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(54) **DETERGENT COMPOSITIONS**

REINIGUNGSMITTELZUSAMMENSETZUNGEN

COMPOSITIONS DE DETERGENTS

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EP 0 543 911 B2

Description

[0001] This invention relates to laundry detergent compositions and more especially to laundry detergent compositions that incorporate little or no phosphorus containing materials. Laundry detergent compositions of this type have become widely available as a result of public concern over, and/or legislative action to control, the environmental impact of aqueous effluent from untreated or partially treated domestic sewage containing dissolved phosphates.

[0002] The commercial introduction of zero-phosphate detergent products, whilst meeting the primary objective of reducing the phosphate load on the environment arising from detergent products, has added to formulation complexity and has also increased the load on the environment of organic materials. Zero phosphate compositions employ a combination of materials to replace the phosphate builder, the principal component usually being a water insoluble sodium aluminosilicate zeolite supplemented by a mixture of water soluble inorganic and polymeric organic salts.

[0003] Much effort has been expended by those working in the field in developing such multi-component builder systems, the need for which arises from the difficulty of finding a single material that will carry out all of the functions previously performed by the phosphate builder. Although not completely characterised, these functions include chelation of both Ca^{++} and Mg^{++} ion hardness together with peptisation and suspension of the soils removed from fabrics during the washing process.

[0004] It has now been found that the use of crystalline or so-called layered silicates (known per se) in particular combinations of detergent builder components provides enhanced performance and permits certain other materials to be reduced in level or omitted altogether from the resultant particulate detergent products. In preferred embodiments of the invention, cleaning performance equivalent to that of existing products can be obtained at a significantly lower level of usage of the detergent builder components, thereby reducing the load on the environment. Other advantages include enhanced dispensing characteristics, i.e. dispersion and/or dissolution of the particulate product at the start of the wash cycle in an automatic domestic washing machine, a reduction in insoluble precipitates on fabrics (ash) and a reduction in fabric damage.

[0005] EP-A-405,122 describes detergent compositions containing crystalline layered silicate and zeolite builders. EP-A-337, 219 describes detergent compositions containing crystalline layered silicate and an oxygen bleaching component. JP 1-153800 describes concentrated fabric softening granular detergent compositions containing bentonite, crystalline layered silicate and zeolite components.

[0006] According to the present invention there is provided a particulate detergent composition comprising an oxygen bleach and comprising

a) from 5% to 50% by weight of one or more anionic, nonionic, ampholytic, zwitterionic or cationic surfactants or a mixture of any thereof;

(b) from 10% to 60% of a detergent builder system comprising a mixture of

i) from 20% to 60% by weight of the mixture of a sodium aluminosilicate zeolite;

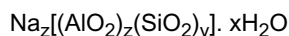
ii) from 10% to 30% by weight of the mixture of a water soluble monomeric or oligomeric organic carboxylate chelating agent; and

iii) from 10% to 65% by weight of the mixture of a crystalline layered sodium silicate having the composition $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$, wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20; and

(c) up to 40% of non-surfactant, non-builder detergent ingredients which comprise the oxygen bleach.

[0007] There is also provided a method of preparing a detergent composition according to any one of Claims 1-18 wherein the crystalline layered sodium silicate (b)(iii) is added as a finely divided particulate solid to one or more particulate solids comprising component (a) component (b)(i) & (ii) and component (c).

[0008] Preferably component (b)(iii) of the builder system is α , β , γ , or δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and component (b)(i) is a synthetic hydrated zeolite of unit cell formula



wherein z and y are at least 6, the ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276.

[0009] Preferably also the monomeric or oligomeric organic carboxylate chelating agent has a first carboxyl logarithmic acidity constant (pK_1) of less than 9, preferably of from 2 to 8.5.

[0010] The present invention concerns a particulate detergent composition incorporating one or more surfactants and a detergent builder system composed of three principal components viz. a sodium aluminosilicate zeolite, a water soluble monomeric or oligomeric organic carboxylate chelating agent and a crystalline layered sodium silicate. Compo-

sitions in accordance with the invention, also contain an oxygen bleach and optionally other, non surfactant, non-builder detergent ingredients.

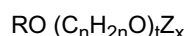
[0011] A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,664,961 issued to Norris on May 23, 1972.

[0012] Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C₁₂-C₁₈ fatty source, preferably from a C₁₆-C₁₈ fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants are alkyl sulphates having from 12 to 22, preferably 14 to 18 carbon atoms in the alkyl radical, optionally in admixture with ethoxy sulphates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. The cation in each instance is again an alkali metal cation, preferably sodium.

[0013] One class of nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene 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.

[0014] Especially preferred nonionic surfactants of this type are the C₉-C₁₅ primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C₁₄-C₁₅ primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C₁₂-C₁₄ primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

[0015] Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

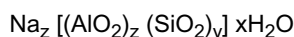
[0016] A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C₈-C₂₀, preferably C₁₀-C₁₄ N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

[0017] Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C₈-C₁₆, preferably C₁₀-C₁₄ N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

[0018] The detergent compositions can comprise from 5% to 50% by weight of surfactant but usually comprises from 5% to 30%, more preferably from 5% to 15% by weight. Combinations of surfactant types are preferred, more especially anionic-nonionic and also anionic-nonionic-cationic blends. Particularly preferred combinations are described in GB-A-2040987 and EP-A-0087914. Although the surfactants can be incorporated into the compositions as mixtures, it is preferable to control the point of addition of each surfactant in order to optimise the physical characteristics of the composition and avoid processing problems. Preferred modes and orders of surfactant addition are described hereinafter.

[0019] The second essential component of compositions in accordance with the invention is a detergent builder system comprising a mixture of sodium aluminosilicate zeolite, a water soluble monomeric or oligomeric carboxylate chelating agent and a crystalline layered sodium silicate in defined amounts.

[0020] Whilst a range of aluminosilicate ion exchange materials can be used, preferred sodium aluminosilicate zeolites have the unit cell formula

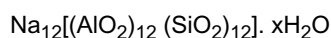


wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate materials are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water.

[0021] The above aluminosilicate ion exchange materials are further characterised by a particle size diameter of from 0.1 to 10 micrometers, preferably from 0.2 to 4 micrometers. The term "particle size diameter" herein represents

the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The aluminosilicate ion exchange materials are further characterised by their calcium ion exchange capacity, which is at least 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 300 mg eq./g to 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterised by their calcium ion exchange rate which is at least 130 mg equivalent of CaCO_3 /litre/minute/(g/litre) [2 grains Ca^{++} /gallon/minute/(gram/gallon)] of aluminosilicate (anhydrous basis), and which generally lies within the range of from 130 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [2 grains/gallon/minute/ (gram/gallon)] to 390 mg equivalent of CaCO_3 /litre/minute/ (gram/litre) [6 grains/gallon/minute/(gram/gallon)], based on calcium ion hardness. Optimum aluminosilicates for builder purposes exhibit a calcium ion exchange rate of at least 260 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [4 grains/gallon/minute/(gram/gallon)].

