight of said polyoxyalkylene moiety; d is 1 when M^2 is N+ and is 0 when M^2 is N; n is at least about 16 for said cationic monoamines, is at least about 6 for said cationic diamines and is at least about 3 for said cationic polyamines; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1;

and wherein the ratio of (a) to (b) is from 1:95 to 95:1;

with the proviso that if the detergent composition is a liquid detergent composition the water-soluble cationic compound having clay soil removal/anti-redeposition properties is selected from the group consisting of (2) and (3) and mixtures thereof.

Detailed description of the invention

An essential feature of the present invention is a water-soluble cationic compound which has particulate/ clay-soil removal/anti-redeposition properties and which is selected from the group consisting of cationic mono-di- and polyamines.

If present in liquid detergent compositions of the present invention, as described hereinafter, the water-soluble cationic compound which has clay-soil removal/anti-redeposition properties is selected from the group consisting of cationic di- and polyamines.

The ratio of the water-soluble cationic compound to the cationic surfactant is from 1:95 to 95:1, more preferably from 1:8 to 12:1, more preferably from 1:5 to 6:1, most preferably from 1:2 to 3:1.

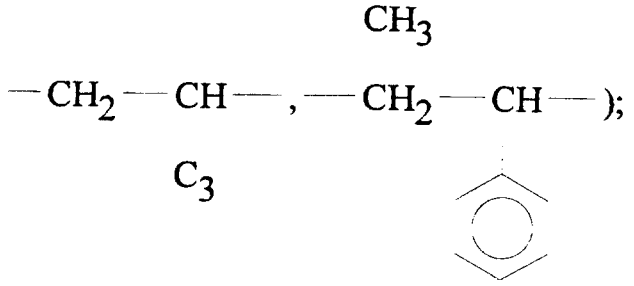
If present in detergent compositions in accord with the inevntion the water-soluble cationic compound is preferably present at a level of from 0.01% to 30%, more preferably from 0.1% to 15% , most preferably from 0.2% to 3.0% by weight of the detergent composition.

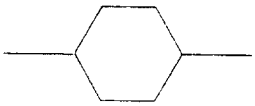
Cationic amines

The water-soluble cationic compounds of the present invention useful in the detergent compositions or components thereof of the present invention include ethoxylated cationic monoamines, ethoxylated cationic diamines and ethoxylated cationic polyamines as previously defined.

In the preceding formulas for the cationic amines, R^1 can be branched

(e.g.



cyclic (e.g. ),

or most preferably linear

(e.g. $-CH_2CH_2-$, $-CH_2CH_2CH_2-$)

alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene. R^1 is preferably C_2-C_6 alkylene for the ethoxylated cationic diamines. Each R^2 is preferably methyl or the moiety -L-X; each R^3 is preferably C_1-C_4 alkyl or hydroxyalkyl, and most preferably methyl.

The positive charge of the N+ groups is offset by the appropriate number of counter anions. Suitable counter anions include Cl-, Br-, SO_3^{-2}, PO_4^{-2}, $MeOSO_3$- and the like. Particularly preferred counter anions are Cl- and Br-.

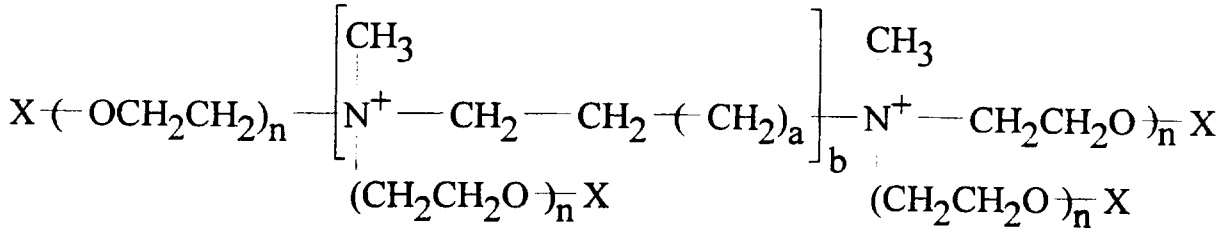
X can be a nonionc group selected from hydrogen (H), C_1-C_4 alkyl or hydroxyalkyl ester or ether groups, or mixtures thereof. Preferred esters or ethers are the acetate ester and methyl ether, respectively. The particularly preferred nonionic groups are H and the methyl ether.

In the preceding formulas, hydrophilic chain L usually consists entirely of the polyoxyalkylene moiety -$[(R^6O)_m(CH_2CH_2\text{-}O_n)]$-. The moieties -$(R^6O)$m- and -$(CH_2CH_2O)$n- of the polyoxyalkylene moiety can be mixed together or preferably form blocks of -$(R^6O)_m$- and -$(CH_2CH_2O)_n$- moieties. R^6 is preferably C_3H_6 (propylene); m is preferably from 0 to about 5 and is most

preferably 0, i.e. the polyoxyalkylene moiety consists entirely of the moiety -$(CH_2CH_2O)_n$-. The moiety -$(CH_2CH_2O)_n$- preferably comprises at least about 85% by weight of the polyoxyalkylene moiety and most preferably 100% by weight (m is O).

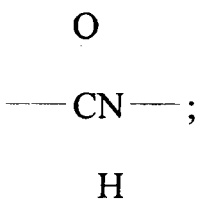
In the preceding formulas, M^1 and each M^2 are preferably an N+ group for the cationic diamines and polyamines.

Preferred ethoxylated cationic monoamines and diamines have the formula:



wherein X and n are defined as before, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0. For preferred cationic monoamines (b=0), n is preferably at least about 16, with a typical range of from about 20 to about 35. For preferred cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

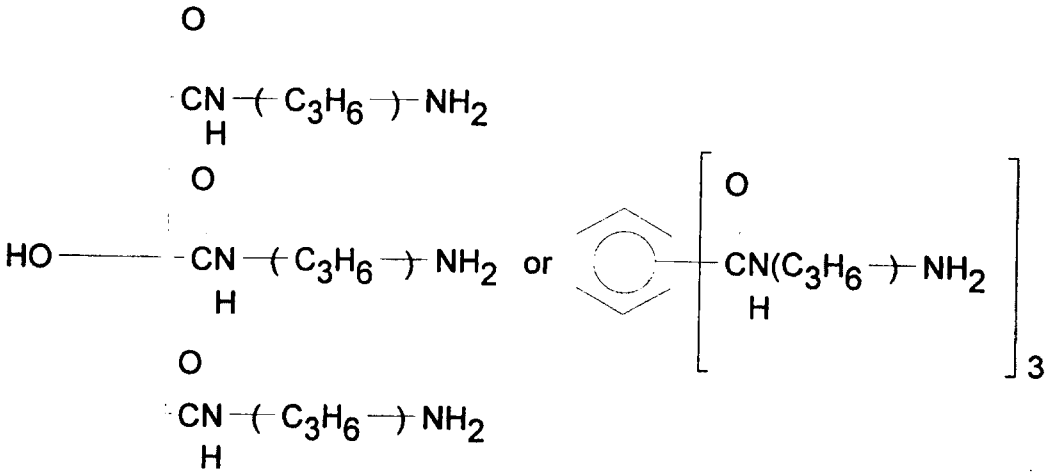
In the preceding formula for the ethoxylated cationic polyamines, R4 (linear, branched, or cyclic) is preferably a substituted C_3-C_6 alkyl, hydroxyalkyl or aryl group; A^1 is preferably



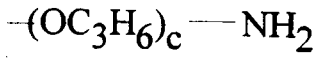
n is preferably at least about 12, with a typical range of from about 12 to about 42; p is preferably from 3 to 6. When R^4 is a substituted aryl or alkaryl group, q is preferably 1 and R^5 is preferably C_2-C_3 alkylene. When R^4 is a substituted alkyl, hydroxyalkyl, or alkenyl group, and when

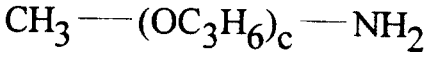
q is 0, R^5 is preferably a C_2-C_3 oxyalkylene moiety; when q is 1, R^5 is preferably C_2-C_3 alkylene.

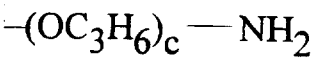
These ethoxylated cationic polyamines can be derived from polyamino amides such as:



These ethoxylated cationic polyamines can also be derived from polyaminopropyleneoxide derivatives such as:







wherein each c is a number from 2 to about 20.

Cationic surfactant

Another essential component of the detergent composition or components thereof of the invention is a cationic surfactant, selected from the group consisting of cationic ester surfactants, cationic mono-alkoxylated amine

surfactants, cationic bis-alkoxylated amine surfactants and mixtures thereof.

The ratio of the water-soluble cationic compound to the cationic surfactant is from 1:95 to 95:1, more preferably from 1:8 to 12:1, more preferably from 1:5 to 6:1, most preferably from 1:2 to 3:1.

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 ester surfactant

The detergent composition or component thereof in accord with the invention contains a cationic ester surfactant.

If present in a detergent compostion the cationic ester surfactant is preferably present at a level from 0.1% to 20.0%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3.0% by weight of the detergent composition.

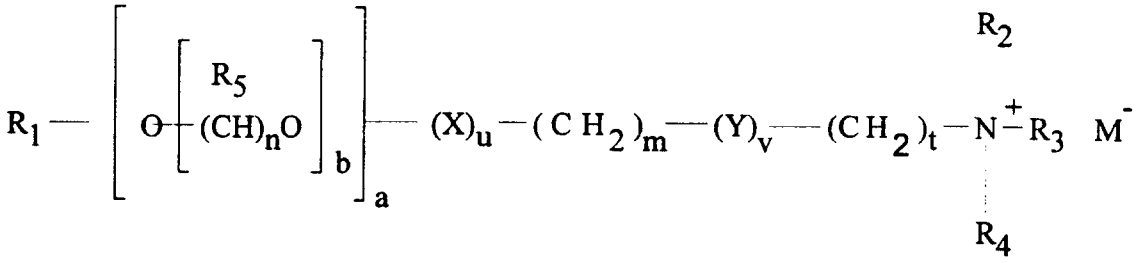
The cationic ester surfactant of the present invention is a, preferably water dispersible, compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group.

Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

In one preferred aspect the ester linkage and cationically charged group are separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), preferably from three to eight atoms, more preferably from three to five atoms, most preferably three atoms. The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures

thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain. Thus spacer groups having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example $-CH_2-O-CH_2-$ and $-CH_2-NH-CH_2-$ linkages are included. In a preferred aspect the spacer group chain comprises only carbon atoms, most preferably the chain is a hydrocarbyl chain.

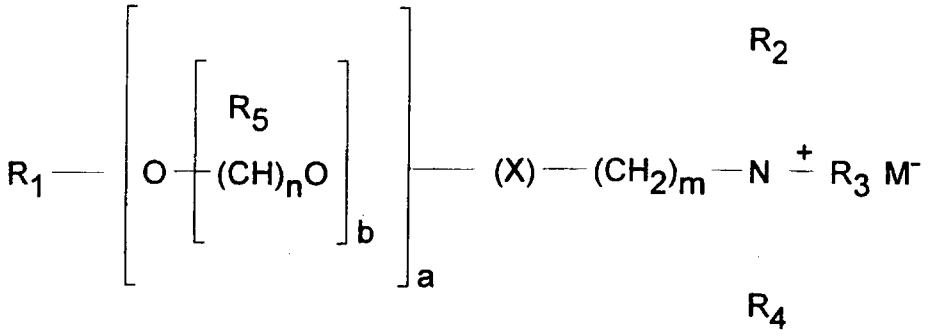
Preferred cationic ester surfactants are those having the formula:



wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain or M^-. $N^+(R_6R_7R_8)(CH_2)_s$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R_2, R_3, R_4, R_6, R_7, and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl and hydroxy-alkenyl groups having from 1 to 4 carbon atoms and alkaryl groups; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

Preferably M is selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably methyl sulfate, chloride, bromide or iodide.

