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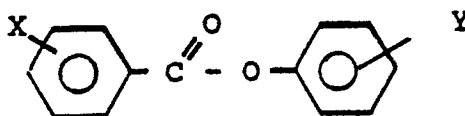
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54 **Aluminosilicate built detergent bleach compositions.**

57 A phosphate-free aluminosilicate built detergent bleach composition having really effective cleaning and stain removal performances at lower wash temperatures of 40°C and below, which composition comprises at least one detergent-active material, from 15% to about 40% by weight of a water-insoluble aluminosilicate cation exchange material, from 0.5% to about 3% by weight of a polyphosphonate compound, from 5% to about 35% by weight of an inorganic peroxide compound and from about 1% to about 10% by weight of a peroxybenzoic acid bleach precursor having the formula:



wherein X is H, NO₂, C₁-C₄ straight or branched chain alkyl, Cl or Br; and Y is H, CO₂⁻M⁺, SO₃⁻M⁺

$\text{SO}_4^{2-}\text{M}^+$, NO_2 , Cl or Br; M being a water-soluble cation.

ALUMINOSILICATE BUILT DETERGENT BLEACH COMPOSITIONS

The invention relates to phosphate-free detergent bleach compositions. In particular it relates to aluminosilicate built laundry detergent bleach compositions having improved cleaning and stain-removal performances, effective at low washing temperatures.

5 The role and value of phosphate detergency builders in laundry detergent compositions are well-known. In recent years, however, the use of phosphate builders, such as the alkali metal triphosphates, has come under scrutiny because of the suspicion that soluble phosphate species accelerate the eutrophication of water bodies. In a number of countries phosphate legislations have already forced detergent manufacturers to radically reduce the phosphate level of detergent compositions down to substantially zero. The need
10 exists, therefore, for a built laundry detergent composition with zero phosphate level but which is comparable to a conventional triphosphate built composition in overall detergency effectiveness.

Furthermore, with the present trend to lower fabric washing temperatures, there is an incentive to improve on the formulations of detergent compositions so as to be effective at lower washing temperatures of e.g. 40° C and below.

15 Water-insoluble aluminosilicates, commonly known as zeolites, have been used in detergent compositions as important alternative builders to phosphates (see, for example, GB-A-1429143; GB-A-1470250; GB-A-1504211; GB-A-1529454 and US-A-4064062). Bleaching experiments have indicated, however, that the bleach performances of aluminosilicate built formulations are well below those of phosphate built products.

In EP-A-70079 it has been proposed to improve activated persalt bleach performance in aluminosilicate
20 built compositions by addition thereto of a nitrilotriacetic acid compound (NTA). Apart from the still existing uncertainty around the use of NTA in various countries with regard to environmental consequences, the compositions as disclosed in EP-A-70079 are not particularly effective at temperatures around 40° C and below.

It is an object of the present invention to provide an improved phosphate-free aluminosilicate built
25 detergent composition having really effective cleaning and stain-removal performances at low wash temperatures of 40° C and below without the above drawbacks.

It has now been found that the above object can be achieved if the bleach system used therein comprises an inorganic peroxide compound and a peroxybenzoic acid bleach precursor as defined hereinafter combined with at least 0.5% by weight of a polyphosphonate sequestering agent.

30 Polyphosphonates have already been suggested for use in detergent compositions containing aluminosilicates. For example, German Offenlegungsschrift 2,544,035; 2,539,071; 2,527,388; 2,559,631 and Austrian Patent N° 338,947 all disclose the use of various polyphosphonates notably as dispersing agents in aluminosilicate built products.

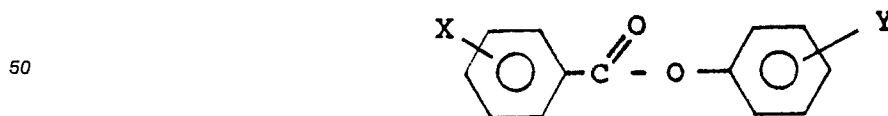
GB Patent 1,392,284 and GB Patent Application 2,113,730 discloses polyphosphonates, particularly
35 ethylene diamine tetra methylene phosphonic acid, as peroxide bleach stabilizer.

