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⑤④ **Granular detergent compositions containing film-forming polymers.**

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## Description

## Technical field

The present invention relates to granular detergent compositions containing a detergent surfactant, an aluminosilicate ion exchange material, a water-soluble neutral or alkaline salt and a film-forming polymer. The compositions herein, which contain no or only low levels of phosphate materials and from 0.5 % to less than 3 % by weight of alkali metal silicate materials, provide granules having both superior free-flowing characteristics and solubility in the laundering solution.

Granular detergent compositions have, in the past, often contained high concentrations of phosphate builder materials, particularly sodium tripolyphosphate. When a crutcher mix containing sodium tripolyphosphate is spray-dried, it is believed that enough mixed-phosphate hydrolysis products are formed to inhibit phosphate crystal growth. The hydrolysis products are concentrated in the liquid phase which finally dries to an amorphous glassy phosphate material. This glassy material effectively « cements » the finely crystalline granule walls together, producing granules exhibit very desirable physical properties, i. e., crisp, durable and free-flowing granules. Moreover, the glassy phosphate material readily disintegrates in the laundering solution so that no insoluble residue is left on the fabrics.

Alkali metal silicates are usually included in granular detergents at low levels for corrosion inhibition and processing reasons. When phosphate builders are removed from detergents, the level of silicate is often increased severalfold since it also dries to a tough glassy film capable of strengthening granule walls and enhancing free-flowing characteristics. Silicates having a lower  $\text{SiO}_2$  to alkali metal oxide ration (e. g., 1.6-2.0) are usually selected because they are more water-soluble than the higher ratio silicates. However, exposure of the silicate to carbon dioxide during drying and storage can shift its ratio to a higher value and reduce its solubility, resulting in detergent granules which do not completely disintegrate in the laundering solution, and an unacceptably high level of insoluble material being deposited on fabrics. The insolubles problem can be particularly severe when the detergent composition also contains the water-insoluble aluminosilicate material herein since higher levels of silicates (e. g., above 3 %) enhance the deposition of the aluminosilicates onto fabrics.

## Background art

U.S. Patent 3,985,669, Krummel, et al., issued October 12, 1976, describes the use of low levels (i. e., about 0.5 % to 3 %) of alkali metal silicates in granular detergent compositions also containing aluminosilicate builder materials to provide both corrosion inhibition and crispness benefits without enhancing deposition of the aluminosilicates onto fabrics.

U.S. Patent 4,072,621, Rose, issued February 7, 1978, discloses the addition of a water-soluble copolymer of a vinyl compound and maleic anhydride to granular detergents containing aluminosilicate builders. The compositions provide improved granule physical properties, particularly relating to reduced dustiness, and improved cleaning performance in the presence of appreciable amounts of orthophosphate and pyrophosphate, such as formed by the hydrolysis of polyphosphates during spray-drying operations. The compositions disclosed in the examples contain 20 % by weight of phosphate materials.

British Patent 2,048,841, published December 17, 1980, discloses the use of polymeric acrylamides to stabilize aqueous suspensions of zeolites. The suspensions are said to be suitable for spray-drying to obtain detergent compositions.

DE-A-2,615,698, published October 20, 1977, describes stable suspensions containing aluminosilicates, dispersing agents which can include polymers containing carboxylic and/or hydroxyl groups, and stabilization agents. The suspensions are said to be useful in the manufacture of spray-dried detergents.

DE-A-2,854,484, published June 26, 1980, discloses stable zeolite suspensions containing polyacrylamides or copolymers thereof with acrylic acid. The suspensions are said to be useful as sequestering agents in spray-dried detergent compositions.

European Patent Application 215 indicates that polyphosphate builders are very effective sequestrants of hardness cations but that by reason of their undesirable effects on the water supply it has been proposed to use aluminosilicates as builders to remove hardness cations. However, the action of the aluminosilicates tends to be slow. In order to overcome this difficulty and improve the performance of the builder, (especially with regard to the removal of bleachable stains), a copolymer based on maleic acid is to be in the detergent composition.

European Patent Application 216 relates to the improvement of suds control in laundry operations by means of a multi-component suds-regulating system containing a liquid hydrocarbon and either an insoluble solid hydrocarbon or an ester of an alcohol and an acid together with a hydrophobic silica suds-regulating agent. The composition may contain, as a supplementary component, a certain copolymer based on maleic acid which can act as slurry-processing aid.

European Patent Application 1853 refers to the effectiveness of polyphosphate builders as sequestrants of undesirable hardness cations and mentions that, by reason of the undesirability of their effects on the water supply, it has been proposed to use aluminosilicates. However, it is stated that the

aluminosilicates are deficient ; for example, in the field of removal of oxidisable stains. In order to deal with this problem the Application proposes the use of certain specific types of aluminosilicate, together with a polyphosphonate. It is mentioned that an optional component is the maleic acid copolymer which is, in fact, that mentioned in European Patent Application 215.

5 European Patent Application 10247 relates to a phosphate-free detergent composition containing aluminosilicates as well as a number of other ingredients. The composition may additionally contain soil-suspending agents which are water-soluble colloids of mainly organic nature.

DE-A1-2 412 837 (Henkel) relates to compositions for washing or bleaching textiles such as untreated cotton. The compositions may comprise a surfactant, a builder, a bleach and a crystalline, water-insoluble  
10 aluminosilicate. The compositions may also comprise a calcium sequestering or precipitating agent, such as a polyacrylate.

The compositions are prepared, for instance as shown in Example 2, by mixing together in water to form a slurry the dried aluminosilicate, the bleach, a precipitation delayer and a spray dried powder containing the remaining components. The slurry is then diluted as necessary for use.

