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(54) **Detergent compositions.**

(57) A detergent composition for fabric washing comprises detergent-active compounds and a detergency builder system comprising maximum aluminium zeolite P and a citrate.

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DETERGENT COMPOSITIONS

TECHNICAL FIELD

The present invention relates to detergent compositions, especially particulate detergent compositions, suitable for the laundering of fabrics in domestic or commercial washing machines, containing a detergency builder system which is a combination of a specific aluminosilicate and a citrate builder salt.

BACKGROUND AND PRIOR ART

Detergent compositions for heavy-duty fabric washing conventionally contain materials - detergency builders - to lower the concentration of calcium water hardness ions in the wash liquor and thus to give good detergency in hard water as well as in soft water.

Alkali metal aluminosilicate ion-exchangers, especially the crystalline sodium aluminosilicate zeolite 4A, are now well-known replacements for the inorganic phosphates traditionally used as detergency builders in fabric washing detergents. It is also well known that zeolites show certain deficiencies in detergency building, as compared with phosphates, and that supplementary building power is generally desirable. In many zero-phosphate premium detergent powders now on the European market, homo- or copolymers of acrylic acid are included for this purpose.

It is also known to include citric acid and/or its salts in detergent compositions, but these compounds are well-known to be poor sequestrants of calcium ions and to contribute little to detergency building.

Detergent compositions built with crystalline aluminosilicate (zeolite) and also containing citrates are specifically disclosed in GB 1 473 201 (Henkel), GB 1 429 143 (Procter & Gamble), GB 1 470 250 (Procter & Gamble), EP 1310A (Procter & Gamble), EP 1853A (Procter & Gamble), EP 75 796B (Procter & Gamble), GB 2 095 274B (Colgate-Palmolive), DE 2 336 182C (Lion), EP 234 867A (Clorox), and also in our copending European Patent Application No. 90 311 672.1 filed on 24 October 1990.

Water-softening or detergency building granules based on zeolites and citrates are disclosed in EP 243 908A (Henkel), DE 3 144 297A (Degussa), and EP 22 023A (Union Carbide).

EP 313 143A (Unilever) discloses bleaching detergent compositions containing aluminosilicate (15-40 wt%), citric acid or alkali metal citrate (1-15 wt%), and a solid organic peroxyacid (1-15 wt%). EP 313 144A (Unilever) describes and claims bleaching detergent compositions containing aluminosilicate (15-40 wt%), citric acid or alkali metal citrate (1-15 wt%), an inorganic peroxy compound (5-35 wt%), and a peroxybenzoic acid bleach precursor (1-10 wt%). Both specifications claim improved cleaning and bleaching performance when a builder system based on zeolite and citrate is used in conjunction with these specific bleach systems.

Our copending Application of even date (Case C3367), claiming the priority of British Patent Application No. 90 06171.4 filed on 19 March 1990, describes and claims detergent compositions, containing aluminosilicate and citrate in specific amounts and ratios, which exhibit unexpectedly good detergency even though the bleach systems mentioned above are absent.

EP 384 070A (Unilever) describes and claims a novel zeolite P (maximum aluminium zeolite P, or zeolite MAP) having an especially low silicon to aluminium ratio, not greater than 1.33 and preferably not greater than 1.15. This material is demonstrated to be a more efficient detergency builder than conventional zeolite 4A.

The present invention is based on the discovery that the novel combination of zeolite MAP and citrate provides an especially effective detergency builder system.

EP 419 036A (Unilever), to be published on 27 March 1991, describes and claims a detergency builder additive for use in a Baukasten (building block) product in conjunction with a separately packaged main wash detergent powder, the additive comprising:

- (i) at least 50 wt% (anhydrous basis) of a water-insoluble alkali metal aluminosilicate, which may be zeolite MAP;
- (ii) from 15 to 20 wt% of sodium carbonate; and
- (iii) from 2 to 12 wt% of organic sequestrant builder, which may be a water-soluble salt of citric acid.

Such builder additives are specifically disclaimed from the present application.

DEFINITION OF THE INVENTION

In its first aspect, the present invention provides a detergent composition for fabric washing, comprising:

- (i) one or more detergent-active compounds selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and combinations thereof,

(ii) a detergency builder system comprising:

- (a) zeolite P having a silicon to aluminium ratio not exceeding 1.33 (hereinafter zeolite MAP), and
- (b) citric acid and/or a salt thereof;

the ratio of zeolite MAP (a) (anhydrous basis) to citrate (b) (calculated as trisodium citrate dihydrate equivalent) preferably being within the range of from 1:1 to 6:1, more preferably from 1.5:1 to 3:1.

