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(54) Detergent compositions.

(57) A detergent composition suitable for fabric washing comprises detergent-active compounds and a detergency builder composition comprising maximum aluminium zeolite P and a polycarboxylate polymer, preferably an acrylic/maleic copolymer. The composition shows superior detergency compared with compositions containing zeolite A and polymer.

EP 0 502 675 A2

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 polycarboxylate polymer.

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.

Detergent compositions built with crystalline aluminosilicate (zeolite) and also containing polyacrylate or acrylic/maleic copolymer are disclosed, for example, in EP 221 777A, EP 240 356A, EP 270 240A, EP 340 013A, EP 358 473A, EP 367 339A, EP 390 251A and EP 352 135A (Unilever); EP 215A, EP 63 399A, EP 66 915A, EP 130 640A and EP 137 669A (Procter & Gamble); EP 228 011A and EP 291 869A (Henkel); and EP 229 671A (Kao).

Water-softening or detergency building granules based on zeolites and polycarboxylate polymers are disclosed in EP 184 794A, EP 243 908A and EP 344 629A (Henkel), EP 289 767A and EP 289 768A (Degussa), GB 1 568 420 and GB 2 210 055A (Colgate), DE 3 316 513A (Benckiser), and DE 3 707 806A (Dispo-Kommerz AG).

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 polycarboxylate polymer provides an especially effective detergency builder system.

EP 419 036A (Unilever), 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 polycarboxylate polymer.

Such builder additives are specifically disclaimed from the present application.

DEFINITION OF THE INVENTION

In one aspect, the present invention provides a detergent composition suitable 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) a polycarboxylate polymer in acid and/or salt form,

the ratio of zeolite MAP (a) (anhydrous basis) to polycarboxylate polymer (b) preferably being within the range of from 2:1 to 10:1, more preferably from 4.5:1 to 9.5:1.

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

(a) zeolite MAP (as defined above), and

(b) a polycarboxylate polymer in acid and/or salt form,

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% of polycarboxylate polymer;

the ratio of zeolite MAP (a) (anhydrous basis) to polycarboxylate polymer preferably being within the range of from 2:1 to 10:1, more preferably from 4.5:1 to 9.5:1.

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

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 C_8-C_{15}; primary and secondary alkyl sulphates, particularly C_{12}-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; 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 C_{12}-C_{15} 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 polycarboxylate polymer.

Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably not greater than 1.20, more preferably not greater than 1.15 and most desirably not greater than 1.10.

Zeolite MAP and its use in detergent compositions are described and claimed in EP 384 070A (Unilever).

The silicone to aluminium ratio is preferably within the range of from 0.9 to 1.33, and more preferably within the range of from 0.9 to 1.2.

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.

The second essential component of the detergency builder system of the invention is a polycarboxylate polymer. This term is used to mean a water-soluble polymeric polycarboxylic acid, a water-soluble salt of a polymeric polycarboxylic acid, or a mixture of these.

Preferred polycarboxylate polymers are homo- and copolymers of acrylic acid and/or maleic acid, in acid and/or salt form. Especially preferred polymers are acrylic acid homopolymers, and acrylic/maleic copolymers. The acrylic/maleic copolymers disclosed in EP 25 551B (BASF) are of particular interest.

Polymeric polycarboxylates which may suitably be used, alone or in combination, in the compositions of the present invention include the following:

Polymer type	Trade name	Supplier	Average m wt
Polyacrylate	Versicol* E5	Allied Colloids	3500
Polyacrylate	Versicol* E7	Allied Colloids	27 000

Polymer type	Trade name	Supplier	Average m wt
Polyacrylate	Versicol* E9	Allied Colloids	70 000
Polyacrylate	Narlex* LD 30	National Adhesives	5000
Polyacrylate	Narlex* LD 34	National Adhesives	25 000
Polyacrylate	Acrysol* LMW-10	Röhm & Haas	1000
Polyacrylate	Acrysol* LMW-20	Röhm & Haas	2000
Polyacrylate	Acrysol* LMW-45	Röhm & Haas	4500
Polyacrylate	Acrysol* A1-N	Röhm & Haas	60 000
Polyacrylate	Sokalan* PA-20	BASF	2500
Polyacrylate	Sokalan* PA-40	BASF	15 000
Polyacrylate	Sokalan* PA-70	BASF	70 000

Polymer type	Trade name	Supplier	Average m wt
Polyacrylate	Sokalan* PA-110	BASF	250 000
Ethylene/ maleic acid	EMA*	Monsanto	
Methyl vinyl ether/maleic acid	Gantrez* AN 119	GAF Corporation	
Acrylate/ maleate	Sokalan* CP5, CP7	BASF	
Acrylic phosphinate	DKW*	National Adhesives	
Acrylic phosphinate	Belsperse*	Ciba-Geigy	

*denotes Trade Mark

The weight ratio of aluminosilicate to polymer is preferably within the range of from 2:1 to 10:1, more preferably from 4.5:1 to 9.5:1.