In a preferred aspect, the cationic ester surfactant is selected from those having the formula:

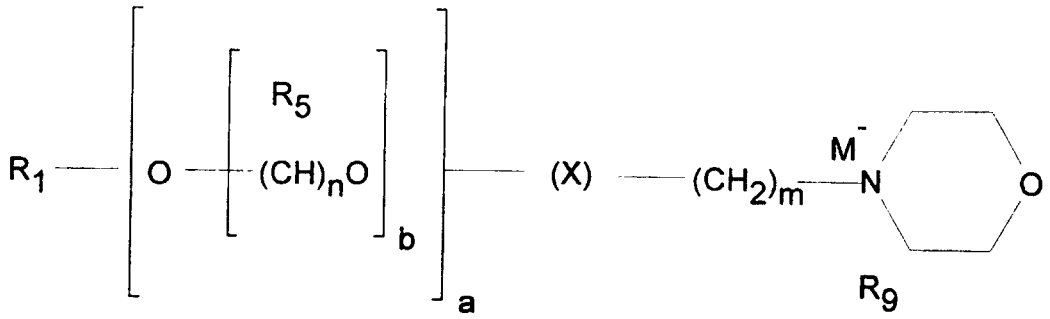


wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain; X is selected from the group consisting of COO, OCO, OCOO, OCONH and NHCOO; R_2, R_3, and R_4 are independently selected from the group consisting of alkyl and hydroxyalkyl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the value of n lies in the range of from 0 to 8, the value of b lies in the range from 0 to 20, the value of a is either 0 or 1, and the value of m is from 3 to 8.

More preferably R_2, R_3 and R_4 are independently selected from a C_1-C_4 alkyl group and a C_1-C_4 hydroxyalkyl group. In one preferred aspect at least one, preferably only one, of R_2, R_3 and R_4 is a hydroxyalkyl group. The hydroxyalkyl preferably has from 1 to 4 carbon atoms, more preferably 2 or 3 carbon atoms, most preferably 2 carbon atoms. In another preferred aspect at least one of R_2, R_3 and R_4 is a C_2-C_3 alkyl group, more preferably two C_2-C_3 alkyl groups are present.

In a preferred aspect two of R_2, R_3 and R_4 and the nitrogen of the cationically charged group from part of a ring structure. Preferably, the ring structure contains another nitrogen atom or more preferably, an oxygen atom, or mixtures thereof. Preferably, the ring structure contains 5 to 8 atoms, most preferably 6 atoms.

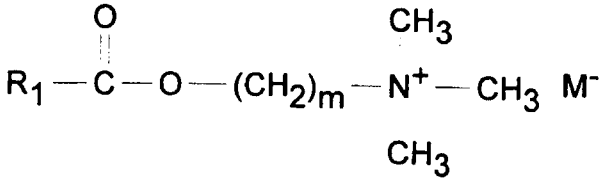
In a highly preferred aspect two of R_2, R_3 and R_4 and the nitrogen of the cationically charged group from part of a morpholino ring structure or a substituted morpholino ring structure. Highly preferred cationic ester surfactants of this type are the esters having the formula:



wherein R_1 is a C_5-C_{31} linear or branched alkyl, alkenyl or alkaryl chain; X is selected from the group consisting of COO, OCO, OCOO, OCONH and NHCOO; R_9 is selected from the group consisting of alkyl, alkenyl, hydroxyalkyl and hydroxy-alkenyl groups having from 1 to 4 carbon atoms and alkaryl groups; and R_5 is independently H or a C_1-C_3 alkyl group; wherein the value of n lies in the range of from 0 to 8, the value of b lies in the range from 0 to 20, the value of a is either 0 or 1, and the value of m is from 3 to 8.

More preferably R_2, R_3 and R_4 are independently selected from a C_1-C_4 alkyl group and a C_1-C_4 hydroxyalkyl group. In one preferred aspect at least one, preferably only one, of R_2, R_3 and R_4 is a hydroxyalkyl group. The hydroxyalkyl preferably has from 1 to 4 carbon atoms, more preferably 2 or 3 carbon atoms, most preferably 2 carbon atoms. In another preferred aspect at least one of R_2, R_3 and R_4 is a C_2-C_3 alkyl group, more preferably two C_2-C_3 alkyl groups are present.

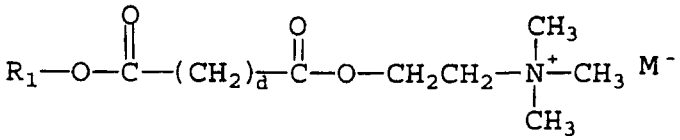
Highly preferred water dispersible cationic ester surfactants are the esters having the formula:

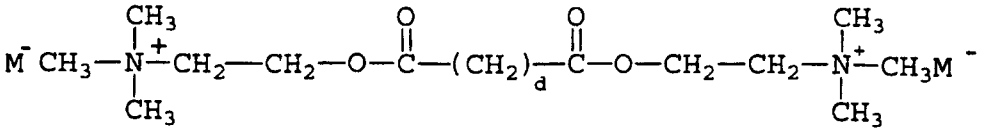


where m is from 1 to 4, preferably 2 or 3 and wherein R_1 is a C_{11}-C_{19} linear or branched alkyl chain.

Particularly preferred choline esters of this type include the stearoyl choline ester quaternary methylammonium halides ($R^1=C_{17}$ alkyl), palmitoyl choline ester quaternary methylammonium halides ($R^1=C_{15}$ alkyl), myristoyl choline ester quaternary methylammonium halides ($R^1=C_{13}$ alkyl), lauroyl choline ester methylammonium halides ($R^1=C_{11}$ alkyl), cocoyl choline ester quaternary methylammonium halides ($R^1=C_{11}$-C_{13} alkyl), tallowyl choline ester quaternary methylammonium halides ($R^1=C_{15}$-C_{17} alkyl), and any mixtures thereof.

Other suitable cationic ester surfactants have the structural formulas below, wherein d may be from 0 to 20.



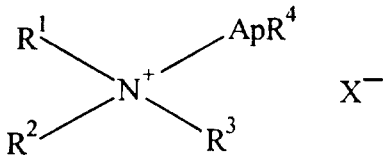


In a preferred aspect the cationic ester surfactant is hydrolysable under the conditions of a laundry wash method.

The particularly preferred choline esters, given above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, preferably in the presence of a solvent such as ethanol, water, propylene glycol or preferably a fatty alcohol ethoxylate such as C_{10}-C_{18} fatty alcohol ethoxylate having a degree of ethoxylation of from 3 to 50 ethoxy groups per mole forming the desired cationic material. They may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then quaternized with trimethylamine, forming the desired cationic material.

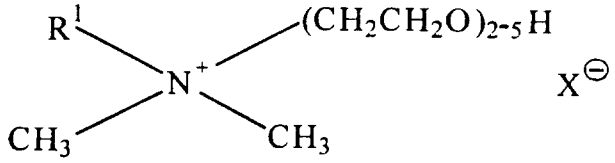
Cationic mono-alkoxylated amine surfactants

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



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 and R^3 are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl; 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 selected from C_1-C_4 alkoxy, especially ethoxy (i.e., $-CH_2CH_2O-$), propoxy, butoxy and mixtures thereof; and p is from 2 to about 30, preferably 2 to about 15, most preferably 2 to about 8.

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.

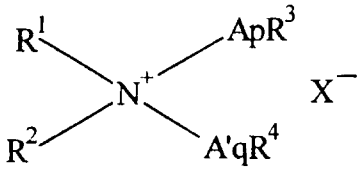
When used in granular detergent compositions cationic mono-alkoxylated amine surfactants wherein the hydrocarbyl substituent R^1 is C_8-C_{11},

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 can range 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.

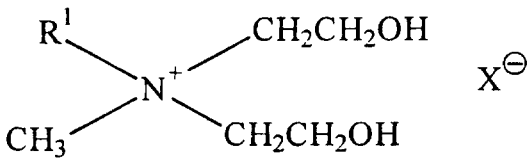
Cationic bis-alkoxylated amine surfactant

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



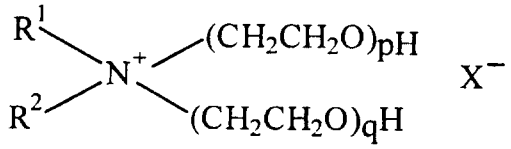
wherein R^1 is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R^2 is an alkyl group containing from one to three carbon atoms, preferably methyl; R^3 and R^4 can vary independently 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.

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.

Cationic polymers

The detergent composition or component thereof in accord with the invention can comprise additional polymeric cationic ethoxylated amine compounds with particulate/ clay-soil removal/ anti-redeposition, selected from the group consisting of water-soluble cationic polymers. These polymers comprise a polymer backbone, at least 2M groups and at least on L-X group, wherein M is a cationic group attached to or integral with the backbone; 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; and L is a hydrophilic chain connecting groups M and X or connecting X to the polymer backbone.

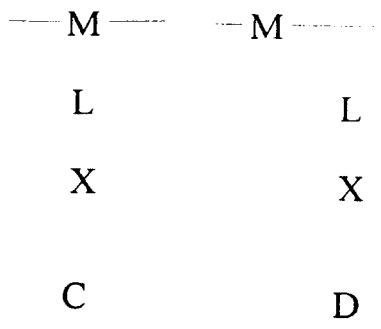
The polymeric cationic ethoxylated amine compounds can be present at a level of from 0.05% to 30%, more preferably from 0.1% to 15%, most preferably from 0.2% to 3% by weight of the detergent composition.

As used herein, the term "polymer backbone" refers to the polymeric moiety to which groups M and L-X are attached to or integral with. Included within this term are oligomer backbones (2 to 4 units), and true polymer backbones (5 or more units).

As used herein, the term "attached to " means that the group is pendent from the polymer backbone, examples of which are represented by the following general structures A and B:

M	M L
L	X
X	
A	B

As used herein, the term "integral with" means that the group forms part of the polymer backbone, examples of which are represented by the following general structures C and D:



C D

Any polymer backbone can be used as long as the cationic polymer formed is water-soluble and has clay soil removal/anti-redeposition properties. Suitable polymer backbones can be derived from the polyurethanes, the polyesters, the polyethers, the polyamides, the polyimides and the like, the polyacrylates, the polyacrylamides, the polyvinylethers, the polyethylenes, the polypropylenes and like polyalkylenes, the polystyrenes and like polyalkarylenes, the polyalkyleneamines, the polyalkyleneimines, the polyvinylamines, the polyalylamines, the polydiallylamines, the polyvinylpyridines, the polyaminotriazoles, polyvinyl alcohol, the aminopolyureylenes, and mixtures thereof.

M can be any compatible cationic group which comprises an N^+ (quarternary), positively charged center. The quarternary positively charged center can be represented by the following general structures E and F:

E F

Particularly preferred M groups are those containing a quarternary center represented by general structure E. The cationic group is preferably positioned close to or integral with the polymer backbone.