In EP-B-0001853 aluminosilicate built detergent compositions are disclosed which contain 0.01-4% by weight of a polyphosphonate sequestering agent and 5-25% by weight of citric acid, citrates or a bicarbonate as pH-regulating agent. These compositions still contain a phosphate builder and are further-
40 more unsatisfactory when used for washing at the low wash temperature region of 40° C and below.

The detergent composition of the invention necessarily contains a peroxybenzoic acid bleach precursor as the bleach activator, which on perhydrolysis generates a peroxybenzoic acid. Other bleach precursors, such as the most commonly used tetraacetylene diamine (TAED), which generates peracetic acid, are much less effective and hence unsuitable for use in the present invention.

Peroxybenzoic acid precursors are known in the art, e.g. from GB-A-836988. Examples thereof are
45 phenylbenzoate; phenyl p-nitrobenzoate; o-nitrophenyl benzoate; o-carboxyphenyl benzoate; p-bromophenyl benzoate; sodium or potassium benzoxyloxy benzenesulphonate; and benzoic anhydride.

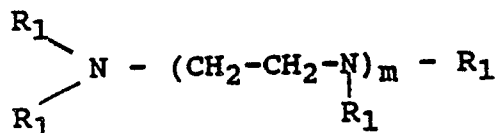
The peroxybenzoic acid precursor compounds usable in the present invention have the formula:



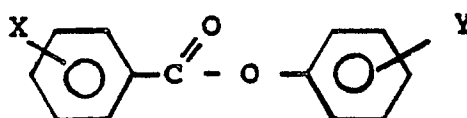
wherein X is H, NO₂, C₁-C₄ straight or branched chain alkyl, Cl or Br; and Y is H, CO₂⁻ M⁺, SO₃⁻ M⁺, SO₄

M^+ , NO_2 , Cl or Br; M being a water-soluble cation, preferably alkali metal cation, particularly Na^+ or K^+ .

Accordingly, the invention provides a phosphate-free detergent bleach composition comprising at least one detergent-active material in an amount of 5% to 40% by weight, a water-insoluble aluminosilicate cation exchange material as main builder in an amount of from 15% to about 40% by weight, and from 0.5% to about 3% by weight of a polyphosphonate compound of the formula:



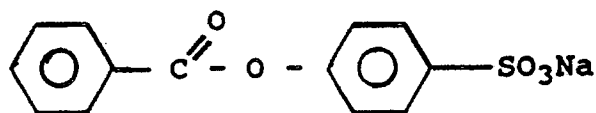
wherein each R_1 is $\text{CH}_2\text{PO}_3\text{H}_2$ or a water-soluble salt thereof, and m is an integer having the value of 0, 1 or 2, characterized in that the composition further contains from about 5% to about 35% by weight of an inorganic peroxide compound, and from about 1% to about 10% by weight of a peroxy benzoic acid bleach precursor having the formula:



wherein X is H, NO_2 , C_1 - C_4 straight or branched chain alkyl, Cl or Br; and Y is H, CO_2M^+ , SO_3M^+ , SO_4M^+ , NO_2 , Cl or Br; M being a water-soluble cation.

It is this unique combination of said class of peroxybenzoic acid bleach precursor with the polyphosphonate sequestering agent underlying the invention that provides for the surprising enhancement of the low temperature bleach performance of aluminosilicate built formulations without the need of phosphate builder.

A preferred peroxybenzoic acid bleach precursor is sodium p-benzoyloxy benzenesulphonate of the formula :



Another preferred peroxybenzoic acid bleach precursor is p-tert-butyl benzoyloxy benzenesulphonate.

