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**EP-A-0 038 591
DE-A-2 545 190
DE-A-2 857 154
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GB-A-1 498 492
GB-A-1 503 363
GB-A-1 528 757**

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Description

Description

5 The present invention relates to additives for detergent compositions, and to detergent compositions containing them. These compositions are particularly, but not essentially, adapted for fabric washing. The invention relates more particularly to substantially phosphate-free detergent compositions.

10 Fabric washing compositions conventionally contain phosphate detergency builders such as sodium tripolyphosphate. In some circumstances it is thought that the use of phosphates in detergent compositions can lead to environmental problems in waste waters. There is therefore a desire to reduce the level of phosphorus, or to eliminate it altogether, in detergent compositions.

15 Water-insoluble aluminosilicate ion exchange materials have been suggested as alternative builders to phosphates; see, for example, GB-1 473 201 and GB-1 473 202 (Henkel). It has been found in practice, however, that these aluminosilicate materials, even in large amounts, tend to be undesirably slow in their exchange of cations, especially at low temperatures, resulting in inferior detergency. It has accordingly been suggested that supplementary water-soluble builders should be used in combination with these aluminosilicates to raise the detergency to an acceptable level. These supplementary builders are generally materials that are efficiency sequestrant builders in their own right, for example, alkali metal tripolyphosphates, nitrilotriacetates and poly- α -hydroxyacrylates. High levels of these materials are, however, not generally desirable in detergent compositions for cost or environmental reasons.

20 We have now discovered that surprisingly good detergency results are obtained by using, in combination with an aluminosilicate builder, relatively small amounts of both a specific organic sequestrant builder (nitrilotriacetic acid or a salt thereof) and a specific organic precipitant builder (a defined soap or soap blend). The detergency results obtained using ternary systems of this type have surprisingly been found to be better than would have been expected from consideration of the results obtained using the corresponding binary aluminosilicate/sequestrant and aluminosilicate/precipitant systems, so that decreased amounts of the supplementary builders can be used, giving cost savings and environmental advantages.

25 It is known that the detergency builder properties of aluminosilicates are enhanced by the addition of water-soluble complexing agents such as sodium tripolyphosphate. This effect has been explained in terms of the so-called "carrier molecule model": see, for example, P Berth, J. Am. Oil Chemists' Soc., 55, 52 - 53 (1978). The complexing agent is able to take up polyvalent water hardness ions (notably Ca^{2+} , but also Mg^{2+}) from solid surfaces (such as the surface of a textile fibre) and pass them on to the aluminosilicate ion-exchanger after transport through the aqueous medium. The complexing agent forms a chelate complex with the hardness ion which on arrival at the surface of the aluminosilicate dissociates.

30 It is not easy to envisage a similar mechanism with precipitant builders, such as soaps, since these remove hardness ions from the wash liquor by the virtually irreversible formation of a precipitate (insoluble calcium or magnesium salt).

35 It is thus unexpected that addition of a soap to an aluminosilicate/sequestrant system gives a substantial improvement in detergency builder properties.

40 The present invention accordingly provides a detergent composition as set out in the appended claim 1.

Component (b) (ii) will hereinafter be referred to as NTA.

Thus the subject of the invention is a detergent composition comprising a ternary builder system consisting of aluminosilicate, soap and NTA.

45 In GB-1 498 492 (Henkel) and DE-2 539 110 (Henkel) there are disclosed detergent compositions, built with aluminosilicate and NTA, in which the detergent-active system includes soap; the soap is, however, present only in small quantities. GB-1 528 943 (Henkel) discloses spray-dried detergent powders containing soap as a part of the detergent-active system and built with zeolite and sodium tripolyphosphate (1 : 1); the powders exemplified contain very low levels of NTA.

50 EP-38 591 (Procter & Gamble) discloses detergent compositions built with aluminosilicate in which the detergent-active agents used include soaps of C_{16} - C_{22} unsaturated fatty acids. These soaps function in the compositions as detergent-active agents, assisting in soil removal and cool-water detergency; the aluminosilicate is said to assist in keeping the unsaturated soap from forming an insoluble curd. The unsaturated soaps are not, accordingly, functioning as builders by precipitating calcium from the wash liquor as an insoluble calcium soap. The soap compositions disclosed in EP-38 591 may contain some unsaturated soap, but only at low levels so as not to detract from the detergent activity of the preferred unsaturated materials.

55 The unsaturated soaps disclosed in EP-38 591 are unsuitable for use in the compositions of the present invention, because their calcium salts are not sufficiently insoluble in water. The predominantly saturated soaps used according to the invention, on the other hand, have highly insoluble calcium salts. Calcium present in the wash liquor is removed in the form of insoluble calcium soaps; the soaps themselves thus function as builders rather than as detergent-active agents.

