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(71) Applicant: UNILEVER NV
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

(84) CH DE ES FR IT LI NL SE

(71) Applicant: UNILEVER PLC
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)

(84) GB

(72) Inventor: Emery, Wiliam Derek
64 Plymyard Avenue Bromborough
Wirral Merseyside L62 6BP(GB)
Inventor: Barnes, Stephen George
7 Vernon Avenue Hooton
South Wirral L66 6AL(GB)
Inventor: Sims, Peter Stanford
71 Dee Banks Chester
Cheshire, CH3 5UX(GB)

(74) Representative: Tan, Bian An, Ir. et al
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

(54) Non-phosphorus detergent bleach compositions.

(57) Non-phosphorus aluminosilicate built detergent bleach compositions having really effective cleaning and stain-removal performances at low wash temperatures of 40° C and below comprise 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; and

(c) from about 1% to about 15% by weight of a solid organic peroxyacid.

EP 0 313 143 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).

In EP-B-0001853 aluminosilicate built detergent compositions are described 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 temperature region of 40° C and below.

It is known that organic peroxyacids as a class are effective bleaching agents in the lower temperature region of, say, 40°-60° C. Bleaching experiments have indicated that organic peroxyacids, e.g. 1,2-diperoxydodecanedioic acid, provide effective bleaching and stain removal at 40° C in a phosphate-built detergent formulation but, remarkably, they are much less effective in a non-phosphate, aluminosilicate built detergent composition.

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 using a solid organic peroxyacid compound as principal bleaching agent 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 materials;

(b) from about 1% to about 15% by weight of citric acid or an alkali metal citrate; and

(c) from about 1% to about 15% by weight of a solid organic peroxyacid compound;

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_{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 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 (C_9-C_{18}) 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 (C_8-C_{20}) with sodium bisulphate and those derived by reacting paraffins with SO_2 and Cl_2 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 C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolyzing the reaction product. Suitable soaps are the alkali metal salts of long chain C_8-C_{22} 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 (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

Examples of suitable nonionic detergent compounds which may be used include the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6-C_{22}) phenols, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8-C_{18}) 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

$$M_z\,[(AlO_2)_z\,(SiO_2)_y]\,xH_2O \qquad I$$

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 $CaCO_3$ water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion- exchange materials herein are still further characterized by their calcium ion- exchange rate which is at least about 2 grains Ca^{++}/gallon/minute/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

$$Na_{12}[(AlO_2)_{12}\,(SiO_2)_{12}]\,xH_2O$$

wherein x is from about 20 to about 30, especially about 27. Zeolite X of formula Na_{86} [$(AlO_2)86)(SiO_2)_{106}$] .276 H_2O is also suitable, as well as Zeolite HS of formula Na_6 [$(AlO_2)_6$ $(SiO_2)_6$] 7.5 H_2O).

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. $C_6H_5O_7.Na_3.2H_2O$.

A further essential component of the compositions herein is from about 1% to about 15% by weight, preferably from 2% to 8% by weight of a solid organic peroxyacid compound. The organic peroxyacid compounds used in the present invention are solid at room temperature and should preferably have a melting point of at least 50° C.

Such peroxyacid compounds are the organic peroxyacids and water-soluble salts thereof having the general formula:

$$HO\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}R\text{-}Y,$$

wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms, and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution. Such Y groups can include, for example:

$$-\overset{\overset{O}{\|}}{C}-OM; \quad -\overset{\overset{O}{\|}}{C}-O-OM; \quad \text{or} \quad -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OM$$

wherein M is H or a water-soluble, salt-forming cation. The organic peroxyacids and salts thereof usable in the present invention can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid may have the general formula:

$$HO\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_n\text{-}Y$$

wherein Y can be H, $-CH_3$, $-CH_2Cl$,

$$-\overset{\overset{O}{\|}}{C}-OM, \quad -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OM \quad \text{or} \quad -\overset{\overset{O}{\|}}{C}-O-OM$$

and n can be an integer from 6 to 20.

Peroxydodecanoic acids, peroxytetradecanoic acids and peroxyhexadecanoic acids are the most preferred compounds of this type, particularly 1,2-diperoxy-dodecanedioic acid, 1,14-diperoxytetradecanedioic acid and 1,16-diperoxyhexadeca nedioic acid. Examples of other preferred compounds of this type are diperoxyazelaic acid, diperoxyadipic acid and diperoxysebacic acid.

When the organic peroxyacid is aromatic, the unsubstituted acid may have the general formula:

$$HO\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}C_6H_4\text{-}Y$$

wherein Y is, for example, hydrogen, halogen, alkyl,

$$-\overset{\overset{O}{\|}}{C}-OM, \quad -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OM \quad \text{or} \quad -\overset{\overset{O}{\|}}{C}-O-OM.$$

The percarboxy and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents such as halogen or sulphonate groups. Examples of suitable aromatic peroxyacids and salts thereof include monoperoxyphthalic acid, diperoxyterephthalic acid, 4-cholorodiperoxyphthalic acid, diperoxyisophthalic acid, m-chloroperoxybenzoic acid, pnitroperoxybenzoic acic, and peroxy-alpha-napthoic acid. A preferred aromatic peroxyacid is diperoxyisophthalic acid.

A particularly preferred peroxyacid for use in the present invention is 1,12-diperoxydodecanedioic acid.

Suitable salts of peroxyacids are preferably the magnesium salts, such as are described in EP-A-0105689.

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 80,000, preferably from about 5000 to about 50,000; and mixtures thereof.

The detergent bleach compositions of the invention are alkaline and will advantageously give a solution pH (2-10 g/1) of from 8-10.5, 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.

