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(54) **DETERGENT COMPOSITION**

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COMPOSITION DETERGENTE

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Description

Technical field

[0001] The present invention relates to detergent compositions containing a quaternary ammonium cationic component and a polymeric component having pendant carboxylic functionality, which are suitable for use in laundry and dishwashing methods.

Background to the invention

[0002] The satisfactory removal of greasy soils/stains, that is soils/stains having a high proportion of triglycerides or fatty acids, is a challenge faced by the formulator of detergent compositions for use in laundry and dish washing methods. Surfactant components have traditionally been employed in detergent products to facilitate the removal of such greasy soils/stains. In particular, surfactant systems comprising cationic surfactants are known for use in greasy soil/stain removal.

[0003] For example, EP-B-21,491 discloses detergent compositions containing a nonionic/cationic surfactant mixture and a builder mixture comprising aluminosilicate and polycarboxylate builder. The cationic surfactant may be a cationic ester. Improved particulate and greasy/oily soil removal is described.

[0004] US-A-4,228,042 discloses biodegradable cationic surfactants, including cationic ester surfactants for use in detergent compositions to provide greasy/oily soil removal. The combination of these cationic surfactants with nonionic surfactants in compositions designed for particulate soil removal is also described.

[0005] Polymeric compounds are also known components of detergent compositions. They are generally incorporated in detergent compositions as soil suspension agents.

[0006] It has been found that the stain and greasy soil removal properties of detergent compositions incorporating both a quaternary ammonium cationic component and a polymeric component having pendant carboxylic functionality are surprisingly enhanced when the two components are used within a specific ratio. The use of the combination of components within the specific ratio also enables the overall quantity of one or both components to be reduced whilst achieving the same, or improved cleaning performance.

[0007] All documents cited in the present description are, in relevant part, incorporated herein by reference.

Summary of the Invention

[0008] A detergent composition of the present invention comprises a hard acid which is a quaternary ammonium cationic component and up to 1.7% by weight total detergent composition of hard base which is a polymeric component having pendant carboxylic functionality, and wherein the ratio of cationic component to polymeric component is from 10:1 to 1:3, the composition comprising less than 20% by weight phosphate component.

[0009] In a preferred aspect of the invention, the ratio of cationic component to polymeric component is from 5:1 to 1:2. The ratio may be 5:1 to 1:1. In a further preferred aspect said cationic component comprises a cationic surfactant of the formula:

$$R^1R^2{}_mR^3{}_{3-m}N^+A^-$$

wherein R^1 represents a C_{6-24} alkyl or alkenyl group or a C_{6-12} alkaryl group, each R^2 independently represents a $(C_nH_{2n}O)_xR^4$ group where n is 1 to 4 and x is from 1 to 14 and R^4 represents hydrogen (preferred), methyl or ethyl, the sum total of $C_nH_{2n}O$ groups in $R^2{}_m$ being from 1 to 14, each R^3 group independently represents a C_{1-12} alkyl or alkenyl group, an aryl group or a C_{1-6} alkaryl group, m is 1, 2 or 3, and A is a counterion providing electrical neutrality.

Detailed description of the invention

Cationic Component

[0010] An essential element of the detergent compositions of the invention is a quaternary ammonium cationic component. Preferably this cationic component is a surfactant. The cationic component is preferably present at a level from 0.5 % to 20.0%, more preferably from 0.1% to 10%, most preferably from 1.0% to 5.0% or even below 1.5% by weight of the detergent composition.

[0011] Any quaternary ammonium cationic surfactant may be used however, according to a preferred aspect of the invention, the cationic component comprises a surfactant selected from compounds of the formula.

$$R^1R^2{}_mR^3{}_{3-m}N^+A^-$$

wherein R^1 represents a C_{6-24} alkyl or alkenyl group or a C_{6-12} alkaryl group, each R^2 independently represents a $(C_nH_{2n}O)_xR^4$ group where n is 1 to 4 and x is from 1 to 14 and R^4 represents hydrogen (preferred), methyl or ethyl, the sum total of $C_nH_{2n}O$ groups is $R^2{}_m$ being from 1 to 14, each R^3 group independently represents a C_{1-12} alkyl or alkenyl group, an aryl group or a C_{1-6} alkaryl group, m is 1, 2 or 3, and A is a counterion providing electrical neutrality.

[0012] Particularly preferred surfactants have R^2 equal to $-CH_2CH_2OH$, each R^3 independently selected from C_{1-4} alkyl, preferably methyl and m is 1 or 2. Preferably R^1 is a linear C_{6-14} alkyl group. C_{8-10} alkyl groups have been found to be particularly useful. C_{12-14} alkyl groups have also been found to be particularly useful.

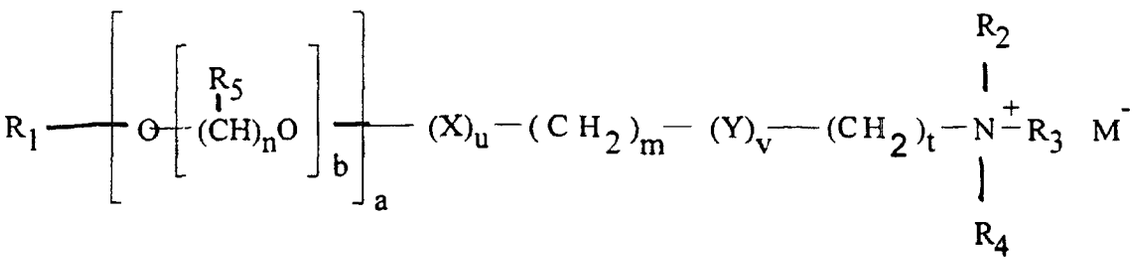
[0013] Preferably the cationic component is a monoquaternary ammonium compound.

[0014] The cationic component surfactant of the present invention is preferably a water dispersible compound having surfactant properties.

[0015] The cationic component may comprise a cationic ester surfactant. Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

[0016] In preferred cationic ester surfactants the ester linkage (i.e. -COO-) and cationically charged group of the cationic ester 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.

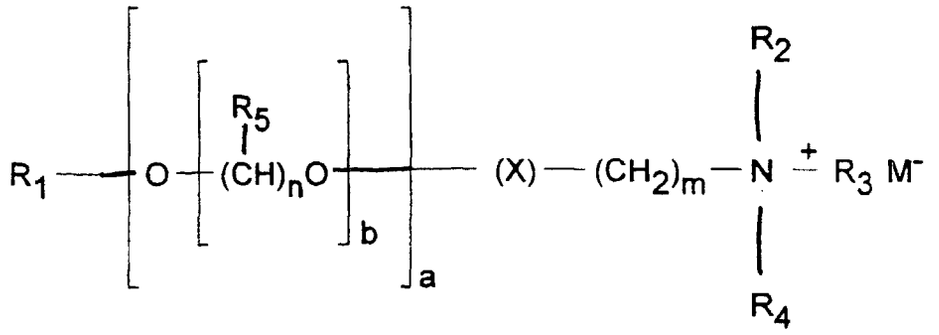
[0017] Preferred cationic ester surfactants are those having the formula:



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.

[0018] Preferably M is selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably methyl sulfate, chloride, bromide or iodide.