60 The soaps used in the compositions of the invention consist to an extent of at least 60 %, preferably at least 80 %, of saturated soaps. Advantageously 100 % saturated material may be used.

65 The soap preferably contains both longer-chain (C_{18} and above) and shorter-chain (C_{14} and below) material. The longer the chain, the higher the insolubility of the calcium salt, and thus the greater the efficiency of the soap as a builder. Shorter chain-length soaps, however, although forming less insoluble calcium salts, can also

be effective detergency builders because of their lower molecular weight and accordingly greater weight-effectiveness. The shorter-chain soaps are especially valuable under low temperature washing conditions.

Shorter-chain soaps themselves (generally the sodium salts) also have better solubility than the longer-chain materials, and the presence of some short-chain material along with longer-chain soaps can enhance overall soap solubility.

In general, for efficient building, the soap used in the detergent additive of the invention preferably contains at least 5 % by weight, more preferably at least 8 %, of material having a chain length of C₁₈ and above. It may also be advantageous, from the point of view of solubility, for the soap used in the detergent additive of the invention to contain at least 1 %, preferably at least 3 %, of material being a chain length of C₁₄ and below.

When predominantly longer-chain soaps are used in the detergent additive of the invention, the soap or mixture of soaps contains at least 60 % by weight, preferably at least 80 % by weight, of material having a chain length of C₁₈ and above. It is also advantageous from the point of view of solubility, for the soap to contain at least 1 %, preferably at least 3 %, of material having a chain length of C₁₄ and below. This is not essential, however, for products intended for use in conventional medium or high-temperature washing, where the solubility of the soap itself (the sodium or other soluble salt) is not a problem.

Examples of such soaps include hardened tallow (67 % C₁₈ and above) and hardened rapeseed (96.5 % C₁₈ and above).

When predominantly shorter-chain soaps are used in the detergent additive of the invention, the soap or mixture of soaps contains at least 60 % by weight, preferably at least 70 % by weight, of material having a chain length of C₁₄ and below. It preferably also contains at least 5 %, more preferably at least 8 %, of material having a chain length of C₁₈ and above. Such a composition is especially beneficial for lower-temperature washing where the solubility of the soap itself is important in determining good detergency building.

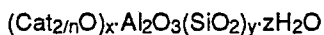
Examples of such soaps include coconut (82 % C₁₄ and below) and palm kernel (73.5 % C₁₄ and below).

The following Table shows the constitution of the four soaps mentioned above:

Soap	Hardened tallow	Hardened rapeseed	Coconut	Palm kernel
Saturated material (%)	100	100	92.5	85.5
Chain length distribution (%)				
C ₁₀ and below	-	-	13.0	7.5
C ₁₂	-	-	49.5	48.5
C ₁₄	3.5	-	19.5	17.5
C ₁₅	0.5	-	-	-
C ₁₆	27.5	3.5	8.5	10.5
C ₁₇	1.5	-	-	-
C ₁₈	66.5	37.2	9.5	16.0
C ₂₀	0.5	6.6	-	-
C ₂₂	-	52.7	-	-

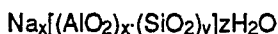
These are of course only exemplary of the many soaps and soap blends that may be used in the detergent composition of the invention.

The detergent composition of the invention also includes a water-insoluble aluminosilicate cation exchange material. This is preferably a crystalline or amorphous material having the general formula:



wherein Cat is a cation having valency n that is exchangeable with calcium (e. g. Na⁺ or K⁺); x is a number from 0.7 - 1.5; y is a number from 1.3 - 4; and z is such that the bound water content is from 10 % to 28 % by weight.

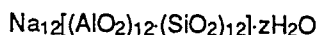
Preferably a crystalline material is used which can be described by the unit cell content:



wherein x and y are integers of at least 6, the ratio of x to y being in the range of 1 : 1 to 1 : 2; and z is such that the bound water content is from 10 % to 28 % by weight.

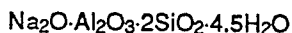
The aluminosilicate preferably has a particle size of from 0.1 to 100 micrometres, ideally between 0.1 and 10 micrometres, and an ion exchange capacity of at least 200 mg CaCO₃ per gram of aluminosilicate (anhydrous basis).

In a preferred embodiment the water-insoluble aluminosilicate is a crystalline material having the formula described by the unit cell content:

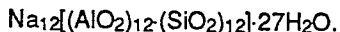


wherein z is from 20 to 30, preferably about 27.

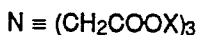
An example of this material is the commercially available product known as Zeolite type A, which is typically:



and is also described by the unit cell content:



The third component of the builder system of the invention is an organic sequestrant builder, namely, nitrilotriacetic acid or a water-soluble salt thereof (NTA). This component may be represented by the following structural formula



wherein X is hydrogen or a solubilizing cation. These compounds may further contain C-bonded substituents of an inert and innocuous nature such as alkyl, e. g. methyl or ethyl, or haloalkyl, e. g. chloromethyl. The nature of said compounds is not particularly critical with the implicit limitation that such substituents be devoid of any tendency to deleteriously affect the desirable properties of the NTA.

