(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 533 392 A2**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number : **92308211.9**

(51) Int. Cl.[5] : **C11D 3/12**

(22) Date of filing : **10.09.92**

(30) Priority : **18.09.91 GB 9119958**

(43) Date of publication of application :
24.03.93 Bulletin 93/12

(84) Designated Contracting States :
CH DE ES FR GB IT LI NL SE

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(54) **Detergent compositions.**

(57) A detergent composition comprises detergent-active compounds and a detergency builder system comprising maximum aluminium zeolite P (zeolite P having a silicon to aluminium ratio not exceeding 1.33) and a lamellar crystalline sodium silicate, preferably Na-SKS-6. The composition is suitable, for example, for washing fabrics.

EP 0 533 392 A2

TECHNICAL FIELD

The present invention relates to detergent compositions, especially particulate detergent compositions, containing a detergency builder system which is a combination of a defined alkali metal aluminosilicate and a defined lamellar crystalline sodium silicate. The invention is especially but not exclusively concerned with compositions suitable for the laundering of fabrics in domestic or commercial washing machines.

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.

US 4 664 839, US 4 728 443 and US 4 820 439 (Hoechst AG) disclose a lamellar crystalline sodium silicate having the composition

$$NaMSi_xO_{2x+1} \cdot yH_2O$$

wherein M denotes sodium or hydrogen, x is a number from 1.9 to 4, and y is a number from 0 to 20. This material is useful as a detergency builder and may be used in conjunction with other detergency builders, for example, zeolite A.

EP 405 122A (Hoechst) discloses a builder for detergents composed of 20-80 wt% of hydrated zeolite and 20-80 wt% of lamellar crystalline sodium silicate. The zeolite is preferably a synthetic material obtained as described in US 4 274 975 (Procter & Gamble). Detergent compositions containing the two materials in ratios of 0.5:1, 1:1 and 2:1 are specifically disclosed.

WO 92 03525A (Procter & Gamble), published on 5 March 1992, discloses particulate laundry detergent compositions containing a three-component non-phosphorus builder system comprising a sodium aluminosilicate zeolite (20-60 wt%), a water-soluble monomeric or oligomeric carboxylate chelating agent such as sodium citrate (10-30 wt%), and a crystalline layered sodium silicate (10-65 wt%), the percentages being based on the builder system. Preferred zeolites specifically mentioned are zeolite A, zeolite X and zeolite HS.

JP 01 153 800A (Lion) discloses textile-softening granular detergent compositions containing detergent-active compounds, bentonite clay, water-soluble crystalline layered sodium silicate of the formula given above, and aluminosilicate (zeolite). Detergent compositions containing zeolite A and layered silicate (Na-SKS-6) in proportions of 3:1, 1:1 and 1:3 are specifically disclosed.

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, preferably not greater than 1.15 and more preferably not greater than 1.07. This material is demonstrated to be a more weight-effective detergency builder than conventional zeolite 4A.

The present invention is based on the discovery that the novel combination of zeolite MAP and lamellar silicate provides an especially effective detergency builder system, the detergency being better than would be predicted from knowledge of the individual builder efficacies of the two materials.

DEFINITION OF THE INVENTION

In its first aspect, the present invention provides a detergent composition 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 lamellar crystalline sodium silicate having the composition

$$NaMSi_xO_{2x+1} \cdot yH_2O$$

wherein M denotes sodium or hydrogen, x is a number from 1.9 to 4, and y is a number from 0 to 20.

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

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

(b) a lamellar crystalline sodium silicate having the composition

$$NaMSi_xO_{2x+1} \cdot yH_2O$$

wherein M, x and y are as defined previously.

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 lamellar silicate as defined above as a detergency builder in a detergency builder composition or a detergent composition 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 inventive step lies in the choice of the detergency builder system, while the detergent-active compound and other optional ingredients may be conventional.

The detergency builder system

The detergency builder system of the invention contains two essential components: zeolite MAP and a lamellar crystalline sodium silicate.

Zeolite MAP and its use in detergent compositions are described and claimed in EP 384 070A (Unilever), the disclosure of which is incorporated herein by reference. 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 more especially material having a 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 lamellar crystalline sodium silicate having the composition

$$NaMSi_xO_{2x+1} \cdot yH_2O$$

wherein M denotes sodium or hydrogen, preferably sodium; x is a number from 1.9 to 4; and y is a number from 0 to 20.

As previously indicated, these materials are described in US 4 664 839, US 4 728 443 and US 4 820 439 (Hoechst AG), the disclosures of which are hereby incorporated by reference. They are crystalline materials and can easily be characterised by means of their X-ray diffraction patterns. Compared with amorphous silicates, they are significantly better binders of calcium and magnesium ions.

Especially preferred are compounds in which x = 2, ie compounds of the formula

$$NaMSi_2O_5 \cdot yH_2O.$$

Both natural and synthetic compounds of this formula are of interest, the synthetic material known as Na-SKS-6 being especially preferred. This material is commercially available from Hoechst AG; its preparation is described, and it is defined in terms of its X-ray diffraction pattern, in the aforementioned US 4 664 839.