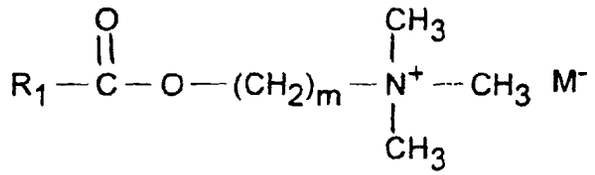
[0019] The cationic ester surfactant may be selected from those having the formula:



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.

[0020] 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.

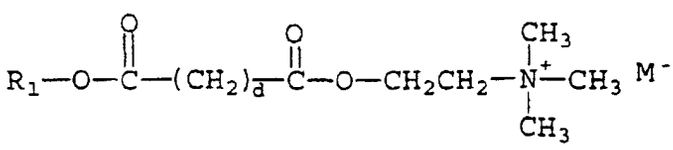
[0021] Highly preferred water dispersible cationic ester surfactants are the esters having the formula:

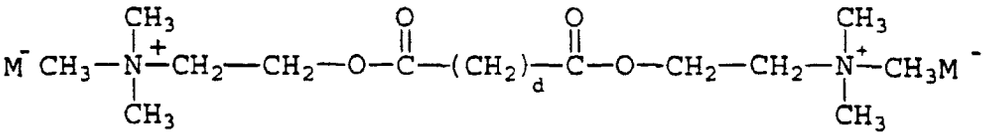


where m is from 1 to 4, preferably 2 or 3 and wherein R_1 is a C_{11}-C_{19} linear or branched alkyl chain.

[0022] 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.

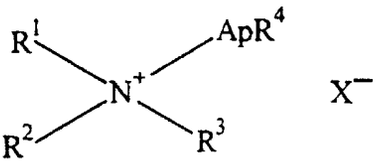
[0023] Other suitable cationic ester surfactants have the structural formulas below, wherein d may be from 0 to 20.



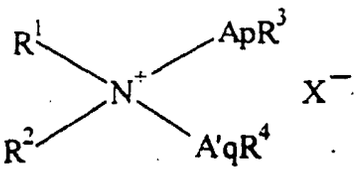


[0024] In a preferred aspect the cationic ester surfactant is hydrolysable under the conditions of a laundry wash method.

[0025] Preferred cationic surfactants include alkoxylated quaternary ammonium (AQA) surfactants of 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. Other preferred cationic surfactants include surfactants of the formula:



and one or more detersive (including fabric care) adjunct materials as disclosed hereinafter, wherein for the AQA surfactant 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; R3 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.

Polymeric Component

[0026] The polymeric component comprises a polymer having a pendant group having a carboxylic functionality (that is to say a group which is not a polymeric linkage group so that it does not form part of the polymer backbone and which has a carboxylic functionality). The polymeric component is generally formed from at least 5%, preferably at least 25% or even at least 50%, more preferably at least 60% and most preferably at least 90% by weight of monomers which result in such pendant groups. The polymeric component preferably has a molecular weight of from 1500 to 150000 most preferably from 2000 to 100000, especially 5000 to 80000. Molecular weight measurements are obtained by GPC using styrene as a standard.

[0027] References herein to carboxylic acid groups also include their salts. Polymeric polycarboxylic materials can

be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid The presence in the polymers herein, of monomeric segments, containing no hard base radicals (such as carboxylate radicals) such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments preferably do not constitute more than about 40% by weight. Acrylic and maleic homopolymers or copolymers are particularly preferred.

[0028] Acrylic/maleic-based coplymers include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably form about 7,000 to 65,000 or even 10,000 to 50,000. The ratio of acrylate to maleate segments in such preferred copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate.

[0029] Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

[0030] The polymer may be any organic polymeric material having a carboxylic functionality pendant group commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions.

[0031] Further 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 include polyacrylates of MWt 1500-5000

[0032] 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.

[0033] 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. These include maleic/acrylic/vinyl alcohol terpolymers. Such materials are disclosed in EP 193,360, including for example the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

[0034] The polymeric component is preferably present as components of any particulate components where they may be beneficial as a binder.

[0035] Detergent compositions of the present invention preferably comprise no greater than 25 % sodium sulphate.

Additional detergent components

[0036] The detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the washing operation for which it is to be used.

[0037] The compositions of the invention preferably contain one or more additional detergent components selected from additional surfactants, additional bleaches, bleach catalysts, alkalinity systems, builders, organic polymeric compounds, additional enzymes, suds suppressors, lime soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

Peroxyacid bleaching system

[0038] A preferred feature of detergent compositions according to the invention is an organic bleaching system. Preferably the bleaching system comprises a hydrogen peroxide source and a 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 the organic peroxyacid bleaching system comprises a preformed organic peroxyacid, which 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

[0039] Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably sodium salt at a level of from 1 % to 40 % by weight, more preferably from 2

% to 30 % by weight and most preferably from 5% to 25% by weight of the compositions.

[0040] 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.

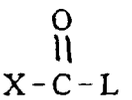
[0041] Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

[0042] 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.

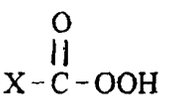
[0043] Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Peroxyacid bleach precursor

[0044] Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



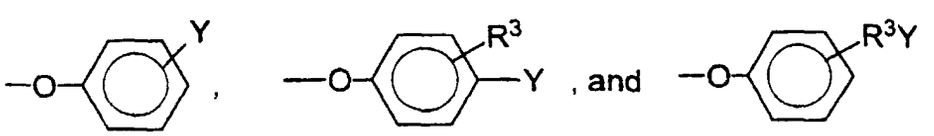
[0045] The peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.05% to 20 % by weight, more preferably from 0.1% to 15 % by weight, most preferably from 0.2% to 10% by weight of the detergent compositions.

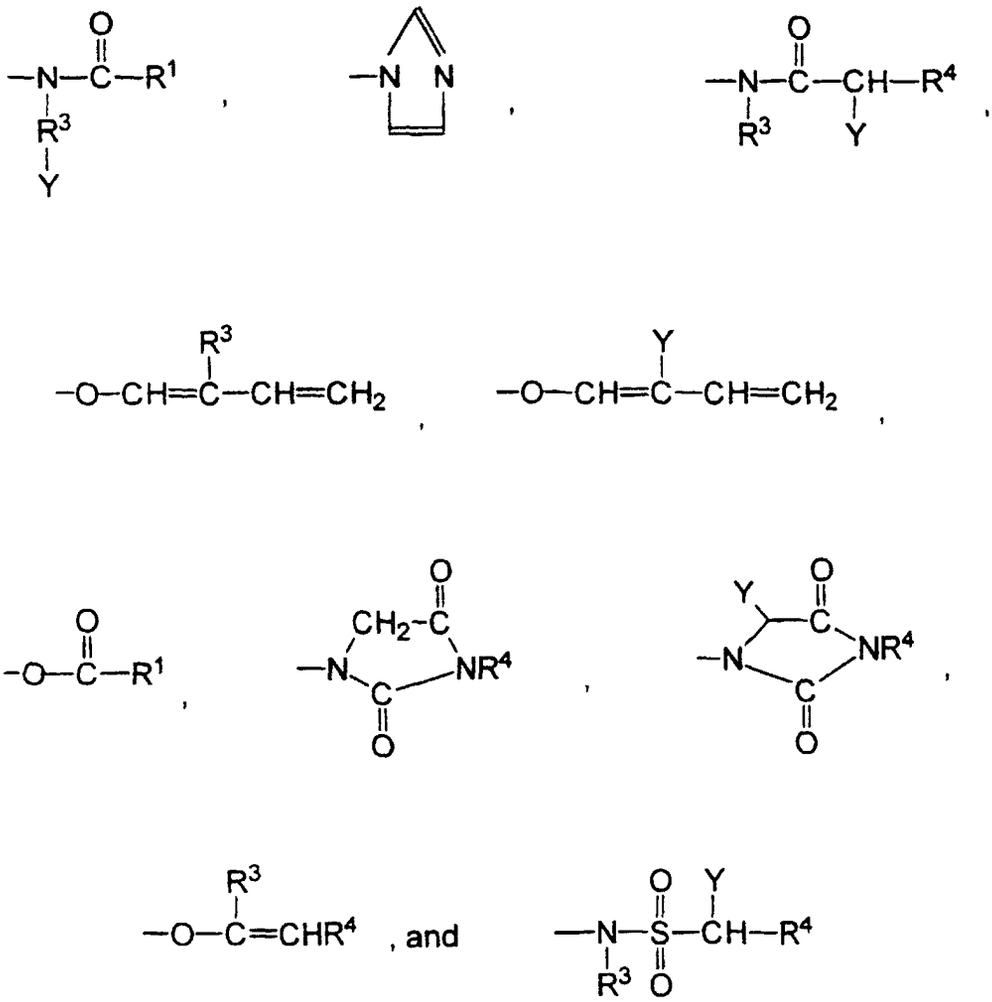
[0046] Suitable peroxyacid bleach precursor compounds typically contain one or more Nor O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials 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