Preferred compounds falling within the ambit of the above-described definition and formula are nitrilotriacetic acid and its alkali metal salts, especially trisodium nitrilotriacetate monohydrate, tripotassium nitrilotriacetate, disodium nitrilotriacetate and dipotassium nitrilotriacetate.

The soap and NTA together constitute up to 75 % by weight of the builder system of the invention, preferably from 20 % to 50 %. The ratio of soap to NTA is from 3 : 1 to 1 : 1.

The detergent composition of the present invention contains an efficient builder system yielding good detergency results.

The detergent composition of the invention contains from 25 % to 70 %, and especially from 28 % to 67 %, of the ternary builder system.

An aluminosilicate content of from 10 % to 60 %, especially from 17 % to 47 %, is preferred.

The content of the specified organic builders (soap plus NTA) preferably will not exceed 40 %, and more preferably does not exceed 27 %. The preferred range for the content of the soap is up to 20 %; for the NTA the preferred range is from 2 % to 10 %.

The detergent compositions of the present invention are preferably substantially free of inorganic phosphate. This is highly desirable for the environmental reasons mentioned earlier. Compositions according to the invention containing no inorganic phosphate have been found to exhibit detergency properties comparable to those of sodium tripolyphosphate-built products.

If desired, however, the compositions may contain inorganic phosphate, but if avoidance of the possible environmental effects of phosphate is in question the level advantageously does not exceed 10 % based on the whole product; levels below 5 % and more especially below 3 % are of particular interest in this connexion. Any phosphate present may, for example, be in the form of alkali metal (preferably sodium) tripolyphosphate, orthophosphate, pyrophosphate or polymeric phosphate.

The detergent composition of the invention may if desired contain other builders in addition to the specified ternary builder system of the invention. As indicated previously, these are preferably non-phosphate materials. Examples of suitable materials include the water-soluble salts of the following acids: ethylenediamine tetracetic acid, polyacrylic acid poly(α -hydroxyacrylic) acid, carboxymethyloxymalonic acid, carboxymethyloxysuccinic acid, oxydiacetic acid, oxydisuccinic acid, citric acid, dipicolinic acid and many more. The polyacetal carboxylates disclosed in US-4 144 126 and US-4 146 495 (Monsanto) and the oxidised polysaccharides disclosed in GB-1 330 121, GB-1 330 122 and GB-1 330 123 (Unilever) may also advantageously be used.

The detergent composition of the invention includes at least 3 % by weight, preferably from about 5 % to about 40 % by weight, more preferably from about 10 % to about 25 % by weight, of synthetic detergent-active material, which may include anionic, nonionic, amphoteric or zwitterionic detergent compounds or mixtures thereof. Many suitable detergent-active compounds are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred detergent compounds which can be used are synthetic anionic and nonionic compounds. The former are usually water soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8 - C_{18}) alcohols produced for example from tallow or coconut oil; sodium and potassium alkyl (C_9 - C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_9 - C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction pro-

ducts of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C₈ - C₂₀) with sodium bisulphate and those derived by reacting paraffins with SO₂ and Cl₂ and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C₁₀ - C₂₀ alpha-olefins, with SO₃ and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C₁₁ - C₁₅) alkyl benzene sulphonates and sodium (C₁₆ - C₁₈) alkyl sulphates.

Examples of suitable nonionic detergent compounds which may be used include in particular the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C₆ - C₂₂) phenols, generally 5 to 25 EO, i. e. 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C₈ - C₁₈) primary or secondary linear or branched alcohols with ethylene oxide, generally 6 to 30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Mixtures of detergent compounds, for example mixed anionic or mixed anionic and nonionic compounds may be used in the detergent compositions, particularly in the latter case to provide controlled low sudsing properties. This is beneficial for compositions intended for use in suds-intolerant automatic washing machines. Anionic and nonionic detergent compounds are advantageously used together in ratios of from 3 : 1 to 1.5 : 1.

Amounts of amphoteric or zwitterionic detergent compounds can also be used in the compositions of the invention but this is not normally desired due to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and/or nonionic detergent compounds.

According to a preferred embodiment of the invention, the detergent composition also contains a bleach system.

The bleach system preferably comprises a peroxy bleach compound which is an inorganic persalt, which is preferably used in conjunction with an activator therefor. The persalt may be, for example, sodium perborate (either the monohydrate or the tetrahydrate) or sodium percarbonate. The activator makes the bleaching more effective at lower temperatures, i. e. in the range from ambient temperature to about 60°C, so that such bleach systems are commonly known as low-temperature bleach systems and are well known in the art. The inorganic persalt acts to release active oxygen in solution, and the activator is usually an organic compound having one or more reactive acyl residues, which cause the formation of peracids, the latter providing for a more effective bleaching action at lower temperatures than can be obtained by use of the peroxy bleach compound alone. The ratio by weight of the peroxy bleach compound to the activator is generally from about 20 : 1 to about 1 : 1, preferably about 15 : 1 to about 2 : 1.