15 DE-A1-2 462 497 (Henkel) is similar to the above mentioned patent to Henkel in that it relates to a process for washing or bleaching textiles such as untreated cotton, but using an aqueous slurry containing an amorphous, water-insoluble aluminosilicate. The slurry may contain a polyacrylate as a calcium sequestering or precipitating agent. The application also relates to aqueous compositions for use in the method.

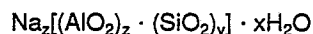
20 The method for preparing the compositions is similar to that given in the previous Henkel patent, as can be seen from Example 2 of this application.

The present invention encompasses a detergent composition comprising :

(a) from 5 % to 40 % by weight of an organic surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof ;

25 (b) from 10 % to 60 % of a finely-divided aluminosilicate ion exchange material selected from the group consisting of :

(1) crystalline aluminosilicate material of the formula :



30

wherein z and y are at least 6, the molar ratio of z to y is from 1.0 to 0.5 and x is from 10 to 264, said material having a particle size diameter of from 0.1  $\mu\text{m}$  to 10  $\mu\text{m}$ , a calcium ion exchange capacity of at least 200 mg.  $\text{CaCO}_3$  eq./g. and a calcium ion exchange rate of at least 0.034 g  $\text{Ca}^{++}$ /liter/minute/g/ 3,79 l ;

35

(2) amorphous hydrated aluminosilicate material of the empirical formula :



40 wherein M is sodium, potassium, ammonium or substituted ammonium, z is from 0.5 to 2 and y is 1, said material having a magnesium ion exchange capacity of at least 50 milligram equivalents of  $\text{CaCO}_3$  hardness per gram of anhydrous aluminosilicate and a  $\text{Mg}^{++}$  exchange rate of at least 0.017 g  $\text{Ca}^{++}$ /liter/minute/g/3.79 l ; and

(3) mixtures thereof ;

(c) from 0.5 % to less than 3 % by weight of alkali metal silicate materials ; and

45

(d) from 5 % to 75 % by weight of a water-soluble neutral or alkaline salt ;

said composition containing less than 10 % by weight of phosphate materials, characterised in that the composition contains

(e) from 0.1 % to 10 % by weight of a film-forming polymer soluble in an aqueous slurry comprising the above components, said film-forming polymer being an at least partially neutralised salt of : a  
50 homopolymer of acrylic acid, hydroxyacrylic acid or methacrylic acid ; a copolymer of acrylic acid, hydroxyacrylic acid or methacrylic acid with a comonomer lacking carboxyl groups ; cellulose acetate sulphate ; cellulose sulfate ; hydroxyethylcellulose sulfate ; methylcellulose sulfate, or hydroxypropylcellulose sulfate, further characterised in that components (a), (b), (c), (d) and (e) have been formed into an aqueous slurry and dried to form granules.

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The film-forming polymer is preferably represented by a copolymer of acrylamide and acrylate having a molecular weight of from 3000 to 100,000 and an acrylamide content of less than 50 %.

The composition preferably contains from 0.5 % to 2 % of a sodium or potassium silicate having a molar ratio of  $\text{SiO}_2$  to alkali metal oxide from 1 to 1.4.

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Detailed description of the invention

The granular detergent compositions of the present invention contain, as essential components, a detergent surfactant, an aluminosilicate ion exchange material, an alkali metal silicate material, a water-soluble neutral or alkaline salt and a film-forming polymer, as described hereinafter. The compositions  
65 contain 0.5 % to less than 3 %, preferably less than 2 %, by weight of alkali metal silicate materials and less

than 10 %, preferably less than 5 %, by weight of phosphate materials. Most preferably, the compositions are substantially free of phosphate materials.

The compositions herein are prepared by drying an aqueous slurry comprising the above components. The slurry generally contains from about 25 % to about 50 % water, whereas the dried granules contain from about 3 % to about 15 % water. The drying operation can be accomplished by any convenient means for example, by using spray-drying towers, both counter-current and co-current, fluid beds, flash-drying equipment, or industrial microwave or oven drying equipment. While not intending to be limited by theory, it is believed that the granular detergents herein exhibit superior free-flowing characteristics because the film-forming polymer dries to a tough, non-sticky, non-hygroscopic film which cements the granule walls together much in the same manner as do the glassy phosphates and silicates. Since the polymer film is readily water-soluble, the granules quickly disintegrate in the laundering solution and leave little or no insoluble residue on the fabrics. Moreover, the film-forming polymer does not enhance the deposition of the aluminosilicate material onto fabrics, as do higher levels of the alkali metal silicates.

#### Organic surfactant

The detergent compositions herein contain from 5 % to 40 % by weight of an organic surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof. The surfactant preferably represents from 10 % to 30 %, and more preferably from 14 % to 20 %, by weight of the detergent composition. Surfactants useful herein are listed in U.S. Patent 3,664,961, Norris, issued May 23, 1972, and in U.S. Patent 3,919,678, Laughlin, et al., issued December 30, 1975. Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980. However, cationic surfactants are generally less compatible with the aluminosilicate materials herein, and thus are preferably used at low levels, if at all, in the present compositions. The following are representative examples of surfactants useful in the present compositions.

Water-soluble salts of the higher fatty acids, i. e., «soaps», are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from 8 to 24 carbon atoms, and preferably from 12 to 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i. e., sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 10 to 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term «alkyl» is the alkyl portion of acyl groups). Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C<sub>8</sub>-C<sub>18</sub> carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkyl benzene sulfonates in which the alkyl group contains from 9 to 15 carbon atoms, in straight chain or branched chain configuration, e. g., those of the type described in United States Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C<sub>11-13</sub> LAS.