In its second aspect, the present invention provides a detergency builder composition comprising:

- (a) zeolite MAP (as defined above), and
- (b) citric acid and/or a salt thereof,

but excluding a composition comprising at least 50 wt% (anhydrous basis) of zeolite MAP, from 15 to 20 wt% of sodium carbonate, and from 2 to 12 wt% (calculated as trisodium citrate dihydrate) of a water-soluble salt of citric acid;

the ratio of zeolite MAP (a) (anhydrous basis) to citrate (b) (calculated as trisodium citrate dihydrate equivalent) preferably being within the range of from 1:1 to 6:1, more preferably from 1.5:1 to 3:1.

In its third aspect, the invention provides a method of washing fabrics, which includes the step of bringing the fabrics into contact with an aqueous wash liquor containing a detergent composition as defined above and/or a detergency builder composition as defined above.

In its fourth aspect, the invention provides the use of citric acid and/or a salt thereof as a detergency builder in a detergency builder composition or a detergent composition for fabric washing containing zeolite MAP.

20 DETAILED DESCRIPTION OF THE INVENTION

The detergent composition

The detergent composition of the invention contains, as essential components, a detergent-active compound, and a detergency builder system.

The detergent-active compound

The detergent compositions of the invention will contain, as essential ingredients, one or more detergent-active compounds (surfactants) which may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are 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-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅; primary and secondary alkyl sulphates, particularly C₁₂-C₁₅ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulposuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the aliphatic C₁₂-C₁₅ primary and secondary alcohols ethoxylated with an average of from 3 to 20 moles of ethylene oxide per mole of alcohol; and alkylpolyglycosides.

Preferred detergent-active systems, suitable for compositions intended for use in automatic fabric washing machines, comprises anionic non-soap surfactant, or nonionic surfactant, or combinations of the two in any ratio, optionally together with soap.

The total amount of detergent-active compounds present may suitably lie in the range of from 5 to 40 wt%.

The detergency builder system

The detergency builder system of the invention contains two essential components: zeolite MAP and a citrate.

Zeolite MAP and its use in detergent compositions are described and claimed in EP 384 070A (Unilever). It is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range of from 0.9 to 1.33, and more preferably within the range of from 0.9 to 1.2.

Of especial interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and having a tetragonally distorted cubic crystal structure.

Especially preferred is zeolite MAP having a silicon to aluminium ratio not greater than 1.07.

Zeolite MAP generally has a calcium binding capacity of at least 150 mg CaO per g of anhydrous aluminosilicate.

Although zeolite MAP like other zeolites contains water of hydration, for the purposes of the present invention amounts and percentages of zeolite are expressed in terms of the anhydrous material.

5 The second essential component of the detergency builder system of the invention is citric acid or a salt thereof, preferably sodium citrate. This salt normally exists in the form of the dihydrate, and for the purposes of the present invention amounts and percentages of citrates are expressed in terms of sodium citrate dihydrate.

It should be understood, however, that the use of other wholly and partially neutralised citric acid salts, and the free acid itself, in equivalent amounts, is also within the scope of the invention.

10 The weight ratio of aluminosilicate to citrate is preferably within the range of from 1:1 to 6:1, more preferably from 1.5:1 to 3:1.

Preferred builder systems

15 Detergent compositions of the invention preferably comprise from 10 to 45 wt%, more preferably from 12 to 30 wt%, of zeolite MAP; and from 2 to 20 wt%, more preferably from 3 to 9 wt% and most preferably from 5 to 8 wt%, of the citrate.

Other builder components

20 The compositions of the invention may be formulated without homo- or copolymers of acrylic acid, for example, polyacrylates or acrylic/maleic copolymers. Preferred compositions are substantially free from such polymers, although compositions containing them are not excluded from the scope of the invention.

25 The amount of soluble silicates in the compositions of the invention is preferably kept to a relatively low level: preferably below 5 wt%, and more preferably below 1 wt%.

The compositions of the invention may advantageously contain alkali metal carbonate, to provide alkalinity rather than for detergency building. The amount of alkali metal, preferably sodium, carbonate may suitably range from 2 to 20 wt%, preferably from 5 to 15 wt%.