The positive charge of the N^+ centres is offset by the appropriate number of counter anions. Suitable counter anions include Cl^-, Br^-, SO_3^{2-}, SO_4^{2-}, PO_4^{2-}, $MeOSO_3^-$ and the like. Particularly preferred counter anions are Cl^- and Br^-.

X can be a nonionic group selected from hydrogen (H), C_1-C_4 alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof. The preferred ester or ether groups are the acetate ester and methyl ether, respectively; The particularly preferred nonionic groups are H and the methyl ether.

The cationic polymers suitable for use in granular detergent compositions or components thereof in accord with the present inventions normally have a ratio of cationic groups M to nonionic groups X of from about 1:1 to about 1:2. However, for example, by appropriate copolymerization of cationic, nonionic (i.e. containing the group L-X), and mixed cationic/nonionic monomers, the ratio of cationic groups M to nonionic groups X can be varied. The ratio of groups M to groups X can usually range from about 2:1 to about 1:10. In preferred cationic polymers, the ratio is from about 1:1 to about 1:5. The polymers formed from such copolymerization are typically random, i.e. the cationic, nonionic and mixed cationc/nonionic monomers copolymerize in a nonrepeating sequence.

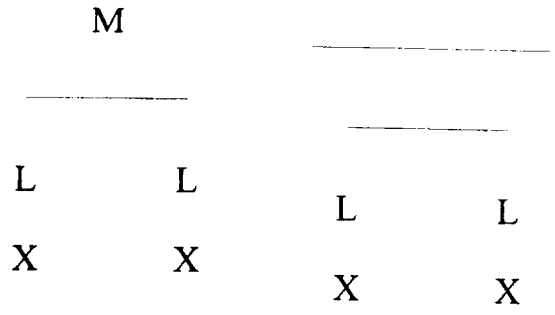
The units which contain groups M and groups L-X can comprise 100% of the cationic polymers of the present invention. However, inclusion of other units (preferably nonionic) in the polymers is also permissible. Examples of other units include acrylamides, vinyl ethers and those containing unquaternized tertiary amine groups (M^1) containing an N centre. These other units can comprise from 0% to about 90% of the polymer (from about 10% to 100% of the polymer being units containing M and L-X groups, including M^1-L-X groups). Normally, these other units comprise from 0% to about 50% of the polymer (from about 50% to 100% of the polymer being units containing M and L-X groups).

The number of groups M and L-X each usually ranges from about 2 to about 200. Typically the number of groups M and L-X are each from

about 3 to about 100. Preferably, the number of groups M and L-X are each from about 3 to about 40.

Other than moieties for connecting groups M and X, or for attachment to the polymer backbone, hydrophilic chain L usually consists entirely of the polyoxyalkylene moiety $-[(R'O)_m(CH_2CH_2O)_n]-$. The moieties $-(R'O)_m-$ and $-(CH_2CH_2O)_n-$ of the polyoxyalkylene moiety can be mixed together, or preferably form blocks of $-(R'O)_m-$ and $-(CH_2CH_2O)_n-$ moieties. R' is preferably C_3H_6 (propylene); m is preferably from 0 to about 5, and most preferably 0; i.e. the polyoxyalkylene moiety consists entirely of the moiety $-(CH_2CH_2O)_n-$. The moiety $-(CH_2CH_2O)_n-$ preferably comprises at least about 85% by weight of the polyoxyalkylene moiety, and most preferably 100% by weight (m is 0). For the moiety $-(CH_2CH_2O)_n-$, n is usually from about 3 to about 100. Preferably n, is from about 12 to about 42.

A plurality (2 or more) of moieties -L-X can also be hooked together and attached to group M or to the polymer backbone, examples of which are represented by the following general structures G and H:

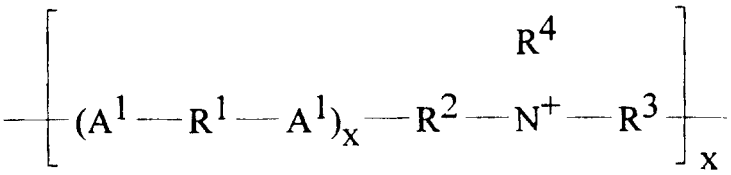


Structures such as G and H can be formed, for example, by reacting glycidol with group M or with the polymer backbone, and ethoxylating the subsequently formed hydroxy groups.

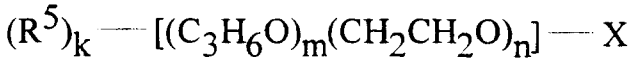
Representative classes of cationic polymers of the present invention are as follows:

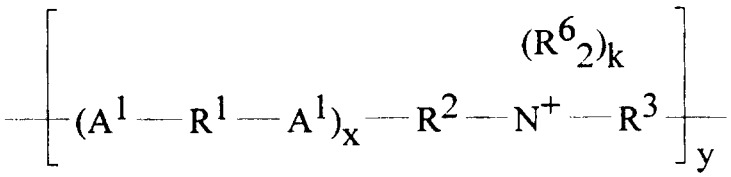
A. Polyurethane, Polyester, Polyether, Polyamide or like Polymers.

One class of suitable cationic polymers are derived from polyurethanes, polyesters, polyethers, polyamides and the like. These polymers comprise units selected from those having formulas I, II and III:

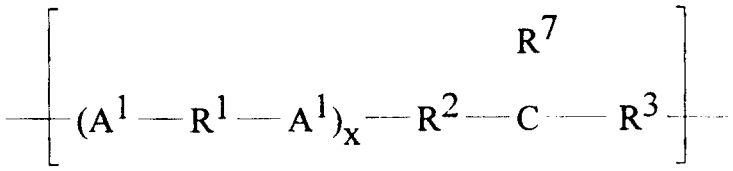


I

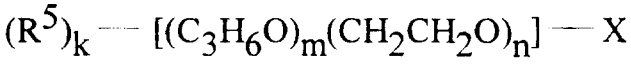




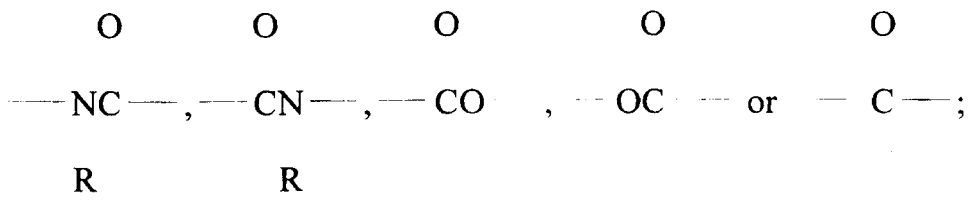
II



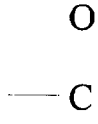
III



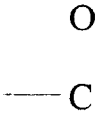
wherein A^1 is



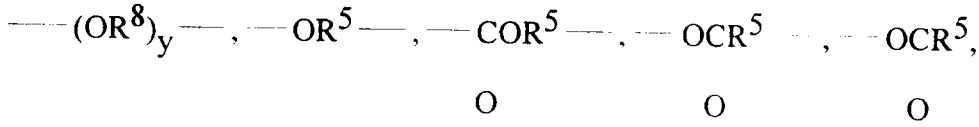
X is 0 or 1; R is H or C_1-C_4 alkyl or hydroxyalkyl; R^1 is C_2-C_{12} alkylene, hydroxyalkylene, alkenylene, cycloalkylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to abut 20 oxyalkylene units provided that no O-O or O-N bonds are formed with A^1; when x is 1, R^2 is $-R^5-$ except when A^1 is

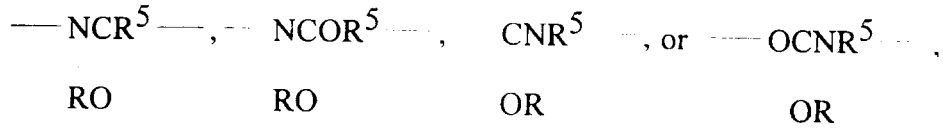


or is $-(OR^8)_y-$ or $-OR^5-$ provided that no O-O or N-O bonds are formed with A^1, and R^3 is $-R^5-$ except when A^1 is



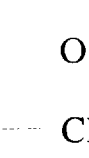
or is $-(R^8O)_y-$ or $-R^5O-$ provided that no O-O or O-N bonds are formed with A^1; when x is 0, R^2 is





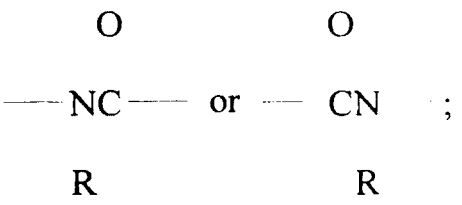
and R^3 is $-R^5-$; R^4 is C_1-C_4 alkyl or hydroxyalkyl, or the moiety $-(R^5)_k-[(C_3H_6O)_m(CH_2CH_2O)_n]-X$; R^5 is C_1-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene, or alkarylene; each R^6 is C_1-C_4 alkyl or hydroxyalkyl, or the moiety $-(CH_2)_r-A^2-(CH_2)s-$, wherein A^2 is -O- or $-CH_2-$; R^7 is H or R^4; R^8 is C_2-C_3 alkylene or hydroxyalkylene; X is H,

24

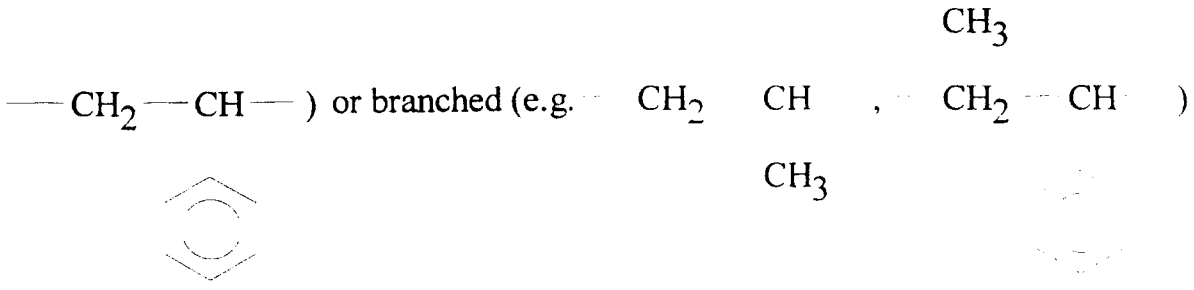


-R^9 or a mixture thereof, wherein R^9 is C_1-C_4 alkyl or hydoxyalkyl; k is 0 or 1; m and n are numbers such that the moiety -$(CH_2CH_2O)_n$- comprises at least about 85% by weight of the moiety -$[(C_3H_6O)_m(CH_2CH_2O)_n]$-; m is from 0 to about 5; n is at least about 3; r is 1 or 2, s is 1 or 2, and r + s is 3 or 4; y is from 2 to about 20; the number of u, v and w are such that there are at least 2 N^+ centers and at least 2 X groups.