[0047] 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.

[0048] Preferred L groups are selected from the group consisting of:





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

[0049] 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

[0050] Alkyl percarboxylic acid bleach precursors from percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

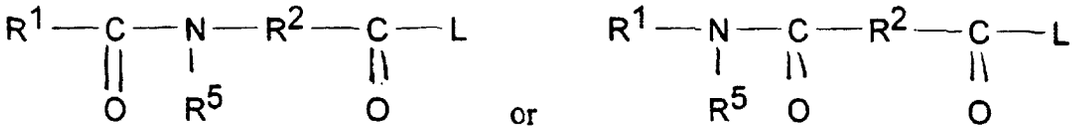
[0051] Preferred alkyl percarboxylic precursor compounds of the imide type include the N-, N^1N^1 tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

[0052] Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5,-trimethyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose. When the bleach precursor hydrophilic, more particularly when it comprises TAED, preferably it is present in amounts of at least 1.5 %, or even at least 3.5% by weight, most preferably at least 5% by weight or

greater of the total detergent composition.

Amide substituted alkyl peroxyacid precursors

[0053] Preferred peroxyacid precursors are amide substituted alkyl peroxyacid precursor compounds, including those of the following general formulae:



wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. R^2 can include alkyl, aryl, wherein said R^2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

[0054] Preferred examples of bleach precursors of this type include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, and the highly preferred (6-nonanamidocaproyl)oxy benzene sulfonate, and mixtures thereof as described in EP-A-0170386.

Perbenzoic acid precursor

[0055] 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

[0056] Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

[0057] Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

[0058] 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.

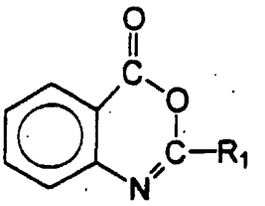
[0059] Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512; 458,396 and 284,292; and in JP 87-318,332.

[0060] Examples of preferred cationic peroxyacid precursors are described in Patent Application No. 9407944.9 and US Patent Application Nos. 08.298903, 08/298650, 08/298904 and 08/298906.

[0061] 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

[0062] Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

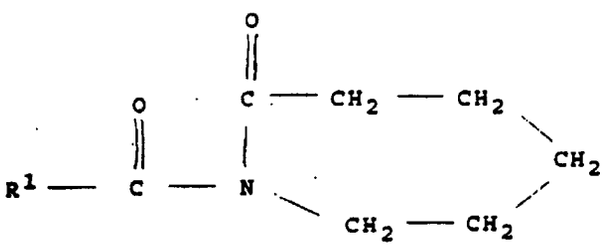


wherein R_1 is an alkyl, alkaryl, aryl, or arylalkyl.

N-acylated lactam precursors

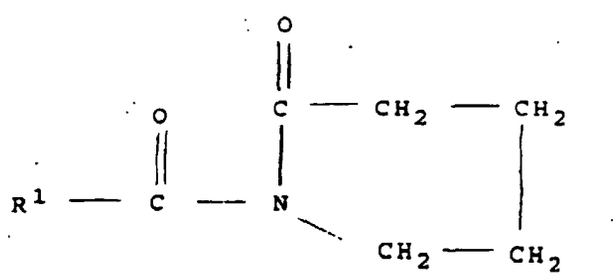
[0063] Still another class of hydrophobic bleach activators are the N-acylated precursor compounds of the lactam class disclosed generally in GB-A-955735. Preferred materials of this class comprise the caprolactams.

[0064] Suitable caprolactam bleach precursors are of the formula:



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

[0065] Suitable valero lactams have the formula:



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

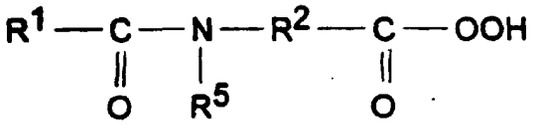
[0066] Mixtures of any of the peroxyacid bleach precursor, herein before described, may also be used.

Preformed organic peroxyacid

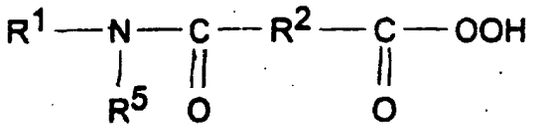
[0067] The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic

peroxyacid bleach precursor compound, a preformed hydrophobic organic peroxyacid , typically at a level of from 0.05 % to 20% by weight, more preferably from 1% to 10% by weight of the composition.

[0068] A preferred class of hydrophobic organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



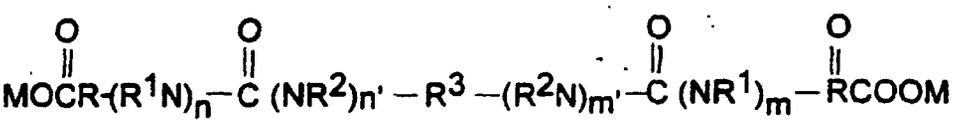
or



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

[0069] Other suitable organic peroxyacids include diperoxyalkanedioc acids, such as diperoxydodecanedioc acid, diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid.

[0070] Other suitable organic peroxyacids include diamino peroxyacids, which are disclosed in WO 95/ 03275, with the following general formula:



wherein:

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

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

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

[0071] Other suitable organic peroxyacids are include the amido peroxyacids which are disclosed in WO 95/ 16673,

with the following general structure:

$$X— Ar— CO— NY— R(Z)— CO— OOH$$

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

$$— CO — NY — R(Z) — CO — OOH$$

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

$$MOOC\text{-}R^1CO\text{-}NR^2\text{-}R^3\text{-}NR^4\text{-}CO\text{-}R^5COOOM$$

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

Additional surfactant

[0072] The detergent compositions of the invention preferably contain an additional surfactant preferably selected from anionic, nonionic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

[0073] 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).

[0074] Where present, ampholytic, amphoteric and zwitteronic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Anionic surfactant

[0075] The detergent compositions of the present invention comprise an 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 tri-ethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

[0076] 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

[0077] 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).

