**EUROPEAN PATENT APPLICATION**

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<th>Application number: 89306334.7</th>
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<td>Date of filing: 23.06.89</td>
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**Priority:** 29.06.88 US 212805

**Date of publication of application:**
03.01.90 Bulletin 90/01

**Designated Contracting States:**
AT BE CH DE ES FR GB GR IT LI LU NL SE

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**Two stage drying of detergent compositions.**

Granular detergent compositions are prepared by forming an aqueous slurry containing tripolyphosphate, pyrophosphate and/or silicate, other neutral or alkaline salt, and optional detergent surfactant, spray drying the slurry in a spray tower to partially dry the granules, and then completing the drying of the granules in a secondary dryer. During the drying process, the granule temperature does not exceed about 90°C to minimize reversion of polyphosphate and formation of silicate insolubles. The resulting granules exhibit improved physical properties versus conventional spray dried granules containing the same water content, or similar physical properties at higher moisture levels.
TWO STAGE DRYING OF DETERGENT COMPOSITIONS

Technical Field

The present invention relates to granular detergent compositions prepared by a two step drying operation that results in granules having a low level of reversion of polyphosphate builder (i.e., reversion of tripolyphosphate to pyrophosphate and orthophosphate, or reversion of pyrophosphate to orthophosphate) and/or improved solubility due to a low level of insoluble silicate formation. After preparing an aqueous slurry comprising the tripolyphosphate, pyrophosphate and/or silicate, other neutral or alkaline salt, water, and optional detergent surfactant, the slurry is spray dried in a spray drying tower in a manner such that the granule temperature does not exceed about 90°C. (As used herein, the granule temperature refers to the bulk granule temperature.) The partially dried granules are then placed in a secondary dryer to complete the drying operation. During the drying process, the granule temperature does not exceed about 90°C to minimize polyphosphate reversion in compositions containing tripolyphosphate and/or pyrophosphate, and to minimize formation of silicate insolubles in compositions containing silicate. Granules prepared by the gentle two stage drying process herein also exhibit improved physical properties, such as better flow characteristics and lower caking grades, versus corresponding spray dried granules containing the same water content. Alternatively, granules exhibiting similar physical properties can be obtained at higher moisture levels when prepared by the present process.

Background of The Invention

Aqueous crutcher mix slurries often contain from about 25% to about 50% by weight of water to allow the slurry to be pumped to the top of spray drying towers. Processes for spray drying large volumes of such slurries in spray drying towers typically utilize inlet air temperatures greater than about 200°C, and often in the range of 300°C to 375°C, in order to remove excess water in the short time (generally about 30 seconds) that the granules remain in the spray drying tower. Crisp, free flowing granules generally contain little free water. However, the amount of free water in the granules varies depending upon the drying conditions (e.g., time, temperature, and air flow) encountered by any particular granule. Some of the granules are over-dried and not only lose all free water, but also bound water or water of hydration. It has been found that when the granule temperature exceeds about 90°C during drying, excessive amounts of tripolyphosphate and pyrophosphate in the granules revert to the lower polyphosphates. It is desirable to minimize the amount of reversion of tripolyphosphate and pyrophosphate, particularly to orthophosphates which can complex with hardness ions and form insoluble deposits on laundered fabrics. Moreover, when the granule temperature exceeds about 90°C, the formation of silicate insolubles increases.

Accordingly, there is a need for a gentle, high volume drying process for granular detergents containing polyphosphate builder and/or silicate to minimize polyphosphate reversion and the formation of silicate insolubles, while still providing granules having good physical properties.

Summary of The Invention

This invention relates to granular detergent compositions prepared by:
(a) forming an aqueous slurry comprising, by weight:
   (1) from 0% to about 50% of a detergent surfactant;
   (2) from about 5% to about 55% of an alkali metal tripolyphosphate or pyrophosphate, or mixtures thereof;
   (3) from about 5% to about 65% of a water-soluble neutral or alkaline salt other than the tripolyphosphate and pyrophosphate in (2); and
   (4) from about 25% to about 50% water;
(b) spray drying the aqueous slurry in a spray tower at an inlet air temperature of at least about 200°C while not exceeding a granule temperature of about 90°C to obtain base granules comprising from about 5% to about 25% by weight of water; and
The invention also relates to granular detergent compositions prepared by:

(a) forming an aqueous slurry comprising, by weight:
   (1) from 0% to about 50% of a detergent surfactant;
   (2) from about 1% to about 50% of an alkali metal silicate having a molar ratio of SiO₂ to alkali metal oxide of from about 1.6 to about 3.2;
   (3) from 0% to about 50% of a finely divided aluminosilicate ion exchange material selected from the group consisting of:
      (i) crystalline aluminosilicate material of the formula:
      \[ Na_{z}[(AlO₂)_{z}·(SiO₂)_{y}]·xH₂O \]
      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 about 0.1 micron to about 10 microns, a calcium ion exchange capacity of at least about 200 mg CaCO₃ eq./g and a calcium ion exchange rate of at least about 2 grains Ca²⁺/gallon/minute/gram/gallon;
      (ii) amorphous hydrated aluminosilicate material of the empirical formula:
      \[ M_{z}(AlO₂·ySiO₂) \]
      wherein \( M \) is sodium, potassium, ammonium, or substituted ammonium, \( z \) is from about 0.5 to about 2 and \( y \) is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO₃ hardness per gram of anhydrous aluminosilicate and a Mg²⁺ exchange rate of at least about 1 grain/gallon/minute/gram/gallon; and
      (iii) mixtures thereof;
   (4) from about 5% to about 65% of a water-soluble neutral or alkaline salt other than the silicate and aluminosilicate in (2) and (3); and
   (5) from about 25% to about 50% water;
(b) spray drying the aqueous slurry in a spray tower at an inlet air temperature of at least about 200°C while not exceeding a granule temperature of about 90°C to obtain base granules comprising from about 5% to about 25% by weight of water; and
(c) drying the base granules in a secondary dryer while not exceeding a granule temperature of about 90°C to obtain granules comprising from about 2% to about 20% by weight of water.