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 30 wt%, more preferably from 3 to 25 wt%, of the lamellar silicate.

The ratio of zeolite MAP (a) (anhydrous basis) to lamellar crystalline silicate (b) is preferably within the range of from 0.1:1 to 10:1, more preferably from 0.2:1 to 7:1. The synergistic effect is particularly marked at ratios ranging from 0.3:1 to 3:1, more especially from 0.5:1 to 2:1.

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 non-ethoxylated nonionic surfactants, for example, alkylpolyglycosides, and alkyl glyceryl ethers and esters.

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%.

Other ingredients

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).

The amount of soluble (amorphous) 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%. However, the presence of sodium carbonate is not essential.

Other materials that may be present in detergent compositions of the invention include fluorescers, antiredeposition 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 any tower (spray-drying) or non-tower process.

In processes based around a spray-drying tower, a base powder is first prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and any ingredients unsuitable for processing via the slurry may then be sprayed on or admixed (postdosed). The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

The zeolite MAP is 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 lamellar silicate is preferably postdosed.

Alternatively, as suggested previously, particulate detergent compositions in accordance with the invention may be prepared by wholly non-tower processes such as granulation.

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 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), 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.

The preferred ratios of zeolite MAP to crystalline lamellar silicate mentioned above for detergent compositions apply equally to separate detergency builder compositions.

A composition of this type may in principle contain no components other than the two essential components (zeolite MAP and lamellar silicate), although in practice it may be desirable to include other ingredients, for example, sodium carbonate, and binders such as nonionic surfactants or cellulose derivatives.

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 lamellar silicate) separately and independently with other detergent ingredients.

Uses of the detergent composition

As the description above indicates, the detergent compositions and detergency builder compositions of the invention are especially suitable for washing textile fabrics, and have been assessed with this end-use in mind. However, the builder system is of potential use and interest for any other type of cleaning product requiring a built detergent system, for example, machine dishwashing compositions.

Examples

The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated. Examples identified by numbers are in accordance with the invention, while those identified by letters are comparative.

EXAMPLES 1 TO 6, A AND B

A detergent composition was prepared to the following formulation:

	wt%
Linear alkylbenzene sulphonate	6.8
Nonionic surfactant (3EO)	3.1
Nonionic surfactant (7EO)	6.9
Soap	1.73
Builder (see below)	31.8
Sodium carboxymethylcellulose	0.83
Sodium carbonate	9.6
Sodium alkaline silicate	0.55
Sodium perborate monohydrate	16.25
Tetraacetylethylenediamine (granule)	6.6
Protease granule (Savinase 6.0T)	1.1
Antifoam granule	1.2
Moisture	to 100.0

The builder systems used in the individual Examples were as follows:

	A, B	1, 4	2, 5	3, 6
(a) Zeolite MAP	31.8	23.8	15.9	8.0
(b) Na-SKS-6	-	8.0	15.9	23.8
Ratio (a):(b)		2.98	1.0	0.34

The zeolite MAP was prepared by a method similar to that described in Examples 1 to 3 of EP 384 070A (Unilever). Its silicon to aluminium ratio was 1.07.

The Na-SKS-6, supplied by Hoechst AG, was as described in US 4 664 839 and US 4 820 439 (Hoechst).

Detergency comparisons were carried out in the Tergotometer using two different test cloths:

Test cloth 1: cotton soiled with oil, silica and ink.

Test cloth 2: cotton soiled with casein.

In all experiments the wash temperature was 40°C, the wash time was 30 minutes, the agitation was 100 rpm, and the liquor to cloth ratio was 20:1. Comparisons were made at two different water hardnesses and product dosages.

Examples A, 1, 2, 3

In this set of experiments the water hardness was 22.5°FH (Ca), 15°FH (Mg), and the product dosage was 3.4 g/litre. The results, expressed as reflectance increases (delta R) at 460 nm, were as follows:

	A	1	2	3	(X)
Test cloth 1	16.6	17.4	18.6	18.5	(< 16.6)
Test cloth 2	19.6	21.1	23.4	23.4	(< 19.6)

The last column represents the predicted result if zeolite MAP were totally replaced by Na-SKS-6 (see Examples C and D below).

Surprisingly, the replacement of zeolite MAP by Na-SKS-6 caused an increase in detergency, reaching a peak in the 1:1 region (Example 2). All combinations of the two builders were better than either builder used alone.

Examples B, 4, 5, 6

In this set of experiments the water hardness was 45°FH (Ca), 30°FH (Mg), and the product dosage was 5.6 g/litre. The results, expressed as reflectance increases (delta R) at 460 nm, were as follows:

	B	4	5	6	(Y)
Test cloth 1	13.6	14.5	15.5	15.5	(< 13.6)
Test cloth 2	14.7	15.6	17.7	16.8	(< 14.7)

Again, the last column represents the predicted result if zeolite MAP were totally replaced by Na-SKS-6 (see Examples C and D below).