The inorganic peroxide compounds usable in the present invention can be true persalts or perhydrates, which liberate hydrogen peroxide in aqueous solution. Examples of inorganic peroxide compounds are the alkali metal perborates, percarbonates, perphosphates and persilicates, the perborates, particularly sodium perborate tetra- and monohydrate being preferred because of their commercial availability.

Within the above ranges of weight percentages, the inorganic peroxide compound and the peroxybenzoic acid bleach precursor in the composition of the invention may be present in a molar ratio of between 0.5:1 and about 20:1, preferably from 1:1 to 10:1. Under certain wash conditions such as are commonly used in the U.S.A. a molar ratio of about 2:1 may be of advantage.

The composition of the invention contains at least one detergent-active material which can be an organic soap or synthetic detergent surfactant material. Generally, from about 5% to 40% by weight of an organic, anionic, nonionic, amphoteric or zwitterionic detergent compound, soap, or mixtures thereof is included. Many suitable detergent-active compounds are commercially available and are fully described in literature, for example in US-A-4222905 and US-A-4239659 and in "Surface Active Agents and Detergents", Vol. I and II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds which can be used are synthetic anionic, soap and nonionic compounds. The first-mentioned 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_{20}) alcohols produced, for example, from tallow or coconut oil; sodium and potassium alkyl (C_9 - C_{20})

benzene sulphonates, particularly sodium linear secondary alkyl (C₁₀-C₁₅) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those esters 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 (C₉-C₁₈) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphates 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 hydrolyzing with a base to produce a random sulphonate; olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C₁₀-C₂₀ alpha-olefins, with SO₃ and then neutralizing and hydrolyzing the reaction product. Suitable soaps are the alkali metal salts of long chain C₈-C₂₂ fatty acids such as the sodium soaps of tallow, coconut oil, palmkernel oil, palm oil or hardened rapeseed oil fatty acids or mixtures thereof. The preferred anionic detergent compounds are sodium (C₁₁-C₁₅) alkyl benzene sulphonates and sodium (C₁₅-C₁₈) alkyl sulphates.

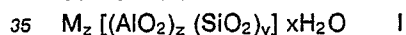
Examples of suitable nonionic detergent compounds which may be used include the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C₆-C₂₂) phenols, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C₈-C₁₈) primary or 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 ethylene diamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulfoxides.

Mixtures of detergent-active 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.

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

The detergent composition of the invention also contains a water-insoluble aluminosilicate cation-exchange material in an amount of from 15% to about 40% by weight, preferably from 20% to 35% by weight.

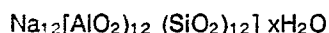
The aluminosilicate can be crystalline or amorphous in character, preferred materials having the unit cell formula I:



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

The aluminosilicate ion-exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns, preferably from about 0.2 micron to about 4 microns. 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 herein are usually further characterized by their calcium ion-exchange capacity, which is at least about 200 mg. equivalent of CaCO₃ water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion-exchange materials herein are still further characterized by their calcium ion-exchange rate which is at least about 2 grains Ca⁺⁺/gallon/minute/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from about 2 grains/ gallon/minute/gram/gallon to about 6 grains/gallon/minute/gram/gallon, based on calcium ion hardness. Optimum aluminosilicates for builder purposes exhibit a calcium ion-exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

Aluminosilicate ion-exchange materials useful in the practice of this invention are commercially available and can be naturally occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion-exchange materials is discussed in US-A-3985669. 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 about 20 to about 30, especially about 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 $\text{Na}_6 [(\text{AlO}_2)_6 (\text{SiO}_2)_6] \cdot 7.5 \text{H}_2\text{O}$.

The polyphosphonate compounds usable in the present invention are as defined hereinbefore. Effectively, the amount of polyphosphonate compound in the composition is from 0.5% to about 3% by weight. Amounts of lower than 0.5% are inadequate to give the desired benefit, and levels of higher than 3% by weight will give no added benefit. A preferred level of polyphosphonate compound is from 1% to 2% by weight of the composition.

Suitable polyphosphonate compounds are, for example, aminotri(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid) and diethylene triamine penta(methylene phosphonic acid).