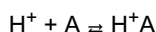
[0022] Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available and can be naturally occurring materials, but are preferably synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in US Patent No. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite X, Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A and has the formula



wherein x is from 20 to 30, especially 27. Zeolite X of formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$ is also suitable, as well as Zeolite HS of formula $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6] \cdot 7.5 \text{H}_2\text{O}$.

[0023] The water-soluble monomeric or oligomeric organic carboxylate chelating agent can be selected from a wide range of compounds but preferably has a first carboxyl logarithmic acidity/constant (pK_1) of less than 9, preferably of between 2 and 8.5, more preferably of between 4 and 7.5.

[0024] The logarithmic acidity constant is defined by reference to the equilibrium



where A is the fully ionized carboxylate anion of the builder salt.

[0025] The equilibrium constant is therefore

$$K_1 = \frac{(\text{H}^+ \text{A})}{(\text{H}^+) (\text{A})}$$

and $\text{pK}_1 = \log_{10} K_1$.

[0026] For the purposes of this specification, acidity constants are defined at 25°C and at zero ionic strength. Literature values are taken where possible (see Stability Constants of Metal-Ion Complexes, Special Publication No. 25, The Chemical Society, London): where doubt arises they are determined by potentiometric titration using a glass electrode.

[0027] Preferred carboxylates can also be defined in terms of their calcium ion stability constant ($\text{pK}_{\text{Ca}^{++}}$) defined, analogously to pK_1 , by the equations

$$\text{pK}_{\text{Ca}^{++}} = \log_{10} K_{\text{Ca}^{++}}$$

where

$$K_{\text{Ca}^{++}} = \frac{(\text{Ca}^{++} \text{A})}{(\text{Ca}^{++}) (\text{A})}$$

[0028] Preferably, the polycarboxylate has a $\text{pK}_{\text{Ca}^{++}}$ in the range from about 2 to about 7 especially from about 3 to about 6. Once again literature values of stability constants are taken where possible. The stability constant is defined at 25°C and at zero ionic strength using a glass electrode method of measurement as described in Complexation in Analytical Chemistry by Anders Ringbom (1963).

[0029] The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

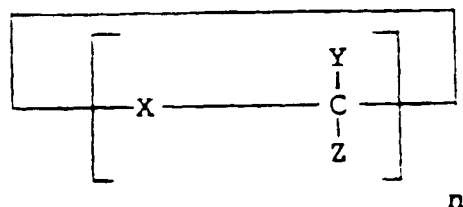
[0030] Monomeric and oligomeric builders can be selected from acyclic, alicyclic, heterocyclic and aromatic carbox-

ylates having the general formulae

(a)

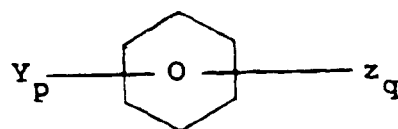


(b)



or

(c)



wherein R_1 represents H, C_{1-30} alkyl or alkenyl optionally substituted by hydroxy, carboxy, sulfo or phosphono groups or attached to a polyethylenoxy moiety containing up to 20 ethyleneoxy groups; R_2 represents H, C_{1-4} alkyl, alkenyl or hydroxy alkyl, or alkaryl, sulfo, or phosphono groups;

X represents a single bond; O; S; SO; SO_2 ; or NR_1 ;

Y represents H; carboxy; hydroxy; carboxymethyloxy; or

C_{1-30} alkyl or alkenyl optionally substituted by hydroxy or carboxy groups;

Z represents H; or carboxy;

m is an integer from 1 to 10;

n is an integer from 3 to 6;

p, q are integers from 0 to 6, $p + q$ being from 1 to 6; and wherein, X, Y and Z each have the same or different representations when repeated in a given molecular formula, and wherein at least one Y or Z in a molecule contain a carboxyl group.

[0031] Suitable carboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 821,368, 821, 369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. 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.

[0032] 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. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

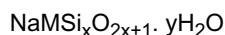
[0033] Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadi-

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

5 **[0034]** Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

[0035] The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, eg. citric acid or citrate/citric acid mixtures are also contemplated as components of builder systems useful in the present invention.

10 **[0036]** The third element of the builder system is a crystalline layered sodium silicate having the general formula



15 wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purposes of the present invention x, in the general formula above can have a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the α -, β -, γ - and δ -forms of $\text{Na}_2\text{Si}_2\text{O}_5$. These materials are available from Hoechst AG FRG 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.

20 **[0037]** Other detergent builder materials can also form part of the builder system but are not essential elements thereof. Such materials can be organic or inorganic in nature.

[0038] Inorganic builder materials that can form optional elements of the builder system for the purposes of the invention include alkali metal carbonates, bicarbonates and silicates. Suitable organic materials include the organic phosphonates and amino polyalkylene phosphonates although these materials are less preferred where the minimisation of phosphorus compounds in the compositions is desired.

25 **[0039]** Other suitable water soluble organic salts are the homo-or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 30 20,000 to 70,000, especially about 40,000. These materials are normally used at levels of from 0.5% to 10% by weight more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

[0040] The optional builder materials, if present, will total no more than 25% by weight of the composition normally less than 20% and most usually less than 15% by weight.

[0041] For the purposes of compositions in accordance with the invention, the builder system will comprise from 35 10% to 60% by weight of the compositions, more preferably from 20% to 60% by weight. Within the builder system, the sodium aluminosilicate zeolite will comprise from 20% to 60% by weight of the mixture, the monomeric or oligomeric carboxylate will comprise from 10% to 30% by weight of the mixture and the crystalline layered silicate will comprise from 10% to 65% by weight of the mixture. More preferably the zeolite is present in an amount of from 25% to 50%, the monomeric or oligomeric carboxylate comprises from 15% to 25% and the layered silicate from 20% to 50% by weight 40 of the builder system. Preferably also the builder system incorporates a combination of auxiliary inorganic and organic builders such as sodium carbonate and maleic anhydride/acrylic acid copolymers in amounts of up to 25%.

[0042] Compositions in accordance with the invention also contain up to 40% of non-surfactant non detergent builder components including an oxygen bleach and optionally other ingredients. Anti-redeposition and soil-suspension agents, optical brighteners, soil release agents, dyes and pigments are examples of such optional ingredients and can 45 be added in varying amounts as desired.