[0078] 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.

[0079] 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.

[0080] 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. When C_{12} akyl benzene sulfonate is incorporated into the detergent compositions of the invention, it may be present in an amount below 8% by weight of the composition.

Anionic sulfonate surfactant

[0081] 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. When C_{12} alkyl benzene sulfonate is incorporated into the detergent compositions of the invention, it may be present in an amount below 8 % by weight of the composition.

Anionic carboxylate surfactant

[0082] 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.

[0083] Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_2O)_x\ CH_2COO^-M^+$ 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.

[0084] 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

[0085] 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-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Alkoxylated nonionic surfactant

[0086] Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

[0087] 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

[0088] 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

[0089] 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, prefer-

able 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

[0090] 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

[0091] 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.

[0092] 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

[0093] Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

[0094] 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 $C_{10\text{-}18}$ acylamido alkyl dimethylamine oxide.

[0095] A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

[0096] Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

[0097] 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 $C_{12\text{-}18}$ dimethylammonio hexanoate and the $C_{10\text{-}18}$ acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Alkalinity

[0098] In the detergent compositions of the present invention preferably a alkalinity system is present to achieve optimal cationic ester surfactant performance. The alkalinity system comprises components capable of providing alkalinity species in solution. By alkalinity species it is meant herein: carbonate, bicarbonate, hydroxide, the various silicate anions, percarbonate, perborates, perphosphates, persulfate and persilicate.

Such alkalinity species can be formed for example, when alkaline salts selected from alkali metal or alkaline earth carbonate, bicarbonate, hydroxide or silicate, including crystalline layered silicate, salts and percarbonate, perborates, perphosphates, persulfate and persilicate salts and any mixtures thereof are dissolved in water.

[0099] Examples of carbonates are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

[0100] Suitable silicates include the water soluble sodium silicates with an SiO_2: Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.0 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2: Na_2O ratio of 2.0 is the most preferred silicate.

[0101] Preferred crystalline layered silicates for use herein have the general formula

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

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a value of 2, 3 or 4 and is preferably 2. The most preferred material is δ-$Na_2Si_2O_5$, available from Hoechst AG as NaSKS-6.

Water-soluble builder compound

[0102] The detergent compositions of the present invention preferably contain a water-soluble builder compound, typically present at a level of from 1 % to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60 % by weight of the composition.

[0103] 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.

[0104] The carboxylate or polycarboxylate builder can be momomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

[0105] 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.

[0106] The parent acids of 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.

[0107] 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.

[0108] 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.

[0109] The compositions of the invention contain less than 20% by weight phosphate component, preferably less than 15%, or even less than 10 % or 5% by weight phosphate component. Thus, if phosphate builders are present as the phosphate component, lower amounts are preferred.

Partially soluble or insoluble builder compound

[0110] The detergent compositions of the present invention may contain a partially soluble or insoluble builder compound, typically present at a level of from 1 % to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60 % weight of the composition.

[0111] Examples of largely water insoluble builders include the sodium aluminosilicates.

[0112] 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.

[0113] 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 Zeolite MAP 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.

Bleach catalyst

[0114] The compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

[0115] Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6$(1,4,7-triazacyclononane)$_4$-$(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

[0116] For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)$(OCH_3)_3$-(PF_6). Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$ and $[Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}bipy_2]$-$(ClO_4)_3$.

[0117] Further suitable bleach catalysts are described, for example, in European patent application No. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Heavy metal ion sequestrant

[0118] The detergent compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

[0119] Heavy metal ion sequestrants are generally present at a level of from 0.005 % to 20%, preferably from 0.1 % to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

[0120] 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.

[0121] 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.

[0122] 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.

[0123] 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.

[0124] EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are also suitable.

Enzyme

[0125] Another preferred ingredient useful in the detergent compositions is one or more additional enzymes.

[0126] Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

[0127] 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.

[0128] 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.

[0129] Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001 % to 2% by weight, preferably 0.001 % to 1% by weight, most preferably from 0.001 % to 0.5% by weight of the compositions.

[0130] 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.

[0131] A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

[0132] 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

[0133] Organic polymeric compounds are preferred additional components of the detergent compositions in accord with the invention. Organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

[0134] 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

[0135] 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.

[0136] Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alkanol antifoam compounds.

[0137] 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.

[0138] 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.

[0139] 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.

[0140] 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.

[0141] 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;

[0142] A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85 °C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

Clay softening system

[0143] The detergent compositions may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent.

[0144] The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058, 3,948,790, 3,954,632 and 4,062,647. European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe suitable organic polymeric clay flocculating agents.

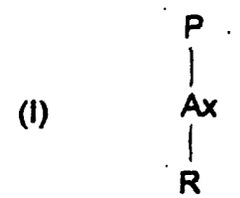
Polymeric dye transfer inhibiting agents

[0145] 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.

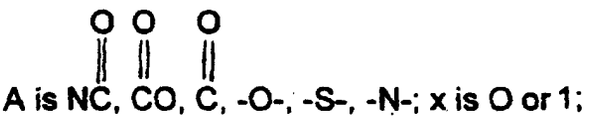
[0146] The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, co-polymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

a) Polyamine N-oxide polymers

[0147] Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :

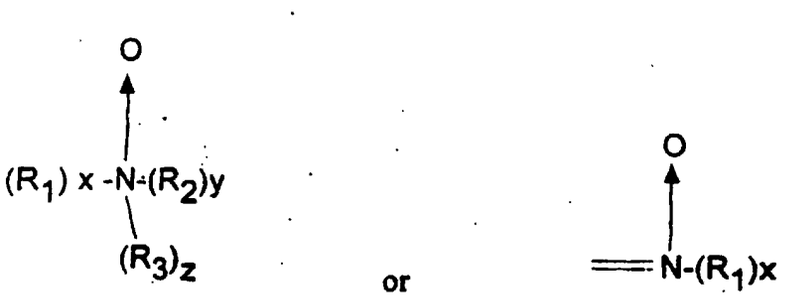


wherein P is a polymerisable unit, and



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.

[0148] 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.

[0149] 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.

[0150] Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the po-

lymerisable 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.

[0151] 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

[0152] 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

[0153] The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinyloxazolidone

[0154] 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.

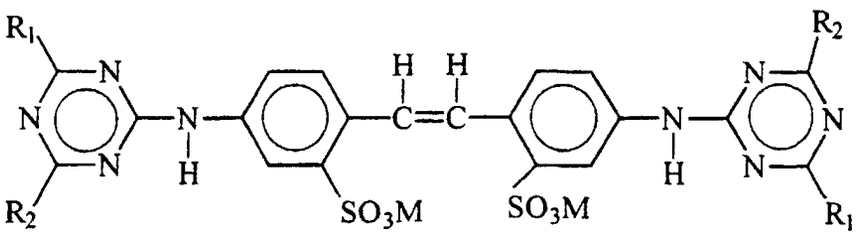
e) Polyvinylimidazole

[0155] 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

[0156] The detergent compositions herein also optionally contain from about 0.005 % to 5% by weight of certain types of hydrophilic optical brighteners.

[0157] 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.

[0158] 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.

[0159] 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.

[0160] When in the above formula, R_1 is aniline, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Cationic fabric softening agents

[0161] Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

[0162] Cationic fabric softening agents are typically incorporated at total levels of from 0.5 % to 15 % by weight, normally from 1% to 5 % by weight.