In the above formulas, A^1 is preferably



A^2 is preferably -O-; x is preferably 1; and R is preferably H. R^1 can be linear (e.g. -CH_2-CH_2-CH_2-,



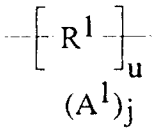
alkylene, hydroxyalkylene, alkenylene, cycloalkylene, alkarylene or oxyalkylene; when R^1 is a C_2-C_3 oxyalkylene moiety, the number of oxyalkylene units is preferably from about 2 to about 12; R^1 is preferably C_2-C_6 alkylene or phenylene, and most preferably C_2-C_6 alkylene (e.g. ethylene, propylene, hexamethylene). R^2 is preferably -OR^5- or -$(OR^8)_y$-; R3 is preferably -R^5O- or -$(OR^8)_y$-; R^4 and R^6 are preferably methyl. Like R^1, R^5 can be linear or branched, and is preferably C_2-C_3 alkylene; R^7 is preferably H or C_1-C_3 alkyl; R^8 is

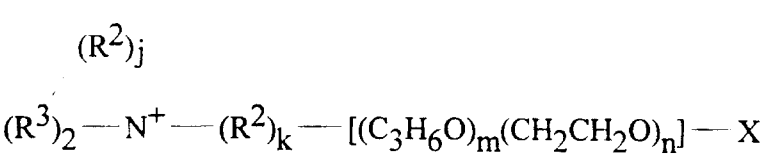
preferably ethylene; R^9 is preferably methyl; X is preferably H or methyl; k is preferably 0; m is preferably 0, r and s are each preferably 2; y is preferably from 2 to about 12.

In the above formulas, n is preferably at least about 6 when the number of N^+ centers and X groups is 2 or 3; n is most preferably at least about 12, with a typical range of about 12 to about 42 for all ranges of u + v + w. For homopolymers (v and w are 0), u is preferably from about 3 to about 20. For random compolymers (u is at least 1 or preferably 0), v and w are each preferably from about 3 to about 40.

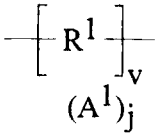
B. Polyacrylate, Polyacrylamide, Polyvinylether or Like Polymers

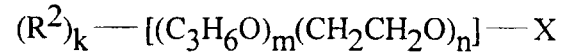
Another class of suitable cationic polymers are derived from polyacrylates, polyacrylamides, polyvinylethers and the like. These polymers comprise units selected from those having formulas IV, V and VI.



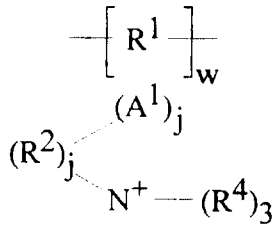


IV

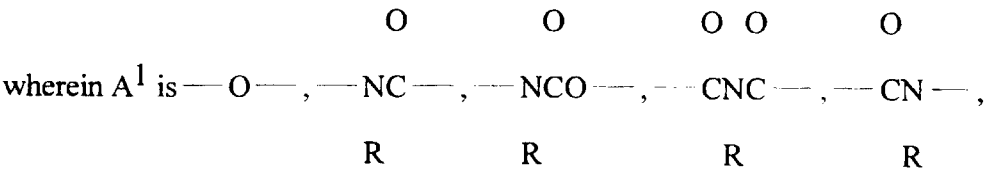




V



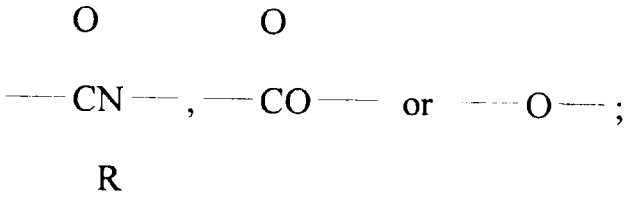
VI

wherein A^1 is —O—, 

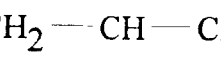
R is H or C_1-C_4 alkyl or hydroxyalkyl; R^1 is substituted C_2-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or C_2-C_3 oxyalkylene; each R^2 is C_1-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene; each R^3 is C_1-C_4 alkyl or hydroxyalkyl, the moiety $-(R^2)_k-[(C_3H_6O)_m(CH_2CH_2O)_n]-X$, or together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$, wherein A^2 is -O- or $-CH_2-$; each R^4 is C_1-C_4 alkyl or hydroxyalkyl, or two R^4 together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$; X is H,

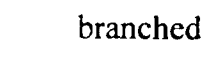
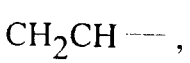
-R^5 or mixture thereof, wherein R^5 is C_1-C_4 alkyl or hydroxalkyl; j is 1 or 0; k is 1 or 0; m and n are numbers such that the moiety -$(CH_2CH_2O)_n$- comprises at least about 85% by weight of the moiety -$[(C_3H_6O)_m(CH_2CH_2O)_n]$-; m is from 0 to about 5; n is at least about 3; r is 1 or 2, s is 1 or 2 and r + s is 3 or 4; the number of u, v and w are such that there are at least 2N+ centres and at least 2 X groups.

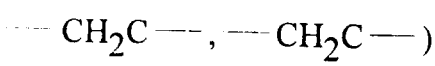
In the above formulas, A^1 is preferably



A^2 is preferably -O-; R is preferably H. R^1 can be linear

(e.g. ) or

branched (e.g.  ,  ,



substituted alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene; R^1 is preferably substituted C_2-C_6 alkylene or substituted C_2-C_3 oxyalkylene, and most preferably

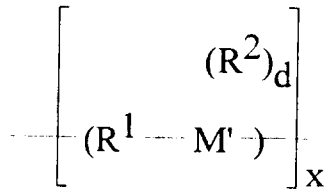
$$\text{---}CH_2CH\text{---} \quad \text{or} \quad \text{---}CH_2\text{---}\overset{CH_3}{\underset{}{C}}\text{---} .$$

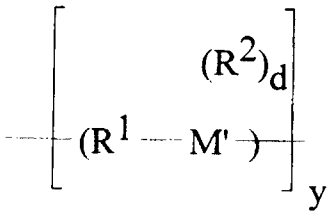
Each R^2 is preferably C_2-C_3 alkylene, each R^3 and R^4 are preferably methyl; R^5 is preferably methyl; X is preferably H or methyl; j is preferably 1; k is preferably 0; m is preferably 0; r and s are each preferably 2.

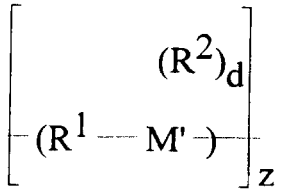
In the above formulas, n, u, v and w can be varied according to the n, u, v and w for the polyurethane and like polymers.

C. Polyalkyleneamine, Polyalkyleneimine or like polymers.

Another class of suitable cationic polymers are derived from polyalkyleneamines, polyalkyleneimines and the like. These polymers comprise units selected from those having formulas VII and VIII and IX.







wherein R^1 is C_2-C_{12} alkylene, hydroxyalkylene, alkenylene, cycloalkylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R^2 is C_1-C_4 alkyl or hydroxyalkyl, or the moiety -$(R^3)_k$-$[(C_3H_6O)_m(CH_2CH_2O)_n]$-X; R^3 is C_1-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene; M' is an N+ or N centre; X is H,

$$CR^4,$$

O

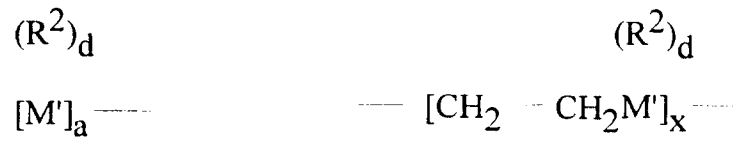
-R^4 or mixture thereof, wherein R^4 is C_1-C_4 alkyl or hydroxyalkyl; d is 1 when M' is N+ and is 0 when M' is N; e is 2 when M' is N+ and is 1 when M' is N; k is 1 or 0; m and n are numbers such that the moiety -

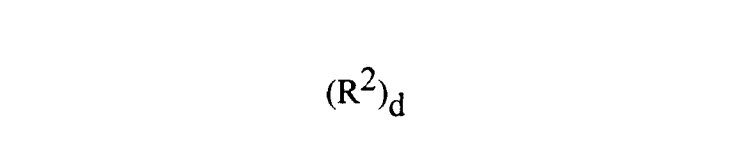
$(CH_2CH_2O)_n$- comprises at least about 85% by weight of the moiety -$[(C_3H_6O)_m(CH_2CH_2O)_n]$-; m is from 0 to about 5; n is at least about 3; the number of x, y and z are such that there are at least 2M' groups, at least 2N+ centres and at least 2 X groups.

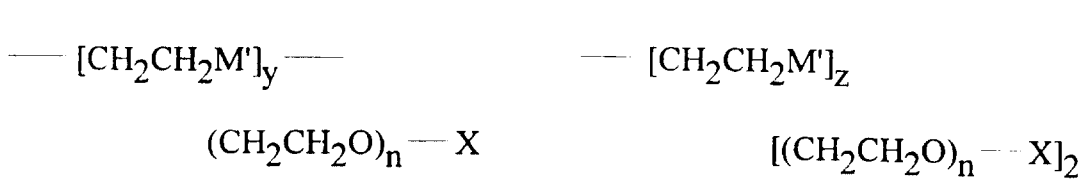
In the above formulas, R^1 can be varied like R^1 of the polyurethene and like polymers; each R^2 is preferably methyl or the moiety -$(R^3)_k$-$[(C_3H_6O)_m(CH_2CH_2O)_n]$-X; R^3 is preferably C_2-C_3 alkylene; R^4 is preferably methyl; X is preferably H; k is preferably 0; m is preferably 0.

In the above formulas, n is preferably at least about 6 when the number of M' and X groups is 2 or 3; n is most preferably at least about 12, with a typical range of from about 12 to about 42 for all ranges of x + y + z. Typically, x + y + z is from 2 to about 40 and preferably from 2 to about 20. For short chain length polymers, x + y + z can range from 2 to 9 with from 2 to 9 N+ centres and from 2 to 11 X groups. For long chain length polymers, x + y + z is at least 10, with a preferred range of from 10 to about 42. For the short and long chain length polymers, the M' groups are typically a mixture of from about 50 to 100% N+ centres and from 0 to about 50% N centres.

Preferred cationic polymers within this class are derived from the C_2-C_3 polyalkyleneamines (x + y + z is from 2 to 9) and polyalkyleneimines (x + y + z is at least 10, preferably from 10 to about 42). Particularly preferred cationic polyalkyleneamines and polyalkyleneimines are the cationic polyethyleneamines (PEA's) and polyethyleneimines (PEI's). These preferred cationic polymers comprise units having the general formula:

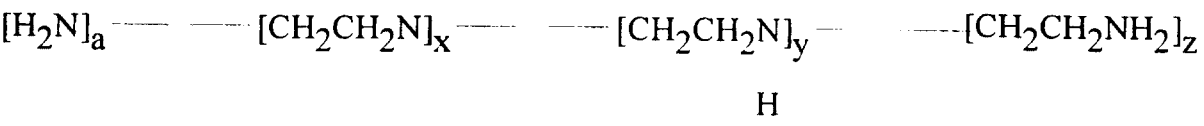






wherein R^2 (preferably methyl), M', X, d, x, y, z and n are defined as before; a is 1 or 0.

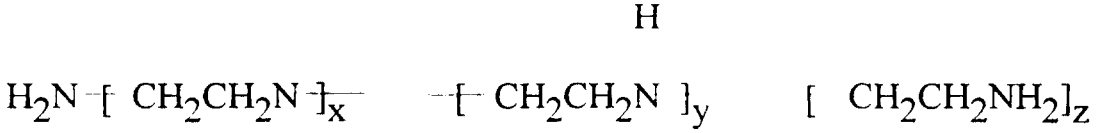
Prior to ethoxylation, the PEAs used in preparing cationic polymers of the present invention have the following general formula:



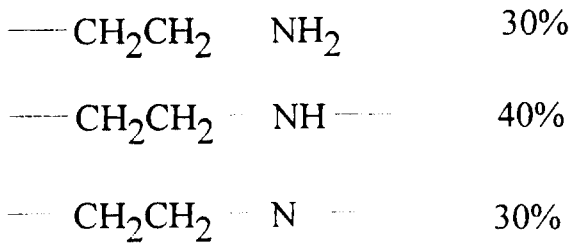
wherein x + y + z is from 2 to 9, and a is 0 or 1 (molecular weight of from about 100 to about 400). Each hydrogen atom attached to each nitrogen atom represents an active site for subsequent ethoxylation. For preferred PEAs, x + y + z is from about 3 to about 7 (molecular weight is from about 140 to about 310). These PEA's can be obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See US Pat. No. 2,792,372 to Dickson, issues May 14, 1957, which describes the preparation of PEAs.

