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(54) Aluminosilicate-agglomerates and detergent compositions containing them.

(57) A composition is described herein which contains aluminosilicate materials characterized in their ability to exchange sodium ions for calcium and magnesium ions. The composition also contains, in an intimate mixture with the aluminosilicate, an inorganic salt and a specific low level of certain water-soluble detergent surfactants as agglomerating compounds. The particulate composition described above is suitable for water softening per se or for admixture into detergent compositions.

Croydon Printing Company Ltd.

ALUMINOSILICATE-AGGLOMERATES AND DETERGENT COMPOSITIONS CONTAINING THEM

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Background

1. Field of the Invention

The present invention relates to compositions of matter which are useful for water softening or as detergent builders.

2. Description of the Art

Aluminosilicates which have high calcium and magnesium exchange rates and capacity have been added to water softening and detergent products to remove water hardness. Effective removal of calcium and magnesium ions from water when considered in the context of detergent products is important in that those ions can precipitate anionic surfactants rendering the former less effective in fabric cleaning. Moreover, if the calcium and magnesium ions are not removed from water used for washing, these ions will interact with soils on the fabrics thus interfering with soil removal.

U.S. Patent 3,985,669, issued October 12, 1976, Krummel et al, describes the formulation of a detergent composition containing aluminosilicates and alkali metal silicates. In Krummel et al the silicates are present at a very low level to avoid the interaction with the aluminosilicate. This product is formed by spray drying all of the components in the composition including the aluminosilicate and the alkali metal silicate. Said patent is incorporated herein by reference.

It has been found that the incorporation of the aluminosilicate materials into detergent and water softening compositions described above presents great difficulties. For instance, if aluminosilicates are to be admixed into the composition as a dry material, a considerable quantity of dust can be generated by improper handling of the finely divided aluminosilicate. Moreover, the aluminosilicates per se are not free flowing. It is also noted that if the aluminosilicate materials with which the present invention is concerned are admixed dry with the remainder of a composition, that segregation of the fine aluminosilicate materials will occur during packing and transportation of the finished product. The segregation is extremely undesirable in that when the consumer uses the product the lack of uniformity may result in over-usage or under-usage.

The present invention is an improvement on U.S. Patent 4,096,081, Phenicie et al, issued June 20, 1978 and incorporated herein by reference. This patent teaches agglomeration of the aluminosilicate particles using an organic agglomerating agent and an inorganic salt. This agglomerate can be admixed with conventional spray-dried detergent granules.

Throughout the specification and claims, percentages and ratios are by weight and temperatures are in degrees centigrade unless otherwise indicated.

Summary of the Invention

A free-flowing particulate water softening composition comprising an intimate mixture of:

(a) from about 60% to about 95% of an aluminosilicate detergency builder, preferably
  (i) an amorphous aluminosilicate;
  (ii) a hydrated crystalline zeolite selected from the group consisting of Zeolite A, X, and P having a particle size of from about 0.1 to about 25 microns; and
  (iii) mixtures thereof having a calcium ion exchange capacity of at least about 200 mg eq./g (four milliequivalents/g.); and a calcium ion exchange rate of at least about 2 grains/gallon/minute gram;
(b) from about 1% to about 4% of synthetic anionic detergent surfactants which are relatively hardness insensitive;
(c) from about 1% to about 10% of an inorganic salt and being essentially free of silicates; and
(d) balance water.

Detailed Description of the Invention

The aluminosilicate detergency builder of this invention comprise both amorphous and crystalline aluminosilicates as is well known in the art. U.S. Patent 4,096,081 contains a description of such builders. Zeolites A, X and P are preferred, with Zeolite A being most preferred.

An essential feature of the ion exchange builder materials herein is that they be in a hydrated form, i.e., contain at least about 10% by weight of water. Highly preferred Zeolite A aluminosilicates herein contain the theoretical maximum of from about 18% to about 22%

(wt.) water in their crystal matrix. It has been found, for example, that less highly hydrated Zeolite A aluminosilicates, e.g., those with about 6% water, do not function effectively as ion exchange builders when employed in the context of a laundry detergent composition.