A preferred polyphosphonate compound is ethylene diamine tetra(methylene phosphonic acid) or its water-soluble salts, known as EDTMP, which is preferably used in the form of its calcium complex, i.e. $\text{Ca}_n\text{-EDTMP}$ (n being from 1-3), as disclosed in US-A-4,259,200.

Preferably, the composition of the invention will also include an enzyme, particularly proteolytic enzymes. Suitable proteolytic enzymes are normally solid, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the composition of the present invention. Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*, such as the commercially available subtilisins Maxatase®, as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase®, as supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of *Bacillus* having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade names Esperase® and Savinase®. The preparation of these and analogous enzymes is described in British Patent Specification No 1,243,784.

The amount of proteolytic enzymes used in the composition of the invention ranges from 0.001% to 10% by weight, preferably from 0.01% to 5% by weight, depending upon their activity. They are generally incorporated in the form of granules, prills or "marumes" in an amount such that the final washing product has a proteolytic activity of from about 2-20 Anson units per kilogram of final product.

Apart from the components already mentioned, the detergent composition herein can contain any of the conventional additives and adjuncts in the amounts in which such materials are normally employed in fabric washing compositions. Examples of such additives include lather boosters such as alkanolamides, particularly the monoethanolamides derived from palmkernel and coconut fatty acids; lather depressants such as alkyl phosphates, silicones and waxes; anti-redeposition agents such as sodium carboxymethyl cellulose (SCMC), polyvinyl pyrrolidone (PVP) and the cellulose ethers such as methylcellulose and ethyl hydroxyethyl cellulose; stabilizers such as ethylene diamine tetraacetate; fabric-softening agents; inorganic salts such as sodium sulphate and sodium carbonate; and - usually present in very minor amounts - fluorescent agents, perfumes, other enzymes such as proteases, amylases and lipases; germicides and colourants.

Polycarboxylate polymers, though not essential, may also be included as desired in amounts of from e.g. about 0.5% to 6% by weight of the total composition. The polycarboxylate polymers herein are preferably selected from co-polymeric polycarboxylic acids and their salts derived from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid or mesaconic acid as a first monomer and ethylene, methyl vinyl ether, acrylic acid or metacrylic acid as a second monomer, the co-polymer comprising at least about 10 mole%, preferably at least about 20 mole% of polycarboxylic acid units and having weight average molecular weights of at least about 10,000, preferably at least about 30,000; homopolyacrylates and homopolymethacrylates having a weight average molecular weight of from about 1000 to about 100,000, preferably from about 5000 to about 50,000; and mixtures thereof.

The detergent compositions of the invention are preferably presented in free-flowing particulate, e.g. powdered or granular form, and can be produced by any of the known techniques commonly employed in the manufacture of such washing compositions, but preferably by spray-drying an aqueous slurry comprising the surfactant(s) and the aluminosilicate to form a detergent base powder, to which the heat-sensitive ingredients are added, including the perbenzoic acid bleach precursor, the inorganic percompound, enzymes and optionally some other ingredients as conveniently desirable. The polyphosphonate compound may be present in the base powder, but is preferably added as calcium phosphonate to the spray-dried base powder. The bleach precursor and enzymes are preferably added as granulated particles. It is

preferred that the process used to form the compositions should result in a product having a moisture content of up to about 15%, more preferably from about 7% to about 14% by weight.

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

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Example I

The following particulate non-phosphate detergent composition was prepared by spray-drying an aqueous detergent slurry to form a detergent base powder composition (A) which is combined with a particulate product composition (B).