Bleach system

30 Detergent compositions according to the invention may also suitably contain a bleach system. This preferably comprises one or more peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in conjunction with bleach precursors to improve bleaching action at low temperatures.

The bleach system preferably comprises a peroxy bleach compound, preferably an inorganic persalt, optionally in conjunction with a precursor.

Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

40 Preferred bleach precursors are peracetic acid precursors, especially tetraacetylene diamine (TAED); peroxybenzoic acid precursors; and the novel quaternary ammonium and phosphonium bleach activators disclosed in US 4 751 015 and US 4 818 426 (Lever Brothers Company), more especially cholyl p-sulphophenyl carbonate (CSPC).

If desired, the bleach system may also include a bleach stabiliser (heavy metal sequestant).

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Dicarboxylic acid structurant

The invention is especially, but not exclusively, concerned with detergent compositions in particulate form.

50 Particulate compositions of the invention may advantageously contain a dicarboxylic acid powder structurant.

Suitable materials include succinic acid, adipic acid, glutaric acid and mixtures thereof. The acids may be employed in free acid or in salt (wholly or partially neutralised) form. The dicarboxylic acid is suitably employed in an amount within the range of from 0.5 to 5 wt%. A commercial mixture of adipic acid (maximum 33 wt%), glutaric acid (maximum 50 wt%) and succinic acid (maximum 31 wt%) is available from BASF, Ludwigshafen, Germany under the trade mark Sokalan DCS, and a similar mixture of sodium salts under the trade mark Sokalan DCN.

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Particulate detergent compositions containing succinates as powder structurants are described and claimed in EP 61 295B (Unilever).

Other ingredients

Other materials that may be present in detergent compositions of the invention include fluorescers, anti-redeposition agents, inorganic salts such as sodium sulphate, enzymes, lather control agents, fabric softening agents, pigments, coloured speckles, and perfumes. This list is not intended to be exhaustive.

Preparation of the detergent compositions

Detergent compositions of the invention may be prepared by any suitable method. The particulate detergent compositions which are the preferred embodiment of the invention are suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on or postdosing those ingredients unsuitable for processing via the slurry.

The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

Both the zeolite MAP and the citrate builder component are suitable for inclusion in the slurry, although it may be advantageous for processing reasons for part of the zeolite MAP to be incorporated post-tower.

The particulate detergent compositions of the invention may be prepared to any suitable bulk density. Compositions having bulk densities of at least 400 g/l, more preferably at least 500 g/l, are of especial interest.

The detergency builder composition

The detergency builder system of the invention may exist as a composition in its own right that may be used for water softening or added to the wash liquor to enhance the performance of an unbuild or underbuilt detergent composition in hard water.

Such a composition may, for example, form the building or water-softening component of a Baukasten (building block) detergent composition as described and claimed in EP 419 036A (Unilever), to be published on 27 March 1991, in which a main wash powder is supplied together with separately packaged additives (builder, bleach) that need only be used when the wash conditions demand them.

A typical composition of this type might contain from 50 to 80 wt% zeolite MAP (anhydrous basis), and from 5 to 30 wt% sodium citrate.

A composition of this type may in principle contain no components other than the two essential components (zeolite MAP and citrate), although in practice it may be desirable to include other ingredients, for example, sodium carbonate, and binders such as nonionic surfactants or cellulose derivatives. However, as mentioned above, builder additives of the specific composition claimed in EP 419 036A are disclaimed and do not form part of the present invention.

A builder composition of the type under discussion may also be used as a raw material or premix in the manufacture of more fully formulated detergent compositions. However, the invention also includes within its scope detergent compositions prepared by admixing the two builder materials (zeolite MAP and citrate) separately and independently with other detergent ingredients.

The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated.