[0043] Anti-redeposition and soil-suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include copolymers of maleic anhydride with ethylene, methylvinyl ether, acrylic or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally 50 used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

[0044] Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance 55 on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

[0045] However one advantage of compositions in accordance with the present invention is their ability to maintain the suspension of insoluble particulate solids (ash) with reduced levels of polymeric polycarboxylate builder/anti

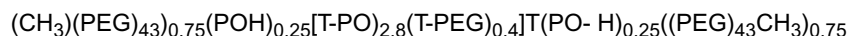
redeposition agents or even, in preferred compositions of the invention, with no polymeric polycarboxylate present. Thus a level of polymeric polycarboxylate of 5% in conventional products can be halved, i.e. to 2.5% with no increase in fabric ash level in compositions according to the present invention. If the polymeric polycarboxylate is removed entirely only a slight increase in fabric ash takes place in contrast to a virtual doubling of the ash level if the polymer is removed from a conventional formulation.

[0046] Compositions in accordance with the invention also show robustness in hardness control in under built situations, i.e. where insufficient detergent builder is available to control all of the mineral hardness present. This benefit is believed to arise because of the ability of the ternary builder system components to redistribute the calcium and magnesium hardness ions amongst themselves in underbuilt situations, taking advantage of the enhanced affinity of the crystalline layered silicate component for magnesium ion.

[0047] A further benefit provided by compositions in accordance with the present invention is a reduction in damage to fabrics arising from the washing process. This loss is believed to arise from the interaction of heavy metal ions deposited on fabrics during the washing process with oxygen bleaches. Fabrics washed in compositions of the present invention show a level of deposition of heavy metal ions and a reduced tensile strength loss, relative to compositions in which the crystalline layered silicate component is replaced by a conventional amorphous silicate

[0048] Preferred optical brighteners are anionic in character, examples of which are disodium 4,4¹-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)stilbene-2,2¹-disulphonate, disodium 4, 4¹-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2,2¹-disulphonate, disodium 4,4¹-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2,2¹-disulphonate, monosodium 4¹,4¹¹-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4¹-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2¹-disulphonate, disodium 4,4¹-bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2¹-disulphonate, disodium 4,4¹-bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2¹-disulphonate and sodium 2(stilbyl-4¹¹-(naphtho-1¹, 2¹:4,5)-1,2,3 - triazole-2¹¹-sulphonate.

[0049] Soil-release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0272033. A particular preferred polymer in accordance with EP-A-0272033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_0-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pcOC}_6\text{H}_4\text{CO})$.

[0050] Certain polymeric materials such as polyvinyl pyrrolidones typically of MW 5000-20000, preferably 10000-15000, also form useful agents in preventing the transfer of labile dyestuffs between fabrics during the washing process.

[0051] Another optional but highly preferred ingredient is a particulate inorganic perhydrate bleach. Any particulate inorganic perhydrate bleach can be used, in an amount of from 3% to 40% by weight, more preferably from 8% to 25% by weight and most preferably from 12% to 20% by weight of the compositions. Preferred examples of such bleaches are sodium perborate monohydrate and tetrahydrate and mixtures thereof.

[0052] Another preferred ingredient is a peroxy carboxylic acid bleach precursor, commonly referred to as a bleach activator, which is preferably added in a prilled or agglomerated form. Examples of suitable compounds of this type are disclosed in British Patent Nos. 1586769 and 2143231 and a method for their formation into a prilled form is described in European Published Patent Application No. 0062523. Preferred examples of such compounds are tetracetyl ethylene diamine and sodium 3, 5, 5 trimethyl hexanoyloxybenzene sulphonate.

[0053] Bleach activators are normally employed at levels of from 0.5% to 10% by weight, more frequently from 1% to 8% and preferably from 2% to 6% by weight of the composition.

[0054] Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms, exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

[0055] As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50 m²/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

[0056] A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3,933, 572. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors.

[0057] An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

[0058] The suds suppressors described above are normally employed at levels of from 0.001% to 0.5% by weight of the composition, preferably from 0.01% to 0.1% by weight.

5 **[0059]** The preferred methods of incorporation comprise either application of the suds suppressors in liquid form by spray-on to one or more of the major components of the composition or alternatively the formation of the suds suppressors into separate particulates that can then be mixed with the other solid components of the composition. The incorporation of the suds modifiers as separate particulates also permits the inclusion therein of other suds controlling materials such as C₂₀-C₂₄ fatty acids, microcrystalline waxes and high MW copolymers of ethylene oxide and propylene
10 oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al U.S. Patent No. 3,933,672.

[0060] Another optional ingredient useful in the present invention is one or more enzymes.

[0061] Preferred enzymatic materials include the commercially available amylases, neutral and alkaline proteases, lipases, esterases and cellulases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in U.S. Patent 3,533,139.
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[0062] Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1,400,898. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A-1514276 and EP-B-0011340. Their combination with mono C₁₂-C₁₄ quaternary ammonium salts is disclosed in EP-B-0026528. Other useful organic fabric softening agents are the dilong chain amides as disclosed in
20 EP-B-0242919. Additional organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0299575 and 0313146.

[0063] Levels of smectite clay are normally in the range from 5% to 15%, more preferably from 8% to 12% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of
25 from 0.5% to 5% by weight, normally from 1% to 3% by weight, whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. Where a portion of the composition is spray dried, these materials can be added to the aqueous slurry fed to the spray drying tower, although in some instances it may be more convenient to add them as a dry mixed particulate,
30 or spray them as a molten liquid on to other solid components of the composition.

[0064] The compositions of the invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation and preferred methods involve combinations of these techniques. A preferred method of making the compositions involves a combination of spray drying, agglomeration in a high speed mixer and dry mixing.

[0065] Preferred detergent compositions in accordance with the invention also comprise at least two particulate
35 multi-ingredient components. The first component comprises at least 20%, conventionally from 30% to 70%, but more preferably no more than 40% by weight of the composition and the second component from 1% to 50%, more preferably 10% to 40% by weight of the composition.

[0066] The first component comprises a particulate incorporating an anionic surfactant in an amount of from 0.75% to 35% by weight of the powder and one or more inorganic and/or organic salts in an amount of from 99.25% to 65%
40 by weight of the powder. The particulate can have any suitable form such as granules, flakes, prills, marumes or noodles but is preferably granular. The granules themselves may be agglomerates formed by pan or drum agglomeration or by in-line mixers but are preferably spray dried particles produced by atomising an aqueous slurry of the ingredients in a hot air stream which removes most of the water. In certain processes, the spray dried granules forming the first component may themselves be subjected to densification steps, eg. by high speed cutter mixers, to increase density
45 before being reagglomerated. For illustrative purposes, the first component is described hereinafter as a spray dried powder as this constitutes a preferred embodiment of the invention.