A second essential feature of the ion exchange builder materials herein is their particle size range. Of course, the amorphous aluminosilicates inherently have a small particle size (ca. 0.01 micron - 5 micron diameter). However, the crystalline aluminosilicates must have a small particle size in the range disclosed herein. Proper selection of small particle sizes results in fast, highly efficient builder materials. Moreover, the small particle size of the preferred aluminosilicates herein (≤10 microns) presumably accounts for the fact that they are not noticeably deposited on fabrics from an aqueous laundering liquor. This nondeposition is, of course, desirable when the aluminosilicates are employed as detergent builders.

The amorphous aluminosilicate ion exchange builder/water softening materials herein can be prepared according to the following procedure:

(a) Admix sodium aluminate ($NaAlO_2$) and sodium hydroxide in water to form a mixture having the following (preferred) weight ratios of the components:

$H_2O/NaAlO_2 = 2.9:1$
$H_2O/NaOH = 5.2:1$
$NaAlO_2/NaOH = 1.8:1$.

The temperature of the mixture is adjusted to about 20°C-70°C, preferably about 50°C. If prepared at lower temperatures, the mixture of aluminate and sodium hydroxide is not a true solution and may contain a small quantity of finely dispersed particulate materials.

(b) Add a sodium silicate solution (ca. 37% wt. solid; 3.2:1 SiO_2/Na_2O ratio) rapidly to the mixture of step (a). This rapid mixing step can be carried out using a vessel employed with an efficient agitator; alternatively, the two mixtures at the desired temperature can be metered into an inline mixer which can be part of a dominant bath system to provide a continuous process. The ratio of $NaAlO_2$ to sodium silicate (anhydrous basis) is about 1.6:1.

(c) Heat the mixture of step (b) rapidly to 75°C to 95°C (preferably 80°C - 85°C) and maintain at this temperature for 10 minutes to 60 minutes (preferably 10 minutes - 20 minutes).

(d) Cool the slurry from step (c) to about 50°C and filter. Recover the resulting filter cake and wash in water using a sufficient quantity of water to yield a wash water/solids (anhydrous basis) weight ratio of about 2.0:1 (preferred). Repeat the filtration and washing operations.

The filter cake prepared by the foregoing process comprises a mixture of crystalline aluminosilicate and amorphous aluminosilicate in approximately a 1:1 (wt.) ratio. The material from the filter cake exhibits a rapid and efficient uptake of both Ca^{++} and Mg^{++} ions. The filter cake is useful per se as an ion exchange material. For use in powdered or granular detergent compositions, it is preferred to dry the filter cake only the minimum amount to eliminate free moisture, using a drying temperature below about 175°C to avoid excessive dehydration. Preferably, the drying is performed at 100°C to 105°C.

The amorphous aluminosilicate of this invention can, if desired, be separated from the amorphous-crystalline mixture prepared in the foregoing manner by simply suspending the filter cake mixture in water. When thus suspended, the crystalline portion of the mix settles out (over a period of about 1-6 hours), whereas the amorphous material remains suspended in the aqueous medium. The amorphous material can be separated by decantation or other physical means. Of course, low speed centrifugation can be employed to more rapidly separate the amorphous component from the crystalline component of the mixtures herein.

Both the crystalline and amorphous aluminosilicate ion exchangers herein are further characterized by their calcium ion exchange capacity which is preferably at least about 200 mg. equivalent of $CaCO_3$ hardness/gram of aluminosilicate, calculated on an anhydrous basis, and which preferably lies within the range of about 300 mg. eq./g. to about 352 mg. eq./g.

The ion exchange materials herein are further characterized by their calcium ion exchange rate which is at least about 2 grains

(Ca^{++})/gal./min./g. of aluminosilicate (anhydrous basis). Optimum aluminosilicates for builder purposes exhibit a Ca^{++} exchange rate of at least about 4 gr./gal./min./g.

The amorphous aluminosilicate ion exchanges herein are further characterized by their magnesium exchange capacity, which is at least about 50 mg. eq. of $CaCO_3$ hardness/gram of aluminosilicate, calculated on an anhydrous basis, and which generally lies within the range of about 50 mg. eq./g. to 150 mg. eq./g. or greater.

The amorphous ion exchange materials herein are still further characterized by their magnesium ion exchange rate which is at least about 1 grain (Mg^{++})/gal./min./g. of aluminosilicate (anhydrous basis). Optimum aluminosilicates for builder purposes exhibit a magnesium exchange rate of at least about 2 gr./gal./min./g.

