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(54) **Stable detergent compositions comprising bleaching agents.**

(57) Granular detergent compositions comprising certain bleaching agents having improved stability of those bleaching agents. The compositions comprise:

- i) a granular component comprising water-insoluble silicate which comprises magnesium, aluminium, or a mixture of these, and water-soluble silicate; and
- ii) a granular component comprising a bleaching agent chosen from the group comprising alkalimetal percarbonate, peroxyacid, perimidic acid or combinations of these.

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The present invention concerns the improved stability of certain bleaching agents in detergent compositions. In particular it relates to the improved stability of percarbonate bleach particles.

Percarbonate bleach is currently being proposed as an alternative to perborate bleach which has commonly been used in detergent compositions in the past. Sodium percarbonate is an attractive perhydrate for use in detergent compositions because it dissolves readily in water, is weight efficient and, after giving up its available oxygen, provides a useful source of carbonate ions for detergency purposes. However, one problem is that percarbonate is less stable in granular detergents than perborate. In particular this stability problem is more apparent when water-insoluble silicates such as aluminosilicates and/or clays are present in the composition.

Aluminosilicates and clays are common components of granular detergents. Certain aluminosilicates are employed most commonly for their ability to complex with metal ions such as calcium and magnesium which are present in hard water, and certain clays are used for their ability to impart softness to fabrics. However the presence of heavy metal ions in these components is unavoidable.

Particulate detergent components comprising clays have been proposed in the prior art.

GB 2 121 843, published on 8th April 1982 describes the use of silicate as a binder for clay particles. EP-A 340 004, published on 2nd November, 1989, describes the use of anionic surfactant as the binder for clay particles and also suggests that silicate may be used in addition. The use of such particles in bleaching compositions comprising perborate is disclosed.

However, neither mentions the stability problems associated with percarbonate bleach, or suggests ways in which this problem may be solved.

WO92/6163, published on 16th April, 1992, suggests that the percarbonate stability problem arises predominantly from the presence of heavy metal ions which catalyse the decomposition of the percarbonate, and proposes to limit such ions as well as to control moisture to inhibit the catalysed degradation of the bleaching agent. The application also mentions the possibility of coating percarbonate with protective layer (including silicate), and adding chelants to the compositions to immobilise the heavy metal ions. However further improvements are still sought which would allow improvements in percarbonate stability in formulations containing aluminosilicates and/or clays, in order to give more flexibility to formulate compositions which comprise certain bleaching agents.

It has now been found that the presence of water-soluble silicate in the aluminosilicate/clay particle greatly improves percarbonate stability. This development offers a number of advantages, including the possibility to formulate compositions with increased levels of clay, and to make products having a higher level of moisture than was previously possible.

Summary of the Invention

The present invention relates improvements in the stability of granular detergent compositions comprising certain bleaching agents. The compositions of the invention comprise:

- i) a granular component comprising water-insoluble silicate which comprises magnesium, aluminium, or a mixture of these, and water-soluble silicate; and
- ii) a granular component comprising a bleaching agent chosen from the group comprising alkalimetal percarbonate, peroxyacid, perimidic acid or combinations of these.

Detailed Description of the Invention

The present invention relates to a granular detergent composition comprising

- i) a granular component comprising water-insoluble silicate which comprises magnesium, aluminium, or a mixture of these, and water-soluble silicate; and
- ii) a granular component comprising a bleaching agent chosen from the group comprising alkalimetal percarbonate, peroxyacid, perimidic acid or combinations of these.

The invention particularly relates to aluminosilicates and clays of natural origin, because these minerals frequently comprise heavy metal ions such as iron, copper and manganese.

In a preferred embodiment, the present invention comprises clays of the smectite type, for example, a trioctahedral mineral of the hectorite type, or a dioctahedral mineral of the montmorillonite type.

Furthermore the clay may be modified by the addition of cationic or amino organic compounds.

Preferably, in this embodiment of the invention, the granular detergent composition will comprise clay at a level of at least 5% by weight of the granular detergent composition.

The water-soluble silicate preferably has a ratio of SiO_2 to Na_2O of between 2.0:1 and 3.3:1.