The minimum degree of ethoxylation required for preferred clay soil removal/anti-redeposition performance can vary depending upon the number of units in the PEA. Where y + z is 2 or 3, n is preferably at least about 6. Where y + z is from 4 to 9, suitable benefits are achieved when n is at least about 3. For preferred cationic PEAs, n is at least about 12, with a typical range of about 12 to about 42.

The PEIs used in preparing the polymers of the present invention have a molecular weight of at least about 440 prior to ethoxylation, which represents at least about 10 units. Preferred PEIs used in preparing these polymers have a molecular weight of from about 600 to about 1800. The polymer backbone of these PEIs can be represented by the general formula:



wherein the sum of x, y, and z represents a number of sufficient magnitude to yield a polymer having the molecular weights previously specified. Although linear polymer backbones are possible, branch chains can also occur. The relative proportions of primary, secondary and tertiary amine groups present in the polymer can vary, depending on the manner of preparation. The distribution of amine groups is typically as follows:

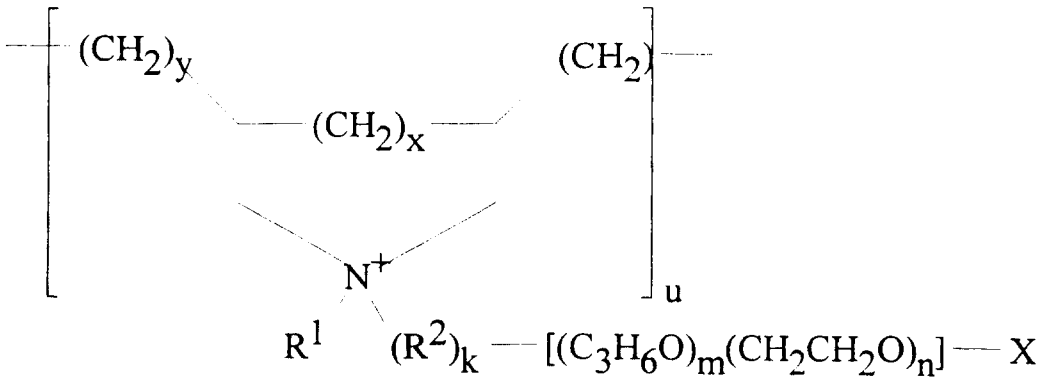


Each hydrogen atom attached to each nitrogen atom of the PEI represents an active site for subsequent ethoxylation. These PEIs can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing PEIs are disclosed in US Pat. No. 2,182,306 to Ulrich et al., issued Dec. 5, 1939; US Pat No. 3,033,746 to Mayle et al., issued May 8, 1962; US Pat. No. 2,208,095 to Esselmann et al., issued July 16, 1940; US Pat. No. 2,806,839 to Crowther, issued Sept. 17, 1957; and US Pat. No. 2,533,696 to Wilson, issued May 21, 1951 (all herein incorporated by reference).

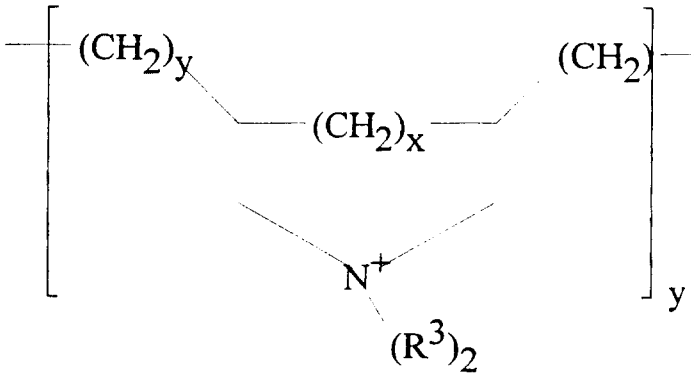
As defined in the preceding formulas, n is at least about 3 for the cationic PEIs. However, it should be noted that the minimum degree of ethoxylation required for suitable clay soil removal/anti-redeposition performance can increase as the molecular weight of th PEI increases, especially much beyond about 1800. Also, the degree of ethoxyalation for preferred polymers increases as the molecular weight of the PEI increases. For PEIs having a molecular weight of at least about 600, n is preferably at least about 12, with a typical range of from about 12 to about 42. For PEIs having a molecular weight of at least 1800, n is preferably at least about 24, with a typical range of from about 24 to about 42.

D. Diallylamine Polymers

Another class of suitable cationic polymers are those derived from the diallylamines. These polymers comprise units selected from those having formulas X and XI:



X



XI

wherein R^1 is C_1-C_4 alkyl or hydroxyalkyl, or the moiety $-(R^2)_k-[(C_3H_6O)_m(CH_2CH_2O)_n]-X$; R^2 is C_1-C_{12} alkylene, hydroxyalkylene, alkylene, arylene or alkarylene; each R^3 is C_1-C_4 alkyl or hydroxyalkyl, or together form the moiety $-(CH_2)_r-A-(CH_2)_s-$, wherein A is -O- or -CH_2-; X is H,

$$-CR^4,$$

$$O$$

$-R^4$ or mixture thereof, wherein R^4 is C_1-C_4 alkyl or hydroxyalkyl; k is 1 or 0; m and n are numbers such that the moiety $-(CH_2CH_2O)_n-$ comprises at least about 85% by weight of the moiety $-[(C_3H_6O)_m(CH_2CH_2O)_n]-$; m is from 0 to about 5; n is at least about 3; r is 1 or 2, s is 1 or 2, and r + s is 3 or 4; x is 1 or 0; y is 1 when x is 0 and 0 when x is 1; the number of u and v are such that there are at least 2N+ centres and at least 2 X groups.

In the above formulas, A is preferably -O-; R^1 is preferably methyl; each R^2 is preferably C_2-C_3 alkylene; each R^3 is preferably methyl; R^4 is preferably methyl; X is preferably H; k is preferably 0; m is preferably 0; r and s are each preferably 2.

In the above formulas, n is preferably at least about 6 when the number of N+ centres and X groups are each 2 or 3, n is preferably at least 12, with a typical range of from about 12 to about 42 for all range of u + v. Typically, v is 0, and u is from 2 to about 40, and preferably from 2 to about 20.

Additional detergent components

The detergent compositions or components thereof in accord with 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 or components thereof of the invention preferably contain one or more additional detergent components selected from additional surfactants, alkalinity systems, builders, bleach, bleach precursors, bleach catalysts, organic polymeric compounds, enzymes, suds suppressors, lime soap dispersants, additional soil suspension and anti-redeposition agents soil releasing agents, perfumes and corrosion inhibitors.

Additional surfactant

The detergent compositions or compositions thereof in accord with the invention preferably contain an additional surfactant selected from anionic, nonionic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples

are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch).

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

Anionic surfactant

The detergent compositions or compositions thereof in accord with the present invention preferably comprise an additional anionic surfactant. Essentially any anionic surfactants useful for detersive purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

In detergent compositions one or more anionic surfactants can be present at a level of from 1% to 25%, more preferably from 4% to 15%, most preferably from 5% to 12% by weight of the detergent composition.

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.

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_{10}-C_{18} 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 $RO(CH_2CH_20)_x\ CH_2C00\text{-}M^+$ 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 $RO\text{-}(CHR_1\text{-}CHR_2\text{-}O)\text{-}R_3$ 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.

Alkoxylated nonionic surfactant

Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the

nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic alkoxylated alcohol surfactant

The condensation products of aliphatic alcohols with from 1 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 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are 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

Suitable fatty acid amide surfactants include 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

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic

group containing from 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 10 to 18 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.

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 or compositions thereof in accord with the present invention preferably contain a water-soluble builder compound, typically present in the detergent compositions 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 momomeric 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.

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

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions 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 or components thereof in accord with the present invention may contain a partially soluble or insoluble builder compound, typically present in detergent compositions 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 $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]. 276\ H_2O$.

Another preferred aluminosilicate zeolite is zeolite MAP builder. The zeolite MAP can be present at a level of from 1% to 80%, more preferably from 15% to 40% by weight of the compositions.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

In a preferred aspect the zeolite MAP detergent builder has a particle size, expressed as a d_{50} value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres.

The d_{50} value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer. Other methods of establishing d_{50} values are disclosed in EP 384070A.

Heavy metal ion sequestrant

The detergent compositions or components thereof in accord with the invention can 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 in detergent compositions 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.

Organic peroxyacid bleaching system

A preferred feature of detergent compositions or components thereof in accord with the invention is an organic peroxyacid bleaching system. In

one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic 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 a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Inorganic perhydrate bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in detergent compositions 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.

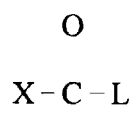
Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

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.

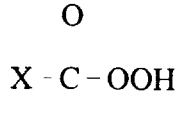
Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

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 perhydroloysis the structure of the peroxyacid produced is



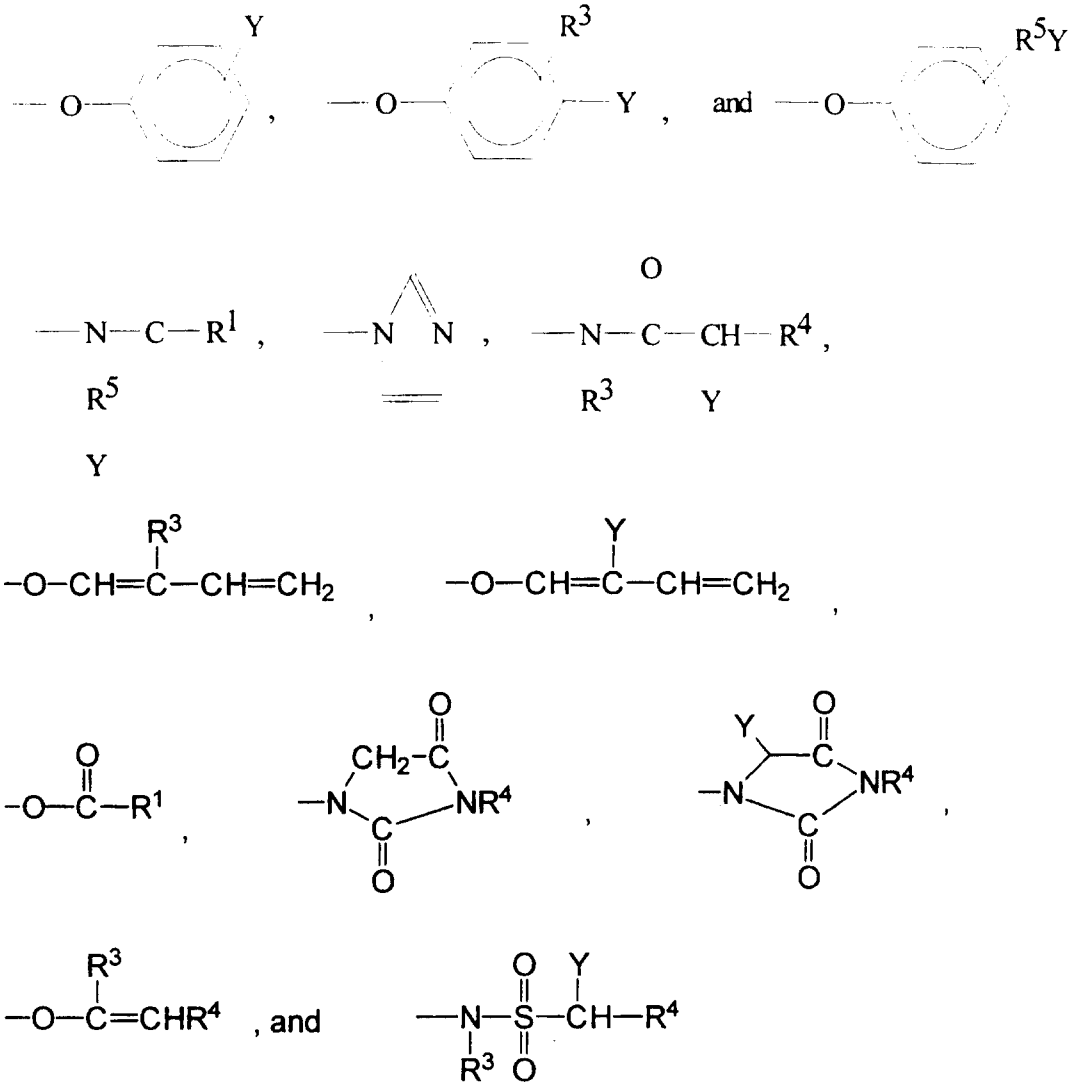
Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight of the detergent compositions.

