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(54) Detergent composition

(57) A detergent composition is disclosed having improved particulate stain control properties which comprises a conventional surfactant, a detergency builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and a biodegradable sucrose-based polymer.

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Description

The present invention relates to a detergent composition and, in particular, to improvements in the detergency performance of laundry detergent compositions comprising zeolites as a sequestering agent for water hardness.

Detergent compositions for fabric washing conventionally contain detergency builders which lower the concentration of calcium and magnesium water hardness ions in the wash liquor and thereby provide good detergency effect in both hard and soft water.

Conventionally, inorganic phosphates, such as sodium tripolyphosphate, have been used as builders for laundry detergents. More recently, alkali metal aluminosilicate ion-exchangers, particularly crystalline sodium aluminosilicate zeolite A, have been proposed as replacements for the inorganic phosphates.

For example, EP 21 491A (Procter & Gamble) discloses detergent compositions containing a building system which includes zeolite A, X or P (B) or a mixture thereof. EP 384070A (Unilever) discloses specific zeolite P materials having an especially low silicon to aluminium ratio not greater than 1.33 (hereinafter referred to as zeolite MAP) and describes its use as a detergency builder. To date, however, zeolite A is the preferred aluminosilicate detergency builder in commercially available products.

It is also known in the art that polymeric soil release agents can be employed in order to sustain good soil suspension, to assist in particulate stain removal at high temperatures and to achieve ash control. A problem associated with conventional polymeric soil release agents, howver, is that they are not biodegradable. Efforts have therefore been made to develop an acceptable polymeric soil release agent which is biodegradable. For example EP A 0 465 287 describes detergent compositions containing a biodegradable graft polysaccharide and zeolite 4A is exemplified. JP 940426 in the name of Nippon Synthetic Chem. Ind. describes certain biodegradable detergent polymers.

However, not all biodegradable polymers are stable in alkaline detergent compositions based on zeolite A upon elevated moisture and temperature conditions, particularly when the composition has a low or zero phosphate content.

We have surprisingly found that the stability of sucrose-based polymers is improved in detergent compositions containing zeolite MAP. The improvement is particularly evident in alkaline detergents having a pH of greater than 9.25.

We have found that a combination of zeolite MAP and a sucrose-based polymer results in improved soil suspension properties, improved particulate stain removal at high temperatures and ash control. Not only is the sucrose- based polymer biodegradable, and hence environmentally acceptable, but also its use in combination with zeolite MAP results in enhanced properties and improved compatibility.

Thus, the present invention provides a detergent composition comprising:

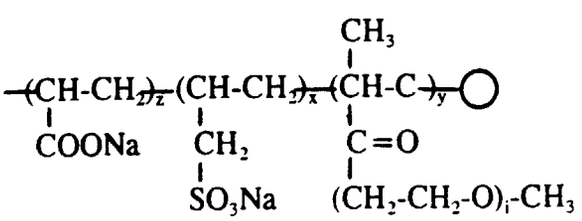
a) a surfactant selected from anionic. nonionic, cationic, amphoteric and zwitterionic detergent - active compounds and mixtures thereof;

b) a detergency builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and

c) a sucrose-based polymer.

The detergent composition according to the invention may be any conventional form including liquid and particulate detergents but granular detergent compositions are preferred.

The sucrose-based polymer may be any suitable polymer based on sucrose including copolymers of sucrose with acrylic or methacrylic graft comonomer components and having a molecular weight of, for example, 1000 to 200,000, preferably 2000 to 100,000. Suitable sucrose based polymers are commercially available such as a copolymer of sucrose, acrylate and sodium methallyl sulphonate (Chemische Fabrick Stockausen AG) molecular weight 2000 - 100,000 and having the structural formula:



x, y and z are integers

Such polymers may be made, for example, by dissolving the sucrose in alcohol, adding the monomers and/or comonomers and a suitable redox catalyst for the graft reaction, distilling off aqueous alcohol solution under reduced pressure and neutralising with an aqueous alkaline solution. A suitable general method is disclosed in WO93/02118.

The sucrose-based polymer is employed in the detergent composition in an amount of 0.05 to 30% by weight, based on the composition. Preferably the polymer is employed in an amount of 0.5 to 15% by weight and most preferably 1 to 10% by weight based on the detergent composition.

The detergent composition according to the invention contains, as an essential ingredient, one or more surfactants selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent-active compounds and mixtures thereof. Such surfactants are well known and described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II by Schwartz, Perry and Berch.

Examples of suitable anionic surfactants include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; C_{12}-C_{15} primary alkyl sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Examples of suitable nonionic surfactants include alkoxylated adducts of fatty alcohols containing an average of from 3 to 10 alkylene oxide groups per molecule. Preferred alkoxylated adducts of fatty alcohols contain an average of less than 5 alkylene oxide groups per molecule, for example less than 4 alkylene oxide groups per molecule e.g. 3.5 and usefully 3 alkylene oxide groups per molecule or less and usefully also greater than 0.5, or 1, or 2 alkylene oxide groups per molecule.