Other anionic surfactants herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from 8 to 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl group contains from 10 to 20 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from 10 to 20 carbon atoms in the alkyl group and from 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

Water-soluble nonionic surfactants are also useful in the compositions of the invention. Such nonionic materials include compounds produced by the condensation of alylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e. g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from 3 to 12 moles of ethylene oxide per mole of alkyl phenol.

5 Preferred nonionics are the water-soluble condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 3 to 12 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 9 to 15 carbon atoms with from 4 to 8 moles of ethylene oxide per mole of alcohol.

10 Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; and water-soluble sulfoxides  
15 containing one alkyl moiety of from 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and at least one aliphatic  
20 substituent contains an anionic water-solubilizing group.

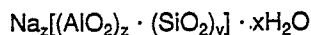
Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from 8 to 18 carbon atoms.

Particularly preferred surfactants herein include linear alkybenzene sulfonates containing from 11 to 14 carbon atoms in the alkyl group; tallowalkyl sulfates; coconutalkyl glyceryl ether sulfonates; alkyl  
25 ether sulfates wherein the alkyl moiety contains from 14 to 18 carbon atoms and wherein the average degree of ethoxylation is from 1 to 4; olefin or paraffin sulfonates containing from 14 to 16 carbon atoms; alkyl-dimethyl amine oxides wherein the alkyl group contains from 11 to 16 carbon atoms; alkyl-dimethylammonio propane sulfonates and alkyl-dimethylammonio hydroxy propane sulfonates wherein the alkyl group contains from 14 to 18 carbon atoms; soaps of higher fatty acids containing from 12 to 18  
30 carbon atoms; condensation products of C<sub>9</sub>-C<sub>15</sub> alcohols with from 4 to 8 moles of ethylene oxide, and mixtures thereof.

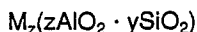
Specific preferred surfactants for use herein include: sodium linear C<sub>11-13</sub> alkylbenzene sulfonate; triethanolamine C<sub>11-13</sub> alkylbenzene sulfonate; sodium tallow alkyl sulfate; sodium coconut alkyl glyceryl ether sulfonate; the sodium salt of a sulfated condensation product of a tallow alcohol with 4  
35 moles of ethylene oxide; the condensation product of a coconut fatty alcohol with 6 moles of ethylene oxide; the condensation product of tallow fatty alcohol with 11 moles of ethylene oxide; 3 - (N,N - dimethyl - N - coconutalkylammonio - 2 - hydroxypropane - 1 - sulfonate; 3 - (N,N - dimethyl - N - coconutalkylammonio) - propane - 1 - sulfonate; 6 - (N - dodecylbenzyl - N,N - dimethylammonio) hexanoate; dodecyl dimethyl amine oxide; coconut alkyldimethyl amine oxide; and the water-soluble  
40 sodium and potassium salts of coconut and tallow fatty acids.

#### Aluminosilicate ion exchange material

The detergent compositions herein also contain from 10 % to 60 %, preferably from 15 % to 40 %, and  
45 more preferably from 18 % to 30 %, by weight of crystalline aluminosilicate ion exchange material of the formula



wherein z and y are at least 6, the molar ratio of z to y is from 1.0 to 0.5 and x is from 10 to 264. Amorphous  
50 hydrated aluminosilicate materials useful herein have the empirical formula



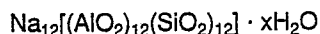
wherein M is sodium, potassium, ammonium or substituted ammonium, z is from 0.5 to 2 and y is 1, said  
55 material having a magnesium ion exchange capacity of at least 50 milligram equivalents of CaCO<sub>3</sub> hardness per gram of anhydrous aluminosilicate.

The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from 10 % to 28 % of water by weight if crystalline, and potentially even higher amounts of water if amorphous. Highly preferred crystalline aluminosilicate ion exchange materials contain from 18 % to 22 % water in  
60 their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from 0.1 μm to about 10 μm. Amorphous materials are often smaller, e.g., down to less than 0.01 μm. Preferred ion exchange materials have a particle size diameter of from 0.2 μm to 4 μm. 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, micro-  
65 scopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion

exchange materials herein are further characterized by their calcium ion exchange capacity, which is at least 200 mg. equivalent of  $\text{CaCO}_3$  water hardness/g. of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from 300 mg. eq./g. to 352 mg. eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least 0.034 g  $\text{Ca}^{++}$ /liter/minute/gram/3.79 l, and generally lies within the range of from 0.034 g/liter/minute/gram/3.79 l to about 0.102 g/liter/minute/gram/3.79 l, based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a calcium ion exchange rate of at least 0.068 g/liter/minute/gram/3.79 l.

The amorphous aluminosilicate ion exchange materials have a  $\text{Mg}^{++}$  exchange capacity of at least 50 mg. eq.  $\text{CaCO}_3$ /g. (12 mg.  $\text{Mg}^{++}$ /g.) and a  $\text{Mg}^{++}$  exchange rate of at least 0.017 g  $\text{Ca}^{++}$ /liter/minute/gram/3.79 liter. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units) (0.15 nm).

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Patent 3,985,669, Krummel, et al., issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula



wherein x is from 20 to 30, especially 27.