In another embodiment of the invention, the water-soluble silicate may be partly added to the granular component comprising the clay, and partly dry mixed with the remainder of the composition. The dry mixed portion of the water-soluble silicate in this embodiment should comprise less than 10% by weight of the granular detergent composition.

5 In another embodiment of the invention alkalimetal percarbonate has a granular form, the outer surface of the granules being substantially coated in order to further improve the stability of the bleach. Preferably the coating of the alkalimetal percarbonate particles comprises less than 2% by weight of silicate.

In a most preferred embodiment of the invention, the granular detergent composition comprises at least 12% by weight of zeolite and less than 1% by weight of any of the chelating agents chosen from the group
10 of aminocarboxylates, aminophosphonates, polyfunctionally-substituted aromatic chelating agents, or mixtures of these.

The various components mentioned above will now be described in more detail.

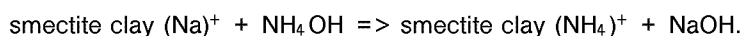
The granular compositions of the present invention comprise, firstly, a component comprising water-insoluble silicate, and water-soluble silicate (this component is described hereinafter as the "silicate
15 component").

The water-insoluble silicates of the present invention include clays which may be either unmodified or organically modified. Those clays which are not organically modified can be described as expandable, three-layered clays, i.e., aluminosilicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100g. of clay and preferably at least 60 meq/100 g. of clay. The starting clays for the
20 organically modified clays can be similarly described. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

There are two distinct classes of smectite-type clays that can be broadly differentiated on the basis of the numbers of octahedral metal-oxygen arrangements in the central layer for a given number of silicon-oxygen
25 atoms in outer layers. A more complete description of clay minerals is given in "Clay Colloid Chemistry" by H. van Olphen, John Wiley & Sons (Interscience Publishers), New York, 1963. Chapter 6, especially pages 66-69.

The family of smectite (or montmorillonoid) clays includes the following trioctahedral minerals: talc; hectorite; saponite; sauconite; vermiculite; and the following dioctahedral minerals: prophyllite; montmoril-
30 lonite; volchonskoite and nontronite.

The clays employed in these compositions contain cationic counterions such as protons, sodium ions, potassium ions, calcium ions, and lithium ions. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange
35 reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation :



40 Since in the foregoing equilibrium reaction, an equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq/100g). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration, or by a methylene blue procedure, all as fully set forth in Grimshaw,
45 "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971). The cation exchange capacity of a clay material relates to such factors as the expandable properties of the clay, the charge of the clay (which in turn is determined at least in part by the lattice structure), and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. of kaolinites to about 150 meq/100 g., and greater, for certain smectite clays.

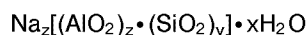
50 In a preferred embodiment of the invention a smectite-type clay is present in the clay/aluminosilicate component. sodium, potassium, lithium, magnesium, calcium clays may be used.

Preferred smectite-type clays are sodium montmorillonite, potassium montmorillonite, sodium hectorite and potassium hectorite. The clays used herein have a particle size range of up to about 1 micron.

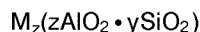
Any of the clays used herein may be either naturally or synthetically derived. However the present
55 invention has been found to be particularly useful when natural clays are used owing to the generally higher levels of heavy metal ions which are present in natural minerals.

In addition to, or in place of the clays described above, another family of water-insoluble silicates which may be used in the present invention are described below.

One example is crystalline aluminosilicate ion exchange material of the formula :



- 5 wherein z and y are at least about 6, the molar ratio of z to y is from about 1.0 to about 0.4 and z is from about 10 to about 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula :



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wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2 and y is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO_3 hardness per gram of anhydrous aluminosilicate. Hydrated sodium Zeolite A with a particle size of from about 1 to 10 microns is preferred.

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The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from about 1.5% to about 35% by weight, preferably from 5% to 22% by weight, and more preferably 10% to 15% by weight of water by weight if crystalline, and potentially even higher amounts of water if amorphous. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns. Amorphous materials are often smaller, e.g., down to less than about 0.01 micron. Preferred ion exchange materials have a particle size diameter of from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter by weight of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion exchange materials herein are usually further characterized by their calcium ion exchange capacity, which is at least about 200 mg equivalent of CaCO_3 water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least about 2 grains Ca^{++} /gallon/minute/gram/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/minute/gram/gallon, based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a calcium ion exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

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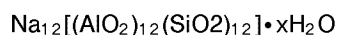
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The amorphous aluminosilicate ion exchange materials usually have a Mg^{++} exchange of at least about 50 mg eq. CaCO_3 /g (12 mg Mg^{++} /g) and a Mg^{++} exchange rate of at least about 1 grain/gallon/minute/gram/gallon. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units).