[0067] An important characteristic of the principal anionic surfactant in the first component is that it should have a low rate of solubility in aqueous media at the water temperatures that prevail during the fill step of the wash cycle in an automatic washing machine. With respect to European wash habits the water temperature during the fill step is predominantly in the range from 5°C to 20°C, more usually from 7°C to 12°C.
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[0068] Suitable anionic surfactants for the purposes of the first component have been found to be linear alkyl sulfate salts in which the alkyl group has an average of from 16 to 22 carbon atoms, and linear alkyl carboxylate salts in which the alkyl group has an average of from 16 to 24 carbon atoms.

[0069] The alkyl groups for both types of surfactant are preferably derived from natural fats such as tallow. Shorter chain alkyl sulfates or carboxylates, in which the alkyl group is derived from sources comprising a mixture of alkyl moieties more than 40% of which contain 14 or less carbon atoms, are less suitable as they cause the first component to form a gel like mass during dissolution.
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[0070] The level of anionic surfactant in the spray dried powder forming the first component is from 0.75% to 4% by

weight, more usually 2.5% to 25% preferably from 3% to 20% and most preferably from 5% to 15% by weight. Water-soluble surfactants such as linear alkyl benzene sulphonates can be included or alternatively may be applied subsequently to the spray dried powder by spray on.

[0071] The other major ingredient of the spray dried powder is one or more inorganic or organic salts that provide the crystalline structure for the granules. The inorganic and/or organic salts may be water-soluble or water-insoluble, the latter type being comprised by the, or the major part of the, water-insoluble builders where these form part of the builder system. Suitable water soluble inorganic salts include the alkali metal carbonates, bicarbonates, sulphates and borates. Alkali metal silicates can also be present in the spray dried granule provided that aluminosilicate does not form part of the spray dried component.

[0072] It is preferred that at least part of the aluminosilicate builder be incorporated into the spray dried granule and, as indicated above, where this takes place, any silicate present should not form part of the spray dried component. In these circumstances incorporation of the silicate can be achieved in several ways, e.g. by producing a separate silicate containing spray dried particulate, by incorporating the silicate into an agglomerate of other ingredients, or more preferably by adding the silicate as a dry mixed solid ingredient.

[0073] Any of the previously mentioned optional builder salts can also be incorporated in the spray dried powder forming the first component. The spray dried powder can also include some or even all of the water soluble monomeric or oligomeric carboxylate chelating agent but this is less preferred as it tends to inhibit the rapid solution of this ingredient. The organic and/or inorganic salts comprise from 60% to 90% by weight of the first component, more preferably from 70% to 90% and most preferably from 75% to 85% by weight.

[0074] The spray dried powder also normally contains up to 15% by weight of miscellaneous ingredients.

[0075] In preferred compositions where the first component is a spray dried powder, optional ingredients included in the first component should be heat stable to the extent necessary to withstand the temperatures encountered in the spray drying process. Where the first component is a spray dried powder it will normally be dried to a moisture content of from 7% to 11% by weight, more preferably from 8% to 10% by weight of the spray dried powder. Moisture contents of powders produced by other processes such as agglomeration may be lower and can be in the range 1-10% by weight.

[0076] The particle size of the first component is conventional and preferably not more than 5% by weight should be above 1.4 mm, while not more than 10% by weight should be less than 0.15 mm in maximum dimension. Preferably at least 60% and most preferably at least 80% by weight of the powder lies between 0.7 mm and 0.25 mm in size. For spray dried powders, the bulk density of the particles should lie in the range from 350 g/litre to 650g/litre but is conventionally in the range from 540 to 600 g/litre. Bulk densities in the upper part of the range from 600-650 g/litre are particularly useful where production of so called concentrated products is desired. Bulk densities above this range may be produced if the spray dried powder is subjected to further processing steps such as size reduction in a high speed cutter/mixer followed by compaction. Alternatively, processes other than spray drying may be used to form the powder.

[0077] A second component of a preferred composition in accordance with the invention is a particulate containing a water soluble surfactant.

[0078] This may be anionic, nonionic, cationic or semipolar in type or a mixture of any of these. Suitable surfactants are listed hereinbefore but preferred surfactants are linear C₁₁-C₁₅ alkyl benzene sulfonates and fatty C₁₄-C₁₈ methyl ester sulphonates.

[0079] The second component may have any suitable physical form i.e. it may take the form of flakes, prills, marumes, noodles, ribbons, or granules which may be spray-dried or non spray-dried agglomerates. Although the second component could in theory comprise the water soluble surfactant on its own, in practice at least one organic or inorganic salt is included to facilitate processing. This provides a degree of crystallinity, and hence acceptable flow characteristics, to the particulate and may be any one or more of the organic or inorganic salts present in the first component.

[0080] The particle size range of the second component is not critical but should be such as to obviate segregation from the particles of the spray dried first component when blended therewith. Thus not more than 5% by weight should be above 1.4 mm while not more than 10% should be less than 0.15 mm in maximum dimension.

[0081] The bulk density of the second component will be a function of its mode of preparation. Thus, in spray dried granular form the second component may have a density of from 350 g/litre to 650 g/litre but more preferably will be in the range from 500 g/litre to 630 g/litre. The preferred form of the second component however is a mechanically mixed agglomerate which may be made by adding the ingredients dry or with an agglomerating agent to a pan agglomerator, Z blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050 F.R.G. By this means the second component can be given a bulk density in the range from 650 g/litre to 1190 g/litre more preferably from 750 g/litre to 850 g/litre. This is particularly useful in formulating the so called 'concentrated' products.

[0082] Preferred compositions include a level of alkali metal carbonate in the second component corresponding to

an amount of from 3% to 15% by weight of the composition, more preferably from 5% to 12% by weight. This will provide a level of carbonate in the second component of from 20% to 40% by weight.

[0083] A highly preferred ingredient of the second component is also a hydrated water insoluble aluminosilicate ion exchange material of the synthetic zeolite type, described hereinbefore, present at from 10% to 35% by weight of the second component. The amount of water insoluble aluminosilicate material incorporated in this way is from 1% to 10% by weight of the composition, more preferably from 2% to 8% by weight. If the second component is spray dried, it is important that it does not contain both silicate and aluminosilicate ingredients for the reasons stated hereinbefore. In such circumstances, the silicate may be incorporated in the first component or, if that also contains aluminosilicate, may be added as a solid, together with other dry mixed materials, to the first and second components.

[0084] In one process for preparing the second component, the surfactant salt is formed in situ in an inline mixer. The liquid acid form of the surfactant is added to a mixture of particulate anhydrous sodium carbonate and hydrated sodium aluminosilicate in a continuous high speed blender such as a Lodige KM mixer and neutralised to form the surfactant salt whilst maintaining the particulate nature of the mixture. The resultant agglomerated mixture forms the second component which is then added to other components of the product. In a variant of this process, the surfactant salt is pre-neutralised and added as a viscous paste to the mixture of the other ingredients. In this variant, the mixer serves merely to agglomerate the ingredients to form the second component.