EXAMPLESExamples 1 and 2, Comparative Example A

Detergent powders containing zeolite MAP and citrate were prepared to the following formulations (in parts by weight):

		<u>1</u>	<u>2</u>
5	Linear alkylbenzene sulphonate	7.00	7.00
	Nonionic surfactant (7EO)	3.00	3.00
	Nonionic surfactant (3EO)	6.00	6.00
	Soap	1.50	1.50
10			
	Zeolite MAP (anhydrous basis) (a)	26.00	24.00
	Sodium citrate (2 aq basis) (b)	5.40	5.40
15			
	Antifoam granules	2.00	2.00
	Sodium carbonate	12.00	12.00
	TAED granules	7.00	7.00
20			
	Sodium perborate monohydrate	15.00	15.00
	Dequest 2047	0.75	0.75
	Enzyme (Savinase 6.0T)	0.50	0.50
25			
	Fluorescer	0.20	0.20
	Sodium carboxymethyl cellulose	0.50	0.50
30			
		<u>1</u>	<u>2</u>
	Ratio (a):(b)	4.80	4.40
	Total (a)+(b) (parts)	31.40	29.40

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Comparative Example A was identical to Example 1 except that the zeolite MAP was replaced by 26.00 parts of zeolite 4A.

The zeolite MAP was prepared on a pilot scale by the method described in Examples 1 to 3 of EP 384 070A (Unilever). Its silicon to aluminium ratio was 1.10 and it had a tetragonally distorted cubic crystal structure.

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Detergency was measured in a tergotometer in 26° (French) hard water (Ca:Mg ratio 4:1) at 60°C and a product dosage of 4 g/l. Test cloths as described below were washed together with a white ballast load. The results, expressed as reflectance differences at 460 nm (δR_{460}), were as follows:

Test cloths

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- (1) oil/silica/ink soil on cotton;
- (2) Indian ink/olive oil soil on polyester/cotton;
- (3) Indian ink/olive oil soil on cotton.

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	<u>Test cloth</u>	<u>1</u>	<u>2</u>	<u>A</u>
5	(1)	24.6	25.6	23.6
	(2)	16.6	14.5	14.1
10	(3)	25.7	25.6	22.5

These results show the superior building capacity of zeolite MAP/citrate as compared with zeolite 4A/citrate.

15 Examples 3 and 4, Comparative Examples B and C

Formulations containing lower percentages of zeolite MAP and citrate were prepared as follows:

20	Linear alkylbenzene sulphonate	6.00
	Nonionic surfactant (7EO)	2.75
	Nonionic surfactant (3EO)	4.25
25	Soap	1.75
	Zeolite MAP (anhydrous basis) (a)	12.00
30	Sodium citrate (2 aq basis) (b)	see below
	Antifoam granules	1.20
	Sodium carbonate	14.00
35	Sodium silicate	0.55
	TAED granules	3.00
	Sodium perborate tetrahydrate	20.00
40	Dequest 2047	0.75
	Enzyme (Savinase 6.0T)	0.40
	Fluorescer	0.21
	Sodium carboxymethyl cellulose	0.83
45	Moisture and salts	10.00

The zeolite MAP used was the same as that used in Examples 1 and 2.

50 The builder systems of the various formulations were as shown below: Sokalan (Trade Mark) CP5 ex BASF AG, Ludwigshafen, Germany is an acrylic/maleic copolymer.

<u>Example</u>	<u>3</u>	<u>4</u>	<u>B</u>	<u>C</u>
Zeolite MAP (a)	12.0	12.0	12.0	12.0
Citrate (b)	6.0	8.0	-	-
Sokalan CP5	-	-	-	2.0
Ratio (a):(b)	2.0	1.5	-	-
Total (a) + (b)	18.0	20.0	-	-

Detergency was measured in a tergotometer in 15° (French) hard water (Ca:Mg ratio 4:1) at 40°C and a product dosage of 4 g/l. Test cloths as described below were washed together with a white ballast load. The results, expressed as reflectance differences at 460 nm ($\delta\delta R_{460}$) as compared with Comparative Example C, were as follows:

Test cloths:

- (1), (2): as in Examples 1 and 2;
 (4) proteinaceous (casein) soil on cotton.

<u>Test cloth</u>	<u>3</u>	<u>4</u>	<u>B</u>
(1)	0.2	0.6	-1.1
(2)	2.9	3.5	1.6
(4)	0.8	0.9	0.1
	*	*	*

Claims

1 A detergent composition for fabric washing, comprising:

(i) one or more detergent-active compounds selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and combinations thereof,

(ii) a detergency builder system comprising:

(a) alkali metal aluminosilicate and

(b) citric acid and/or a salt thereof.

characterised in that the alkali metal aluminosilicate is zeolite P having a silicon to aluminium ratio not exceeding 1.33 (hereinafter zeolite MAP).