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Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Pat. No. 3,985,669, Krummel et al., issued Oct. 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite M, Zeolite P and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula :



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wherein x is from about 20 to about 30, especially about 27 and has a particle size generally less than about 5 microns.

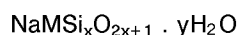
An essential feature of the present invention is the presence of water-soluble silicate in the same particle as the clay/aluminosilicate. Water-soluble silicates which are suitable for use in the present invention may be amorphous or layered.

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Such silicates may be characterised by the ratio of SiO_2 to Na_2O in their structure. In the present invention, this ratio may typically lie in the range of from 3.3:1 to 2.0:1, preferably 3.3:1 to 2.4:1, more preferably 3.3:1 to 2.8:1, most preferably 3.3:1 to 3.0:1.

Crystalline layered sodium silicates have the general formula :

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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 164 514 and methods for their preparation are disclosed in DE-A 34 17 649 and DE-A 37 42 043. For the purpose of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is) and preferred examples of this formula comprise the α -, β -, γ -, δ - forms of $\text{Na}_2\text{Si}_2\text{O}_5$. These materials are available from Hoechst AG, Germany, as, respectively, NaSKS-5, NaSkS-7, NaSKS-11 and NaSKS-6. The most preferred material is δ - $\text{Na}_2\text{Si}_2\text{O}_5$, NaSKS-6.

The laundry detergent compositions incorporating the bleaching compositions of the present invention preferably comprise amorphous silicate or crystalline layered silicate at a level of from 1% to 40% by weight of the composition, more preferably from 1% to 20% by weight.

The water-soluble silicate which is present in the finished composition may be partly added to the clay/aluminosilicate component, and partly added to the rest of the composition by some other means. Such means includes the dry mixing of silicate particles. Suitable silicate particles may be prepared by spray drying although alternative processing routes will be evident to the man skilled in the art. Furthermore the man skilled in the art of detergent formulation will choose different types of silicate for use in the various components of the composition. For example a layered silicate and/or a low ratio silicate may be dry added, whereas a higher ratio silicate may be chosen for use in the clay/aluminosilicate component of the same composition.

It is preferred that the silicate component of the present invention comprises less than 25% by weight of water-soluble silicate and preferably from 3% to 15% by weight. When dry added water-soluble silicate is used, it is preferred that less than 10% by weight of the finished composition is dry added water-soluble silicate.

The granular compositions of the present invention further comprise a granular component comprising a bleaching agent chosen from the group comprising alkalimetal percarbonate, peroxyacid, perimidic acid or combinations of these. (This component is described hereinafter as the "bleaching component")

Percarbonate will generally be solid and granular in nature. It may be added to granular detergent compositions without additional protection. However, such granular compositions may utilise a coated form of the material which provides better storage stability for the percarbonate in the granular product.

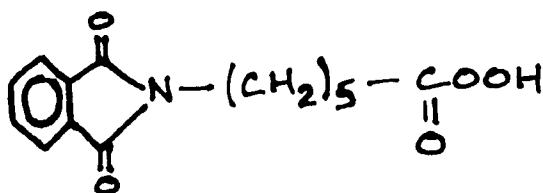
The sodium salt of percarbonate is preferred for use in the present invention. Sodium percarbonate is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Most commercially available material includes a low level of a heavy metal sequestrant such as EDTA, 1-hydroxyethylidene 1,1-diphosphonic acid (HEDP) or an amino-phosphonate, that is incorporated during the manufacturing process. For the purposes of the present invention, the percarbonate may be incorporated into detergent compositions without additional protection, but preferred embodiments of the invention utilise a coated form of the material. Suitable coating materials include the alkali and alkaline earth metal carbonates and sulphates or chlorides. The most preferred coating material comprises a mixed salt of alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB 1 466 799, granted to Interlox on 9th March, 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1:200 to 1:4, more preferably from 1:100 to 1:10, and most preferably from 1:50 to 1:20. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $\text{Na}_2\text{SO}_4 \cdot n \cdot \text{Na}_2\text{CO}_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Another suitable coating material is sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}$ ratio from 1.6:1 to 3.4:1, preferably 2.8:1, applied as an aqueous solution to give a level of less than 2% of silicate solids by weight of percarbonate. Magnesium silicate can also be included in the coating.