[0085] In a particularly preferred process for making compositions in accordance with the invention, part of the spray dried product comprising the first granular component is diverted and subjected to a low level of nonionic surfactant spray on before being reblended with the remainder. The second granular component is made using the preferred process described above. The first and second components together with other dry mix ingredients such as the carboxylate chelating agent, inorganic peroxygen bleach, bleach activator, soil-release polymer, silicate and enzyme are then fed to a conveyor belt, from which they are transferred to a horizontally rotating drum in which perfume and silicone suds suppressor are sprayed on to the product. In highly preferred compositions, a further drum mixing step is employed in which a low (approx. 2% by weight) level of finely divided crystalline aluminosilicate is introduced to increase density and improve granular flow characteristics.

[0086] Compositions in accordance with the invention can also benefit from delivery systems that provide transient localised high concentrations of product in the drum of an automatic washing machine at the start of the wash cycle, thereby also avoiding problems associated with loss of product in the pipework or sump of the machine.

[0087] Delivery to the drum can most easily be achieved by incorporation of the composition in a bag or container from which it is rapidly releasable at the start of the wash cycle in response to agitation, a rise in temperature or immersion in the wash water in the drum. Alternatively the washing machine itself may be adapted to permit direct addition of the composition to the drum e.g. by a dispensing arrangement in the access door.

[0088] Products comprising a detergent composition enclosed in a bag or container are usually designed in such a way that container integrity is maintained in the dry state to prevent egress of the contents when dry, but are adapted for release of the container contents on exposure to a washing environment, normally on immersion in an aqueous solution.

[0089] Usually the container will be flexible, 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.

[0090] In a variant of the bag or container product form, laminated sheet products can be employed in which a central flexible layer is impregnated and/or coated with a composition and then one or more outer layers are applied to produce a fabric-like aesthetic effect. The layers may be sealed together so as to remain attached during use or may separate on contact with water to facilitate the release of the coated or impregnated material.

[0091] An alternative laminate form comprises one layer embossed or deformed to provide a series of pouch-like containers into each of which the detergent components are deposited in measured amounts, with a second layer overlying the first layer and sealed thereto in those areas between the pouch-like containers where the two layers are in contact. The components may be deposited in particulate, paste or molten form and the laminate layers should prevent egress of the contents of the pouch-like containers prior to their addition to water. The layers may separate or may remain attached together on contact with water, the only requirement being that the structure should permit rapid release of the contents of the pouch-like containers into solution. The number of pouch-like containers per unit area of substrate is a matter of choice but will normally vary between 500 and 25,000 per square metre.

[0092] Suitable materials which can be used for the flexible laminate layers in this aspect of the invention include, among others, sponges, paper and woven and non-woven fabrics.

[0093] However the preferred means of carrying out the process of the invention is to introduce the composition into

the liquid surrounding the fabrics that are in the drum via a reusable dispensing device having walls that are permeable to liquid but impermeable to the solid composition.

[0094] Devices of this kind are disclosed in European Patent Application Publication Nos. 0343069 and 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 cycle. 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.

[0095] The invention is illustrated in the following non limiting Examples, in which all percentages are on a weight basis unless otherwise stated.

[0096] In the detergent compositions, the abbreviated component identifications have the following meanings:

C ₁₂ LAS :	Sodium linear C ₁₂ alkyl benzene sulphonate
TAS :	Sodium tallow alcohol sulphate
C _{14/15} AS :	Sodium C ₁₄ -C ₁₅ alkyl sulphate
TAE _n :	Tallow alcohol ethoxylated with n moles of ethylene oxide per mole of alcohol
45E7 :	A C ₄ -C ₁₅ predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
CnAE _{E6.5} :	A C ₁₂ -C ₁₃ primary alcohol condensed with 6.5 moles of ethylene oxide.
PEG :	Polyethylene glycol (MW normally follows)
TAED :	Tetraacetyl ethylene Diamine
Silicate :	Amorphous Sodium silicate (SiO ₂ :Na ₂ O ratio normally follows)
NaSKS-6 :	Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
Carbonate :	Anhydrous sodium carbonate
CMC :	Sodium carboxymethyl cellulose
Zeolite A :	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (AlO ₂ SiO ₂) ₁₂ · 27H ₂ O having a primary particle size - the range from 1 to 10 micrometers
Polyacrylate :	Homopolymer of acrylic acid of MW 4000
Citrate :	Sodium citrate trihydrate
Photoactivated Bleach :	Tetra sulphonated Zinc phthalocyanine
MA/AA :	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000.
MVEMA :	Maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of 240,000. This material was prehydrolysed with NaOH before addition.
Perborate :	Sodium perborate tetrahydrate of nominal formula NaBO ₂ · 3H ₂ O · H ₂ O ₂
Perborate monohydrate :	Anhydrous sodium perborate bleach empirical formula NaBO ₂ · H ₂ O ₂
Enzyme :	Mixed proteolytic and amylolytic enzyme sold by Novo Industrie AS.
Brightener :	Disodium 4,4'-bis(2-morpholino-4-anilino-s-triazin-6-ylamino)stilbene-2,2'-disulphonate.
DETPMP :	Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060
Mixed Suds Suppressor :	25% paraffin wax mp 50°C, 17% hydrophobic silica, 58% paraffin oil.

EXAMPLE I

[0097] The granular detergent products were prepared having compositions as shown below in parts by weight.

	A	B
C ₁₂ LAS	4.4	4.4
TAS	4.0	4.0
45E7	3.7	3.7
TAE ₁₁	1.1	1.1
Zeolite A	18.2	8.0

(continued)

	A	B
NaSKS-6	-	11.0
Citrate	9.25	6.0
MA/AA	4.9	4.9
TAED	5.0	5.0
Perborate	10.0	10.0
Perborate monohydrate	6.0	6.0
DETPMP	0.19	0.19
Enzyme	1.40	1.40
Silicate (2.0 ratio)	4.0	-
Carbonate	15.5	9.0
Suds suppressor	0.55	0.55
CMC	0.8	0.8
Photoactivated bleach	20 ppm	20 ppm
Perfume	0.43	0.43
Brightener	0.24	0.24
Moisture & Misc.	10.34	6.29

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[0098] Both products were made by a combination of spray drying, agglomeration and dry mixing techniques. A spray dried powder was made incorporating all of the TAS, approximately one quarter of the LAS, all of the Maleic anhydride/acrylic acid copolymer, DETPMP, CMC and brightener and part of the carbonate and zeolite builders. For Product A approximately 82% of the zeolite and 65% of the carbonate were included in the spray dried portion, while for Product B approximately 60% of the zeolite and 45% of the carbonate were added in this way. The spray dried product was passed through a Lodige KM high speed mixer/cutter and the 45E7 nonionic was sprayed on to the granules. The treated granules were then transferred to a conveyor belt. The remainder of the LAS, carbonate and zeolite were processed in a Lodige KM high speed mixer to form agglomerated particles which were fed to the conveyor belt. The other dry solid ingredients viz. the citrate, silicate, perborate and bleach activator were also added to the belt at the same time. Finally the mixed particulates were subjected to a low intensity blending step in a mix drum, during which step the perfume and suds suppressor were sprayed on to the particulates to form the finished product.