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

Leaving groups

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

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, R^5 is an alkenyl chain containing from 1 to 8 carbon atoms, 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 $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and $O<--N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ 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.

Alkyl percarboxylic acid bleach precursors

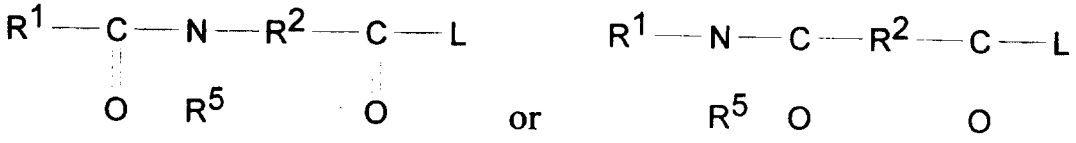
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

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

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

Amide substituted alkyl peroxyacid precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic acid precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammmonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter

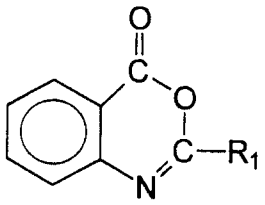
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

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

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

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:

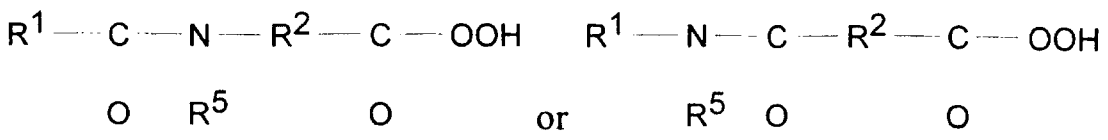


wherein R_1 is H, alkyl, alkaryl, aryl, or arylalkyl.

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 organic peroxyacid , typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

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



wherein R^1 is an alkyl, 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. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Enzyme

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

Preferred additional enzymatic materials include the commercially available cellulases, endolases, lipases, cutinases, amylases, neutral and alkaline proteases, esterases, 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 in the detergent compositions 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 or components thereof 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, not being an quaternised ethoxylated (poly) amine clay-soil removal/ anti-redeposition agent in accord with the invention.

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.

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.

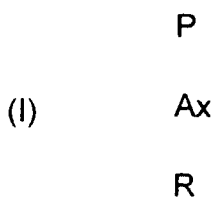
Polymeric dye transfer inhibiting agents

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, whereby these polymers can be cross-linked polymers.

a) Polyamine N-oxide polymers

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



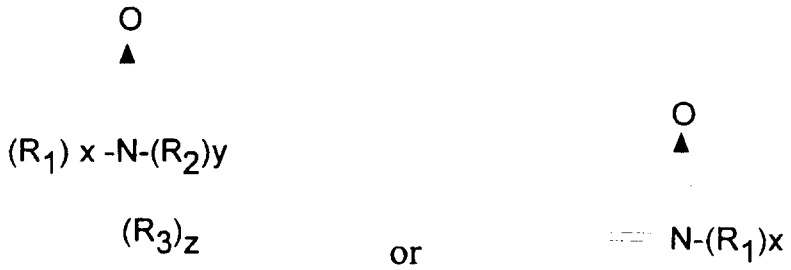
(I)

wherein P is a polymerisable unit, and

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 vailable 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.

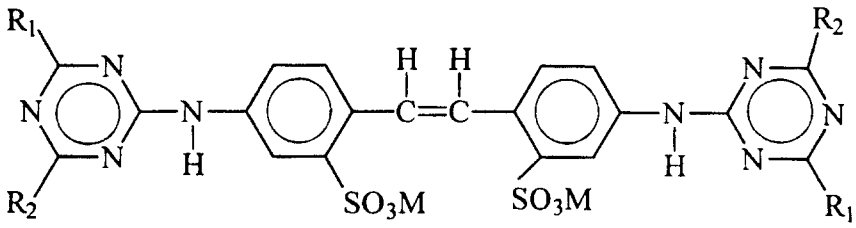
e) Polyvinylimidazole

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.

Polymeric Soil Release Agent

Known polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present detergent compositions or components thereof. If utilized in detergent compositions, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the backbone, for example as described in U.S.

4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C_1-C_4 alkyl celluloses and C_4 hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100

and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.;

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.

Near neutral wash pH dergent formulation

While the detergent compositions of the present invention are operative within a wide range of wash pHs (e.g. from about 5 to about 12), they are particularly suitable when formulated to provide a near neutral wash pH, i.e. an initial pH of from about 7.0 to about 10.5 at a concentration of from about 0.1 to about 2% by weight in water at 20°C. Near neutral wash pH formulations are better for enzyme stability and for preventing stains from setting. In such formulations, the wash pH is preferably from about 7.0 to about 10.5, more preferably from about 8.0 to about 10.5, most preferably from 8.0 to 9.0.

Preferred near neutral wash pH detergent formulations are disclosed to European Patent Application 83.200688.6, filed May 16, 1983, J.H.M. Wertz and P.C.E. Goffinet.

Highly preferred compositions of this type also preferably contain from about 2 to about 10% by weight of citric acid and minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, enzymes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides, dyes, perfumes and brighteners, such as those described in US Patent 4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference).

Form of the compositions

The detergent component of the invention can be made via a variety of methods, including dry-mixing and agglomerating of the various compounds comprised in the detergent component.

The detergent component preferably forms part of a detergent composiiton.
The compositions in accordance with the invention can take a variety of physical forms including granular, tablet, flake, pastille and bar forms. The compositions can also be in the form of a nonaqueous liquid, gel or paste, which means that they are substantially nonaqueous (or anhydrous) in character. While very small amounts of water may be incorporated into such compositions as an impurity in the essential or optional components, the amount of water should in no event exceed about 5% by weight of the compositions herein. More preferably, water content of the nonaqueous detergent compositions herein will comprise less than about 1% by weight.

The compositions in accord with the present invention can also be used in or in combination with bleach additive compositions, for example comprising chlorine bleach.

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation. The quaternised clay-soil removal/ anti-redeposition agent in accord with the present

invention can be added to the other detergent components by dry-mixing, agglomeration (preferably combined with a carrier material) or as a spray-dried component.

The mean particle size of the components of granular compositions in accordance with the invention, comprising the water-soluble cationic clay-soil removal/anti-redeposition compounds, should preferably be such that no more that 15% of the particles are greater than 1.8mm in diameter and not more than 15% of the particles are less than 0.25mm in diameter. Preferably the mean particle size is such that from 10% to 50% of the particles has a particle size of from 0.2mm to 0.7mm 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 sieves, preferably 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.

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 10g 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.

The dispensing device containing the detergent product is placed inside the drumat the commencement of the wash, before, simultaneously with or after the washing machine has been loaded with laundry. 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 arrangemnt 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
CxyAS	:	Sodium C_{1x} - C_{1y} alkyl sulfate
C46SAS	:	Sodium C_{14} - C_{16} secondary (2,3) alkyl sulfate
CxyEzS	:	Sodium C_{1x}-C_{1y} alkyl sulfate condensed with z moles of ethylene oxide
CxyEz	:	C_{1x}-C_{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
CEQ	:	$R_1COOCH_2CH_2.N^+(CH_3)_3$ with R_1 = C_{11}-C_{13}
QAS 1	:	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with R_2 = C_{12} - C_{14}
QAS 2	:	$R_2.N^+(CH_3)_2(C_2H_4OH)_2$ with R_2 = C_{10} - C_{14}
Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils
CFAA	:	C_{12}-C_{14} (coco) alkyl N-methyl glucamide
TFAA	:	C_{16}-C_{18} alkyl N-methyl glucamide
TPKFA	:	C_{12}-C_{14} topped whole cut fatty acids

STPP	:	Anhydrous sodium tripolyphosphate
TSPP	:	Tetrasodium pyrophosphate
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
Zeolite MAP	:	Hydrated sodium aluminosilicate zeolite MAP having a silicon to aluminium ratio of 1.07
NaSKS-6	:	Crystalline layered silicate of formula δ-$Na_2Si_2O_5$
Citric acid	:	Anhydrous citric acid
Borate	:	Sodium borate
Carbonate	:	Anydrous 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 = 2.0:1)
Sodium sulfate	:	Anhydrous sodium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850μm
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
CMC	:	Sodium carboxymethyl cellulose
Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
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 by	:	Amylolytic enzyme of activity 120KNU/g sold NOVO Industries A/S under the tradename Termamyl 120T
Lipase	:	Lipolytic enzyme of activity 100KLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase	:	Endoglucanase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4 formula	:	Sodium perborate tetrahydrate of nominal $NaBO_2.3H_2O.H_2O_2$
PB1	:	Anhudrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
Percarbonate	:	Sodium percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
NOBS the	:	Nonanoyloxybenzene sulfonate in the form of sodium salt
TAED	:	Tetraacetylethylenediamine
Mn catalyst	:	Mn^{IV}_2(m-O)$_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2(PF_6)_2$, as described in U.S. Pat. Nos. 5,246,621 and 5,244,594.
DTPA	:	Diethylene triamine pentaacetic acid
DTPMP under the	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto Tradename Dequest 2060
Photoactivated bleach	:	Sulfonated Zinc Phthlocyanine encapsulated in dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyry)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
EDDS	:	Ethylenediamine-N, N'-disuccinic acid
QEA1 C_6H_{12}-N^+- wherein n=from	:	bis($(C_2H_5O)(C_2H_4O)_n$) (CH_3) -N^+- (CH_3) bis((C_2H_5O)-$(C_2H_4O)_n$), 20 to 30