Other optional ingredients

[0163] Other optional ingredients suitable for inclusion in the compositions of the invention include colours and filler salts, with sodium sulfate being a preferred filler salt.

pH of the compositions

[0164] The present compositions preferably have a pH measured as a 1 % solution in distilled water of at least 8.5, preferably from 9.0 to 12.5, most preferably from 9.5 to 11.0.

Form of the compositions

[0165] The compositions in accordance with the invention can take a variety of physical forms including granular, tablet, bar and liquid forms. The compositions are particularly the so-called concentrated granular detergent compositions adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

[0166] 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.

[0167] The mean particle size of the components of granular compositions in accordance with the invention should preferably be such that no more that 5 % of particles are greater than 1.7mm in diameter and not more than 5 % of particles are less than 0.15mm in diameter.

[0168] The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

[0169] 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 furmel 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.

[0170] To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

Surfactant agglomerate particles

[0171] The cationic ester surfactant herein, preferably with additional surfactants, is preferably present in granular

compositions in the form of surfactant agglomerate particles, which may take the form of flakes, prills, marumes, noodles, ribbons, but preferably take the form of granules. The most preferred way to process the particles is by agglomerating powders (e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderbom 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name).

[0172] A high active surfactant paste comprising from 50% by weight to 95% by weight, preferably 70 % by weight to 85 % by weight of surfactant is typically used. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used. An operating temperature of the paste of 50°C to 80°C is typical.

Laundry washing method

[0173] Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

[0174] 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.

[0175] Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

[0176] 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.

[0177] 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.

[0178] Especially preferred dispensing devices are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing process. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

[0179] 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

[0180] 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

[0181] In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS :	Sodium linear C_{12} alkyl benzene sulfonate
TAS :	Sodium tallow alkyl sulfate
C45AS :	Sodium C_{14}-C_{15} linear alkyl sulfate
CxyEzS :	Sodium C_{1x}-C_{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
C45E7 :	A C_{14-15} predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
C25E3 :	A C_{12-15} branched primary alcohol condensed with an average of 3 moles of ethylene oxide
C25E5 :	A C_{12-15} branched primary alcohol condensed with an average of 5 moles of ethylene oxide
CEQ I :	$R_1COOCH_2CH_2.N^+(CH_3)_3$ with $R_1 = C_{11}$-C_{13}
CEQ II :	$R_1COOCH_2CH_2CH_2N^+(CH_3)_3$ with $R_1 = C_{11}$-C_{13}
CEQ III :	$R_1COOCH_2CH_2N^+(CH_3)_2(CH_2CH_2OH)$ with $R_1 = C_{11}$-C_{13}
CEQ IV :	$R_1COOCH_2CH_2N^+(CH_3CH_2)_2(CH_3)$ with $R_1 = C_{11}$-C_{13}
QAS I :	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12}$ - C_{14}
QAS II :	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_8$ - C_{10}
Soap :	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
TFAA :	C_{16}-C_{18} alkyl N-methyl glucamide
TPKFA :	C12-C14 topped whole cut fatty acids
STPP :	Anhydrous sodium tripolyphosphate
Zeolite A :	Hydrated Sodium Aluminosilicate of formula $Na_{12}(AlO_2SiO_2)_{12}$. $27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers
NaSKS-6 :	Crystalline layered silicate of formula δ -Na_2Si_2O5
Citric acid :	Anhydrous citric acid
Carbonate :	Anhydrous sodium carbonate with a particle size between 200μm and 900μm
Bicarbonate :	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
Silicate :	Amorphous Sodium Silicate (SiO_2:Na_2O; 2.0 ratio)
Sodium sulfate :	Anhydrous sodium sulfate
Citrate :	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850μm
MA/AA :	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
CMC :	Sodium carboxymethyl cellulose
Protease :	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
Alcalase :	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
Cellulase :	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
Amylase :	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
Lipase :	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
Endolase :	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
PB4 :	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
PB1 :	Anhydrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
Percarbonate :	Sodium Percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
NOBS :	Nonanoyloxybenzene sulfonate in the form of the sodium salt
NAC-OBS :	(Nonanamido caproyl) oxybenzene sulfonate in the form of the sodium salt.
NACA :	6 nonylamino - 6 oxo - capronic acid.
TAED :	Tetraacetylethylenediamine
DTPMP :	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060

Photoactivated :	Sulfonated Zinc Phthlocyanine encapsulated in bleach dextrin soluble polymer
Brightener 1 :	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2 :	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
HEDP :	1,1-hydroxyethane diphosphonic acid
PVNO :	Polyvinylpyridine N-oxide
PVPVI :	Copolymer of polyvinylpyrolidone and vinylimidazole
SRP 1 :	Sulfobenzoyl end capped esters with oxyethylene oxy and terephtaloyl backbone
SRP 2 :	Diethoxylated poly (1, 2 propylene terephtalate) short block polymer
Silicone antifoam :	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

[0182] In the following Examples all levels are quoted as % by weight of the composition:

Example 1

[0183] The following laundry detergent compositions A to F are examples 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
CEQ I	0.2	0.8	1.0	2.0	1.0	0.7
CEQ II	-	0.5	0.5	0.7	2.0	0.8
QAS I	-	-	0.8	-	-	0.8
QAS II	0.8	-	-	-	-	-
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
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
PB4	9.0	9.0	9.0	9.0	9.0	9.0
NAC OBS	2.5	1.5	3.0	4.0	3.2	2.2
DETPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
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
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

[0184] The following granular laundry detergent compositions G to I of bulk density 750 g/litre are examples 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
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
CEQ II	0.8	2.0	2.0
CEQ III	0.4	1.0	0.5
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Sodium sulfate	39.8	-	14.3
PB4	5.0	12.7	-
TAED	0.5	1.6	-
NAC OBS	1.0	1.2	1.3
DETPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Protease	0.26	0.85	0.85
Lipase	0.15	0.15	0.15
Cellulase	0.28	0.28	0.28
Amylase	0.1	0.1	0.1
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
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

[0185] The following detergent formulations are examples according to the present invention where J is a phosphorus-containing detergent composition, K is a zeolite-containing detergent composition and L is a compact detergent

composition:

	J	K	L
Blown Powder			
STPP	19.0	-	19.0
Zeolite A	-	24.0	-
C45AS	9.0	6.0	13.0
CEQ I	-	2.0	-
CEQ II	-	-	2.0
CEQ III	2.0	-	-
MA/AA	1.5	1.2	1.2
LAS	6.0	7.8	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DTPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10.0
PB1	4.0	4.0	0
NAC OBS	3.0	4.2	1.0
Photoactivated bleach	0.02	0.02	0.02
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.25	0.30	0.15
Dry mixed sodium sulfate	3.0	3.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

Example 4

[0186] The following detergent formulations are examples according to the present invention:

	Q
LAS	6.0

(continued)

	Q
QAS I	1.0
CEQ III	0.4
CEQ IV	0.4
TFAA	1.0
C25E5/C45E7	6.5
C45E3S	7.5
STPP	9.0
Silicate	5.0
Carbonate	7.5
Bicarbonate	7.5
DTPMP	1.0
SRP 1	0.2
MA/AA	1.5
CMC	0.4
Protease	1.0
Amylase	0.4
Lipase	0.1
Cellulase	0.05
Photoactivated bleach (ppm)	45ppm
Brightener 1	0.2
PB1	2.0
NAC OBS	1.0
Balance (Moisture and Miscellaneous)	100