[0099] These products were then compared in a split bundle wash testing programme to enable the assessment of cleaning and stain removal performance. The test programme was designed, and contained sufficient replicates, to permit statistical treatment of the results. Product A was used in an amount of 95g per load whereas Product B was used in an amount of 79g per load. The difference reflected the higher concentration of ingredients per 100 parts of Product B and thus the need to use less weight in order to provide the same levels of non builder ingredients. The test programme used AEG Lavamat 980 automatic washing machines set to the No. 2 cycle. The machines were charged with water of 25° German Hardness having a 3:1 Ca:Mg ratio. Testing was carried out at three temperatures, viz. 40°C, 60°C and 95°C, for which respectively, fabric loads of 1.81 kg 2.25 kg, and 2.72 kg were employed. Each load comprised a mixture of naturally soiled white cotton fabric articles together with swatches soiled with a variety of stains viz. greasy, clay soil, enzymatic and bleachable, to permit the assessment of whiteness and stain removal performance. Each swatch comprised half of a pair, the other half being washed in the same machine using the comparison product. After washing, the fabrics were dried at ambient temperature and were then subjected to panelling by expert judges using a 1-5 Scheffe scale to characterise differences in whiteness and stain removal performance between Products A and B at the selected temperatures.

[0100] The panelling showed significant advantages for Product B over Product A on greasy and clay stains at 40°C and on clay stains at 95°C, the overall stain removal performance of the products being otherwise statistically indistinguishable. Useful performance advantages therefore exist for a composition incorporating a builder system in accordance with the present invention over a prior art composition. Moreover, such advantages can be obtained with a significant reduction (13.0 parts) in the level of builder ingredients.

EXAMPLE II

[0101] A comparison of the amount of deposited inorganic material on fabrics subjected to multiple washes was made between Product B in Example I and a non-phosphate laundry detergent (UK Ariel Ultra (trademark) manufactured in UK by Procter & Gamble Limited).

[0102] The washing conditions comprised the mainwash cycle of a Miele Hydromatic W698 (Ca:Mg = 3:1) and a wash temperature of 95°C. Each product was used to wash a load comprising 2.72 kg of new cotton terry towelling fabric and the respective washed loads were then subjected to a further 14 complete wash cycles.

[0103] A sample of the fabric from each load was then weighed, incinerated and the residue weighed to provide a value for the inorganic material deposited during the wash cycles.

[0104] Results were as follows:

Product	Dosage/wash (g)	Ash (wt%)
Ariel Ultra (trademark)	125g	0.698%
Product B	102g	0.483%

[0105] The results indicate that compositions in accordance with the invention produce lower levels of inorganic salt deposition than those obtained with commercially available non-phosphate detergent products.

EXAMPLE III

[0106] The following composition is in accordance with the invention and is made in the same manner as product B of Example I.

C ₁₂ LAS	6.80
TAS	2.20
45E7	3.27
TAE ₁₁	1.00
Zeolite A	13.00
NaSKS-6	11.00
Citrate	6.00
MA/AA	4.25
Carbonate	9.00
TAED	5.00
Perborate Monohydrate	12.50
DETPMP	0.19
Enzyme	1.20
CMC	0.48
Photactivated Bleach	20 ppm
Brightener	0.24
Suds Suppressor	0.49
Perfume	0.43
Moisture & Misc.	8.70

EXAMPLE IV

[0107] Three detergent products C,D and E were prepared in the manner of, and having compositions identical to, Composition B of Example I other than the builder system differences shown below (values are in parts by weight in the composition).

	C	D	E
Zeolite A	13.0	13.0	13.0
Citrate	6.0	6.0	6.0
NaSKS-6	11.0	11.0	-
Silicate (2.0 Ratio)*	-	-	13.75
MA/AA	4.25	2.0	2.0

*supplied as 80% active, providing 11.0 parts on an anhydrous basis

[0108] The products were used to conduct full scale washing machine tests in which terry towelling cotton swatches were included with 4 kg of clean fabric ballast loads and subjected to multiple wash cycles to determine the levels of heavy metal ions (Fe and Mn) and total ash (inorganic salts) building up on the fabrics after repeated washing. A heavy metal ion 'spike' of 2.5 ppm Fe as FeCl_3 and 0.2 ppm Mn as MnCl_2 was added to the water fed to the machines.

[0109] The wash conditions were

Machine Type	Miele Hydromatic W698	
Machine Cycle	95°C Cotton	
Water Hardness	Newcastle upon Tyne (UK) City Water adjusted to give 25° German Hardness with Ca:Mg ratio of 3:1. (This water source typically contains 0-3ppm Cu).	
Artificial Soil	20g/load of a mixture made up of	
	Palmitic Acid	250g
	Stearic Acid	250g
	Garden Clay	200g
	Dirty Motor Oil	150g
	Glyceryl trioleate	150g
	Iron Oxide (Fe_2O_3)	5.36g

[0110] The swatches are subjected to 25 wash cycles and then analysed for heavy metal ion content (ppm) and total inorganic salt content (ash). The latter required the burning of a weighed terry towelling fabric swatch in a flame for 3 minutes followed by calcination at 800°C for 2 1/2 hours. The ash was then analysed for the elements below and reported as a fraction of the original sample weight.

[0111] Results were as follows:

	C	D	E
Fe ppm	8.8	9.9	27.2

(continued)

	C	D	E
Mn ppm	1.9	3.5	12.4
Cu ppm	1.4	2.3	7.0
Ca+Mg%	0.42	0.46	1.05
Si and Al%	0.18	0.27	0.49

[0112] It can be seen that cotton fabrics washed in Products C + D, comprising compositions in accordance with the invention, display similar ash and heavy metal ion contents. However Composition D contains a level of polymeric polycarboxylate auxiliary builder which is < 50% of that used conventionally, showing that the use of the ternary builder system of the invention provides enhanced robustness to detergent compositions.

[0113] The results for Products C + D, when compared with those of Comparative Product E, also show the reduction in the level of deposited inorganic salts (ash) arising from the use of the ternary builder system relative to prior art builder systems. More particularly, the comparison of Products C + D with Product E shows the significant reduction in heavy metal ion levels on fabrics resulting from use of the compositions of the invention. Fabric heavy metal ion content can be directly correlated with Tensile Strength Loss in fabrics which is believed to arise from catalytic decomposition of inorganic perhydrate bleaches on the surface of the fabrics.