Water-soluble neutral or alkaline salt

The granular detergents of the present invention additionally contain from 5 % to 75 %, preferably from 10 % to 60 %, and more preferably from 20 % to 50 %, by weight of a water-soluble neutral or alkaline salt. The neutral or alkaline salt has a pH in solution of seven or greater, and can be either organic or inorganic in nature. The salt assists in providing the desired density and bulk to the detergent granules herein. While some of the salts are inert, many of them also function as detergency builder materials in the laundering solution.

Examples of neutral water-soluble salts include the alkali metal, ammonium or substituted ammonium chlorides, fluorides and sulfates. The alkali metal, and especially sodium, salts of the above are preferred. Sodium sulfate is typically used in detergent granules and is a particularly preferred salt herein.

Other useful water-soluble salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, polyhydroxysulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above. However, as previously described, the present compositions contain from 0.5 % to less than 3 %, preferably less than 2 %, by weight of silicate materials and less than 10 %, preferably less than 5 %, by weight of phosphate materials. Most preferably, the compositions are substantially free of phosphates.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1 - hydroxy - 1,1 - diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2 - triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581 ; 3,213,030 ; 3,422,021 ; 3,422,137 ; 3,400,176 and 3,400,148.

Examples of non-phosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a molar ratio of  $\text{SiO}_2$  to alkali metal oxide of from 0.5 to 4.0, preferably from 1.0 to 2.4.

Water-soluble, non-phosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxysulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Highly preferred polycarboxylate builders herein are set forth in U.S. Patent No. 3,308,067, Diehl, issued March 7, 1967. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Other useful builders herein are sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentanetetracarboxylate phlorog-

lucinol trisulfonate, and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield, et al., and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield, et al. These polyacetal carboxylates can be prepared by bringing together under  
 5 polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

Other detergency builder materials useful herein are the "seeded builder" compositions disclosed  
 10 in Belgian Patent No. 798,856, issued October 29, 1973. Specific examples of such seeded builder mixtures are: 3:1 wt. mixtures of sodium carbonate and calcium carbonate having 5  $\mu\text{m}$  particle diameter; 2.7:1 wt. mixtures of sodium sesquicarbonate and calcium carbonate having a particle diameter of 0.5  $\mu\text{m}$ ; 20:1 wt. mixtures of sodium sesquicarbonate and calcium hydroxide having a particle diameter of 0.01  $\mu\text{m}$ ; and a 3:3:1 wt. mixture of sodium carbonate, sodium aluminate and  
 15 calcium oxide having a particle diameter of 5  $\mu\text{m}$ .

#### Film-forming polymer

The compositions of the present invention also contain from 0.1 % to 10 %, preferably from 0.5 % to 7  
 20 %, and more preferably from 1 % to 4 % by weight of a film-forming polymer soluble in an aqueous slurry comprising the organic surfactants, aluminosilicate materials, alkali metal silicate materials and neutral or alkaline salts herein. It will be appreciated that the polymer must be at least partially soluble in the slurry for it to dry to a film capable of cementing the granule walls together as the slurry is dried. For optimum granule physical properties, the polymer should be substantially soluble in the slurry, and is  
 25 preferably completely soluble in the slurry. The slurry will typically comprise a surfactant phase and the insoluble aluminosilicate material suspended in a solution (often saturated) of the neutral or alkaline salt, which preferably comprises sodium sulfate. The slurry will usually be alkaline in nature due to the presence of the aluminosilicate material and either anionic surfactants or alkaline salts. Since the slurry will generally be a strong electrolyte solution, optimum solubility of the polymer is obtained when it is in  
 30 the form of an at least partially neutralised or substituted alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanol ammonium) salt. The alkali metal, especially sodium, salts are most preferred. While the molecular weight of the polymer can vary over a wide range, it preferably is from 1000 to 500,000, more preferably is from 2000 to 250,000 and most preferably is from 3000 to 100,000.

Suitable film-forming polymers herein include homopolymers of acrylic acid, hydroxyacrylic acid or  
 35 methacrylic acid or a copolymer of acrylic acid, hydroxyacrylic acid or methacrylic acid with a comonomer lacking carboxyl groups. The copolymers can be formed of mixtures of the said carboxylic acids with or without other copolymerisable monomers, or they can be formed from one only of the said carboxylic acids with other copolymerisable monomers. In either case, the percentage by weight of the polymer units derived from non-carboxylic acids is preferably less than 50 %. Suitable copolymerisable  
 40 monomers include, for example, vinyl chloride, vinyl alcohol, furan, acrylonitrile, vinyl acetate, methyl acrylate, methyl methacrylate, styrene, vinyl methyl ethyl, vinyl ethyl ether, vinyl propyl ether, acrylamide, ethylene and propylene.

The preferred polymers of the above group are the homopolymers and copolymers of acrylic acid, hydroxyacrylic acid, or methacrylic acid, which in the case of the copolymers contain at least 50 %, and  
 45 preferably at least 80 %, by weight of units derived from the acid. Particularly preferred polymers are sodium polyacrylate and sodium polyhydroxyacrylate.

The polymerisation of acrylic acid homo- and copolymers can be accomplished using free-radical initiators, such as alkali metal persulphates, acyl and aryl peroxides, acyl and aryl peresters and aliphatic azocompounds. The reaction can be carried out in situ or in aqueous or non-aqueous solutions or  
 50 suspensions. Chain-terminating agents can be added to control the molecular weight. These polymerisation techniques are well known in the art. It will be appreciated that instead of using a single polymeric aliphatic carboxylic acid, mixtures of two or more of the said polymeric carboxylic acids can be used to prepare the above polymers.