Example 5

[0187] The following detergent formulations are examples according to the present invention:

	T	U	V
Blown Powder			
CEQ II	-	0.4	1.5
CEQ IV	0.8	0.8	1.5
Zeolite A	30.0	22.0	6.0
Sodium sulfate	19.0	5.0	7.0
MA/AA	1.5	1.5	1.2
LAS	14.0	12.0	22.0
C45AS	7.0	7.0	7.0
Silicate	-	1.0	5.0
Soap	-	-	2.0

(continued)

	T	U	V
Blown Powder			
Brightener 1	0.2	0.2	0.2
Carbonate	8.0	16.0	20.0
Spray On			
C45E7	1.0	1.0	1.0
Dry additives			
PVPVI/PVNO	0.5	0.5	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.1	0.1	0.1
Cellulase	0.1	0.1	0.1
NACA	3.4	6.1	4.5
Sodium sulfate	-	6.0	-
Balance (Moisture and Miscellaneous)	100	100	100

Example 6

[0188] The following high density and bleach-containing detergent formulations are examples according to the present invention:

	W	X	Y
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodim sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
CEQ II	0.2	0.5	2.4
CEQ III	0.3	0.9	-
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	1.3	1.7	1.7
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3

(continued)

	W	X	Y
Spray On			
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
NAC OBS	6.0	2.0	5.0
NACA	2.0	1.8	1.2
PB1	14.0	7.0	10.0
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
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 7

[0189] The following high density detergent formulations are examples according to the present invention:

	Z
Agglomerate	
C45AS	11.0
CEQ III	0.6
Zeolite A	15.0
Carbonate	4.0
MA/AA	1.3
CMC	0.5
DTPMP	0.4
Spray On	
C25E5	5.0
Perfume	0.5
Dry Adds	
HEDP	0.5

(continued)

	Z
Dry Adds	
SKS 6	13.0
Citrate	3.0
NAC OBS	4.1
TAED	1.6
Percarbonate	20.0
SRP 1	0.3
Protease	1.4
Lipase	0.4
Cellulase	0.6
Amylase	0.6
Silicone antifoam	5.0
Brightener 1	0.2
Brightener 2	0.2
Balance (Moisture and Miscellaneous)	100
Density (g/litre)	850

Example 8

[0190] The following liquid detergent formulations are examples according to the present invention:

	AB	AC	AD	AE	AF	AG	AH	AI
CEQ I	0.4	1.0	0.8	0.4	2.0	2.5	-	3.5
CEQ II	0.6	1.2	0.7	0.4	1.2	-	3.5	-
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
QAS	-	-	-	-	3.0	1.0	-	-
MA/AA	1.6	1.4	1.0	0.6	1.2	0.9	0.4	1.4
TPKFA	2.0	-	13.0	2.0	-	15.0	7.0	7.0
Rapeseed fatty acids	-	-	-	5.0	-	-	4.0	4.0
Citric acid	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl/tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Oleic acid	4.0	2.0	1.0	-	1.0	-	-	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.-
Mono Ethanol Amine	-	-	-	5.0	-	-	9.0	9.0

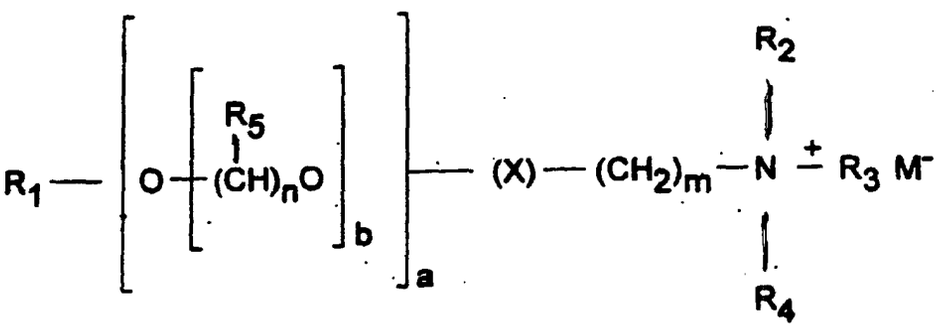
(continued)

	AB	AC	AD	AE	AF	AG	AH	AI
Tri Ethanol Amine	-	-	8	-	-	-	-	-
NaOH up to pH	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2
Ethoxylated tetraethylene pentamine	0.5	-	0.5	0.2	-	-	0.4	0.3
NAC OBS	1.0	1.0	0.5	1.0	2.0	1.2	1.0	1.6
NACA	0.7	1.1	1.8	1.5	1.9	2.1	1.4	1.0
PB_4	2.0	2.6	3.1	3.0	3.1	3.5	2.9	2.5
SRP 2	0.3	-	0.3	0.1	-	-	0.2	0.1
PVNO	-	-	-	-	-	-	-	0.10
Protease	0.5	0.5	0.4	0.25	-	0.5	0.3	0.6
Alcalase	-	-	-	-	1.5	-	-	-
Lipase	-	0.10	-	0.01	-	-	0.15	0.15
Amylase	0.25	0.25	0.6	0.5	0.25	0.9	0.6	0.6
Cellulase	-	-	-	0.05	-	-	0.15	0.15
Endolase	-	-	-	0.10	-	-	0.07	-
Boric acid	0.1	0.2	-	2.0	1.0	1.5	2.5	2.5
Na formate	-	-	1.0	-	-	-	-	-
Ca chloride	-	0.015	-	0.01	-	-	-	-
Bentonite clay	-	-	-	-	4.0	4.0	-	-
Suspending clay SD3	-	-	-	-	0.6	0.3	-	-
Balance (Moisture and Miscellaneous)	100	100	100	100	100	100	100	100

Claims

1. A detergent composition comprising anionic surfactant and 0.5 to 20% by weight a quaternary ammounium cationic component and up to 1.7% by weight of polymeric component having pendant carboxylic functionality, and wherein the ratio of cationic component to polymeric component is from 10:1 to 1:3, the compositon comprising less than 20% by weight phosphate component.

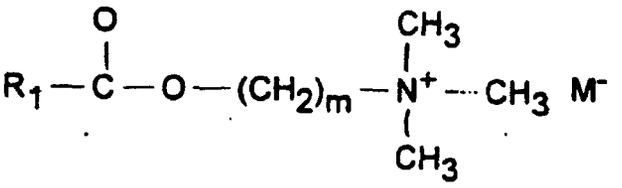
2. A detergent composition according to claim 1 in which the quaternary ammonium compound is a surfactant of the formula



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.

3. A detergent composition according to claim 1 in which the quaternary ammonium compound is a surfactant of 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.

4. A detergent composition according to claim 1 wherein the cationic component comprises a cationic surfactant of the formula:

$$R^1R^2{}_mR^3{}_{3-m}N^+A^-$$

wherein R^1 represents a C_{6-24} alkyl or alkenyl group or a C_{6-12} alkaryl group, each R^2 independently represents a $(C_nH_{2n}O)_xR^4$ group where n is 1 to 4 and x is from 1 to 14 and R^4 represents hydrogen (preferred), methyl or ethyl, the sum total of $C_nH_{2n}O$ groups in $R^2{}_m$ being from 1 to 14, each R^3 group independently represents a C_{1-12} alkyl or alkenyl group, an aryl group or a C_{1-6} alkaryl group, m is 1, 2 or 3, and A is a counterion providing electrical neutrality.

