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Non-phosphorus detergent bleach compositions.

Non-phosphorus aluminosilicate built detergent bleach composition having really effective cleaning and stain removal performances at low wash temperatures of 40°C and below, comprising at least one detergent-active material selected from anionic, nonionic, amphoteric, zwitterionic detergent compounds and soaps and mixtures thereof, and

- (a) from about 15% to about 40% by weight of a water-insoluble aluminosilicate cation-exchange material;
- (b) from about 1% to about 15% by weight of citric acid or an alkali metal citrate;
- (c) from about 5% to about 35% by weight of an inorganic peroxide compound; and
- (d) from about 1% to about 10% by weight of a peroxybenzoic acid bleach precursor.

EP 0 313 144 A2

NON-PHOSPHORUS DETERGENT BLEACH COMPOSITIONS

This invention relates to non-phosphorus detergent bleach compositions. In particular it relates to aluminosilicate built laundry detergent bleach compositions having improved cleaning and stain-removal performances.

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 exists, therefore, for a built laundry detergent composition with zero or reduced phosphate levels 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.

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-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 or citrates as pH-regulating agent. These compositions are unsatisfactory when used for washing at the low wash temperature region of 40° C and below.

It is an object of the present invention to provide an improved aluminosilicate built detergent composition having really effective cleaning and stain-removal performances at low wash temperatures of 40° C and below.

It has now been found that the above object can be achieved by having incorporated therein an inorganic peroxide compound and a peroxybenzoic acid bleach precursor as the principal bleach system together with citric acid or an alkali metal citrate.

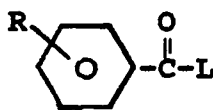
Thus, according to the invention, there is provided a non-phosphorus detergent bleach composition comprising at least one detergent-active material and :

- (a) from about 15% to about 40% by weight of a water-insoluble aluminosilicate cation-exchange material;
- (b) from about 1% to about 15% by weight of citric acid or an alkali metal citrate;
- (c) from about 5% to about 35% by weight of an inorganic peroxide compound; and
- (d) from about 1% to about 10% of a peroxybenzoic acid bleach precursor.

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 phenylbenzoate; phenyl p-nitrobenzoate; o-nitrophenyl benzoate; o-carboxyphenyl benzoate; p-bromophenyl benzoate; sodium or potassium benzoyloxybenzenesulphonate; and benzoic anhydride.

The compounds have the general formula :

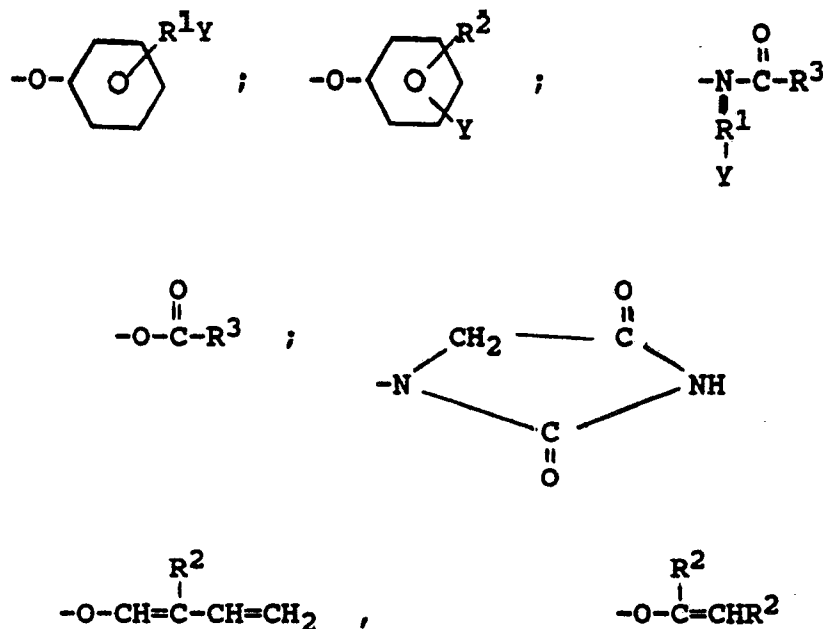


wherein R is H or a substituent selected from -NO₂ and halogens, and L is a leaving group, the conjugate acid of which has a pKa in the range of from about 6 to about 13.

L can be essentially any suitable leaving group that is displaced from the bleach precursor as a consequence of the nucleophilic attack on the bleach precursor by the perhydroxide anion, HOO⁻. This

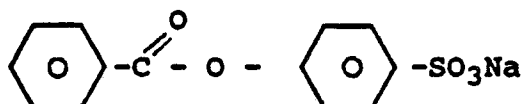
perhydrolysis reaction results in the formation of the peroxybenzoic acid. Generally, for a group to be a suitable leaving group, it must exert an electron-attracting effect, which facilitates the nucleophilic attack by the perhydroxide anion. Leaving groups that exhibit such behaviour are those in which their conjugate acid has a pKa in the range of from 6 to 13, preferably from about 7 to about 11, and most preferably from 8 to 11.