The ion exchange properties of the aluminosilicates herein can conveniently be determined by means of a calcium ion electrode and a divalent ion electrode. In this technique the rate and capacity of Ca^{++} and Mg^{++} uptake from an aqueous solution containing a known quantity of Ca^{++} and Mg^{++} ions are determined as a function of the amount of aluminosilicate ion exchange material added to the solution. More specifically, the ion exchange rates of the amorphous and mixed amorphous-crystalline aluminosilicates herein are determined as follows. The aluminosilicate prepared in the foregoing manner is added in the sodium form to 150 ml. of aqueous solution containing 4.7 gr./gal. Ca^{++} and 2.4 gr./gal. Mg^{++} (measured as $CaCO_3$) at a concentration of 0.06% (wt.), pH of 10.0, and with gentle stirring of the solution. The rate of calcium depletion is measured using the calcium electrode (commercially available; Orion) and the rate of total calcium and magnesium depletion is determined using the general divalent cation electrode. Magnesium ion removal is thereafter determined by the difference in readings. The rate of depletion is determined for each cation by taking measurements at appropriate time intervals. Total depletion from the solution is calculated after ten minutes, which corresponds to the normal wash time in an aqueous laundering process. Rate curves for calcium depletion, magnesium depletion and mixed calcium and magnesium depletion can be plotted as gr./gal. *v*. time.

Calcium exchange capacity of the aluminosilicates herein can be determined by a simple titration method. In practice the aluminosilicate sample is equilibrated with a known excess of Ca^{++}. After equilibration and uptake of the calcium ion, the excess calcium ion remaining in solution is determined by a standard titration with EDTA, using a standard Eriochrome Black T Indicator. Magnesium ion capacity is determined titrimetrically, in similar fashion.

As noted hereinabove, both the crystalline and amorphous aluminosilicates herein exhibit excellent rates of exchange and capacities for calcium ions. Moreover, the amorphous material herein additionally provides rapid and efficient uptake of magnesium ions. Accordingly, a mixture of crystalline and amorphous material can provide mixed Ca^{++}/Mg^{++} hardness control.

Preferably, the compositions of this invention are essentially free of the organic agglomerating agents of U.S. Patent 4,096,081.

The surfactant agglomerating agents of this invention include the following.

Preferably the detergent component of the present invention is a water-soluble salt of: an ethoxylated sulfated alcohol with an average degree of ethoxylation of about 1 to about 10 and an alkyl chain length of from about 8 to about 20; an alkyl benzene sulfonate with an average alkyl chain length between about 9 and about 15, preferably from about 11 to about 13, and most preferably about 11.8 carbon atoms; a C_6-C_{20} alpha-sulfocarboxylic acid or ester thereof having 1 to 14 carbon atoms in the alcohol radical; a C_8-C_{18} secondary paraffin sulfonate; a C_{10}-C_{18} olefin sulfonate or mixtures thereof; or other hardness insensitive anionic surfactant. Such preferred detergents are discussed below. Blends of surfactants which exhibit hardness resistance (insensitivity) can be used as well.

An especially preferred alkyl ether sulfate detergent component of the present invention is a mixture of alkyl ether sulfates, said mixture having an average (arithmetic mean) carbon chain length within the range of about 12 to 16 carbon atoms, preferably from about 14 to 15 carbon atoms, and an average (arithmetic mean) degree of ethoxylation of from about 1 to 4 moles of ethylene oxide, preferably from about 2 to 3 moles of ethylene oxide.

Specifically, such preferred mixtures comprise from about 0 to 10% by weight of mixture of C_{12-13} compounds, from about 50 to 100% by weight of mixture of C_{14-15} compounds, and from about 0 to 45% by weight of mixture of C_{16-17} compounds, and from about 0 to 10% by weight of a mixture of C_{18-19} compounds. Further, such preferred alkyl ether sulfate mixtures comprise from about 0 to 30% by weight of mixture of compounds having a degree of ethoxylation of 0, from about 45 to 95% by weight of mixture of compounds having a degree of ethoxylation from 1 to 4, from about 5 to 25% by weight of mixture of compounds having a degree of ethoxylation from 5 to 8, and from about 0 to 15% by weight of mixture of compounds having a degree of ethoxylation greater than 8. The sulfated condensation products of ethoxylated alcohols of 8 to 24 alkyl carbons and with from 1 to 30, preferably 1 to 4 moles of ethylene oxide may be used in place of the preferred alkyl ether sulfates discussed above.