5. A detergent composition according to claim 4 wherein R^2 is $-CH_2CH_2OH$, R^3 is (independently) C_{1-4} alkyl, m is 1 or 2 and R^1 is a linear C_{6-14} alkyl group.

6. A detergent composition according to claim 4 in which R^2 is $-CH_2CH_2OH$, R^3 is (independently) C_{1-4} alkyl, m is 1 or 2 and R^1 is a C_{8-10} alkyl group.

7. A detergent composition according to claim 4 or claim 6 in which R^1 is a C_{8-10} alkyl group.

8. A detergent composition according to any preceding claim wherein the cationic component is present in an amount below 1.5%.

9. A detergent composition according to claim 1 comprising no greater than 25% by weight sodium sulphate.

10. A detergent composition according to any preceding claim additionally comprising a bleach precursor compound, the amount of bleach precursor in the composition being at least 1.5% by weight when the bleach precursor is a hydrophilic bleach precursor.

11. A detergent composition according to claim 10 wherein the hydrophilic bleach precursor is tetracetylethylenediamine.

12. A detergent composition according to any preceding claim comprising less than 8% by weight of sodium linear C_{12} alkyl benzene sulfonate.

13. A detergent composition according to any preceding claim wherein the polymer component is present in amounts from 0.01% to 1.4% by weight.

14. A detergent composition according to any preceding claim wherein said polymeric component comprises an acrylic, maleic or succinic acid/salt polymer.

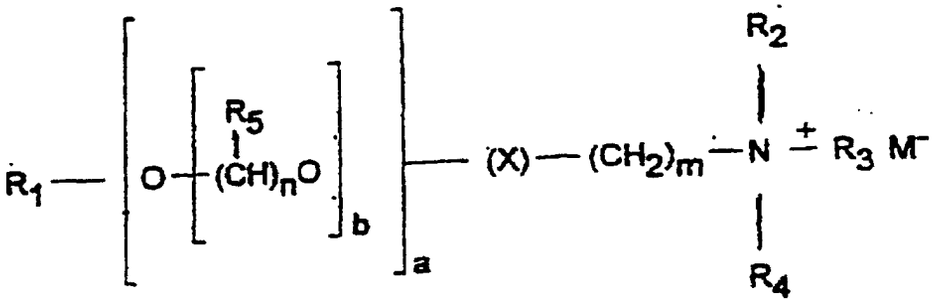
15. A detergent composition according to any preceding claim wherein said polymeric component has a molecular weight of from 2000 to 150,000.

16. A method of washing laundry in a domestic washing machine in which a dispensing device containing an effective amount of a solid detergent composition according to any of claims 1 to 15 is introduced into the drum of the washing machine before the commencement of the wash, wherein said dispensing device permits progressive release of said detergent composition into the wash liquor during the wash.

Patentansprüche

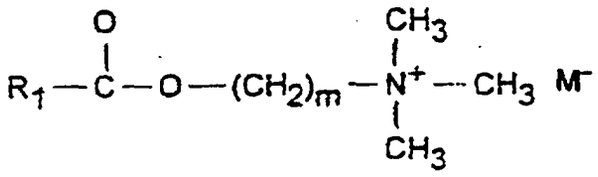
1. Detergenszusammensetzung, umfassend anionisches Tensid und 0,5 bis 20 Gew.-% einer quaternären kationischen Ammoniumkomponente, und bis zu 1,7 Gew.-% polymere Komponente mit Carboxylfunktionalität in der Seitenkette, und wobei das Verhältnis von kationischer Komponente zu polymerer Komponente 10:1 bis 1:3 beträgt, wobei die Zusammensetzung weniger als 20 Gew.-% Phosphatkomponente umfasst.

2. Detergenszusammensetzung nach Anspruch 1, wobei die quaternäre Ammoniumverbindung ein Tensid der Formel ist



worin R_1 eine lineare oder verzweigte C_5-C_{31}-Alkyl-, Alkenyl- oder Alkarylkette ist; X aus der Gruppe gewählt ist, bestehend aus COO, OCO, OCOO, OCONH und NHCOO; R_2, R_3 und R_4 unabhängig gewählt sind aus der Gruppe, bestehend aus Alkyl- und Hydroxyalkylgruppen mit 1 bis 4 Kohlenstoffatomen; und R_5 unabhängig H oder eine C_1-C_3-Alkylgruppe ist; wobei der Wert von n im Bereich von 0 bis 8 liegt, der Wert von b im Bereich von 0 bis 20 liegt, der Wert von a entweder 0 oder 1 ist, und der Wert von m 3 bis 8 ist.

3. Detergenszusammensetzung nach Anspruch 1, wobei die quaternäre Ammoniumverbindung ein Tensid der Formel ist



worin m 1 bis 4 ist, vorzugsweise 2 oder 3, und worin R_1 eine lineare oder verzweigte C_{11}-C_{19}-Alkylkette ist.

4. Detergenszusammensetzung nach Anspruch 1, wobei die kationische Komponente ein kationisches Tensid der Formel umfasst:

$$R^1R^2{}_mR^3{}_{3-m}N^+A^-$$

worin R^1 eine C_{6-24}-Alkyl- oder Alkenylgruppe oder eine C_{6-12}-Alkarylgruppe bedeutet, jedes R^2 unabhängig eine

$(C_nH_{2n}O)_xR^4$-Gruppe bedeutet, worin n 1 bis 4 ist und x 1 bis 14 ist, und R^4 Wasserstoff (bevorzugt), Methyl oder Ethyl bedeutet, wobei die Gesamtsumme der $C_nH_{2n}O$-Gruppen in $R^2{}_m$ 1 bis 14 beträgt, jede R^3-Gruppe unabhängig eine C_{1-12}-Alkyl- oder Alkenylgruppe, eine Arylgruppe oder eine C_{1-6}-Alkarylgruppe bedeutet, m 1, 2 oder 3 ist, und A ein Gegenion ist, das elektrische Neutralität vorsieht.

5. Detergenszusammensetzung nach Anspruch 4, wobei R^2 $-CH_2CH_2OH$ ist, R^3 (unabhängig) C_{1-4}-Alkyl ist, m 1 oder 2 ist, und R^1 eine lineare C_{6-14}-Alkylgruppe ist.

6. Detergenszusammensetzung nach Anspruch 4, wobei R^2 $-CH_2CH_2OH$ ist, R^3 (unabhängig) C_{1-4}-Alkyl ist, m 1 oder 2 ist, und R^1 eine C_{8-10}-Alkylgruppe ist.

7. Detergenszusammensetzung nach Anspruch 4 oder Anspruch 6, wobei R^1 eine C_{8-10}-Alkylgruppe ist.

8. Detergenszusammensetzung nach mindestens einem vorangehenden Anspruch, wobei die kationische Komponente in einer Menge unterhalb 1,5% vorliegt.

9. Detergenszusammensetzung nach Anspruch 1, umfassend nicht mehr als 25 Gew.-% Natriumsulfat.

10. Detergenszusammensetzung nach mindestens einem vorangehenden Anspruch, umfassend zusätzlich eine Bleichvorläuferverbindung, wobei die Menge des Bleichvorläufers in der Zusammensetzung mindestens 1,5 Gew.-% beträgt, wenn der Bleichvorläufer ein hydrophiler Bleichvorläufer ist.