Claims

1. A particulate detergent composition comprising an oxygen bleach and comprising
 - a) from 5% to 50% by weight of one or more anionic, nonionic, ampholytic or cationic surfactants or a mixture of any thereof;
 - (b) from 10% to 60% of a detergent builder system comprising a mixture of
 - i) from 20% to 60% by weight of the mixture of a sodium aluminosilicate zeolite;
 - ii) from 10% to 30% by weight of the mixture of a water soluble monomeric or oligomeric organic carboxylate chelating agent; and
 - iii) from 10% to 65% by weight of the mixture of a crystalline layered sodium silicate having the composition $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$, wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20; and
 - (c) up to 40% of non-surfactant, non-builder detergent ingredients which comprise the oxygen bleach.
2. A particulate detergent composition according to claim 1 wherein, in component (b)(iii), x has a value of 2.
3. A detergent composition according to either one of claims 1 and 2 wherein, in component (b)(iii), M is sodium.
4. A detergent composition according to any one of claims 1-3 wherein the component (b)(iii) is α , β , γ or δ - $\text{Na}_2\text{Si}_2\text{O}_5$.
5. A detergent composition according to any one of claims 1-4 wherein the sodium aluminosilicate zeolite is a hydrated synthetic zeolite having a Calcium ion exchange capacity of at least 200 mg eq CaCO_3 water hardness per g of zeolite calculated on an anhydrous basis.
6. A detergent composition according to any one of claims 1-5 wherein the synthetic hydrated zeolite has a unit cell formula

$$\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$$
 wherein z and y are at least 6, the ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276.
7. A detergent composition according to any one of claims 1-6 wherein the sodium aluminosilicate zeolite is hydrated Zeolite A, X, B or HS.

8. A detergent composition according to any one of the preceding claims wherein the monomeric or oligomeric organic carboxylate chelating agent has a first carboxyl logarithmic acidity constant (pK_1) of less than 9.
9. A detergent composition according to any one of claims 1-8 wherein the monomeric or oligomeric organic carboxylate chelating agent has a pK_1 of from 2 to 8.5, preferably of from 4 to 7.5.
10. A detergent composition according to any one of claims 1-9 wherein the component (b)(ii) comprises a monomeric poly carboxylate.
11. A detergent composition according to any one of claims 1-10 wherein component (b)(ii) comprises an aliphatic monomeric poly carboxylate containing from 2 to 4 carboxyl groups.
12. A detergent composition according to any one of claims 1-11 wherein component (b)(ii) comprises citric acid, a water soluble citrate salt or a mixture thereof.
13. A detergent composition according to any one of the preceding claims wherein component (b) also includes one or more auxiliary builders.
14. A detergent composition according to claim 13 wherein the auxiliary builder is selected from amino polyalkylene phosphonates, alkali metal carbonates and bicarbonates, homo-/or copolymeric 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, and mixtures thereof.
15. A detergent composition according to any one of the preceding claims comprising from 5% to 30% of component a), from 20% to 60% of component b) and from 20% to 40% of other detergent ingredients.
16. A detergent composition according to any preceding claim wherein the oxygen bleach is an inorganic perhydrate.
17. A detergent composition according to any preceding claim wherein the oxygen bleach includes an organic peroxy acid precursor.
18. A detergent composition according to any one of the preceding claims wherein component (c) includes a detergent enzyme.
19. A method of preparing a detergent composition according to any one or claims 1-18 wherein the crystalline layered sodium silicate (b)(iii) is added as a finely divided particulate solid to one or more particulate solids comprising component a) component (b)(i) and (ii) and, component (c).

Patentansprüche

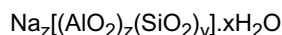
1. Eine partikuläre Waschmittel-Zusammensetzung, welche eine Sauerstoffbleiche umfaßt und umfaßt:
 - a) zu 5 Gew.-% bis 50 Gew.-% ein oder mehrere anionische, nichtionische, ampholytische oder kationische Tenside oder eine Mischung beliebiger hievon;
 - b) zu 10 % bis 60 % ein Waschmittel-Buildersystem, welches eine Mischung von
 - i) 20 % bis 60 %, bezogen auf das Gewicht der Mischung, Natriumaluminosilikat-Zeolith,
 - ii) 10 % bis 30 %, bezogen auf das Gewicht der Mischung, wasserlöslichem monomeren oder oligomeren Carboxylat-Chelatbildner; und
 - iii) 10 % bis 65 %, bezogen auf das Gewicht der Mischung, kristallinem Natriumschichtsilikat mit der Zusammensetzung $NaMSi_xO_{2x+1} \cdot yH_2O$, worin M für Natrium oder Wasserstoff steht, x für eine Zahl von 1,9 bis 4 steht und y für eine Zahl von 0 bis 20 steht; umfaßt, und
 - c) bis zu 40 % nicht-oberflächenaktive, Nicht-Builder-Waschmittel-Bestandteile, welche die Sauerstoffbleiche umfassen.
2. Eine partikuläre Waschmittel-Zusammensetzung nach Anspruch 1, in welcher in Komponente (b)(iii) x einen Wert 2 hat.

3. Eine Waschmittel-Zusammensetzung nach einem der Ansprüche 1 und 2, in welcher in Komponente (b)(iii) M für Natrium steht.

4. Eine Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 3, in welcher die Komponente (b)(iii) alpha-, beta-, gamma- oder delta- $\text{Na}_2\text{Si}_2\text{O}_5$ ist.

5. Eine Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 4, in welcher der Natriumaluminosilikat-Zeolith ein hydratisierter synthetischer Zeolith mit einer Tauschkapazität für Kalziumion von mindestens 200 mg eq CaCO_3 Wasserhärte pro Gramm Zeolith, berechnet auf wasserfreier Basis, ist.

6. Eine Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 5, in welcher der synthetische hydratisierte Zeolith für die Einheitszelle eine Formel



hat, in welcher z und y für mindestens 6 stehen, das Verhältnis von z zu y 1,0 bis 0,5 beträgt und x für mindestens 5, vorzugsweise 7,5 bis 276, steht.

7. Eine Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 6, in welcher der Natriumaluminosilikat-Zeolith hydratisierter Zeolith A, X, B oder HS ist.

8. Eine Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, in welcher der monomere oder oligomere organische Carboxylat-Chelatbildner eine erste logarithmische Aciditätskonstante (pK_1) des Carboxyls von weniger als 9 hat.

9. Eine Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 8, in welcher der monomere oder oligomere organische Carboxylat-Chelatbildner eine pK_1 von 2 bis 8,5, vorzugsweise von 4 bis 7,5, hat.