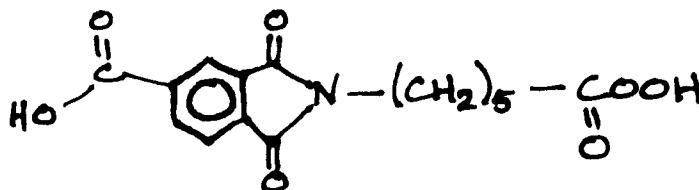
Where the bleaching processes utilising the compositions of the invention are carried out at least in part at temperatures lower than about 60°C , the compositions of the invention may contain bleaching agents more suited to low temperature bleaching. These will include, for example, preformed organic peracids and perimidic acids.

The following are examples of preformed peroxy acids or perimidic acids which are useful in the present invention:

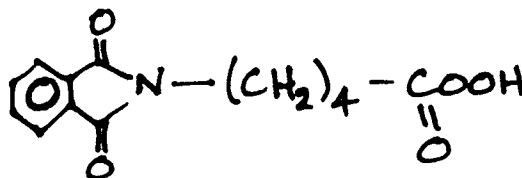
PAP: N,N phthaloylaminoperoxy caproic acid



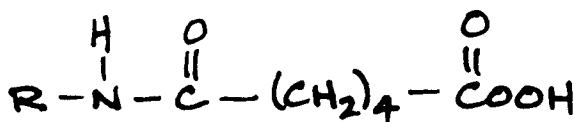
C-PAP: 2-carboxy-phthaloylaminoperoxy caproic acid



PAPV: N,N phthaloylaminoperoxy valeric acid



NAPAA: Nonyl amide of peroxy adipic acid



DPDA: 1, 12 diperoxydodecanedioic acid

Peroxycarboxylic acid and ring substituted peroxybenzoic acid

Monoperoxyphtalic acid (magnesium salt, hexahydrate) Diperoxycarboxylic acid

Optional Ingredients:

In addition to the components described above, the compositions of the present invention may also include other optional ingredients which may be useful in detergent compositions. Such optional ingredients will now be described in more detail below.

Surfactants

Surfactants are selected from the group consisting of anionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof. Anionic surfactants are preferred. Surfactants useful herein are listed in U.S. Pat. No. 3,664,961, Norris, issued May 23, 1972, and in U.S. Pat. No. 3,919,678, Laughlin et al., issued Dec. 30, 1975. Useful cationic surfactants also include those described in U.S. Pat. No. 4,222,905, Cockrell, issued Sept. 16, 1980, and in U.S. Pat. 4,239,659, Murphy, issued Dec. 16, 1980. However, cationic surfactants are generally less compatible with the aluminosilicate materials herein, and thus are preferably used at low levels, if at all, in the present compositions. The following are representative examples of surfactants useful in the present compositions.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably

from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbonatoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkyl benzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight or branched chain configuration, e.g., those of the type described in U.S. Pat. Nos. 2,220,099 and 2,477,383.

Other anionic surfactants herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; watersoluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to about 20 carbon atoms in the alkane moiety.

Also useful are the sulphonation products of fatty acid methyl esters containing a alkyl group with from 10 to 20 carbon atoms. Preferred are the C16-18 methyl ester sulphonates (MES)

Water-soluble nonionic surfactants are also useful as secondary surfactant in the compositions of the invention. Such nonionic materials include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 16 carbon atoms, in either a straight chain or branched chain configuration, with from about 4 to 25 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 4 to 25 moles of ethylene oxide per more of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 4 to 25 moles of ethylene oxide per mole of alcohol; and condensation products of propylene glycol with ethylene oxide.