The other film-forming polymers useful herein are cellulose acetate sulfate, cellulose sulfate,  
 55 hydroxyethyl cellulose sulfate, methylcellulose sulfate and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

Particularly preferred polymers for use herein are copolymers of acrylamide and acrylate having a molecular weight of from 3,000 to 100,000, preferably from 4,000 to 20,000 and an acrylamide content of less than 50 %, preferably less than 20 %, of the polymer. Most preferably, the polymer has a molecular  
 60 weight of from 4,000 to 10,000 and an acrylamide content of from 5 % to 15 %. Such a polymer acts to increase the percentage of a crutcher mix that is in the aqueous (lye) phase. This improves the rate at which droplets of the crutcher mix will dry in a spray tower and can desirably increase the density of the resulting detergent granules when, for example, large amounts of sodium sulfate or other high-density inorganic salt is in the lye phase.

65 It has also been found, surprisingly, that a mixture of the preferred polyacrylamide copolymer and

from 0.5 % to 2 %, preferably from 0.5 % to 1 %, by weight of a low-ratio silicate, i.e., one having a ratio of from 1.0 to 1.4, provides optimum granule structure and solubility. In an especially preferred aspect, the crutcher mix contains additional alkalinity, e.g. by way of added sodium carbonate at a level from 1 % to 30 % or its alkalinity equivalent, as a water-soluble inorganic material and contains less than 50 % sodium sulfate, by weight of the finished product, preferably less than 30 %, to achieve normal densities without additional additives.

Other ingredients commonly used in detergent compositions can be included in the compositions of the present invention. These include colour speckles, bleaching agents and bleach activators, suds boosters or suds suppressors, anti-tarnish and anti-corrosion agents, soil suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, pH adjusting agents, non-builder alkalinity sources, hydrotropes, enzymes, enzyme-stabilizing agents, and perfumes.

The following non-limiting examples illustrate the detergent compositions of the present invention.

All percentages, parts, and ratios used herein are by weight unless otherwise specified.

The following granular detergent compositions were evaluated using the indicated tests.

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#### Compression test

The granules are poured into a standard cylinder and compressed by applying a 20 pound (9.08 Kg) weight for about 60 seconds. The difference in height in inches (cm) is the compression grade. Lower numbers are therefore better. Grades of less than about 30 inches (76.2 cm) are acceptable.

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#### Cake test

The compressed, unsupported cylinder of granules created by the compression test is fractured by applying a weight to the top until the cylinder fractures. The weight in pounds (Kg) required to fracture the cylinder is the cake grade. For products prepared in a small 10' (3.05 m) diameter tower, grades of less than about 20 pounds (9.08 Kg) are acceptable.

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#### Black fabric test

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The detergent composition is dissolved in water under standard conditions and filtered with suction through a black knit fabric and graded against photographic standards. Grades of 8 to 10 are acceptable.

#### Example I (comparative)

35

| Component   | Parts |
|---|-------|
| Sodium C <sub>12</sub> alkyl benzene sulfonate                    | 7.0   |
| Sodium C <sub>14-15</sub> alkyl polyethoxy <sub>2.2</sub> sulfate | 5.5   |
| Sodium tallow alkylsulfate  | 5.5   |
| Hydrated sodium Zeolite A (avg. diameter of 3 µm)                 | 24.4  |
| Sodium silicate (1.6 r)   | 8.5   |
| Sodium sulfate  | 24.6  |
| Water   | 7.6   |
| Sodium carbonate (admixed)  | 14.6  |

50

The above composition had a black fabric grade of 4. Grades of 10 were obtained when the 8.5 parts of sodium silicate was replaced with : 0.8 parts of sodium cellulose sulfate and 7.7 parts of sodium sulfate ; and 3 parts of sodium cellulose sulfate and 5.5 parts of sodium sulfate.

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(See Table page 9)

65



## Examples

| Component  | II             | III             | IV               | V               | VI              | VII             | VIII            |
|--|----------------|-----------------|------------------|-----------------|-----------------|-----------------|-----------------|
| Sodium C <sub>12</sub> alkyl benzene sulfonate                         |                |                 | 6.2              |                 |                 |                 |                 |
| Sodium C <sub>14-15</sub> alkyl polyethoxy <sub>2,2</sub> sulfate      |                |                 | 4.9              |                 |                 |                 |                 |
| Sodium tallow alkylsulfate   |                |                 | 4.9              |                 |                 |                 |                 |
| Hydrated sodium Zeolite A (avg. diameter of 3 µm)                      | 20             | 20              | 20               | 25              | 25              | 25              | 25              |
| Sodium silicate (1.6 r)  | 2              | 0               | 0                | 0               | 0               | 0               | 0               |
| Sodium silicate (1.0 r)  | 0              | 2               | 2                | 1               | 2               | 2               | 2               |
| Sodium carbonate (crutched)  | 0              | 0               | 0                | 0               | 20              | 20              | 5               |
| Sodium carbonate (admixed)   | 13             | 13              | 13               | 13              | 0               | 0               | 15              |
| Polyacrylamide/acrylate sodium<br>(M. Wt. of 4000—10,000; 5—15% anide) | 2              | 2               | 2                | 2               | 2               | 1               | 2               |
| Water  |                |                 |                  | 5—6%            |                 |                 |                 |
| Miscellaneous minors and sodium sulfate                                |                |                 |                  | balance         |                 |                 |                 |
| Cake grade (pounds)<br>(kilograms)                                     | 1—3<br>0.4—1.3 | 6—14<br>2.7—6.3 | 12—20<br>5.4—9.0 | 1—11<br>0.4—4.9 | 5—10<br>2.2—4.5 | 5—10<br>2.2—4.5 | 8—12<br>3.6—5.4 |
| Compression grade (inches)<br>(centimeters)                            | 9—12<br>23—30  | 12—14<br>30—36  | 16—18<br>41—46   | 10—15<br>25—38  | 8—14<br>20—35   | 8—14<br>20—35   | 11—14<br>28—35  |
| Black fabric grade (initial)   | 7'             | 9               | 10               | 9               | 10              | 10              | 10              |
| Black fabric grade (aged)<br>(line powder)                             | 6'             | 8.5             | 9                | 8.5             | 10              | 10              | 10              |