QEA2 wherein to 30	:	bis((C_2H_5O)-$(C_2H_4O)_n$) (CH_3) N^+ R_1, R_1 is C_4-C_{12} alkyl group and n=from 20
QEA3	:	tri{(bis((C_2H_5O)-$(C_2H_4O)_n$)(CH_3)-N^+)-$(CONC_3H_6)$}-C_3H_6O, wherein n=from 20 to 26
PEGX x	:	Polyethylene glycol, with a molecular weight of
PEO	:	Polyethylene oxide, with a molecular weight of 50,000
TEPAE	:	Tetraethylenepentaamine ethoxylate
PVP	:	Polyvinylpyrolidone polymer
PVNO	:	Polyvinylpyridine N-oxide
PVPVI	:	Copolymer of polyvinylpyrolidone and vinylimidazole
SRP 1	:	Sulfobenzoyl and 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
Wax	:	Paraffin wax

In the following examples all levels are quoted as % by weight of the composition:

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
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
C46AS	1.0	2.0	2.5	-	3.0	4.0
C68AS	3.0	2.0	5.0	7.0	1.0	0.5
QAS 1	-	-	0.8	-	-	1.0
CEQ	0.8	0.9	-	1.2	1.4	-
Zeolite A	18.1	18.1	16.1	18.1	18.1	18.1
Zeolite MAP	-	4.0	3.5	-	-	-
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sodium 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	9.0	9.0	9.0
TAED	1.5	1.5.	1.0	1.5	-	1.5
Mn Catalyst	-	0.03	0.07	-	-	-
DTPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.2	0.2	0.3	0.3
EDDS	-	-	0.4	0.2	-	-
QEA 1	1.0	0.8	0.7	1.2	-	0.5
QEA 2	-	-	-	-	1.0	0.5

Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.4	0.3	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
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 2

The following granular laundry detergent compositions G to I of particular utility under European machine wash conditions were prepared in accord with the invention:

	G	H	I
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25E3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
QAS 1	0.8	2.0	2.0
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
Zeolite MAP	2.0	-	-
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	-	14.3
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4

PB4	5.0	12.7	-
Percarbonate	5.0	-	12.7
TAED	0.5	3.1	-
Mn Catalyst	0.04	-	-
DTPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
QEA 1	0.9	1.2	-
QEA 2	-	-	1.0
Protease	0.26	0.85	0.85
Lipase	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28
Amylase	0.4	0.1	0.1
PVP	0.9	1.3	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%			

Example 3

The following detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention.

	J	K	L	M
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	-	27.0	-	20.0
STPP	24.0	-	24.0	-
Sulfate	9.0	6.0	13.0	-
MA/AA	2.0	4.0	6.0	4.0
Silicate	7.0	3.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
QEA 1	0.8	1.0	1.4	0.5
QEA 2	-	-	-	0.5
Brightener	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	0.4	0.4	0.2	0.4
Spray on				
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
QAS 2	1.4	0.8	0.4	-
CEQ	-	-	0.4	1.2
Perfume	0.3	0.3	0.3	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
Sulfate	3.0	3.0	5.0	10.0
Carbonate	6.0	13.0	15.0	14.0
PB1	-	-	-	1.5
PB4	18.0	18.0	10.0	18.5
TAED	3.0	2.0	-	2.0
EDDS	-	2.0	2.4	-
Protease	1.0	1.0	1.0	1.0

Lipase	0.4	0.4	0.4	0.2
Amylase	0.2	0.2	0.2	0.4
Photoactivated bleach	-	-	-	0.15
Total	100.0	100.0	100.0	100.0

Example 4

The following granular detergent formulations were prepared in accord with the invention. Formulation N is particularly suitable for usage under Japanese machine wash conditions. Formulations O to S are particularly suitable for use under US machine wash conditions.

	N	O	P	Q	R	S
Blown powder						
LAS	22.0	5.0	4.0	9.0	8.0	7.0
C45AS	7.0	7.0	6.0	-	-	-
C46AS	-	4.0	3.0	-	-	-
C45E35	-	3.0	2.0	8.0	5.0	4.0
Zeolite A	6.0	16.0	14.0	19.0	16.0	14.0
MA/AA	6.0	3.0	3.0	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sodium Sulfate	7.0	18.3	11.3	24.0	19.3	19.3
Silicate	5.0	1.0	1.0	2.0	1.0	1.0
Carbonate	28.3	9.0	7.0	25.7	8.0	6.0
QEA 1	0.9	0.9	-	-	0.5	1.1
QEA 2	-	-	0.8	1.0	-	-
QEA 3	-	-	0.4	-	-	-
PEG 4000	0.5	1.5	1.5	1.0	1.5	1.0
Sodium oleate	2.0	-	-	-	-	-
DTPA	0.4	-	0.5	-	-	0.5
Brightener	0.2	0.3	0.3	0.3	0.3	0.3
Spray on						
C25E9	1.0	-	-	-	-	-
C45E7	-	2.0	2.0	0.5	2.0	2.0
QAS 1	0.8	1.8	1.4	2.2	0.6	1.0
Perfume	1.0	0.3	0.3	1.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	-	5.0	5.0
LAS	-	2.0	2.0	-	2.0	2.0
Zeolite A	-	7.5	7.5	-	7.5	7.5
HEDP	-	1.0	-	-	2.0	-

Carbonate	-	4.0	4.0	-	4.0	4.0
PEG 4000	-	0.5	0.5	-	0.5	0.5
Misc (water etc)	-	2.0	2.0	-	2.0	2.0
Dry additives						
TEAD	1.0	2.0	3.0	1.0	3.0	2.0
PB4	-	1.0	4.0	-	5.0	0.5
PB1	6.0	-	-	-	-	-
Percarbonate	-	5.0	12.5	-	-	-
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.5	-	6.0	-	-	0.6
Cumeme sulfonic acid	-	2.0	2.0	-	2.0	2.0
Lipase	0.4	0.4	0.4	-	0.4	0.4
Cellulase	0.1	0.2	0.2	-	0.2	0.2
Amylase	0.1	0.3	0.3	-	-	-
Protease	1.0	0.5	0.5	0.5	0.5	0.5
PVPVI	-	0.5	0.5	-	-	-
PVP	0.5	0.5	0.5	-	-	-
PVNO	-	0.5	0.5	-	-	-
SRP1	-	0.5	0.5	-	-	-
Silicone antifoam	-	0.2	0.2	-	0.2	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0

Example 5

The following granular detergent formulations were prepared in accord with the invention. Formulations W and X are of particular utility under US machine wash conditions. Y is of particular utility under Japanese machine wash conditions

	T	U	V
Blown Powder			
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
CEQ	0.5	1.1	-
QAS 1	0.5	-	1.5
C45AS	8.0	7.0	7.0
Silicate	-	1.0	5.0
Soap	-	-	2.0
Brightener 1	0.2	0.2	0.2
QEA 1	0.6	2.0	1.0
Carbonate	8.0	16.0	20.0
DTPMP	-	0.4	0.4
Spray On	-	1.0	5.0
C45E7	1.0	1.0	1.0
Dry additives			
HEDP	1.0	-	-
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
TEAD	-	6.1	4.5
PB1	11.0	5.0	6.0
Sodium Sulfate	-	6.0	-
Balance (Moisture and Misc.)			

Example 6

The following granular detergent compositions of particular utility under European wash conditions were prepared in accord with the invention.

	W	X
Blown powder		
Zeolite A	20.0	-
STPP	-	20.0
LAS	6.0	6.0
C68AS	2.0	2.0
QAS1	1.6	0.8
Silicate	3.0	8.0
MA/AA	4.0	2.0
CMC	0.6	0.6
QEA 1	0.9	0.6
QEA 3	0.1	-
Brightener 1	0.2	0.2
DTPMP	0.4	0.4
Spray on		
C45E7	5.0	5.0
Silicone antifoam	0.3	0.3
Perfume	0.2	0.2
Dry additives		
Carbonate	14.0	9.0
PB1	1.5	2.0
PB4	18.5	13.0
TAED	2.0	2.0
Photoactivated bleach	15 ppm	15 ppm
Protease	1.0	1.0
Lipase	0.2	0.2
Amylase	0.4	0.4
Cellulase	0.1	0.1
Sulfate	10.0	20.0
Balance (Moisture and Misc.)		

Density (g/litre)	700	700

Example 7

The following detergent compositions, according to the present invention were prepared:

	Y	Z	AA
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
QAS1	-	1.5	1.5
CEQ	1.5	-	-
DTPMP	0.4	0.2	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
QEA 1	1.0	2.5	0.6
Mn Catalyst	0.03	-	-
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
Percarbonate	-	7.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
EDDS	-	2.0	-
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0

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 Misc.)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 8

The following detergent formulations, according to the present invention were prepared:

	BB	CC	DD	EE
LAS	20.0	14.0	24.0	22.0
QAS1	0.7	1.0	1.2	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
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	-	-
Percarbonate	-	5.0	9.0	15.0
DTPMP	0.7	1.0	-	-
QEA 1	0.4	1.2	0.5	2.0
QEA 3	0.4	-	-	-
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	-	-
HEDP	-	-	2.3	-
TEAD	2.0	1.0	-	-
Balance (Moisture and Miscellaneous)				

Example 9

The following liquid detergent formulations of particular utility under US machine wash conditions were prepared in accord with the invention.

	FF	GG	HH	II	JJ
LAS	11.5	8.8	-	3.9	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	15.7	-
C23E9	-	2.7	1.8	2.0	1.0
QAS2	0.8	-	-	-	0.6
C23E7	3.2	-	-	-	-
CEQ	-	1.4	0.7	0.9	0.4
CFAA	-	-	5.2	-	3.1
TPKFA	1.6	-	2.0	0.5	2.0
Citric acid (50%)	6.5	1.2	2.5	4.4	2.5
Calcium formate	0.1	0.06	0.1	-	-
Sodium formate	0.5	0.06	0.1	0.05	0.05
Sodium cumene sulfonate	4.0	1.0	3.0	1.18	-
Borate	0.6	-	3.0	2.0	2.9
Sodium hydroxide	5.8	2.0	3.5	3.7	2.7
Ethanol	1.75	1.0	3.6	4.2	2.9
1, 2 propanediol	3.3	2.0	8.0	7.9	5.3
Monoethanolamine	3.0	1.5	1.3	2.5	0.8
TEPAE	1.6	-	1.3	1.2	1.2
Protease	1.0	0.3	1.0	0.5	0.7
Lipase	-	-	0.1	-	-
Cellulase	-	-	0.1	0.2	0.05
Amylase	-	-	-	0.1	-
QEA1	0.4	0.7	1.4	1.2	1.1
SRP1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Water/minors to 100%					

Example 10

The following liquid detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention:

	KK	LL	M	NN	OO	PP	RR	SS
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
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
QAS1	-	-	-	-	3.0	1.0	-	-
CEQ	1.1	2.0	3.0	1.7	-	-	2.5	2.2
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0
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	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0
Triethanolamine	-	-	8.0	-	-	-	-	-
TEPAE	0.5	-	0.5	0.2	-	-	0.4	0.3
DTPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-
QEA1	0.7	0.9	1.1	1.0	1.6	1.0	0.4	0.6
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	-

SRP2	0.3	-	0.3	0.1	-	-	0.2	0.1
Boric acid	0.1	0.2	1.0	2.0	1.0	1.5	2.5	2.5
Calcium chloride	-	0.02	-	0.01	-	-	-	-
Bentonite clay	-	-	-	-	4.0	4.0	-	-
Water/minors to 100%	100	100	100	100	100	100	100	100
NaOH up to pH	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2

Example 11

The following liquid detergent compositions of particular utility under Japanese machine wash conditions were prepared in accord with the invention.