Other useful nonionic surfactants are based upon natural renewable sources such as glucose. Alkyl polyglucoside (APG), preferably those containing from 10 to 20 carbon atoms and an average of from 1 to 4 glucose groups. Also useful are nonionic surfactants based on polyhydroxy fatty acid amides which contain an alkyl group with from 10 to 20 carbon atoms, for example tallow N-methyl glucamine.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be either straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent

contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

Particularly preferred surfactants herein include tallow alkyl sulfates; coconutalkyl glyceryl ether sulfates; alkyl ether sulfates wherein the alkyl moiety contains from about 14 to 18 carbon atoms and wherein the average degree of ethoxylation is from about 1 to 4; olefin or paraffin sulfonates containing from about 14 to 16 carbon atoms; alkyldimethylamine oxides wherein the alkyl group contains from about 11 to 16 carbon atoms; alkyldimethylammonio propane sulfonates and alkyldimethylammonio hydroxy propane sulfonates wherein the alkyl group contains from about 14 to 18 carbon atoms; soaps of higher fatty acids containing from about 12 to 18 carbon atoms; condensation products of C9-C15 alcohols with from about 3 to 8 moles of ethylene oxide, and mixtures thereof.

Useful cationic surfactants include water-soluble quaternary ammonium compounds of the form $R_4R_5R_6R_7N^+X^-$, wherein R_4 is alkyl having from 10 to 20, preferably from 12-18 carbon atoms, and R_5 , R_6 and R_7 are each C_1 to C_7 alkyl preferably methyl; X^- is an anion, e.g. chloride. Examples of such trimethyl ammonium compounds include C_{12-14} alkyl trimethyl ammonium chloride and cocalkyl trimethyl ammonium methosulfate.

Specific preferred surfactants for use herein include: alpha-olefin sulphonates; triethanolammonium C_{11-13} alkylbenzene sulfonate; alkyl sulfates, (tallow, coconut, palm, synthetic origins, e.g. C_{45} , etc.); sodium alkyl sulfates; methyl ester sulphonate; sodium coconut alkyl glyceryl ether sulfonate; the sodium salt of a sulfated condensation product of a tallow alcohol with about 4 moles of ethylene oxide; the condensation product of a coconut fatty alcohol with about 6 moles of ethylene oxide; the condensation product of tallow fatty alcohol with about 11 moles of ethylene oxide; the condensation of a fatty alcohol containing from about 14 to about 15 carbon atoms with about 7 moles of ethylene oxide; the condensation product of a C_{12-13} fatty alcohol with about 3 moles of ethylene oxide; 3-(N,N-dimethyl-N-coconutalkylammonio)-2-hydroxypropane-1-sulfonate; 3-(N,N-dimethyl-N-coconutalkylammonio)-propane-1-sulfonate; 6-(N-dodecylbenzyl-N,N-dimethylammonio) hexanoate; dodecyldimethylamine oxide; coconutalkyldimethylamine oxide; and the water-soluble sodium and potassium salts of coconut and tallow fatty acids.

Detergency Builders

Any compatible detergency builder or combination of builders or powder can be used in the process and compositions of the present invention.

The detergent compositions herein can contain aluminosilicates which have already been described in detail herein.

The granular detergents of the present invention can contain neutral or alkaline salts which have a pH in solution of seven or greater, and can be either organic or inorganic in nature. The builder salt assists in providing the desired density and bulk to the detergent granules herein. While some of the salts are inert, many of them also function as detergency builder materials in the laundering solution.

Examples of neutral water-soluble salts include the alkali metal, ammonium or substituted ammonium chlorides, fluorides and sulfates. The alkali metal, and especially sodium, salts of the above are preferred. Sodium sulfate is typically used in detergent granules and is a particularly preferred salt. Citric acid and, in general, any other organic or inorganic acid may be incorporated into the granular detergents of the present invention as long as it is chemically compatible with the rest of the agglomerate composition.

Other useful water-soluble salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, and polyhydroxysulfonates. Preferred are the alkali metal, especially sodium, salts of the above.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate. (Suitable silicates having been described above).

Polymers

Also useful are various organic polymers, some of which also may function as builders to improve detergency. Included among such polymers may be mentioned sodium carboxy-lower alkyl celluloses, sodium lower alkyl celluloses and sodium hydroxy-lower alkyl celluloses, such as sodium carboxymethyl cellulose, sodium methyl cellulose and sodium hydroxypropyl cellulose, polyvinyl alcohols (which often also include some polyvinyl acetate), polyacrylamides, polyacrylates and various copolymers, such as those of maleic and acrylic acids. Molecular weights for such polymers vary widely but most are within the range of 2,000 to 100,000.