The detergent composition of the invention preferably contains from about 5 % to about 30 % by weight of the peroxy bleach compound, and about 0.1 to about 15 % by weight of the activator. The total amount of the bleach system ingredients preferably lies within the range of from 5 % to 35 % by weight, especially from about 6 % to about 30 % by weight.

Typical examples of suitable peroxy bleach compounds are alkali metal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persulfates and perphosphates, of which sodium perborate is preferred.

Activators for peroxybleach compounds have been amply described in the literature, including British Patents 836,988, 855,735, 907,356, 907,358, 970,950, 1,003, 310 and 1,246,339, US Patents 3,332,882 and 4,128,494, Canadian Patent 844,481 and South African Patent 68/6,344. Specific suitable activators include:

- (a) N-diacylated and N,N'-polyacylated amines, such as N,N,N',N'-tetraacetyl methylene diamine and N,N,N',N'-tetraacetyl ethylene diamine, N,N-diacetylaniline, N,N-diacetyl-p-toluidine; 1,3-diacylated hydantoins such as, for example, 1,3-diacetyl-5,5-dimethyl hydantoin and 1,3-dipropionyl hydantoin; α-acetoxy-(N,N')-polyacetylmalonamide, for example α-acetoxy-(N,N')-diacetylmalonamide;
- (b) N-alkyl-N-sulphonyl carbonamides, for example the compounds N-methyl-N-mesyl-acetamide, N-methyl-N-mesyl-benzamide, N-methyl-N-mesyl-p-nitrobenzamide, and N-methyl-N-mesyl-p-methoxybenzamide;
- (c) N-acylated cyclic hydrazides, acylated triazones or urazoles, for example monoacetylmaleic acid hydrazide;
- (d) O,N,N-trisubstituted hydroxylamines, such as O-benzoyl-N,N-succinyl hydroxylamine, O-acetyl-N,N-succinyl hydroxylamine, O-p-methoxybenzoyl-N,N-succinyl-hydroxylamine, O-p-nitrobenzoyl-N,N-succinyl-hydroxylamine and O,N,N-triacetyl hydroxylamine;
- (e) N,N'-diacyl-sulphurylamides, for example N,N'-dimethyl-N,N'-diacetyl-sulphurylamide and N,N'-diethyl-N,N'-dipropionyl sulphurylamide;
- (f) Triacylcyanurates, for example triacetyl cyanurate and tribenzoyl cyanurate;
- (g) Carboxylic acid anhydrides, such as benzoic anhydride, m-chloro-benzoic anhydride, phthalic anhydride, 4-chlorophthalic anhydride;
- (h) Sugar esters, for example glucose pentaacetate;
- (i) 1,3-diacyl-4,5-diacyloxy-imidazolidine, for example 1,3-diformyl-4,5-diacetoxy-imidazolidine, 1,3-diacetyl-4,5-diacetoxy-imidazolidine, 1,3-diacetyl-4,5-dipropionyloxyimidazoline;
- (j) Tetraacetylglycoluril and tetrapropionylglycoluril;
- (k) Diacylated 2,5-diketopiperazine, such as 1,4-diacetyl-2,5-diketopiperazine, 1,4-dipropionyl-2,5-diketopiperazine and

1,4-dipropionyl-3,6-dimethyl-2,5-diketopiperazine;

(l) Acylation products of propylenediurea or 2,2-dimethylpropylenediurea (2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonane-3,7-dione or its 9,9-dimethyl derivative), especially the tetraacetyl- or the tetrapropionylpropylenediurea or their dimethyl derivatives;

5 (m) Carbonic acid esters, for example the sodium salts of p-(ethoxycarbonyloxy)-benzoic acid and p-(propoxycarbonyloxy)-benzenesulphonic acid.

(n) α -acyloxy-(N,N') polyacyl malonamides, such as α -acetoxy-(N,N') diacetyl malonamide.

10 The N-diacylated and N,N'-polyacylatedamines mentioned under (a) are of special interest, particularly N,N,N',N'-tetraacetyl-ethylenediamine (TAED).