## Claims

1. A detergent composition comprising :

(a) from 5 % to 40 % by weight of an organic surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof ;

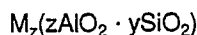
(b) from 10 % to 60 % by weight of a finely-divided aluminosilicate ion exchange material selected from the group consisting of :

(1) crystalline aluminosilicate material of the formula :



wherein z and y are at least 6, the molar ratio of z to y is from 1.0 to 0.5 and x is from 10 to 264, said material having a particle size diameter of from 0.1  $\mu\text{m}$  to 10  $\mu\text{m}$ , a calcium ion exchange capacity of at least 200 mg.  $\text{CaCO}_3$  eq./g. and a calcium ion exchange rate of at least 0,034 g  $\text{Ca}^{++}$ /liter/minute/g/3,79 l ;

(2) amorphous hydrated aluminosilicate material of the empirical formula :



wherein M is sodium, potassium, ammonium or substituted ammonium, z is from 0.5 to 2 and y is 1, said material having a magnesium ion exchange capacity of at least 50 milligram equivalents of  $\text{CaCO}_3$  hardness per gram of anhydrous aluminosilicate and a  $\text{Mg}^{++}$  exchange rate of at least 0,017 g  $\text{Ca}^{++}$ /liter/minute/g/3,79 l ; and

(3) mixtures thereof ;

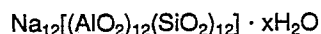
(c) from 0.5 % to less than 3 % by weight of alkali metal silicate materials ; and

(d) from 5 % to 75 % by weight of a water-soluble neutral or alkaline salt ; said composition containing less than 10 % by weight of phosphate materials, characterised in that the composition contains

(e) from 0.1 % to 10 % by weight of a film-forming polymer soluble in an aqueous slurry comprising the above components, said film-forming polymer being an at least partially neutralised salt of : a homopolymer of acrylic acid, hydroxyacrylic acid or methacrylic acid ; or a copolymer of acrylic acid, hydroxyacrylic acid or methacrylic acid with a comonomer lacking carboxyl groups ; cellulose acetate sulfate, cellulose sulfate, hydroxyethylcellulose sulfate, methylcellulose sulfate or hydroxypropylcellulose sulfate, further characterised in that components (a), (b), (c), (d) and (e) have been formed into an aqueous slurry and dried to form granules.

2. A composition according to claim 1 wherein the organic surfactant represents from 10 % to 30 % by weight and is selected from the group consisting of linear alkylbenzene sulfonates containing from 11 to 14 carbon atoms in the alkyl group ; tallowalkyl sulfates ; coconutalkyl glyceryl ether sulfonates ; alkyl ether sulfates wherein the alkyl moiety contains from 14 to 18 carbon atoms and wherein the average degree of ethoxylation is from 1 to 4 ; olefin or paraffin sulfonates containing from 14 to 16 carbon atoms ; alkyl-dimethyl amine oxides wherein the alkyl group contains from 11 to 16 carbon atoms ; alkyl-dimethylammonio propane sulfonates and alkyl-dimethylammonio hydroxy propane sulfonates wherein the alkyl group contains from 14 to 18 carbon atoms ; soaps of higher fatty acids containing from 12 to 18 carbon atoms ; condensation products of  $\text{C}_9$ - $\text{C}_{15}$  alcohols with from 4 to 8 moles of ethylene oxide, and mixtures thereof.

3. A composition according to claim 1 or 2 comprising from 15 % to 30 % by weight of the aluminosilicate ion exchange material of the formula



wherein x is from 20 to 30.

4. A composition according to any of claims 1-3 comprising from 10 % to 60 % by weight of the water-soluble neutral or alkaline salt.

5. A composition according to any of claims 1-4 comprising from 0.5 % to 7 % by weight of the film-forming polymer having a molecular weight of from 1000 to 500,000.

6. A composition according to claim 5 wherein the film-forming polymer is selected from : a copolymer of acrylamide and sodium acrylate having a molecular weight of from 3000 to 100,000 and an acrylamide content of less than 50 %, preferably from 5 % to 15 % ; and sodium polyacrylate or sodium polyhydroxyacrylate.

7. A composition according to claim 1 containing from 0.5 % to 2 % by weight of sodium or potassium silicate having a molar ratio of  $\text{SiO}_2$  to alkali metal oxide of from 1 to 1.4.