Polymeric polycarboxyate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. Such materials include the water-soluble salts of homo-and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Other Optional Ingredients

Other ingredients commonly used in detergent compositions can be included in the compositions of the present invention. These include flow aids, color speckles, bleaching agents and bleach activators, suds boosters or suds suppressors, antitarnish and anticorrosion agents, soil suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, pH adjusting agents, nonbuilder alkalinity sources, hydrotropes, enzymes, enzyme-stabilizing agents, chelating agents and perfumes.

Particulate suds suppressors may also be incorporated in the finished composition by mixing according to the present invention. Preferably the suds suppressing activity of these particles is based on fatty acids or silicones.

Examples

The following silicate particles (comprising montmorillonite clay) were made by spraying an aqueous solution (40%) of sodium silicate with glycerol, on to a montmorillonite clay in a Loedige mixer.

The resulting wet agglomerates were dried to a moisture level of 8% in a fluid bed dryer.

All of the percentages given below are by weight of the finished product composition

Example	1	2	3 (Comparative)
Montmorillonite clay	77.2	77.2	88.6
Sodium Silicate, 2.4 ratio	-	11.9	-
Sodium Silicate, 3.2 ratio	11.9	-	-
Glycerol	2.9	2.9	3.4
Moisture	8	8	8

In examples 4, 5 and 7-10, finished compositions were made using the agglomerated clay particles of examples 1 to 3, and which further comprised particulate sodium percarbonate.

The following abbreviations have been used in the following examples:

LAS:	C13 linear alkyl benzene sulphonate
C16-18 AS:	C16-18 alkyl sulphate
C14-15 AS:	C14-15 alkyl sulphate
C12-15 AE3S:	C12-15 alkyl ether sulphate with an average of 3 ethoxy groups per mole
C14-15AE7:	Ethoxylated nonionic surfactant having a C14-15 alkyl chain and an average of 7 ethoxy groups per mole
C12-13AE3:	Ethoxylated nonionic surfactant having a C12-13 alkyl chain and an average of 3 ethoxy groups per mole
Cationic Surfactant:	Mono alkyl (C13-15) monoethoxy dimethyl ammonium chloride
SKS-6:	Layered silicate (supplied by Hoechst)
(Trade Name)	
TAED:	N,N,N,N-Tetraacetylene diamine
PEG:	Polyethylene glycol with a molecular weight of 4 000 000.
Enzymes:	A mixture of Savinase (having an activity of 4.0 KNPU/g) at a level of 1.4% by weight of the finished composition; and lipolase (having an activity of 100 000

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LU/g) at a level of 0.4 % by weight of the finished product.
Percarbonate particles: Particulate sodium percarbonate. The percarbonate was coated with a mixture of carbonate and sulphate (carbonate : Sulphate ratio = 2.5:1). The coating material being used at a level of 2.5% by weight of the percarbonate. The mean particle size of the coated percarbonate was 580 micrometers.

Examples	4	5	6 (Comparative)	7 (Comparative)
LAS:	7	7	7	7
C16-18 AS:	1.5	1.5	1.5	1.5
C14-15 AS:	2	2	2	2
Cationic Surfactant:	1.5	1.5	1.5	1.5
Zeolite 4A	17	17	17	17
Citrate	5	5	5	5
Silicate (2 Ratio)	3	3	4.8	4.8
Copolymer Acrylic/Maleic	4	4	4	4
Phosphonate	0.4	0.4	0.4	0.4
Carbonate	15	15	28.5	15
PEG	0.5	0.5	0.5	0.5
Enzymes	1.8	1.8	1.8	1.8
TAED	3.5	3.5	3.5	3.5
Percarbonate	13	13	13	13
Clay Particles	15.5	15.5	-	13.5
Clay Particles used from	Example 1	Example 2	-	Example 3
Water/Miscellaneous	-----Balance to 100% -----			

A two kg. sample of each of the examples 4 to 7 was packed in a closed carton and stored at 40 °C and at 32 °C/80% relative humidity. The remaining percarbonate (hydrogen peroxide) was measured after 4 weeks storage.