It is preferred to use the activator in granular form, preferably wherein the activator is finely divided as described in GB-2 053 998B (Unilever). Specifically, it is preferred to have an activator of an average particle size of less than 150 micrometres, which gives significant improvement in bleach efficiency. The sedimentation losses, when using an activator with an average particle size of less than 150 μm , are substantially decreased. 15 Even better bleach performance is obtained if the average particle size of the activator is less than 100 μm . However, too small a particle size gives increased decomposition, dust-formation and handling problems, and although particle sizes below 100 μm can provide for an improved bleaching efficiency, it is desirable that the activator should not have more than 20 % by weight of particles with a size of less than 50 μm . On the other hand, the activator may have a certain amount of particles of a size greater than 150 μm , but it should not 20 contain more than 5 % by weight of particles > 300 μm , and not more than 20 % by weight of particles > 200 μm , preferably > 150 μm . It is to be understood that these particle sizes refer to the activator present in the granules, and not to the granules themselves. The latter have a particle size, the major part of it ranging from 100 to 2000 μm , preferably 250 to 1000 μm . Up to 5 % by weight of granules with a particle size of > 1700 μm and up to 10 % by weight of granules < 250 μm is tolerable. The granules incorporating the 25 activator, preferably in this finely-divided form, may be obtained by granulating a suitable carrier material, such as sodium tripolyphosphate and/or potassium tripolyphosphate with activator particles of the required size. Other granulation methods, e. g. using organic and/or inorganic granulation aids, can also be usefully applied. The granules can be subsequently dried, if required. Basically, any granulation process is applicable, as long as the granule contains the activator, and as long as the other materials present in the granule do not negatively 30 affect the activator.

It is particularly preferred to include in the detergent compositions a stabiliser for the bleach system, for example ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate. These stabilisers can be used in acid or salt form, especially in calcium, magnesium, zinc or aluminium salt form, as described in GB-2 048 930B (Unilever).

35 Apart from the components already mentioned, the detergent compositions of the invention can contain any of the conventional additives in the amounts in which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids; lather depressants such as alkyl phosphates, silicones, or alkyl phosphonic acids incorporated in petroleum jelly, wax or mineral oil; anti-re-deposition agents such as sodium carboxymethylcellulose and cellulose ethers; fabric softening agents; inorganic salts such as sodium sulphate and sodium carbonate; and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases.

It may be desirable to include in the composition an amount of an alkali metal silicate, particularly sodium ortho-, meta- or preferably neutral or alkaline silicate. The presence of such alkali metal silicates at levels of at least about 1 %, and preferably from about 5 % to about 15 % by weight of the composition, is advantageous 45 in decreasing the corrosion of metal parts in washing machines, besides giving processing benefits and generally improved powder properties. The more highly alkaline ortho- and metasilicates would normally only be used at lower amounts within this range, in admixture with the neutral or alkaline silicates.

The composition of the invention is preferably alkaline, but not too strongly alkaline as this could result in fabric damage and also be hazardous for domestic usage. In practice the composition should desirably give a pH of from about 8.5 to about 11 in use in aqueous wash solution. It is preferred in particular for domestic products to have a pH of from about 9.0 to about 10.5 as lower pH's tend to be less effective for optimum 50 detergency building, and more highly alkaline products can be hazardous if misused. The pH is measured at the lowest normal usage concentration of 0.1 % w/v of the product in water of 12°H (Ca), (French permanent hardness, calcium only) at 50°C so that a satisfactory degree of alkalinity can be assured in use at all normal product concentrations. If necessary, up to 10 % by weight of alkali metal carbonate, preferably sodium carbonate, may be included in order to raise the pH and to maintain adequate buffer capacity in the presence of 55 acidic soils.

If carbonate or phosphates are present it may be desirable to include in the composition of the invention one or more antideposition agents, to decrease any tendency to form inorganic deposits on washed fabrics. The amount of any such antideposition agent is normally from about 0.1 % to about 5 % by weight, preferably from about 0.2 % to about 1.5 % by weight of the composition. The preferred antideposition agents are anionic polyelectrolytes, especially polymeric aliphatic carboxylates, or organic phosphonates.

The detergent compositions of the invention should desirably be in free-flowing particulate, for example, powdered or granular form, and can be produced by any of the techniques commonly employed in the manufacture 65

of such washing compositions, for example, by slurry-making and spray-drying processes. It is preferred that the process used to form the compositions should result in a product having a moisture content of not more than about 12 %, more preferably from about 4 % to about 10 % by weight.

The detergent compositions of the invention may also be in the form of bars or tablets, or in liquid form.

The invention will now be illustrated by the following non-limiting Examples.

Examples

In the Examples that follow, the detergencies of wash liquors incorporating various builder systems were compared by measuring the reflectance of a clay-soiled polyester/cotton test cloth before and after washing in the Tergotometer®. The reflectances were measured using a Carl Zeiss Elrepho® Reflectometer and the reflectance increases on washing (ΔR) was taken as a measure of detergency.