As in the first set of experiments, the replacement of zeolite MAP by Na-SKS-6 caused an increase in detergency, reaching a peak in the 1:1 region (Example 5). All combinations of the two builders were better than either builder used alone.

Examples C, D

The experiments described above did not include a comparison with Na-SKS-6 alone.

No direct comparison of the detergencies of Na-SKS-6 and of zeolite MAP as sole builders at the same level has been carried out.

The experiment now described compares the detergencies of Na-SKS-6 and commercial zeolite 4A, and shows that Na-SKS-6 is less than half as weight-effective a builder as the zeolite.

The compositions were as follows:

	C	D
Linear alkylbenzene sulphonate	6.0	6.0
Nonionic surfactant (3EO)	2.75	2.75
Nonionic surfactant (7EO)	4.25	4.25
Soap	1.65	1.65
Zeolite 4A	24.00	-
Na-SKS-6	0.50	45.00
Acrylic/maleic copolymer	4.00	4.00
Sodium carboxymethylcellulose	0.83	0.83
Sodium carbonate	10.00	10.00
Sodium sulphate	33.39	12.89
Sodium perborate monohydrate	7.50	7.50
Tetraacetylethylenediamine (granule)	2.77	2.77
Protease granule (Savinase 6.0T)	0.40	0.40
Antifoam granule	1.00	1.00
Moisture and minor ingredients	-to 100.00-	

Detergencies (delta R_{460}) were compared in the Tergotometer using test cloth 1, at 40°C, water hardnesses of 25°FH and 40°FH (total) and a product dosage of 5 g/litre, and were as follows:

	25°FH	40°FH
Example C (45% SKS-6)	20.8	11.8
Example D (24% zeolite, 0.5% SKS-6)	24.2	13.3

The zeolite 4A used in this experiment was Wessalith P ex Degussa.

Example 14 of EP 384 070A (Unilever) demonstrates that zeolite MAP of silicon to aluminium ratio 1.12, as the sole builder in a detergent composition, gives significantly better detergency on test cloth 1 (referred to as AS 9), at two different product dosages, than does zeolite 4A. Thus zeolite MAP too must be a substantially more weight-effective builder than Na-SKS-6, and it can be predicted that the detergency scores for Na-SKS-6 alone in experiments corresponding to Examples A, 1-3, B and 4-6 would have been considerably lower than those for zeolite MAP alone. The synergistic benefit observed when zeolite MAP is partially replaced by Na-SKS-6 is therefore particularly surprising.

Claims

1 A detergent composition 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 zeolite and a lamellar crystalline sodium silicate, characterised in that the builder system comprises:

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

(b) a lamellar crystalline sodium silicate having the composition

$$NaMSi_xO_{2x+1} \cdot yH_2O$$

wherein M denotes sodium or hydrogen, x is a number from 1.9 to 4, and y is a number from 0 to 20.

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 1.07.

4 A detergent composition as claimed in any preceding claim, characterised in that the weight ratio of zeolite MAP (a) (anhydrous basis) to lamellar crystalline sodium silicate (b) is within the range of from 0.1:1 to 10:1.

5 A detergent composition as claimed in claim 4, characterised in that the weight ratio of (a) to (b) is within the range of from 0.2:1 to 7:1.

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 0.3:1 to 3:1.

7 A detergent composition as claimed in claim 6, characterised in that the weight ratio of (a) to (b) is within the range of from 0.5:1 to 2:1.

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

9 A detergent composition as claimed in claim 8, characterised in that it contains from 12 to 30 wt% (anhydrous basis) of zeolite MAP.

10 A detergent composition as claimed in any preceding claim, characterised in that it contains from 2 to 30 wt% of the lamellar crystalline sodium silicate (b).

11 A detergent composition as claimed in claim 10, characterised in that it contains from 3 to 25 wt% of the lamellar crystalline sodium silicate (b).

12 A detergent composition as claimed in any preceding claim, characterised in that the lamellar crystalline sodium silicate (b) has the composition

$$NaMSi_2O_5 \cdot yH_2O$$

wherein M and y have the meanings given in claim 1.

13 A detergent composition as claimed in claim 12, characterised in that the lamellar crystalline sodium silicate (b) is Na-SKS-6.

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

15 A detergency builder composition comprising zeolite and lamellar crystalline sodium silicate, characterised in that it comprises:

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

(b) a lamellar crystalline sodium silicate having the composition

$$NaMSi_xO_{2x+1} \cdot yH_2O$$

wherein M denotes sodium or hydrogen, x is a number from 1.9 to 4, and y is a number from 0 to 20.

16 A method of washing fabrics, characterised in that it 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 14 and/or a detergency builder composition as claimed in claim 15.

17 Use of a lamellar crystalline sodium silicate having the composition

$$NaMSi_xO_{2x+1} \cdot yH_2O$$

wherein M denotes sodium or hydrogen, x is a number from 1.9 to 4, and y is a number from 0 to 20, as a detergency builder in a detergency builder composition or a detergent composition containing zeolite P having a silicon to aluminium ratio not exceeding 1.33.