## Patentansprüche

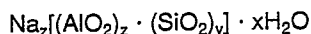
1. Eine Detergenezusammensetzung, enthaltend :

(a) 5 Gew.-% bis 40 Gew.-% eines organischen oberflächenaktiven Mittels, ausgewählt aus der aus

anionischen, nichtionischen, zwitterionischen, ampholytischen und kationischen oberflächenaktiven Mitteln und Mischungen davon bestehenden Gruppe ;

(b) 10 Gew.-% bis 60 Gew.-% eines feinteiligen Aluminosilicationenaustauschmaterials, ausgewählt aus der aus :

5 (1) kristallinem Aluminosilicatmaterial der Formel :



10 worin z und y wenigstens 6 sind, das Molverhältnis von z zu y 1,0 bis 0,5 ist, und x für 10 bis 264 steht, wobei das genannte Material einen Teilchengrößendurchmesser von 0,1 µm bis 10 µm, eine Calciumionenaustauschkapazität von wenigstens 200 mg CaCO<sub>3</sub> Äqu./g und eine Calciumionenaustauschgeschwindigkeit von wenigstens 0,034 g Ca<sup>++</sup>/l/min/g/3,79 l hat ;

(2) amorphem, hydratisiertem Aluminosilicatmaterial der empirischen Formel :

15 
$$\text{M}_z(\text{zAlO}_2 \cdot \text{ySiO}_2)$$

worin M Natrium, Kalium, Ammonium oder substituiertes Ammonium ist, z 0,5 bis 2 ist, und y 1 ist, wobei das genannte Material eine Magnesiumionenaustauschkapazität von wenigstens 50 mg-Äquivalenten CaCO<sub>3</sub>-Härte je g wasserfreies Aluminosilicat und eine Mg<sup>++</sup>-Austauschgeschwindigkeit von wenigstens 20 0,017 g Ca<sup>++</sup>/l/min/g/3,79 l aufweist ; und

(3) Mischungen davon, bestehenden Gruppe ;

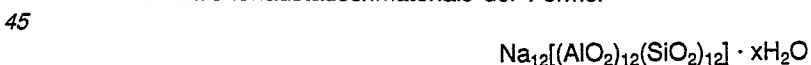
(c) 0,5 Gew.-% bis weniger als 3 Gew.-% Alkalimetallsilicatmaterialien ; und

25 (d) 5 Gew.-% bis 75 Gew.-% eines wasserlöslichen, neutralen oder alkalischen Salzes ; wobei die genannte Zusammensetzung weniger als 10 Gew.-% Phosphatmaterialien enthält ; dadurch gekennzeichnet, daß die Zusammensetzung

(e) 0,1 Gew.-% bis 10 Gew.-% eines filmbildenden, in einer die obigen Komponenten enthaltenden, wässrigen Aufschlämmung löslichen Polymers enthält, wobei das genannte filmbildende Polymer ein wenigstens teilweise neutralisiertes Salz von : einem Homopolymer von Acrylsäure, Hydroxyacrylsäure oder Methacrylsäure ; oder einem Copolymer von Acrylsäure, Hydroxyacrylsäure oder Methacrylsäure mit 30 einem carboxylgruppenfreien Comonomer ; Celluloseacetatsulfat, Cellulosesulfat, Hydroxyethylcellulosesulfat, Methylcellulosesulfat oder Hydroxypropylcellulosesulfat ; ist, weiterhin dadurch gekennzeichnet, daß die Komponenten (a), (b), (c), (d) und (e) in eine wässrige Aufschlämmung gebracht und unter Bildung von Körnern getrocknet worden sind.

2. Eine Zusammensetzung nach Anspruch 1, in der das organische oberflächenaktive Mittel 10 Gew.-% bis 30 Gew.-% ausmacht und aus der Gruppe ausgewählt ist, die aus linearen Alkylbenzolsulfonaten mit 35 11 bis 14 Kohlenstoffatomen in der Alkylgruppe ; Talgalkylsulfaten ; Kokosnußalkylglycerylethersulfonaten ; Alkylethersulfaten, worin der Alkylrest 14 bis 18 Kohlenstoffatome enthält, und worin der mittlere Ethoxylierungsgrad 1 bis 4 beträgt ; Olefin- oder Paraffinsulfonaten mit 14 bis 16 Kohlenstoffatomen ; Alkyldimethylaminoxiden, worin die Alkylgruppe 11 bis 16 Kohlenstoffatome enthält ; Alkyldimethylammonio- 40 propansulfonaten und Alkyldimethylammoniohydroxypropansulfonaten, worin die Alkylgruppe 14 bis 18 Kohlenstoffatome enthält ; Seifen höherer Fettsäuren mit 12 bis 18 Kohlenstoffatomen ; Kondensationsprodukten von C<sub>9</sub>-C<sub>15</sub>-Alkoholen mit 4 bis 8 Mol Ethylenoxid ; und Mischungen davon ; besteht.

3. Eine Zusammensetzung nach Anspruch 1 oder 2, enthaltend 15 Gew.-% bis 30 Gew.-% des Aluminosilicationenaustauschmaterials der Formel



worin x 20 bis 30 ist.

4. Eine Zusammensetzung nach einem der Ansprüche 1 bis 3, enthaltend 10 Gew.-% bis 60 Gew.-% 50 des wasserlöslichen, neutralen oder alkalischen Salzes.

5. Eine Zusammensetzung nach einem der Ansprüche 1 bis 4, enthaltend 0,5 Gew.-% bis 7 Gew.-% des filmbildenden Polymers, das ein Molekulargewicht von 1000 bis 500.000 aufweist.

6. Eine Zusammensetzung nach Anspruch 5, in der das filmbildende Polymer aus : einem Copolymer von Acrylamid und Natriumacrylat mit einem Molekulargewicht von 3000 bis 100.000 und einem 55 Acrylamidgehalt von weniger als 50 %, vorzugsweise 5 % bis 15 % ; und Natriumpolyacrylat oder Natriumpolyhydroxyacrylat ausgewählt ist.

7. Eine Zusammensetzung nach Anspruch 7, enthaltend 0,5 Gew.-% bis 2 Gew.-% Natrium- oder Kaliumsilicat mit einem Molverhältnis von SiO<sub>2</sub> zu Alkalimetalloxid von 1 bis 1,4.