A particularly preferred aliphatic alcohol ethoxylate is a primary alcohol having an average of 12 to 15 carbon atoms in the alkyl chain condensed with an average of three ethoxy groups per mole of alcohol.

Specific examples of suitable alkoxylated adducts of fatty alcohols are Synperonic A3 (ex ICI), which is a C_{13}-C_{15} alcohol with about three ethylene oxide groups per molecule and Empilan KB3 (ex Marchon), which is lauric alcohol 3EO.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula

$$RO(C_nH_{2n}0)_tZ_x$$

wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms: t is from 0 to 10 and n is 2 or 3; x is from 1.1 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

The surfactant will generally be included in the detergent composition in an amount of 3 to 60% by weight, preferably 5 to 40% by weight and most preferably from 10 to 25% by weight of the composition.

According to the present invention the detergency builder system is based on zeolite MAP, optionally in conjunction with one or more supplementary builders. The amount of zeolite MAP employed may range, for example, from 3 to 80 wt%, preferably from 5 to 60 wt%, more preferably from 15 to 40 wt%.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

Zeolite P having a Si:Al ratio of 1.33 or less may be prepared by the following steps:

(i) mixing together a sodium aluminate having a mole ratio NA_20:Al_20_3 within the range of from 1.4 to 2.0 and a sodium silicate having a mole ratio $Si0_2$:Na_20 within the range of from 0.8 to 3.4 with vigorous stirring at a temperature within the range of from 25°C to boiling point usually 95°C, to give a gel having the following composition:

$$Al_20_3 :: (1.75\text{-}3.5)\ Si0_2 : (2.3\text{-}7.5)\ Na_20 : P\ (80\text{-}450)H_20;$$

(ii) ageing the gel composition for 0.5 to 10 hours, preferably 2 to 5 hours, at a temperature within the range of from 70°C to boiling point, usually to 95°C, with sufficient stirring to maintain any solids present in suspension;

(iii) separating the crystalline sodium aluminosilicate thus formed, washing to a pH within the range of from 10 to 12.5, and drying, preferably at a temperature not exceeding 150°C, to a moisture content of not less than 5 wt%.

Preferred drying methods are spray-drying and flash drying. It appears that oven drying at too high a temperature may adversely affect the calcium binding capacity of the product under certain circumstances.

Commercial sodium metasilicate pentahydrate dissolved in water and commercial sodium silicate solution (waterglass) are both suitable silica sources for the production of zeolite P in accordance with the invention. The reactants may be added together in any order either rapidly or slowly. Rapid addition at ambient temperature, and slow addition at elevated temperature (90-95°C) both give the desired product.

Vigorous stirring of the gel during the addition of the reactants, and at least moderate stirring during the subsequent ageing step, however, appear to be essential for the formation of pure zeolite P. In the absence of stirring, various mixtures of crystalline and amorphous materials may be obtained.

Zeolite MAP generally has a calcium binding capacity of at least 150 mg CaO per g of anhydrous aluminosilicate, as measured by the standard method described in GB 1473201 (Henkel). The calcium binding capacity is normally 160 mg CaO/g and may be as high 170 mg CaO/g.

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 notional anhydrous material. The amount of water present in hydrated zeolite MAP at ambient temperature and humidity is generally about 20 wt%.

According to one embodiment a preferred zeolite MAP for use according to the present invention has a d_{50} of < 1.0 micrometre, for example 0.4 to 1.0 micrometres.

According to another embodiment the zeolite MAP has a d_{50} of 1.0 to 10.0 micrometres for example 2.25 to 5 micrometres more particularly 2.75 to 5 micrometres. The quantity "d_{50}" indicates that 50 wt% of the particles have a diameter smaller than that figure.

The particle size is determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope or by means of a laser granulometer.

Zeolite MAP having a larger particle size can be prepared by the conventional techniques as described above while adopting one or more of the following steps:-

a) increasing crystallisation time.

b) increasing the size of the seed crystals used to produce the zeolite;

c) feeding the aluminosilicate gels into the crystallisation stage immediately after they form (i.e. eliminate ageing of gels);

d) screening the zeolite product to remove fine material.

According to one embodiment of the invention the zeolite MAP detergent builder is in powder form.

For convenience in handling, however, the material may be granulated by conventional techniques such as spray drying or by a non-tower method to form larger particles.

In the granular detergent compositions according to the invention, the detergency builder can be zeolite MAP alone or a combination of zeolite MAP with an organic or inorganic cobuilder.

Suitable organic cobuilders can be monomeric or polymeric carboxylates such as citrates or polymers of acrylic, methacrylic and/or maleic acids in neutralised form. Suitable inorganic cobuilders include carbonates, and amorphous and crystalline lamellar sodium silicates.

Suitable crystalline lamellar silicates have the composition:

$$NaMSi_x0_{2x+1} \cdot yH_20$$

where M is sodium or hydrogen, preferably sodium; x is a number from 1.9 to 4; and y is a number from 0 to 20. Such materials are described in US Patents No. 4664839; No. 4728443 and No. 4820439 (Hoechst AG). Especially preferred are compounds in which x = 2 and y = O. The synthetic material is commercially available from Hoechst AG as S-Na_2 Si_20_5 (SKS6) and is described in US Patent No. 4664830.