Preferred builder systems

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 10 wt%, more preferably from 2 to 6 wt%, of the polymer.

Bleach system

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.

Preferred bleach precursors are peracetic acid precursors, especially tetraacetylethylene 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 sequestrant).

Other ingredients

The compositions of the invention may if desired containg water-soluble silicates such as sodium silicate. 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%.

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 polymeric 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 400 g/l, are of especial interest.

The detergency builder composition

The detergency builder system of the invention may be 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 unbuilt 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), 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 2 to 10 wt% polycarboxylate polymer.

A composition of this type may in principle contain no components other than the two essential components (zeolite MAP and polymer), 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 the 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 polymer) 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.

EXAMPLES

Examples 1 to 3, Comparative Example A

Four detergent compositions containing zeolite and polycarboxylate polymer were prepared to the following formulations (in parts by weight):

	parts
Linear alkylbenzene sulphonate	6.80
Nonionic surfactant (7EO)	3.10
Nonionic surfactant (3EO)	6.90
Soap	1.73
Builder system:	
Zeolite MAP or 4A(anhydrous basis))	see below
Acrylic/maleic copolymer)	
Antifoam granules	1.20
Sodium carbonate	9.60
Sodium silicate	0.55
TAED granules	6.60
Sodium perborate monohydrate	16.25
Dequest 2047	0.75
Enzyme (Savinase 6.0T)	1.10
Fluorescer	0.21
Sodium carboxymethyl cellulose	0.83
	55.62

The polymer was an acrylic/maleic copolymer in sodium salt form, Sokalan (Trade Mark) CP5 ex BASF, Ludwigshafen, Germany.

The zeolite MAP was prepared on a pilot scale by a method similar to that described in Examples 1 to 3 of EP 384 070A (Unilever). Its silicon to aluminium ratio was 1.10.

The zeolite 4A was Wessalith (Trade Mark) P powder ex Degussa.

The builder systems of the four compositions were as follows:

	A	1	2	3
Zeolite 4A (anhydr)	27.30	-	-	-
Moisture	7.50			
Zeolite MAP (anhydr)	-	27.30	25.00	22.00
Moisture		7.20	6.60	5.80
Polymer	4.50	4.50	4.50	4.50
Ratio (a):(b)	(6.07)	6.07	5.56	4.89
Total (a)+(b):				
parts	31.80	31.80	29.50	26.50
%	33.50	33.60	32.16	30.14

Detergency was measured in a Candy (Trade Mark) washing machine using the 40°C main wash only cycle. Test cloths as specified below were washed together with a 3 kg soiled load, using two different product dosages and two different water hardnesses.

The results, expressed as reflectance differences at 460 nm (delta R_{460}), were as follows:

Test cloths

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

(i) Water hardness 15° (French), product dosage 4.8 g/l

Test cloth	A	1	2	3
(1)	20.4	23.0	23.6	22.2
(2)	12.5	14.7	13.6	10.7
(3)	27.4	28.1	27.9	26.8
(4)	24.1	24.8	25.2	24.5

(ii) Water hardness 25° (French), product dosage 6.4 g/l

Test cloth	A	1	2	3
(1)	22.9	24.3	24.3	21.6
(2)	11.8	14.5	15.3	10.8
(3)	27.7	28.5	28.4	27.9
(4)	25.3	26.0	25.8	24.7

Example 4, Comparative Example B

Two detergent compositions containing zeolite and polycarboxylate polymer were prepared to the following formulations:

	%	
	B	4
Linear alkylbenzene sulphonate	6.70	6.70
Nonionic surfactant (7EO)	3.07	3.07
Nonionic surfactant (3EO)	6.23	6.23
Soap	1.83	1.83
Builder system:		
Zeolite MAP	-	28.00
Zeolite 4A	28.00	-
Acrylic/maleic copolymer	3.00	3.00
Sodium carbonate	15.08	15.08
Sodium silicate	0.46	0.46
Sodium carboxymethyl cellulose	0.56	0.56
Fluorescer	0.22	0.22
Antifoam granules	1.20	1.20
TAED granules	7.35	7.35
Sodium perborate monohydrate	14.00	14.00
Enzyme (Savinase 6.0T)	1.10	1.10
Moisture	11.00	11.00
	100.00	100.00

The zeolite MAP, zeolite 4A and copolymer were as used in Examples 1 to 3.