Example 7 shows a Percarbonate stability considerably poorer than Example 6 which reflects the detrimental effect of clay particles. Example 5, which contains clay/silicate particles, shows a Percarbonate stability comparable to Example 6, and much better than Example 7. Example 4 shows the best Percarbonate stability of these examples.

Examples	8	9	10
C14-15 AS:	8	8	8
C12-15 AE3S:	1.7	1.7	1.7
C14-15AE7:	6	1.3	6
C12-13AE3:	-	2.6	-
C16-18 N-methyl glucamide	-	2.6	-
Cationic Surfactant:	2	2	2
Zeolite 4A	12	12	12
Citrate	0.8	0.8	0.6
SKS-6 (Trade Name)	8	8	8
Copolymer Acrylic/Maleic	4	4	6.6
Phosphonate	0.2	0.2	0.2
Bicarbonate	-	2.7	-
Carbonate	14	14	14
PEG	0.5	0.5	0.5
Enzymes	1.8	1.8	1.8
TAED	4.5	4.5	6
Percarbonate	13.3	13.3	17
Clay Particles	13.6	13.6	16.5
Clay Particles used from:	Example 2	Example 2	Example 2
Water/Miscellaneous	-----Balance to 100% -----		

The compositions of examples 8 to 10 show good percarbonate stability (less than 20% hydrogen peroxide loss after 2 weeks storage at 32 ° C and 80% relative humidity in closed cartons).

Claims

1. A granular detergent composition comprising
 - i) a granular component comprising water-insoluble silicate which comprises magnesium, aluminium, or a mixture of these, and water-soluble silicate; and
 - ii) a granular component comprising a bleaching agent characterised in that the bleaching agent is chosen from the group comprising alkalimetal percarbonate, peroxyacid, perimidic acid or combinations of these.
2. A granular detergent composition according to claim 1 wherein said water-insoluble silicate is either an aluminosilicate or clay, and is of natural origin.
3. A granular detergent composition according to either of claims 1 or 2 wherein said water-insoluble silicate is a clay is of the smectite type.
4. A granular detergent composition according to claim 3 wherein said clay is a trioctahedral mineral of the hectorite type, or a dioctahedral mineral of the montmorillonite type.
5. A granular detergent composition according to claim 3 wherein said clay is modified by the addition of cationic or amino organic compounds.
6. A granular detergent composition according to any of the previous claims wherein said clay comprises at least 5% by weight of said granular detergent composition.
7. A granular detergent composition according to claim 1 wherein said water-soluble silicate has a ratio of SiO_2 to Na_2O of between 2.0 to 1 and 3.3 to 1.
8. A granular detergent composition according to claim 1 wherein said water-soluble silicate is partly added to the granular component comprising said water-insoluble silicate, and partly dry mixed with the remainder of the composition, and wherein the dry mixed portion of the water-soluble silicate comprises less than 10% by weight of the granular detergent composition.

9. A granular detergent composition according to any of the previous claims wherein the level of water-soluble silicate in the granular component (a) is less than 25% by weight.

5 10. A granular detergent composition according to claim 1 wherein said alkalimetal percarbonate has a granular form, the outer surface of the granules being substantially coated.

11. A granular detergent composition according to claim 10 wherein said coating of said alkalimetal percarbonate particles comprises water-soluble silicate at a level of not more than 2% by weight of percarbonate.

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12. A granular detergent composition according to any of the previous claims wherein said granular detergent composition comprises at least 12% by weight of zeolite and less than 1% by weight of any of the chelating agents chosen from the group of aminocarboxylates, aminophosphonates, polyfunctionally-substituted aromatic chelating agents, or mixtures of these.

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EUROPEAN SEARCH REPORT

Application Number
EP 93 87 0142

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 451 893 (UNILEVER) * page 3, line 3 - line 5; claim 1 * * page 3, line 33 - line 37 * ---	1,9	C11D3/39 C11D17/00 C11D3/12 C11D3/08
X	EP-A-0 377 302 (UNILEVER) * page 4, line 25 - line 27 * * page 3, line 13 - line 18 * ---	1	
A	EP-A-0 021 267 (PQ CORPORATION) * claim 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		14 December 1993	Van Bellinghen, I
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			