In each case a wash liquor was prepared using the ingredients stated below in the concentrations stated below, in 40°FH (Ca) water. The wash liquor was allowed to equilibrate for 15 minutes. Test cloth pieces (four pieces per litre, each measuring 76.2 mm x 76.2 mm) were then added and a 20-minute wash at 80°C, pH 10.0 and 55 rpm agitation was carried out, followed by a rinse in water of the same hardness as that of the water used to prepare the wash liquor.

The ingredients and concentrations were as follows:

	g/litre
Sodium C ₁₀ - C ₁₃ linear alkylbenzene sulphonate	0.195
C ₁₄ - C ₁₅ alcohol ethoxylate (11 EO)	0.09
Hardened tallow soap	0.06
Alkaline silicate	0.15
Sodium sulphate	2.00
Detergent additive according to the invention (as specified in Examples)	2.00 - 5.00

The soap was included for lather control purposes and was present in addition to the soap included in the detergent additive according to the invention.

It will be seen that the detergent additive according to the invention was used at concentrations of from 2.00 to 5.00 g/litre, and the other components of the composition were used at a constant total concentration of 2.495 g/litre, so that the total concentration ranged from 4.495 to 7.495 g/litre. Thus the percentage of the total composition constituted by the detergent additive of the invention at each concentration of the latter was as follows:

Concentration (of detergent additive)	(total)	% Detergent additive in composition
2.00	4.495	44.49
2.50	4.995	50.05
3.00	5.495	54.60
4.00	6.495	61.59
5.00	7.495	66.71

All percentages given in the Examples are by weight and are based on the anhydrous materials.

Example 1

The detergencies of compositions containing a ternary builder system (detergent additive) according to the invention were compared, in 40°FH water at a range of concentrations, with those of control compositions containing single or binary builder systems. The aluminosilicate used was zeolite A, the soap was hardened tallow soap, and the NTA was in the form of its trisodium salt. The results were as follows:

	Reflectance ΔR				
Concentration, g/l	2.0	2.5	3.0	4.0	5.0
Detergent additive					
60 % zeolite/25 % soap/15 % NTA	17.3	22.6	26.1	27.3	27.5
85 % zeolite/15 % NTA	15.2	20.3	24.8	26.2	27.3
75 % zeolite/25 % soap	15.3	18.1	20.9	23.5	25.4
100 % zeolite	14.8	17.4	19.8	22.1	24.3

Example 2

The procedure of Example 1 was repeated using different proportions of zeolite, soap and NTA. The results were as follows:

Concentration, g/l	Reflectance ΔR	
	3.0	4.0
Detergent additive		
70 % zeolite/20 % soap/10 % NTA	24.8	28.3
90 % zeolite/10 % NTA	21.2	24.1
80 % zeolite/20 % soap	18.5	24.0
100 % zeolite	18.7	22.4

Claims

1. A detergent composition comprising a synthetic detergent-active material, a crystalline or amorphous aluminosilicate cation-exchange material and an organic builder, characterised in that it comprises from 25 to 70 % by weight of a ternary builder system consisting of:

- (a) at least 25 % by weight of the crystalline or amorphous aluminosilicate cation-exchange material,
- (b) the balance consisting of:

- (i) at least 15 % by weight, based on (a) plus (b), of one or more water-soluble soaps of C₈ - C₂₂ fatty acids, at least 60 % by weight of the total soap being saturated material,
- (ii) nitrilotriacetic acid or a water-soluble salt thereof,

the weight ratio of (i) to (ii) being from 3 : 1 to 1 : 1.

2. A detergent composition as claimed in Claim 1, characterised in that it comprises:

- (a) from 17 to 47 % by weight of the aluminosilicate,
- (b) (i) up to 20 % by weight of the soap, and
- (b) (ii) from 2 to 10 % by weight of the nitrilotriacetic acid or salt.

3. A detergent composition as claimed in Claim 1 or Claim 2, characterised in that at least 80 % by weight of the soap (i) is saturated material.

4. A detergent composition as claimed in Claim 3, characterised in that the soap (i) consists substantially wholly of saturated material.

5. A detergent composition as claimed in any one of Claims 1 to 4, characterised in that the soap (i) contains at least 5 % by weight of material having a chain length of C₁₈ and above and at least 1 % of material having a chain length of C₁₄ and below.

6. A detergent composition as claimed in Claim 5, characterised in that the soap (i) contains at least 60 % by weight of material having a chain length of C₁₈ and above and at least 1 % of material having a chain length of C₁₄ and below.

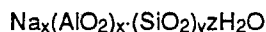
7. A detergent composition as claimed in Claim 6, characterised in that the soap (i) comprises hardened tallow soap and/or hardened rapeseed soap.

8. A detergent composition as claimed in Claim 5, characterised in that the soap (i) contains at least 60 % of material having a chain length of C₁₄ and below and at least 5 % material having a chain length of C₁₈ and above.

9. A detergent composition as claimed in Claim 8, characterised in that soap (i) comprises coconut soap and/or palm kernel soap.