Examples of suitable L are :



wherein R¹ is an alkylene chain containing from 1 to 8 carbon atoms; R² is H or an alkyl chain containing from 1 to 8 carbon atoms; R³ is phenyl or an alkyl chain containing from 5 to 18 carbon atoms; and Y is a solubilizing group, preferably selected from $-\text{SO}_3^-\text{M}^+$, $-\text{COO}^-\text{M}^+$ or $-\text{SO}_4^-\text{M}^+$.

A preferred peroxybenzoic acid bleach precursor is sodium p-benzoyloxybenzene sulphonate of the formula :



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, and persulfates, 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 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 -

C₁₈) alcohols produced, for example, from tallow or coconut oil; sodium and potassium alkyl (C₉-C₂₀) 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 sulphoxides.

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

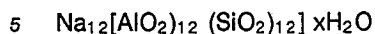


wherein M is a calcium-exchange cation, z and y are at least 6; the molar ratio of z to y is from about 1.0 to about 0.5 and x is at least 5, preferably from about 7.5 to about 276, more preferably from about 10 to about 264. The aluminosilicate materials are in hydrated form and are preferably crystalline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

umino-silicate 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 detergent composition of the invention further contains an alkali metal citrate or citric acid in an amount of from about 1% to about 15%, preferably from 2 to 10%, by weight of the composition. A preferred alkali metal citrate is sodium citrate, particularly trisodium citrate, i.e. $\text{C}_6\text{H}_5\text{O}_7 \cdot \text{Na}_3 \cdot 2\text{H}_2\text{O}$.

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, enzymes such as proteases, amylases and lipases; germicides and colourants.

Polycarboxylate polymers, though not essential, may also be included as desired in amounts of e.g. from 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 10,000, preferably from about 5000 to about 50,000; and mixtures thereof.

The detergent bleach compositions of the invention are alkaline and will advantageously have a solution pH (2-10 g/l) of from 8-11, with an optimal pH of between 8 and 9. A wash pH of, say, 8.5 appears to give the best compromise for achieving good bleaching, detergency and enzymatic soil removal. In order to adjust the pH, buffering agents, such as borax, may be necessary.

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), the aluminosilicate and the alkali metal citrate to form a detergent base powder, to which the heat-sensitive ingredients, including the peroxybenzoic acid bleach precursor, the inorganic percompound, enzymes and optionally some other ingredients as conveniently desirable are added.

Alternatively, the alkali metal citrate can be separately dry-mixed with 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.

Example 1

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).

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	29.9

Washing experiments were carried out with this combined composition without and with added trisodium citrate at levels of 0%, 1%, 2%, 3%, 5%, 10% 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.

The bleaching properties on tea and red-wine stains were measured; the results are given in Table I.

Table I

		ΔR values	
		Tea	Wine
Composition A/B	+ 0% citrate	6.4	20.1
"	+ 1% citrate	8.2	26.3
"	+ 2% citrate	9.6	29.9
"	+ 3% citrate	11.7	32.0
"	+ 5% citrate	13.2	33.9
"	+ 10% citrate	14.4	35.7

Example II

Similar comparative experiments were carried out on tea and red-wine stains, detergency and protein stain removal (enzyme action); the results are shown in Table 2.

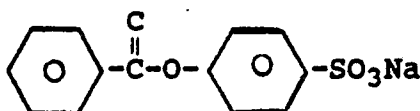
TABLE 2

		ΔR-values			
		Tea	Wine	Detergency	Protein stains
Composition A/B	+ 0% citrate	8.1	24.5	25.6	34.2
"	+ 5% citrate	13.8	32.6	26.3	34.8

From the above results it can be seen that trisodium citrate boosts the bleach performances on tea and wine stains without a negative effect on detergency and enzyme action, i.e. protein soil removal.

Claims

1. A non-phosphorus detergent bleach composition comprising at least one detergent-active material and
- 5 (a) from about 15% to 40% by weight of a water-insoluble aluminosilicate cation-exchange material;
- (b) from about 1% to 15% by weight of citric acid or an alkali metal citrate;
- (c) from about 5% to 35% by weight of an inorganic peroxide compound; and
- (d) from about 1% to 10% by weight of a peroxybenzoic acid bleach precursor.
- 10 2. A composition according to Claim 1, characterized in that it contains :
- from 5 to 40% by weight of said detergent-active material selected from the group consisting of anionic, nonionic, amphoteric, zwitterionic detergent compounds, and soaps and mixtures thereof;
 - from 20 to 35% by weight of said aluminosilicate cation-exchange material; and
 - from 2 to 10% by weight of said citric acid or alkali metal citrate.
- 15 3. A composition according to Claim 1 or 2, characterized in that said peroxybenzoic acid precursor is sodium-p-benzoyloxybenzene sulphonate of the formula :



4. A composition according to Claim 1, 2 or 3, characterized in that said alkali metal citrate is trisodium
- 25 citrate.
5. A composition according to Claim 1, 2, 3 or 4, characterized in that said composition has a solution pH (at 2-10 g/l) of 8-11.
6. A composition according to Claim 5, characterized in that said solution pH is between 8 and 9.

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