10. Eine Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 9, in welcher die Komponente (b)(ii) ein monomeres Polycarboxylat umfaßt.

11. Eine Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 10, in welcher die Komponente (b)(ii) ein aliphatisches monomeres Polycarboxylat umfaßt, das 2 bis 4 Carboxylgruppen enthält.

12. Eine Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 11, in welcher die Komponente (b)(ii) Zitronensäure, ein wasserlösliches Zitratsalz oder eine Mischung hiervon umfaßt.

13. Eine Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, in welcher die Komponente (b) auch einen oder mehrere Hilfsbuilder umfaßt.

14. Eine Waschmittel-Zusammensetzung nach Anspruch 13, in welcher der Hilfsbuilder ausgewählt ist aus Aminopolyalkylenphosphonaten, Alkalimetallcarbonaten und -bicarbonaten, homo- oder copolymeren Polycarbonsäuren oder deren Salzen, in welchen die Polycarbonsäure mindestens zwei Carboxylreste aufweist, die voneinander durch nicht mehr als zwei Kohlenstoffatome getrennt sind, und Mischungen hiervon.

15. Eine Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, die zu 5 % bis 30 % Komponente a), zu 20 % bis 60 % Komponente b) und zu 20 % bis 40 % andere Waschmittel-Bestandteile enthält.

16. Eine Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, in welcher die Sauerstoffbleiche ein anorganisches Perhydrat ist.

17. Eine Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, in welcher die Sauerstoffbleiche eine organische Peroxysäurevorstufe enthält.

18. Eine Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, in welcher die Komponente (c) ein Waschmittel-Enzym enthält.

19. Ein Verfahren zur Herstellung einer Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 18, bei wel-

chem das kristalline Natriumschichtsilikat (b) (iii) als ein fein verteilter partikulärer Feststoff zu einem oder mehreren partikulären Feststoffen, die Komponente (a), Komponente (b)(i) und (ii) und Komponente (c) umfassen, zugesetzt wird.

5 Revendications

1. Composition détergente particulaire comprenant un agent de blanchiment oxygéné et comprenant
 - (a) de 5 à 50 % en poids d'un ou plusieurs tensioactifs anioniques, non ioniques, ampholytes ou cationiques, ou un mélange de plusieurs quelconques d'entre eux;
 - (b) de 10 à 60 % d'un système adjuvant de détergence, comprenant un mélange
 - i) de 20 à 60 % en poids, par rapport au mélange, d'une zéolite de type aluminosilicate de sodium;
 - ii) de 10 à 30 % en poids, par rapport au mélange, d'un agent chélatant de type carboxylate organique, monomère ou oligomère, soluble dans l'eau; et
 - iii) de 10 à 65 % en poids, par rapport au mélange, d'un silicate de sodium lamellaire cristallin ayant la composition $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$, où M est le sodium ou l'hydrogène, x est un nombre de 1,9 à 4 et y est un nombre de 0 à 20 ; et
 - (c) jusqu'à 40 % d'ingrédients autres que des tensioactifs et autres que des adjuvants de détergence qui comprennent l'agent de blanchiment oxygéné.
2. Composition détergente particulaire selon la revendication 1, dans laquelle, dans le constituant (b)(iii), x vaut 2.
3. Composition détergente selon l'une ou l'autre des revendications 1 et 2, dans laquelle, dans le constituant (b)(iii), M est le sodium.
4. Composition détergente selon l'une quelconque des revendications 1 à 3, dans laquelle le constituant (b)(iii) est l' α -, le β -, le γ - ou le δ - $\text{Na}_2\text{Si}_2\text{O}_5$.
5. Composition détergente selon l'une quelconque des revendications 1 à 4, dans laquelle la zéolite de type aluminosilicate de sodium est une zéolite synthétique hydratée ayant une capacité d'échange de l'ion calcium d'au moins 200 mg d'équivalence de dureté de type CaCO_3 par g de zéolite, calculée sur une base anhydre.
6. Composition détergente selon l'une quelconque des revendications 1 à 5, dans laquelle la zéolite hydratée synthétique a une formule de cellule unitaire

$$\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$$
 dans laquelle z et y valent au moins 6, le rapport de z à y est de 1,0 à 0,5, et x vaut au moins 5, et vaut de préférence de 7,5 à 276.
7. Composition détergente selon l'une quelconque des revendications 1 à 6, dans laquelle la zéolite de type aluminosilicate de sodium est une zéolite A, X, B ou HS hydratée.
8. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle l'agent chélatant de type carboxylate organique monomère ou oligomère possède une constante logarithmique d'acidité du premier groupe carboxyle (pK_1) inférieure à 9.
9. Composition détergente selon l'une quelconque des revendications 1 à 8, dans laquelle l'agent chélatant de type carboxylate organique monomère ou oligomère a un pK_1 de 2 à 8,5 et de préférence de 4 à 7,5.
10. Composition détergente selon l'une quelconque des revendications 1 à 9, dans laquelle le constituant (b)(ii) comprend un polycarboxylate monomère.
11. Composition détergente selon l'une quelconque des revendications 1 à 10, dans laquelle le constituant (b)(ii) comprend un polycarboxylate monomère aliphatique contenant de 2 à 4 groupes carboxyle.

12. Composition détergente selon l'une quelconque des revendications 1 à 11, dans laquelle le constituant (b)(ii) comprend de l'acide citrique, un sel citrate soluble dans l'eau ou un de leurs mélanges.

13. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle le constituant (b) comprend aussi un ou plusieurs adjuvants auxiliaires.

14. Composition détergente selon la revendication 13, dans laquelle l'adjuvant auxiliaire est choisi parmi les polyalkylènephosphonates aminés, les carbonates et bicarbonates de métaux alcalins, les acides polycarboxyliques homo- ou copolymères, ou leurs sels, où l'acide polycarboxylique comprend au moins deux radicaux carboxyle séparés l'un de l'autre par au plus deux atomes de carbone, et leurs mélanges.

15. Composition détergente selon l'une quelconque des revendications précédentes, comprenant de 5 à 30 % du constituant (a), de 20 à 60 % du constituant (b) et de 20 à 40 % d'autres ingrédients de détergence.

16. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle l'agent de blanchiment oxygéné est un perhydrate minéral.

17. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle l'agent de blanchiment oxygéné comprend un précurseur d'un peracide organique.

18. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle le constituant (c) comprend une enzyme de détergence.

19. Procédé de préparation d'une composition détergente selon l'une quelconque des revendications 1 à 18, dans lequel le silicate de sodium lamellaire cristallin (b)(iii) est ajouté sous forme d'un solide particulaire finement divisé à un ou plusieurs solides particuliers comprenant le constituant (a), les constituants (b)(i) et (ii), et le constituant (c).