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## Revendications

1. Composition détergente comprenant

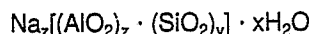
65 (a) 5 % à 40 % en poids d'un tensio-actif organique choisi parmi les tensio-actifs anioniques, nonioniques, zwitterioniques, ampholytiques et cationiques et les mélanges de ceux-ci ;

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(b) 10 % à 60 % en poids d'un échangeur d'ions du type aluminosilicate finement divisé choisi parmi :

(1) un aluminosilicate cristallin de formule :

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dans laquelle z ou y sont au moins égaux à 6, le rapport molaire de z à y est de 1,0 à 0,5 et x est de 10 à 264, cette substance ayant un diamètre de particule compris entre 0,1  $\mu\text{m}$  et 10  $\mu\text{m}$ , une capacité d'échange d'ions calcium d'au moins 200 mg d'équivalents en  $\text{CaCO}_3/\text{g}$  et une vitesse d'échange d'ions calcium d'au

10 moins 0,034 g  $\text{Ca}^{++}/\text{litre}/\text{minute}/\text{g}/3,79 \text{ l}$  ;

(2) un aluminosilicate hydraté amorphe de formule empirique :



15 dans laquelle M est le sodium, le potassium, l'ammonium ou un ammonium substitué, z va de 0,5 à 2 et y est égal à 1, cette substance ayant une capacité d'échange d'ions magnésium d'au moins 50 mg exprimée en équivalents de dureté de  $\text{CaCO}_3$  par gramme d'aluminosilicate anhydre et une vitesse d'échange de  $\text{Mg}^{++}$  d'au moins 0,017 g  $\text{Ca}^{++}/\text{litre}/\text{minute}/\text{g}/3,79 \text{ l}$  ; et

(3) Les mélanges de ceux-ci ; et

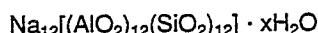
20 (c) de 0,5 % à moins de 3 % de silicates de métaux alcalins, et

(d) 5 % à 75 % en poids d'un sel neutre ou alcalin soluble dans l'eau ; cette composition contenant moins de 10 % de phosphates caractérisée en ce que la composition contient

(e) 0,1 à 10 % en poids d'un polymère susceptible de former une pellicule soluble dans une bouillie aqueuse comprenant les constituants ci-dessus, ce polymère formant pellicule étant un sel au moins  
25 partiellement neutralisé de : un homopolymère de l'acide acrylique, de l'acide hydroxyacrylique ou de l'acide méthacrylique ; ou un copolymère de l'acide acrylique, de l'acide hydroxyacrylique ou de l'acide méthacrylique et d'un monomère dénué de groupes carboxyle ; l'acétate-sulfate de cellulose, le sulfate de cellulose, le sulfate d'hydroxyéthylcellulose, le sulfate de méthylcellulose ou le sulfate d'hydroxypropyl-  
cellulose, caractérisée en outre en ce que les composants (a), (b), (c), (d) et (e) ont été transformés en une  
30 bouillie aqueuse et séchés pour donner des granules.

2. Composition selon la revendication 1, caractérisée en ce que le tensio-actif organique représente 10 % à 30 % en poids et est choisi parmi les alkyl (linéaires) benzènesulfonate contenant 11 à 14 atomes de carbone dans le groupe alkyle ; les alkyl (de suif) sulfates ; les alkyl (de noix de coco) glycéryléthersulfonates ; les alkyléthersulfates dans lesquels la partie alkyle contient 14 à 18 atomes de carbone et dans  
35 lesquels le degré moyen d'éthoxylation est de 1 à 4 ; les oléfine — ou paraffine — sulfonates contenant 14 à 16 atomes de carbone ; les oxydes d'alkyldiméthylamines dans lesquels le groupe alkyle contient 11 à 16 atomes de carbone ; les alkyldiméthylaminopropane-sulfonates et les alkyldiméthylammoniohydroxypropane-sulfonates dans lesquels le groupe alkyle contient 14 à 18 atomes de carbone ; les savons d'acides gras supérieurs contenant 12 à 18 atomes de carbone ; les produits de condensation d'alcools  
40 en  $\text{C}_9\text{-C}_{15}$  et de 4 à 8 moles d'oxyde d'éthylène et les mélanges de ceux-ci.

3. Composition selon la revendication 1 ou 2, caractérisée en ce qu'elle comprend 15 % à 30 % en poids de l'échangeur d'ions du type aluminosilicate de formule :



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dans laquelle x va de 20 à 30.

4. Composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce qu'elle comprend 10 % à 60 % en poids du sel neutre ou alcalin soluble dans l'eau.

5. Composition selon l'une quelconque des revendications 1 à 4, caractérisée en ce qu'elle  
50 comprend 0,5 % à 7 % en poids du polymère formant pellicule ayant un poids moléculaire compris entre 1000 et 500 000.

6. Composition selon la revendication 5, caractérisée en ce que le polymère formant pellicule est choisi parmi : un copolymère d'acrylamide et d'acrylate de sodium ayant un poids moléculaire compris entre 3000 et 100 000 et une teneur en acrylamide inférieure à 50 %, de préférence comprise entre 5 % et  
55 15 % ; et du polyacrylate de sodium ou du polyhydroxyacrylate de sodium.

7. Composition selon la revendication 1, caractérisée en ce qu'elle comprend 0,5 % à 2 % en poids d'un silicate de sodium ou de potassium ayant un rapport molaire à  $\text{SiO}_2$  à l'oxyde de métal alcalin compris entre 1 et 1,4.

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