Additionally, the compositions may optionally include an inorganic peroxide compound, such as the alkali metal perborates, percarbonates, and persilicates, the perborates, particularly sodium perborate tetra- and monohydrates, being preferred because of their commercial availability.

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 alumino-silicate and the alkali metal citrate or citric acid to form a detergent base powder, to which the heat-sensitive ingredients, including the organic peroxyacid, peroxide compound, enzymes and optionally some other ingredients as conveniently desirable are added. Alternatively, the alkali metal citrate does not form part of the base powder and is separately dry-mixed with the spray-dried base powder. 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 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).

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_2CO_3)	2.0
Water and fluorescer (0.13)	7.6
Composition (B)	
Sodium perborate monohydrate	8.0
Anti-foaming agent	2.5
Proteolytic enzyme (Savinase®ex NOVO)	0.5
Diperoxydodecanedioic acid (DPDA)	6.0
Sodium sulphate	33.9

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, detergency and protein stain removal (enzyme action) were measured; the results are given in Table I.

Table I

	ΔR values			
	Tea	Wine	Detergency	Protein stains
Composition A/B + 0% citrate	11.0	30.1	17.1	10.1
" + 1% citrate	13.1	32.5	18.8	9.6
" + 2% citrate	14.2	34.3	18.5	14.1
" + 3% citrate	14.8	35.1	18.4	14.1
" + 5% citrate	16.2	37.4	19.4	21.6
" + 10% citrate	16.4	38.2	18.2	24.3

Two sets of similar comparative experiments were carried out and the results were as follows:

Table 2

	ΔR-values			
	Tea	Wine	Detergency	Protein stains
Composition A/B + 0% citrate	10.1	29.2	17.8	12.1
" + 10% citrate	15.2	37.3	18.5	24.6
Composition A/B + 0% citrate	8.0	25.4	22.3	17.0
" + 5% citrate	15.2	35.0	23.4	30.8

From the above results it can be seen that trisodium citrate boosts the bleach performance on tea stains by about 50%, with large increases on wine and very large increases on protein stains, indicating far better enzyme action, and gives even a slight but noticeable improvement in detergency soil removal. The excellent overall cleaning and bleaching performance of the detergent compositions of the invention at

40 °C is clearly shown.

Example II

The experiments of Example I were repeated using the following powder composition C and a combined composition A^1/B.

Composition C	Parts by weight
Sodium dodecyl benzene sulphonate	9.0
Fatty alcohol-7-ethoxylate	4.0
Zeolite A	24.0
Maleic acid/acrylic acid copolymer (Sokalan ® CP5 ex BASF)	4.0
Sodium carboxymethyl cellulose	0.5
EDTA	0.2
Sodium sulphate	44.1
Fluorescer	0.2
Water	8.0
Diperoxydodecane dioic acid	6.0

Composition A_1 is Composition A without Sokalan CP5 copolymer.

The results are given in the following Table 3.

Table 3

	ΔR Values			
	Tea	Wine	Detergency	Protein stains
Composition C + 0% citrate	6.9	21.6	21.5	27.6
" + 5% citrate	15.4	33.3	22.8	33.0
Composition A^1/B + 0% citrate	6.4	21.2	21.8	17.2
" + 5% citrate	15.2	34.1	22.7	30.4

The results show again the excellent overall cleaning and bleaching performances of the compositions according to the invention as compared with the compositions outside the invention without trisodium citrate.

Examples III-IV

These Examples compare the overall cleaning and bleaching action of composition A/B + citrate of Example I according to the invention with a conventional good quality sodium triphosphate built detergent powder including DPDA of the following composition:

Composition	Parts by weight
Sodium linear alkylbenzene sulphonate	6.0
Nonionic fatty alcohol-7 ethoxylate	7.0
Alkaline sodium silicate	6.0
Sosium triphosphate	25.0
Sodium sulphate	40.1
EDTA	0.1
Sodium carboxymethyl cellulose	0.5
Polymer	1.0
Fluorescer	0.3
Anti-foaming agent	1.0
Water	7.0
Diperoxy dodecanedioic acid	6.0

III) Tergotometer wash, 8 gram/litre dosage, 24° FH water, 40° C, buffered at pH 8.5, 30 min. wash.

	ΔR Values			
	Tea	Wine	Detergency	Protein stains
STP built powder (6% DPDA)	18.2	37.3	23.2	36.8
Composition A/B + 10% citrate	16.5	37.8	23.5	36.3

IV) Miele machine, 40° C, 24° FH water, 8 gram/litre dosage, pH 8.5.

	ΔR Values				
	Tea	Wine	Protein	Detergency	Oily soil
STP built powder (6% DPDA)	17.2	39.9	35.5	32.9	22.8
Composition A/B + 10% citrate	16.5	39.3	36.7	34.7	18.7

Both results of Examples III and IV indicate that the overall bleach and cleaning performances of a non-phosphate, aluminosilicate built detergent composition of the invention and a good quality phosphate built composition are very similar.

Claims

1. 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; and

(c) from about 1% to about 15% by weight of a solid organic peroxyacid compound.

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;
- from 2 to 10% by weight of said citric acid or alkali metal citrate; and
- from 2 to 8% by weight of said organic peroxyacid compound.

3. A composition according to Claim 1 or 2, characterized in that said peroxyacid compound is 1,12-diperoxydodecanedioic acid.

4. A composition according to Claim 1, 2 or 3, characterized in that the composition has a solution pH (at 2-10 g/1) of 8-10.5.

5. A composition according to Claim 4, characterized in that said solution pH is between 8 and 9.