2 A detergent composition as claimed in claim 1, characterised in that the zeolite MAP has a silicon to aluminium ratio not greater than 1.15 and has a tetragonally distorted cubic crystal structure.

3 A detergent composition as claimed in claim 1, characterised in that the zeolite MAP has a silicon to aluminium ratio to aluminium ratio not greater than 1.07.

4 A detergent composition as claimed in any preceding claim, characterised in that the weight ratio of zeolite MAP (a) (anhydrous basis) to citrate (b) (calculated as trisodium citrate dihydrate) is within the range of from 1:1 to 6:1.

5 A detergent composition as claimed in any preceding claim, characterised in that the weight ratio of (a) to (b) is within the range of from 1.5:1 to 3:1.

6 A detergent composition as claimed in any preceding claim, characterised in that it contains from 10 to 45 wt% (anhydrous basis) of zeolite MAP.

7 A detergent composition as claimed in claim 6, characterised in that it contains from 12 to 30 wt% (anhydrous basis) of zeolite MAP.

8 A detergent composition as claimed in any preceding claim, characterised in that it contains from 2 to 20 wt% of the citrate (b).

9 A detergent composition as claimed in claim 8, characterised in that it contains from 3 to 9 wt% of the citrate (b).

10 A detergent composition as claimed in claim 9, characterised in that it contains from 5 to 8 wt% of the citrate (b).

11 A detergent composition as claimed in any preceding claim, characterised in that it is substantially free of homo- or copolymers of acrylic acid.

12 A detergent composition as claimed in any preceding claim, characterised in that it is in particulate form.

13 A detergency builder composition comprising:

(a) alkali metal aluminosilicate, and

(b) citric acid and/or a salt thereof,

characterised in that the alkali metal aluminosilicate (a) is zeolite P having a silicon to aluminium ratio not exceeding 1.33 (hereinafter zeolite MAP),

but excluding a composition comprising at least 50 wt% (anhydrous basis) of zeolite MAP, from 15 to 20 wt% of sodium carbonate, and from 2 to 12 wt% (calculated as trisodium citrate dihydrate) of a water-soluble salt of citric acid.

14 A detergency builder composition as claimed in claim 13, characterised in that the zeolite MAP has a silicon to aluminium ratio not greater than 1.15 and has a tetragonally distorted cubic crystal structure.

15 A detergent composition as claimed in claim 13, characterised in that the zeolite MAP has a silicon to aluminium ratio to aluminium ratio not greater than 1.07.

16 A detergency builder composition as claimed in any one of claims 13 to 15, characterised in that the weight ratio of zeolite MAP (a) (anhydrous basis) to citrate (b) (calculated as trisodium citrate dihydrate) is within the range of from 1:1 to 6:1.

17 A detergency builder composition as claimed in claim 16, characterised in that the weight ratio of (a) to (b) is within the range of from 1.5:1 to 3:1.

18 A method of washing fabrics, characterised by the step of bringing the fabrics into contact with an aqueous wash liquor containing a detergent composition as claimed in any one of claims 1 to 12 and/or a detergency builder composition as claimed in any one of claims 13 to 17.

19 Use of citric acid and/or a salt thereof as a detergency builder in a detergent composition for fabric washing containing alkali metal aluminosilicate, characterised in that the alkali metal aluminosilicate is zeolite P having a silicon to aluminium ratio not exceeding 1.33.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 91302217.4
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D, P, Y	<u>EP - A2 - 0 384 070</u> (UNILEVER) * Claims 1-6,15; page 3, lines 4-8; page 4, lines 36-43; page 5, table 2 * --	1-19	C 11 D 3/12 C 11 D 3/20
D, Y	<u>EP - A2 - 0 313 144</u> (UNILEVER) * Claims 1,2,4; page 5, line 21 * --	1-12, 18,19	
D, Y	<u>DE - A1 - 3 144 297</u> (DEGUSSA) * Claims 1,2; example 2 * --	13-19	
D, E	<u>EP - A2 - 0 419 036</u> (UNILEVER) * Claims 1,7; page 3, lines 42-44 * & AU-A1-61135/90 --	1	
P, X			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	<u>US - A - 3 112 176</u> (W.L. HADEN et al.) * Claim 3; table II; column 1, lines 50-62 * -----		C 11 D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
VIENNA		24-06-1991	REISER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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