11. Detergenszusammensetzung nach Anspruch 10, wobei der hydrophile Bleichvorläufer Tetracetylethylendiamin ist.

12. Detergenszusammensetzung nach mindestens einem vorangehenden Anspruch, umfassend weniger als 8 Gew.-% lineares Natrium-C_{12}-Alkylbenzolsulfonat.

13. Detergenszusammensetzung nach mindestens einem vorangehenden Anspruch, wobei die Polymerkomponente in Mengen von 0,01 bis 1,4 Gew.-% vorliegt.

14. Detergenszusammensetzung nach mindestens einem vorhandenden Anspruch, wobei die polymere Komponente ein Acryl-, Maleinsäure- oder Bemsteinsäure/Salz-Polymer umfasst.

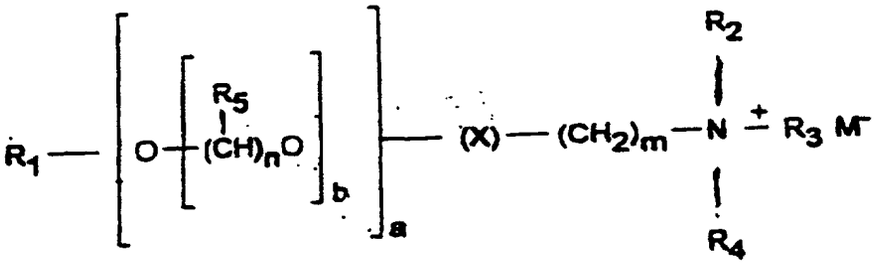
15. Detergenszusammensetzung nach mindestens einem vorangehenden Anspruch , wobei die polymere Komponente ein Molekulargewicht von 2.000 bis 150.000 besitzt.

16. Verfahren zum Waschen von Wäsche in einer Haushaltswaschmaschine, wobei eine Dispensiervorrichtung, welche eine wirksame Menge einer festen Detergenszusammensetzung gemäß mindestens einem der Ansprüche 1 bis 15 enthält, in die Trommel der Waschmaschine eingeführt wird, bevor mit der Wäsche begonnen wird, wobei die Dispensiervorrichtung eine progressive Freisetzung der Detergenszusammensetzung in die Waschlauge während der Wäsche erlaubt.

Revendications

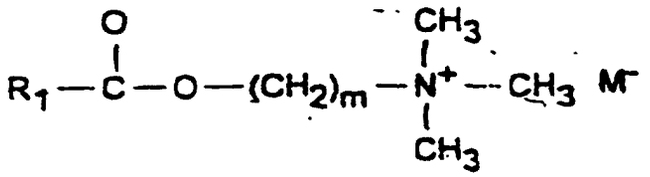
1. Composition détergente comprenant un agent tensioactif anionique et 0,5 à 20 % en poids d'un composant cationique d'ammonium quaternaire et jusqu'à 1,7 % en poids d'un composant polymère ayant une fonctionnalité carboxylique latérale, et dans laquelle le rapport du composant cationique au composant polymère est de 10:1 à 1:3, la composition comprenant moins de 20 % en poids de composant phosphate.

2. Composition détergente selon la revendication 1, dans laquelle le composé d'ammonium quaternaire est un agent tensioactif de formule :



dans laquelle R_1 est une chaîne alkyle, alcényle ou alkaryle linéaire ou ramifiée en C_5-C_{31} ; X est choisi dans le groupe constitué de COO, OCO, OCOO, OCONH et NHCOO ; R_2, R_3 et R_4 sont choisis indépendamment dans le groupe constitué de groupes alkyle et hydroxyalkyle ayant 1 à 4 atomes de carbone ; et R_5 est indépendamment H ou un groupe alkyle en C_1-C_3 ; dans laquelle la valeur de n se situe dans la plage de 0 à 8, la valeur de b se situe dans la plage de 0 à 20, la valeur de a est 0 ou 1, et la valeur de m est 3 à 8.

3. Composition détergente selon la revendication 1, dans laquelle le composé d'ammonium quaternaire est un agent tensioactif de formule :



dans laquelle m a une valeur de 1 à 4, vaut de préférence 2 ou 3, et dans laquelle R_1 est une chaîne alkyle linéaire ou ramifiée en C_{11}-C_{19}.

4. Composition détergente selon la revendication 1, dans laquelle le composant cationique comprend un agent tensioactif cationique de formule :

$$R^1R^2{}_mR^3{}_{3-m}N^+A^-$$

dans laquelle R_1 représente un groupe alkyle ou alcényle en C_{6-24} ou un groupe alkaryle en C_{6-12}, chaque R^2 représente indépendamment un groupe $(C_nH_{2n}O)_xR^4$, où n vaut 1 à 4 et x vaut 1 à 14 et R^4 représente l'hydrogène (préféré), un groupe méthyle ou éthyle, la somme totale des groupes $C_nH_{2n}O$ dans $R^2{}_m$ valant de 1 à 14, chaque groupe R^3 représente indépendamment un groupe alkyle ou alcényle en C_{1-12}, un groupe aryle ou un groupe alkaryle en C_{1-6}, m vaut 1, 2 ou 3, et A est un contre-ion assurant une neutralité électrique.

5. Composition détergente selon la revendication 4, dans laquelle R^2 est $-CH_2CH_2OH$, R^3 est (indépendamment) un groupe alkyle en C_{1-4}, m vaut 1 ou 2 et R^1 est un groupe alkyle linéaire en C_{6-14}.

6. Composition détergente selon la revendication 4, dans laquelle R^2 est $-CH_2CH_2OH$, R^3 est (indépendamment) un groupe alkyle en C_{1-4}, m vaut 1 ou 2 et R^1 est un groupe alkyle en C_{8-10}.

7. Composition détergente selon la revendication 4 ou la revendication 6, dans laquelle R^1 est un groupe alkyle en C_{8-10}.

8. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle le composant cationique est présent en quantité inférieure à 1,5 %.

9. Composition détergente selon la revendication 1, ne comprenant pas plus de 25 % en poids de sulfate de sodium.

10. Composition détergente selon l'une quelconque des revendication précédentes, comprenant en outre un composé précurseur de blanchiment, la quantité de précurseur de blanchiment dans la composition étant d'au moins 1,5 %

en poids lorsque le précurseur de blanchiment est un précurseur de blanchiment hydrophile.

11. Composition détergente selon la revendication 10, dans laquelle le précurseur de blanchiment hydrophile est la tétracétyléthylènediamine.

12. Composition détergente selon l'une quelconque des revendications précédentes, comprenant moins de 8 % en poids d'alkyl-benzènesulfonate de sodium linéaire en C_{12}.

13. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle le composant polymère est présent en quantités de 0,01 % à 1,4 % en poids.

14. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle ledit composant polymère comprend un polymère d'acide/de sel acrylique, maléique ou succinique.

15. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle ledit composant polymère a un poids moléculaire de 2 000 à 150 000.

16. Procédé de lavage de linge dans une machine à laver domestique, dans lequel un dispositif distributeur contenant une quantité efficace d'une composition détergente solide selon l'une quelconque des revendications 1 à 15 est introduit dans le tambour de la machine à laver avant le démarrage du lavage, dans lequel ledit dispositif distributeur permet une libération progressive de ladite composition détergente dans la liqueur de lavage pendant le lavage.