	TT	UU
LAS	27.6	18.9
C45AS	13.8	5.9
C13E8	3.0	3.1
QAS1	2.0	1.0
CEQ	-	0.4
QEA1	0.6	0.9
Oleic acid	3.4	2.5
Citric acid	5.4	5.4
Sodium hydroxide	0.4	3.6
Calcium formate	0.2	0.1
Sodium formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	5.9	5.5
Xylene sulfonic acid	-	2.4
TEPAE	1.5	0.8
Protease	1.5	0.6
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume	0.5	0.3
Water/minors to 100%		

Example 12

The following laundry bar detergent compositions were prepared in accord with the invention.

	VV	WW	XX	YY	ZZ	AB	AC	AD
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
QAS1	1.1	1.4	0.9	0.9	1.0	1.3	2.0	1.5
Sodium laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Calcium carbonate	21.5	-	-	-	-	-	-	-
Sulfate	5.0	-	-	-	-	-	-	-
TSPP	5.0	-	5.0	-	5.0	5.0	2.5	5.0
STPP	5.0	15.0	-	-	-	5.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DTPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
QEA1	0.7	1.1	1.4	0.9	0.6	0.4	1.0	1.0
SRP1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Protease	-	0.12	-	0.08	0.08	-	-	0.1
Lipase	-	0.1	-	0.1	-	-	-	-
Amylase	-	-	0.8	-	-	-	0.1	-
Cellulase	-	0.15	-	-	0.15	-	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.6	-	-	-	-	-	-	-

WHAT IS CLAIMED IS:

1. A detergent composition or component thereof comprising

(a) a cationic surfactant selected from the group consisting of:

(1) cationic ester surfactants;

(2) cationic mono-alkoxylated amine surfactants; and

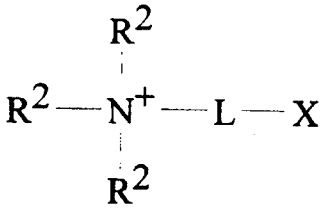
(3) cationic bis-alkoxylated amine surfactants;

(4) mixtures thereof;

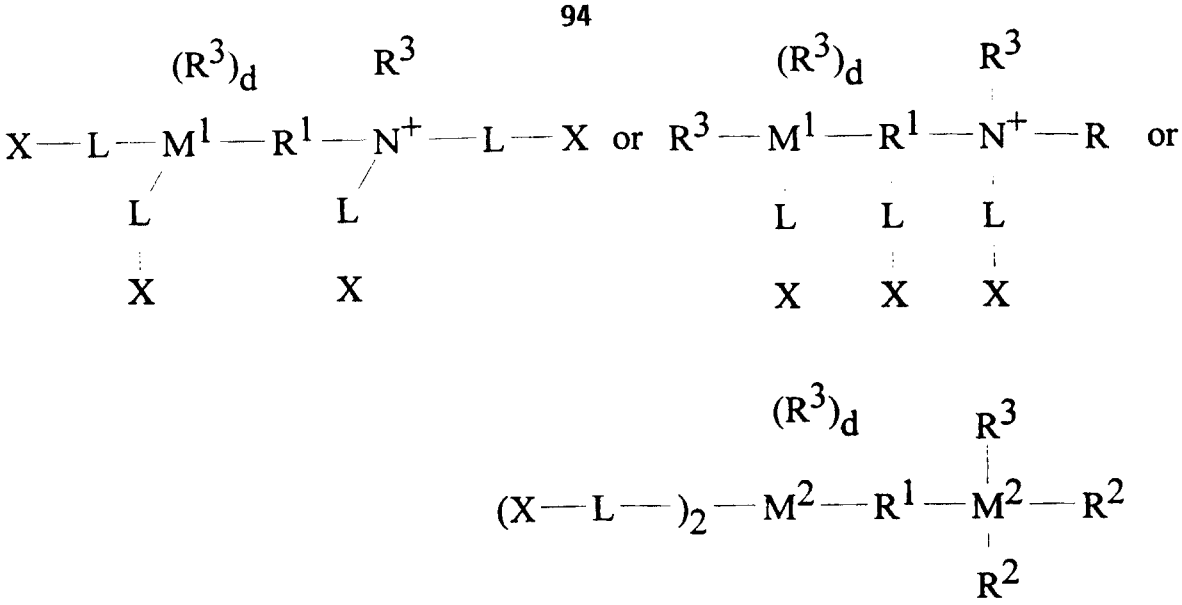
and

(b) a water-soluble cationic compound having clay soil removal/anti-redeposition properties, which is selected from the group consisting of:

1) ethoxylated cationic monoamines having the formula:

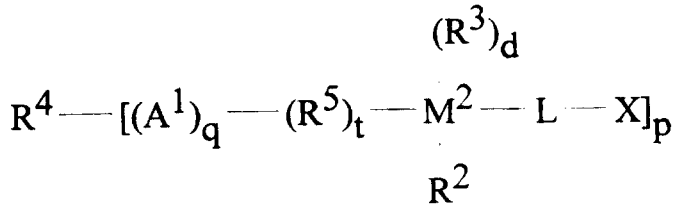


2) ethoxylated cationic diamines having the formula:



wherein M^1 is an N+ or N group; each M^2 is an N+ or N group, and at least one M^2 is an N+ group;

3) ethoxylated cationic polyamines having the formula:



4) mixtures thereof;

wherein A^1 is —NC(R)—, —NCO(R)—, —NCN(R)(R)—, —CN(R)—, —OCN(R)—,

—CO—, —OCO—, —OC—, —CNC(R)— or —O—,

R is H or C_1-C_4 alkyl or hydroxyalkyl, R^1 is C_2-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-N bonds are formed; each R^2 is C_1-C_4 alkyl or hydroxyalkyl, the moiety -L-X, or two R^2 together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$, wherein A^2 is -O- or $-CH_2-$, r is 1 or 2, s is 1 or 2 and r + s is 3 or 4; each R^3 is C_1-C_8 alkyl or hydroxyalkyl, benzyl, the moiety L-X, or two R^3 or one R^2 and one R^3 together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$; R^4 is a substituted C_3-C_{12} alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl group having p substitution sites; R^5 is C_1-C_{12} alkenyl, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to about 20 oxyalkylene units provided that no O-O or O-N bonds are formed; 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; L is a hydrophilic chain which contains the polyoxyalkylene moiety $-[(R^6O)_m(CH_2CH_2O)_n]-$; wherein R^6 is C_3-C_4 alkylene or hydroxyalkylene and m and n are numbers such that the moiety $-(CH_2CH_2O)_n-$ comprises at least about 50% by weight of said polyoxyalkylene moiety; d is 1 when M^2 is N+ and is 0 when M^2 is N; n is at least about 16 for said cationic monoamines, is at least about 6 for said cationic diamines and is at least about 3 for said cationic polyamines; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1;

and wherein the ratio of (a) to (b) is from 1:95 to 95:1;

with the proviso that if the detergent composition is a liquid detergent composition the water-soluble cationic compound having clay soil removal/anti-redeposition properties is selected from the group consisting of (2) and (3) and mixtures thereof.

2. A detergent composition or component thereof according to Claim 1 wherein said ratio is from 1:12 to 8:1.

3. A detergent composition according to Claims 1 or 2 wherein said cationic surfactant is present at a level of from 0.1% to 20% by weight of the composition.

4. A detergent composition according to any of Claims 1 to 3 wherein the cationic surfactant is present at a level of from 0.5% to 3% by weight of the composition.

5. A detergent composition according to any of Claims 1 to 4 wherein said water-soluble cationic compound is present at a level of from 0.01% to 30% by weight of the detergent composition.

6. A detergent composition according to any of Claims 1 to 5 wherein the water-soluble cationic compound is present at a level of from 0.2% to 3% by weight of the detergent composition.

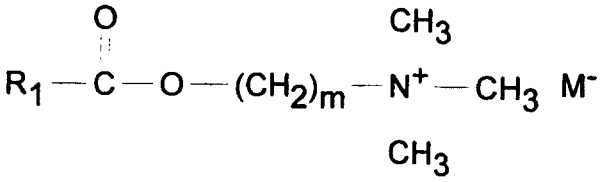
7. A detergent composition or component thereof according to any of Claims 1 to 6 wherein said cationic water-soluble compound is an ethoxylated cationic diamine and is characterized in that R^1 is a C_2-C_6 alkylene.

8. A detergent composition or component thereof according to Claim 7 wherein said ethoxylated cationic diamine is characterized in that R^1 is hexamethylene.

9. A detergent composition or component thereof according to Claims 7 or 8, wherein the ethoxylated cationic diamine is characterized in that each R^2 is methyl or the moiety -L-X, each R^3 is methyl and M^1 and each M^2 are an N^+ group.

10. A detergent composition or component thereof according to any of Claims 1 or 9, wherein m is 0 and n is at least 20.

11. A detergent composition or component thereof according to any of Claim 1 to 10 wherein said cationic ester surfactant is selected from the choline esters having the formula:



wherein m is from 1 to 4 and R_1 is a C_{11}-C_{19} linear or branched alkyl chain.

12. A detergent composition or compponent thereof according to any of Claims 1 to 10 wherein said cationic ester surfactant contains a positively charged amine group, substituted with one or two methyl groups and one or two ethoxy or propoxy groups.

13. A detergent composition or component thereof according to any of Claims 1 to 10, wherein said cationic mono-alkoxylated amine contains a positively charged amine group, which is substituted with one or two methyl groups, one or two C_{10}-C_{18} alkyl groups and one (poly) ethoxy group, with an ethoxylation number of from 1 to 4.

14. A detergent composition or component thereof according to any of Claim 1 to 10 wherein said cationic bis-ethoxylated amine surfactant contains a positively charged amine group, which is substited with one methyl group, one C_{10}-C_{18} alkyl group and two (poly) ethoxy groups, with each independently an ethoxylation number of from 1 to 4.

15. A detergent composition according to any of Claims 1 to 14 wherein a anionic surfactant is present at a level of from 4% to 15% by weight of the detergent composition.

16. A detergent composition or component thereof according to any of Claim 1 to 15 wherein a cationic clay-soil removal/ anti-redeposition polymer is present characterised in that it has a backbone, at least 2M groups and at least one L-X group, wherein M is a cationic group attached to or integral with the backbone and contains an N+ positively charged centre; and L connects groups M and X or connects group X to the polymer backbone; 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; and L is a hydrophilic chain which contains the polyoxyalkylene moiety -$[(R^6O)_m(CH_2CH_2O)_n]$-;

17. A detergent composition according to Claim 16 wherein said cationic polymer is an ethoxylated cationic polymer which has a backbone, selected from the group consisting of the polyurethanes, the polyesters, the polyethers, the polyimides, the polyalkyleneimines and mixtures thereof.

18. A detergent composition according to any of Claims 1 to 17 wherein the composition is formulated in such a manner as to provide a wash pH of from 8.0 to 10.5.

19. A detergent composition according to any of Claims 1 to 18 wherein a heavy metal ion sequestrant is present at a level of from 0.1% to 10% by weight of the detergent composition.

20. A detergent composition according to any of Claims 1 to 19 wherein a surfactant is present, selected from the group consisting of nonionic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

21. A method of washing laundry in a domestic washing machine wherein an effective amount of a detergent composition according to any of Claims 1 to 20 is introduced into the drum of the washing machine, preferably before the commencement of the wash by use of a dispensing device which permits progressive release of said granular detergent composition into the wash liquor during the wash.