Preferred water-soluble organic detergent compounds herein also include alkyl benzene sulfonates (preferably essentially linear, although "hard" ABS may be used) containing from about 9 to 15 carbon atoms in the alkyl group. Examples of the above are sodium and potassium alkyl benzene sulfonates in which the alkyl group contains from about 11 to about 13 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Pat. Nos. 2,220,099 and 2,477,383. Especially valuable are straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 11.8 carbon atoms, abbreviated as $C_{11.2}$LAS.

Another useful detergent compound herein includes the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and their esters with alcohols containing from about 1 to 14, preferably 1 to 2, carbon atoms.

Preferred "olefin sulfonate" detergent mixtures utilizable herein comprise olefin sulfonates containing from 10 to about 18 carbon atoms. Such materials can be produced by sulfonation of olefins by means of uncomplexed sulfur trioxide followed by neutralization under conditions such that any sultones present are hydrolyzed to the corresponding hydroxy-alkane sulfonates. The alpha-olefin starting materials preferably have from 14 to 16 carbon atoms. Said preferred alpha-olefin sulfonates are described in U.S. Pat. No. 3,332,880, incorporated herein by reference.

The secondary paraffin sulfonates embraced in the present invention are essentially linear and contain from about 8 to about 18 carbon atoms, preferably from about 12 to about 16 and more preferably from about 14 to about 15 carbon atoms in the alkyl radical.

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

Other useful detergents include water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 18 carbon atoms in the alkane moiety; beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 18 carbon atoms in the alkane moiety; alkylmethylammoniopropane sulfonates and alkylmethylammoniohydroxypropane sulfonates wherein the alkyl group in both types contains from about 14 to 18 carbon atoms; and alkyl glycerol ether sulfates with from 10 to 18 carbon atoms in the alkyl radical.

A typical listing of the classes and species of detergent compounds useful herein appear in U.S. Pat. No. 3,852,211, to Ohren issued Dec. 3, 1974, incorporated herein by reference. The foregoing list of detergent compounds and mixtures which can be used in the instant compositions is representative of such materials, but is not intended to be limiting.

The compositions comprise from about 1 to about 4%, preferably from about 2% to about 3% of hardness insensitive anionic surfactant. Higher levels of surfactant simply dilute the zeolite without any benefit and can give undesirable physical properties to the agglomerate.

The surfactant improves dispersion of the zeolite as shown hereinafter thus minimizing unacceptable deposits, e.g. on fabrics, and increasing the rate of ion exchange.

The inorganic salts are water soluble and form ions. They promote dispersion of the aluminosilicate as shown to rapidly control the water hardness. Examples of such inorganic salts include those having alkali metal cations such as sodium, or potassium, and having as anions thereof sulfates, chlorides, carbonates, bicarbonates, aluminates and phosphates, and mixtures thereof.

Preferred inorganic salts include sodium sulfate, sodium carbonate, sodium orthophosphate, sodium pyrophosphate, sodium tripolyphosphate, and sodium hexametaphosphate. Especially preferred are sodium sulfate and sodium carbonate. Alkali metal silicates should not be present because of their ability to polymerize the aluminosilicate leading to deposits upon washed fabrics.

When the aluminosilicate, the inorganic salt and the organic surfactant are to be incorporated into a detergent composition, additional surface active agent (detergent surfactant) will be included as a portion of the overall detergent composition since the level of surfactant herein is insufficient to form a complete detergent product.

Exemplary of detergent components which may be used in the present invention are those described in U.S. Patent 3,852,211 to Ohren, issued December 3, 1974, which is herein incorporated by reference.

Composition Preparation

The preparation of the particulate containing the aluminosilicate, the inorganic salt and the detergent surfactant is described as follows:

(a) dispersing the detergent surfactant;

(b) dispersing the inorganic salt into the detergent surfactant;

(c) admixing into the dispersed detergent surfactant the aluminosilicate of the present invention, thereby forming an intimate mixture; and,

(d) solidifying the resultant mass to form the particulate. Alternatively, the detergent surfactant can be sprayed onto a bed of the aluminosilicate and the inorganic salt. Water may be added to the mixture of the detergent surfactant, the inorganic salt, and the aluminosilicate to facilitate mixing. The excess water is then driven off by heating on forming the particulate.