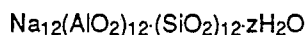
10. A detergent composition as claimed in any one of Claims 1 to 8, characterised in that (ii) is an alkali metal salt of nitrilotriacetic acid.

11. A detergent composition as claimed in any one of Claims 1 to 10, characterised in that the aluminosilicate cation exchange material is a crystalline material having a unit cell of the formula



where x and y are integers of at least 6, the ratio of x to y being in the range of 1 : 1 to 1 : 2; and z is such that the bound water content is from 10 % to 28 % by weight.

12. A detergent composition as claimed in Claim 11, characterised in that the aluminosilicate cation exchange material is a crystalline material having a unit cell of the formula



wherein x is from 20 to 30.

13. A detergent composition as claimed in any one of Claims 1 to 12, characterised in that the ternary builder system contains from 20 to 50 % by weight of component (b), based on the ternary builder system.

14. A detergent composition as claimed in any preceding claim, characterised in that it contains from 5 to 40 % by weight of composition (b), based on the composition.

15. A detergent composition as claimed in any preceding Claim, characterised in that it contains not more than 10 % by weight of inorganic phosphate.

Patentansprüche

1. Detergengzusammensetzung umfassend ein synthetisches Detergens-aktives Material, ein kristallines oder amorphes Aluminosilicat-Kationenaustauschmaterial und einen organischen Builder, dadurch gekennzeichnet, daß sie 25 bis 70 Gew.-% eines ternären Buildersystems umfaßt, bestehend aus:

(a) wenigstens 25 Gew.-% des kristallinen oder amorphen Aluminosilicat-Kationenaustauschmaterials,
(b) der Rest bestehend aus:

(i) wenigstens 15 Gew.-%, basierend auf (a) plus (b), einer oder mehrerer wasser-löslichen Seifen von C₈-C₂₂-Fettsäuren, wobei wenigstens 60 Gew.-% der gesamten Seife gesättigtes Material ist,
(ii) Nitrilotriessigsäure oder ein wasser-lösliches Salz davon,

wobei das Gewichtsverhältnis von (i) zu (ii) 3 : 1 bis 1 : 1 ist.

2. Detergengzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie umfaßt:

(a) 17 bis 47 Gew.-% des Aluminosilicats,
(b) (i) bis zu 20 Gew.-% der Seife, und
(b) (ii) 2 bis 10 Gew.-% der Nitrilotriessigsäure oder des Salzes.

3. Detergengzusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß wenigstens 80 Gew.-% der Seife (i) gesättigtes Material ist.

4. Detergengzusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß die Seife (i) im wesentlichen ganz aus gesättigtem Material besteht.

5. Detergengzusammensetzung nach irgend einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die Seife (i) wenigstens 5 Gew.-% Material mit einer Kettenlänge von C₁₈ und darüber und wenigstens 1 % Material mit einer Kettenlänge von C₁₄ und darunter enthält.

6. Detergengzusammensetzung nach Anspruch 5, dadurch gekennzeichnet, daß die Seife (i) wenigstens 60 Gew.-% Material mit einer Kettenlänge von C₁₈ und darüber und wenigstens 1 % Material mit einer Kettenlänge von C₁₄ und darunter enthält.

7. Detergengzusammensetzung nach Anspruch 6, dadurch gekennzeichnet, daß die Seife (i) gehärtete Talgseife und/oder gehärtete Rapssamenseife umfaßt.

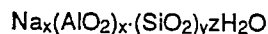
8. Detergengzusammensetzung nach Anspruch 5, dadurch gekennzeichnet, daß die Seife (i) wenigstens 60 % Material mit einer Kettenlänge von C₁₄ und darunter und wenigstens 5 % Material mit einer Kettenlänge von C₁₈ und darüber enthält.

9. Detergengzusammensetzung nach Anspruch 8, dadurch gekennzeichnet, daß die Seife (i) Kokosnußseife und/oder

Palmkernseife umfaßt.

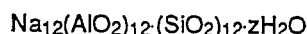
10. Detergengzusammensetzung nach irgend einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß (ii) ein Alkalimetallsalz von Nitrilotriessigsäure ist.

11. Detergengzusammensetzung nach irgend einem der Ansprüche 1 bis 10, dadurch gekennzeichnet, daß das Aluminosilicat-Kationenaustauschmaterial ein kristallines Material mit einer Einheitszelle der Formel



ist, worin x und y ganze Zahlen von wenigstens 6 sind, das Verhältnis von x zu y im Bereich von 1 : 1 bis 1 : 2 ist und z so ist, daß der Gehalt an gebundenem Wasser von 10 bis 28 Gew.-% ist.

12. Detergengzusammensetzung nach Anspruch 11, dadurch gekennzeichnet, daß das Aluminosilicat-Kationenaustauschmaterial ein kristallines Material mit einer Einheitszelle der Formel



ist, worin z 20 bis 30 ist.