The ratio of zeolite (anhydrous basis) to polymer in each case was 9.33, and the total amount of zeolite plus polymer in each case was 31.0.

Detergency was measured in a Miele (Trade Mark) 756 washing machine using the 40°C main wash cycle. Test cloths as specified below were washed together with a 4 kg soiled load, using two different product dosages and two different water hardnesses.

The results, expressed as reflectance differences at 460 nm (delta R_{460}), were as follows:

Test cloths

(1), (3) as in Examples 1 to 3

(5) Indian ink/olive oil/silica plus a small amount of casein, on cotton.

(i) Water hardness 20°(French), Ca:Mg 2.0, product dosage 3.4 g/l

Test cloth	B	4
(1)	18.11	24.48
(3)	31.95	36.05
(5)	21.96	26.38

(ii) Water hardness 40°(French), Ca:Mg 2:1, product dosage 5.6 g

Test cloth	B	4
(1)	14.32	21.07
(3)	27.45	31.01
(5)	18.77	21.29

Example 5

A composition containing lower percentages of zeolite MAP and acrylic/maleic copolymer was prepared as follows:

Linear alkylbenzene sulphonate	6.00
Nonionic surfactant (7EO)	2.75
Nonionic surfactant (3EO)	4.25
Soap	1.75
Zeolite MAP (anhydrous basis) (a)	12.00
Acrylic/maleic copolymer (b)	2.00
Antifoam granules	1.20
Sodium carbonate	14.00
Sodium silicate	0.55
TAED granules	3.00
Sodium perborate tetrahydrate	20.00
Dequest 2047	0.75
Enzyme (Savinase 6.0T)	0.40
Fluorescer	0.21
Sodium carboxymethyl cellulose	0.83
Moisture and salts	10.00

The zeolite MAP and copolymer were the same as those used in Examples 1 to 4.

The ratio of zeolite MAP to copolymer was 6.00 and the total amount of zeolite MAP and copolymer was 14.00.

The composition exhibited excellent cleaning and detergency performance.

Claims

1 A detergent composition suitable 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, and
(ii) a detergency builder system,
characterised in that the detergency builder system (ii) comprises
(a) zeolite P having a silicon to aluminium ratio not exceeding 1.33 (hereinafter zeolite MAP), and
(b) a polycarboxylate polymer in acid and/or salt form.

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.

3 A detergent composition as claimed in claim 1, characterised in that the zeolite MAP has a silicon to aluminium ratio not greater than 1.10.

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

5 A detergent composition as claimed in any preceding claim, characterised in that the weight ratio of zeolite MAP (a) (anhydrous basis) to polymer (b) is within the range of from 2:1 to 10:1.

6 A detergent composition as claimed in claim 5, characterised in that the weight ratio of (a) to (b) is within the range of from 4.5:1 to 9.5:1.

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

8 A detergent composition as claimed in any preceding claim, characterised in that it comprises from 2 to 10 wt% of the polymer (b).

9 A detergent composition as claimed in any preceding claim, characterised in that the polycarboxylate

polymer is a homo- or copolymer of acrylic acid or maleic acid.

10 A detergent composition as claimed in claim 9, characterised in that the polycarboxylate polymer is an acrylic/maleic copolymer.

11 A detergent composition as claimed in any preceding claim, which is in particulate form.

12 A detergency builder composition comprising:

(a) zeolite P having a silicon to aluminium ratio not exceeding 1.33 (hereinafter zeolite MAP), and

(b) a polycarboxylate polymer in acid and/or a salt form,

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% of polycarboxylate polymer.

13 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 claimed in any one of claims 1 to 11 and/or a detergency builder composition as claimed in claim 12.

14 Use of a polycarboxylate polymer in acid and/or a salt form as a detergency builder in a detergency builder composition or a detergent composition suitable for fabric washing containing zeolite P having a silicon to aluminium ratio not exceeding 1.33.