The builder may also include a minor amount of zeolite A, preferably not more than 2 wt% zeolite A or no more than 6 wt% if overdried (i.e. moisture level below 12 wt%).

The total amount of detergency builder in the granular composition generally ranges from 5 to 80 wt%, more preferably 10 to 45 wt%.

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. Suitable persalts include sodium perborate monohydrate tetrahydrate and sodium percarbonate, with sodium percarbonate being most preferred.

Preferred bleach precursors are peracetic acid precursors, such as tetraacetylethylene diamine (TAED); and peroxybenzoic acid precursors, such as sodium benzoyloxybenzene sulphonate (BOBS).

Other materials which may be present in the detergent compositions of the invention include, for example, fluorescers, antiredeposition agents, inorganic salts such as sodium sulphate, enzymes, lather control agents, fabric softening agents, pigments, coloured speckles and perfumes.

The detergent composition according to the invention is preferably free of phosphate or has only a low phosphate content.

The detergent composition preferably has a pH, measured as a 1 wt% solution in distilled water, of above 9.25, preferably above 10.0.

The detergent compositions of the invention may be prepared by any suitable method. The particulate detergent compositions 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 and then other components unsuitable for processing via the slurry can be sprayed on or admixed (post-dosed).

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, where this is employed. is also post-dosed.

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

The granular detergent compositions of the invention may be prepared to any suitable bulk density. The compositions preferably have a bulk density of at least 400 g/l preferably at least 550 g/l, most preferably at least 700 g/l and, with particular preference at least 800 g/l.

High bulk density powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation: in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

According to a further aspect of the invention there is provided a liquid detergent composition, preferably a heavy duty liquid detergent composition comprising a surfactant as previously described, a detergency builder comprising zeolite MAP and a sucrose-based polymer.

According to this embodiment the liquid detergent composition may be of any convenient physical form which may be aqueous or anhydrous. The term "liquid" used herein includes pasty viscous formulations such as gels. The liquid detergent system comprises, as the detergency builder zeolite MAP optionally in combination with other detergency builders such as fatty acids, citric acid or zeolite A.

A preferred co-builder is a lamellar sodium silicate such as SKS-6 which is particularly useful in pasty viscous formulations such as gels or in non-aqueous liquid detergents such as those described in WO92/16608 (Henkel).

The liquid detergent composition generally has a pH of above 9.25, for example 9.25 to 10.5.

The invention is illustrated by the following Example in which the abbreviations have the meanings defined below.

Zeolite	Zeolite MAP having an average particle size of 2.0 μm.
Sucrose Polymer	copolymer of sucrose/acrylate/sodium methallyl sulphonate supplied by Chemische Fabrick Stockhausen AG with a molecular weight of 200 - 100,000
DETPMP	diethylene triamine penta/methylene phosphonic acid), marketed by Monsanto under the Trade Mark Dequest 2060
C14-15AS	sodium C_{14-15} alkyl sulphate

C12-15AE3S	sodium ethoxylated alcohol having a C_{12-15} chain length and an average of 3 ethoxy groups per molecule
C14-15AE7	ethoxylated alcohol having a C_{14-15} chain length and an average of 7 ethoxy groups per molecule
SKS6	crystalline lamellar sodium silicate (Hoechst A.G.)
Percarbonate	sodium percarbonate coated with 2.5% carbonate/sulphate
Citrate	trisodium citrate dihydrate

The following particulate formulation was prepared via post dosing and spray drying

Zeolite	25 %
Sucrose polymer	4 %
DETPMP	0.5 %
C14-15AS	8 %
C12-15AE3S	2 %
C14-15AE7	4 %
SKS6	10 %
Sodium Carbonate	10 %
Percarbonate	15 %
Citrate	5 %
Balance Moisture Misc	100 %

Claims

1. A detergent composition comprising:

   (a) a surfactant selected from anionic, nonionic, cationic, amphoteric and zwitterionic detergent - active compounds and mixtures thereof;
   (b) a detergency builder comprising zeolite P having a silicon to aluminium ratio not greater than 1.33 (zeolite MAP); and
   (c) a sucrose-based polymer.

2. A detergent composition according to claim 1, wherein the composition has a low or zero phosphate content.

3. A detergent composition according to claim 1 or 2, which has a pH (measured as a 1 % by weight solution in distilled water) of above 9.25.

4. A detergent composition according to any one of claims 1 to 3, comprising the sucrose-based polymer in an amount of 0.05 to 30% by weight.

5. A detergent composition according to claim 4, comprising the sucrose-based polymer in an amount of 1 to 10% by weight.

6. A detergent composition according to any one of claims 1 to 5, wherein the zeolite MAP has a silicon to aluminium ratio not greater than 1.15.

7. A detergent composition according to claim 6, wherein the zeolite MAP has a silicon to aluminium ratio not greater than 1.07.

8. A detergent composition according to any of claim 1 to 7, which comprises from 3 to 80 % by weight of zeolite MAP.

9. A detergent composition according to any of claims I to 8 which is in particulate form.