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Composition A	Parts by weight
Sodium linear alkylbenzene sulphonate	9.0
Fatty alcohol-7 ethoxylate	1.5
Maleic acid/acrylic acid copolymer (Sokalan ® CP5 ex BASF)	4.0
Sodium aluminosilicate (Zeolite A)	24.0
Sodium sulphate (anhydrous)	0.3
Sodium carboxymethyl cellulose	0.5
Sodium ethylenediamine tetraacetate (EDTA)	0.2
Sodium carbonate (Na ₂ CO ₃)	2.0
Water and fluorescer (0.13)	7.6
Composition (B)	
Sodium perborate monohydrate	13.0
Anti-foaming agent	2.5
Proteolytic enzyme (Savinase ex NOVO)	0.5
Sodium p-benzoyloxy benzene sulphonate	5.0
Sodium sulphate	29.6

Washing experiments were carried out with this composition without and with added tricalcium complex of EDTMP at a level of 1% by weight in 30 minutes' Tergotometer washes using a dosage of 8 gram/litre in 24 ° FH water at 40 ° C, buffered at pH 8.5.

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The bleaching properties on tea and red-wine stains, detergency and protein stain removal (enzyme action) were measured; the results are given in Table I.

Table I

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	ΔR values			
	Tea	Wine	Detergency	Protein stains
Composition A/B	8.1	24.5	25.6	34.2
" + 1% Ca ₃ EDTMP	14.1	36.8	26.4	27.5

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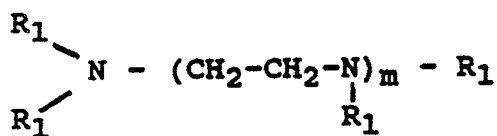
In practice the Ca₃EDTMP can be incorporated in either composition A or composition B, which may be separately packed in two unit sachets or in a two-compartment unit sachet or presented as a combined fully formulated powder composition.

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Claims

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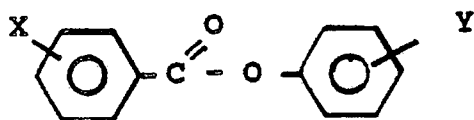
1. A phosphate-free aluminosilicate built detergent bleach composition comprising at least one detergent-active material in an amount of 5% to 40% by weight, a water-insoluble aluminosilicate cation exchange material as main builder in an amount of from 15% to about 40% by weight, and from 0.5% to about 3% by weight of a polyphosphonate compound of the formula:



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wherein each R_1 is $CH_2PO_3H_2$ or a water-soluble salt thereof, and m is an integer having the value of 0, 1 or 2, characterized in that the composition further contains from about 5% to about 35% by weight of an inorganic peroxide compound, and from about 1% to about 10% by weight of a peroxy benzoic acid bleach precursor having the formula:

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wherein X is H , NO_2 , C_1 - C_4 straight or branched chain alkyl, Cl or Br ; and Y is H , $CO_2^-M^+$, $SO_3^-M^+$, $SO_4^-M^+$, NO_2 , Cl or Br ; M being a water-soluble cation.

2. A composition according to claim 1, characterized in that it further contains a proteolytic enzyme in an amount such that the washing product has a proteolytic activity of from about 2 to 20 Anson units per kilogram of product.

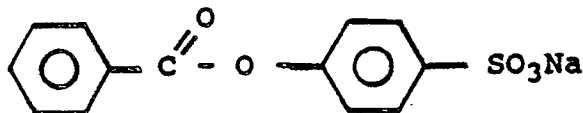
3. A composition according to claim 1 or 2, characterized in that said polyphosphonate compound is present in an amount of 1% to 2% by weight of the composition.

4. A composition according to claim 1, 2 or 3, characterized in that said polyphosphonate compound is ethylene diamine tetra (methylene phosphonic acid) or its water-soluble salt.

5. A composition according to claim 4, characterized in that said ethylene diamine tetra (methylene phosphonic acid) is present in the form of its calcium complex.

6. A composition according to any of the above claims, characterized in that said peroxybenzoic acid bleach precursor is sodium-p-benzoyloxy benzene sulphonate of the formula:

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7. A composition according to any one of the above claims 1-6, characterized in that said aluminosilicate cation exchange material is a zeolite selected from the group consisting of Zeolite A, Zeolite B, Zeolite X, Zeolite HS and mixtures thereof.

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