In a preferred method, sulfuric acid is added to the synthesis liquor of the aluminosilicate to neutralize excess caustic (while staying above pH 9) and form Na_2SO_4. The surfactant is then dispersed in the slurry and the product is spray or flash dried.

Another preferred method of preparing the particulate of the present invention is to spray the mixture of the aluminosilicate, the inorganic salt and the detergent surfactant to form granules of the size compatible with normal detergent particles. It is to be understood, however, that the product can take several forms, e.g. cakes, flakes, prills, or granules which are reduced by conventional methods to the appropriate size.

The preferred method of preparing the particulate of the present invention is by spray-drying or spray cooling the mass to form the particulate. It is essential when spray-drying is employed that the aluminosilicate should not be dehydrated beyond the point where its ion exchange capacity is adversely affected. Also, certain of the surfactants which are heat sensitive should not be heated to the extent at which they begin to decompose.

When a spray-drying operation is used to prepare the agglomerate the apparatus for conducting the drying operating may be a multilevel spray-drying tower such as that described in U.S. Patent 3,629,950 and 3,629,955 issued to Davis et al, both of which are herein incorporated by reference.

In preparing the particulate of the present invention the detergent surfactant will be present at from about 1/2% to about 4%, preferably from about 1-1/2% to about 2-1/2% by weight while the aluminosilicate will be present at from about 60% to about 95%, preferably from about 70% to about 80% by weight.

The inorganic salts which promote lessened friability are used at a level of from about 1/2% to about 10%, preferably from about 2% to about 4%. Larger amounts of the inorganic salts may be utilized in the particulate, however, the benefit reaches a maximum at about 5% and additional amounts merely take up more formula room.

Composition Utilization

When the particulate of the present invention is utilized as a water softener for laundering purposes, it is simply added to the wash tub or washing machine, preferably before the fabrics and the detergent composition are introduced and after the water has been introduced into the container.

When the particulate of the present invention is used as part of a complete detergent product admixed with a separate granule containing additional detergent surfactant, the overall product is desirably added to the wash tub or the washing machine before the fabrics and after the water has been added.

The amount of the particulate utilized as a water softening pretreatment is simply an amount sufficient to remove most of the calcium and magnesium ions present in the wash water. As the product of the present invention normally has a density of from about 0.45 gram per cc to about 0.65 gram per cc, sufficient usage of the product will, under most United States conditions, be satisfied by the use of from about 1/4 cup to about 1 cup. Under continental European washing conditions where the water hardness is somewhat greater, the product will normally be used at a level of from about 1/2 cup to about 3 cups.

Laundry detergent products of the present invention as used under U.S. washing conditions at from about 1/2 to about 1-1/2 cups and from about 1 cup to about 3 cups under European washing conditions.

The agglomerate of this invention, when added to a spray-dried detergent granule containing a surfactant to give an agglomerate level of from about 5% to about 80%, preferably from about 10% to about 60% by weight of the total composition, provides a complete detergent composition with little or no apparent formation of insolubles. This is especially important when the spray-dried detergent granule contains large amounts of silicates. In order to avoid segregation, the agglomerate should have a size that is compatible with the detergent granule, e.g., not less than about 100 microns in diameter, preferably not less than about 150 microns in diameter. The agglomerates of this invention do not break down unacceptably under ordinary handling and shipping.

Particle size can be adjusted by sieving and recycling or by adjusting spray drying pressure and nozzle size.

Preferably the agglomerates of this invention are completely free of the agglomerating compounds of U.S. Patent 4,096,081, and especially free of the polyethylene glycol of said patent.

The following are Examples of the present invention:

EXAMPLE I

Detergent compositions were made with the intent of increasing the thoroughness of zeolite builder dispersion in wash water. The expected benefits of increased dispersion are (1) reduced incidence of insoluble aggregates on washed fabrics, and (2) increased rate of zeolite availability for complexation of water hardness.

The method used for evaluating degree of dispersion involved Nephelometer Turbidity Unit (NTU) measurements of wash water concentrations (0.3 g. active zeolite/1. city water at about 9 grains/gallon hardness). A water sample was grabbed after four minutes of normal wash agitation with the zeolite-containing composition present. A higher turbidity reading indicates greater exposed particle surface and thus more effective dispersion. A more sustained turbidity reading after 30 minutes of static observation indicates a slower settling rate and thus a smaller average zeolite aggregate size. Zeolite A, Arogen 2000 from Huber Co., was used in these experiments.