13. Detergengzusammensetzung nach irgend einem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß das ternäre Buildersystem 20 bis 50 Gew.-% der Komponente (b), basierend auf dem ternären Buildersystem, enthält.

14. Detergengzusammensetzung nach irgend einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie 5 bis 40 Gew.-% der Komponente (b), basierend auf der Zusammensetzung, enthält.

15. Detergengzusammensetzung nach irgend einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie nicht mehr als 10 Gew.-% anorganisches Phosphat enthält.

Revendications

1. Une composition détergente comprenant une matière active détergente, une matière échangeuse de cations de type aluminosilicate cristalline ou amorphe et un adjuvant de détergence organique, caractérisée en ce qu'elle comprend:

(a) au moins 25 % en poids de la matière échangeuse de cations de type aluminosilicate cristalline ou amorphe,
(b) le complément consistant en:

(i) au moins 15 % en poids, par rapport au poids total de (a) plus (b), d'un ou plusieurs savons solubles dans l'eau d'acides gras en C_8 - C_{22} , au moins 60 % du poids du savon total étant une matière saturée, et
(ii) l'acide nitrilotriacétique ou un de ses sels solubles dans l'eau,

le rapport pondéral de (i) à (ii) étant de 3/1 à 1/1.

2. Une composition détergente comme revendiquée dans la revendication 1, caractérisée en ce qu'elle comprend:

(a) de 17 à 47 % en poids d'aluminosilicate
(b) (i) jusqu'à 20 % en poids de savon et
(ii) de 2 à 10 % en poids d'acide nitrilotriacétique ou un de ses sels.

3. Une composition détergente comme revendiquée dans la revendication 1 ou la revendication 2, caractérisée en ce qu'au moins 80 % en poids du savon (i) est une matière saturée.

4. Une composition détergente comme revendiquée dans la revendication 3, caractérisée en ce que le savon (i) est constitué essentiellement en totalité de matière saturée.

5. Une composition détergente comme revendiquée dans l'une quelconque des revendications 1 à 4, caractérisée en ce que le savon (i) contient au moins 5 % en poids de matière ayant une longueur de chaîne de C_{18} et plus et au moins 1 % de matière ayant une longueur de chaîne de C_{14} et moins.

6. Une composition détergente comme revendiquée dans la revendication 5, caractérisée en ce que le savon (i) contient au moins 60 % en poids de matière ayant une longueur de chaîne de C_{18} et plus et au moins 1 % d'une matière ayant une longueur de chaîne de C_{14} et moins.

7. Une composition détergente comme revendiquée dans la revendication 6, caractérisée en ce que le savon (i) est

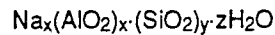
constitué de savon de suif durci et/ou de savon de colza durci.

5 8. Une composition détergente comme revendiquée dans la revendication 5, caractérisée en ce que le savon (i) contient au moins 60 % de matière ayant une longueur de chaîne de C₁₄ et moins et au moins 5 % de matière ayant une longueur de chaîne de C₁₈ et plus.

9. Une composition détergente comme revendiquée dans la revendication 8, caractérisée en ce que le savon (i) comprend du savon de coprah et/ou du savon de palmiste.

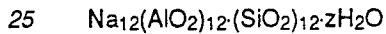
10 10. Une composition détergente comme revendiquée dans l'une quelconque des revendications 1 à 9, caractérisée en ce que (ii) est un sel de métal alcalin de l'acide nitrilotriacétique.

15 11. Une composition détergente comme revendiquée dans l'une quelconque des revendications 1 à 10, caractérisée en ce que la matière échangeuse de cations de type aluminosilicate est une matière cristalline ayant une maille de formule:



20 dans laquelle x et y sont des entiers supérieurs ou égaux à 6, le rapport de x à y étant dans la gamme de 1/1 à 1/2, et z est tel que la teneur en eau liée est de 10 % à 28 % en poids.

12. Une composition détergente comme revendiquée dans la revendication 11, caractérisée en ce que la matière échangeuse de cations de type aluminosilicate est une matière cristalline ayant une maille de formule



dans laquelle z est de 20 à 30.

30 13. Une composition détergente comme revendiquée dans l'une quelconque des revendications 1 à 12, caractérisée en ce que le système adjuvant ternaire contient de 20 à 50 % en poids du composant (b), par rapport au poids du système adjuvant ternaire.

35 14. Une composition détergente comme revendiquée dans l'une quelconque des revendications 1 à 13, caractérisée en ce qu'il contient de 5 à 40 % en poids du composant (b) par rapport au poids de la composition.

15. Une composition détergente comme revendiquée dans l'une quelconque des revendications précédentes, caractérisée en ce qu'elle ne contient pas plus de 10 % en poids de phosphate minéral.

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