	Turbidity, NTU	
Composition	Initial Reading	30 Min. Static Reading
A. Zeolite, as received	80	40
B. Zeolite in currently commercial detergent product	175	98
C. Zeolite + sodium sulfate	110	60
D. Zeolite + Na_2So_4 + polyethylene glycol (M.W. 8000) (PEG)	165	90
E. Zeolite + Na_2SO_4 + PEG + C_{14-16} alkyl polyethoxy 2.3 sulfate	255	200
F. Zeolite + Na_2SO_4 + C_{14-16} alkyl polyethoxy 2.3 sulfate	280	250

G. Zeolite + Na_2SO_4 + PEG sodium $C_{11.8}$ alkyl benzene sulfonate ($C_{11.8}$ LAS)	220	165
H. Zeolite + Na_2SO_4 + $C_{11.8}$ LAS	280	190

It is known that electrolytes alone aid in dispersion of aluminosilicates in an aqueous medium, and this is seen in comparing A and C. The addition of a binding and wetting agent, polyethylene glycol (PEG 8000), in D (ref. Patent 4,096,081) improves dispersibility to the level seen with a typical full detergent composition (non-phosphate), as in B. Addition of a relatively hardness-insensitive synthetic surfactant in E and G improves the dispersion, though <u>removal</u> of the PEG (F and H) <u>now</u> shows further benefit in fineness and stability of the zeolite dispersion.

Both of the surfactants in E-H are acceptably hardness insensitive. A tallow alkyl sulfate, for example, would be precipitated by free hardness and rendered ineffective as a zeolite dispersant. It is noted that the higher sustained dispersion at 30 minutes with samples E and F reflect the greater degree of hardness insensitivity of the alkyl polyethoxy sulfate vs. the alkylbenzene sulfonate of G and H.

In all cases, the zeolite was dried from an aqueous slurry of about 50-60% total water to which the other ingredients had been added.

The slurry was heated to about 140°F and mixed thoroughly. This mixture was then dried in a thin film in a 70°C oven until only about 18-20% H_2O remained. The water of hydration in the Zeolite A is generally not removed under these conditions. The dried cake was granulated and screened through a 14 mesh Tyler screen. The resultant density was about 0.58 g./cc. The particle size was mostly greater than about 150 microns. Zeolite delivered to the wash water was controlled at 0.3 g/l. and other components (except in B) were used as: sodium sulfate at 0.01 to 0.03 g./l., PEG 8000 at 0.01 to 0.015 g./l., and synthetic surfactants at 0.008 g./l.

EXAMPLE II

A base granule was spray dried containing:

	Percentage
Sodium $C_{11.8}$ alkyl benzene sulfonate	4.76
Sodium C_{14-16} alkyl polyethoxylate 1.0 sulfate	11.48
Sodium tallow alkyl sulfate	3.36
Sodium silicate (2.0r)	8.4
Sodium carbonate	18.2
Sodium sulfate	47.3
Trisodium sulfosuccinate	2.8
Water and minors	Balance

27.6% of the following admix, formed by spray drying a slurry according to Example 1H, heated to about 175°F and pressure atomized into a pilot scale (10' diameter) spray-drying tower with 500°F inlet air, was mixed with the above base granule and the mixture was sprayed with .9% polyethyleneglycol (M.W. 8000) and 0.14% perfume The admix density was about 0.55-0.58 g./cc. and the particle size was about 90% greater than 150 micron diameter.

Admix composition:

Zeolite A (dry basis)	72.5%
$C_{11.8}$ linear alkylbenzene sulfonate, sodium salt	2.0%
Sodium sulfate	7.5%
Water	18.0%
Total	100.0%

EXAMPLE III (comparison)

Composition of Example II was made using powdered zeolite (as received) admixed to the base granule composition. The resulting detergent product was excessively dusty and free flow was unacceptable due to bridging and surging. Segregation is a further potential problem with this approach.

EXAMPLE IV

The zeolite composition of Example II is metered into a fluidized bed along with other dry ingredients and nonionic surfactant, minors, and perfume are sprayed on.

Composition:

Zeolite composition from Example III	35%
Ethoxylated nonionic ($C_{12,13}$ $E_{6.5}$)	15%
Sodium tripolyphosphate, granular	25%
Sodium carbonate, granular	10%
Sodium sulfate, granular	14%
Water, colorants, perfume, brighteners	1%
	100%

CLAIMS

1. A stable, rapidly-dispersible zeolite detergent builder agglomerate comprising an intimate mixture of:

   (a) from about 60% to about 95% of an aluminosilicate detergency builder, selected from the group consisting of:
      (i) an amorphous aluminosilicate;
      (ii) a hydrated crystalline zeolite selected from the group consisting of Zeolite A, X, and P having a particle size of from about 0.1 to about 25 microns; and
      (iii)mixtures thereof having a calcium ion exchange capacity of at least about 200 mg eq./g (four milliequivalents/g.); and a calcium ion exchange rate of at least about 2 grains/gallon/minute gram;
   (b) from about 1% to about 4% of synthetic anionic detergent surfactant which is relatively hardness insensitive;
   (c) from about 1% to about 10% of an inorganic salt and being essentially free of silicates; and
   (d) balance water.

2. The agglomerate of Claim 1 wherein the aluminosilicate is from about 70% to about 80% by weight, the surfactant is from about 1-1/2% to about 2-1/2% by weight, and the inorganic salt is from about 2% to about 4% by weight.

3. The agglomerate of Claim 2 wherein the surfactant is selected from the group consisting of water-soluble salts of:

   (a) alcohol polyethxylate sulfates wherein the alcohol contains from about 8 to about 20 carbon atoms and the average degree of ethoxylation is from about 1 to about 10;
   (b) alkylbenzene sulfonates with alkyl groups containing from about 9 to about 15 carbon atoms;
   (c) alpha-sulfocarboxylic acids containing from about 6 to about 20 carbon atoms;
   (d) the esters of (s) with alcohols containing up to about 14 carbon atoms;
   (e) secondary paraffin sulfonates containing from about 8 to about 18 carbon atoms;

(f) olefin sulfonates containing from about 8 to about 18 carbon atoms; and

(g) mixtures thereof.

4. The agglomerate of Claim 1 wherein the zeolite is selected from the group consisting of zeolites A, X, P and mixtures thereof.

5. The agglomerate of Claim 1 wherein the zeolite is Zeolite A.

6. The agglomerate of Claims 1, 3, 4, or 5 wherein the inorganic salt is selected from the group consisting of sodium and potassium sulfates, chlorides, carbonates, bicarbonates, aluminates, phosphates, and mixtures thereof.

7. The agglomerate of Claims 1, 3, 4 or 5 wherein the inorganic salt is sodium carbonate or sodium sulfate.

8. The agglomerate of Claim 3 wherein the zeolite is selected from the group consisting of Zeolites A, X, P and mixtures thereof.

9. A detergent composition comprising from about 5% to about 80% of the agglomerate of Claim 1 and from about 20% to about 95% of a spray-dried granule containing a surfactant.

RBA:sp/pw(422)

0050897

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 81 20 1157.5

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	DE - A1 - 2 903 058 (UNILEVER N.V.) * claims 1, 2, 10 to 12; page 5, paragraph 2 to page 6 paragraph 1; page 8, paragraph 2; pages 10 and 11, example 1 * --	1-9
X	DE - A1 - 2 704 003 (PROCTER & GAMBLE CO.) * claims 1, 3, 4, 6, 7, 15, 17, 18, 20 and 23 * & FR - A1 - 2 357 485 & US - A1 - 4 096 081 --	1-3, 6,7
D	US - A - 3 985 669 (H.K. KRUMMEL et al.) --	
A	GB - A - 2 006 257 (PQ CORP.) & DE - A1 - 2 843 709 ----	

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	07-12-1981	SCHULTZE

CLASSIFICATION OF THE APPLICATION (Int. Cl.^{3})

C 11 D 3/08
C 11 D 3/12

TECHNICAL FIELDS SEARCHED (Int. Cl.^{3})

C 11 D 3/00

CATEGORY OF CITED DOCUMENTS

- X: particularly relevant
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- P: intermediate document
- T: theory or principle underlying the invention
- E: conflicting application
- D: document cited in the application
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