The invention further relates to the two stage drying process used to prepare the above granular detergent compositions.

Detailed Description of The Invention

The granular detergent compositions herein are prepared by a process that first requires the preparation of an aqueous crutcher mix slurry comprising alkali metal tripolyphosphate, pyrophosphate, and/or silicate, together with other water-soluble neutral or alkaline salt, and preferably detergent surfactant. A detailed description of the ingredients in the slurry is as follows.

**Detergent Surfactant**

The crutcher mix slurry can contain from 0% to about 50%, preferably from about 5% to about 40%, more preferably from about 10% to about 30%, by weight, of a detergent surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof. The surfactant preferably represents from about 5% to about 40%, more preferably from about 10% to about 50%, most preferably from about 15% to about 40%, by weight of the finished composition. Surfactants useful herein are listed in U.S. Pat. No. 3,864,961, Norris, issued May 23, 1972, and in U.S. Pat. No. 3,919,678, Laughlin, et al, issued Dec. 30, 1975, both incorporated herein by reference. Useful cationic surfactants also include those described in U.S. Pat. No. 4,222,905, Cockrell, issued Sept. 16, 1980, and in U.S. Pat. No. 4,239,659, Murphy, issued Dec. 16, 1980, both incorporated herein by reference.

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 substituted ammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 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. However, anionic synthetic surfactants are preferred herein and the amount of soap in the slurry is generally limited to less than about 5%, preferably less than about 2%, by weight.

Useful anionic synthetic surfactants include the water-soluble salts, preferably the alkali metal, ammonium and substituted ammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and sulfonic acid group. (Included in the term "alkyl" the alkyl portion of acyl groups.) Examples of this group of surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 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, both of which are incorporated herein by reference. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C₁₁₋₁₃LAS.

Other anionic surfactants suitable for use 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 about 1 to about 10 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group; and sodium or potassium sulfates of alkyl ethylene oxide ether sulfates, containing from about 1 to about 10 units of ethylene oxide per molecule and from about 8 to about 20 carbon atoms in the alkyl group.

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

Water-soluble nonionic surfactants are also useful in the compositions of the invention. However, because of their volatility, such nonionics are generally not present in amounts greater than about 10% by weight of the crutcher mix slurry. Preferably, these nonionics represent less than about 5% by weight of the slurry. Most preferably, these nonionics are not present in the slurry. Nonionic surfactants herein include compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyal-kylene 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 about 6 to about 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to about 12 moles of ethylene oxide per mole of alkyl phenol.

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

Semi-polar nonionic surfactants useful herein include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.
Ampholytic surfactants include 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 about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic watersolubilizing group.

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

Cationic surfactants can also be included in laundry compositions of the present invention. Cationic surfactants comprise a wide variety of compounds characterized by one or more organic hydrophobic groups in the cation and generally by a quaternary nitrogen associated with an acid radical. Pentavalent nitrogen ring compounds are also considered quaternary nitrogen compounds. Suitable anions are halides, methyl sulfate and hydroxide. Tertiary amines can have characteristics similar to cationic surfactants at washing solution pH values less than about 8.5. A more complete disclosure of these and other cationic surfactants useful herein can be found in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

Cationic surfactants are often used in detergent compositions to provide fabric softening and/or antistatic benefits. Antistatic agents which provide some softening benefit and which are preferred herein are the quaternary ammonium salts described in U.S. Patent 3,936,537, Baskerville, Jr. et al., issued February 3, 1976, which is incorporated herein by reference. Such materials will normally be present in an amount from about 1% to about 10% by weight of the detergent composition.

Particularly preferred surfactants herein are anionic surfactants selected from the group consisting of the alkali metal salts of C11-13 alkylbenzene sulfonates, C12-18 alkyl sulfates, C12-18 alkyl linear polyethoxy sulfates containing up to about 4 ethylene oxide units, and mixtures thereof.

Alkali Metal Polyphosphate

For certain compositions herein, the crutcher mix slurry further contain from about 5% to about 55%, preferably from about 10% to about 40%, more preferably from about 15% to about 30% of an alkali metal tripolyphosphate or pyrophosphate detergent builder material.

Tripolyphosphates herein may be Form I or Form II, anhydrous or hydrated. Commercially available anhydrous tripolyphosphates typically contain small amounts (e.g., 2-3% by weight) of hydrated material, which aids hydration in the crutcher slurry. Commercially available tripolyphosphates generally also contain about 4% to 12% by weight of a mixture of pyrophosphate and orthophosphate. Of course, the amount of orthophosphate is preferably minimized, as described previously. A particularly preferred material is sodium tripolyphosphate, some of which (e.g., 40-50%) preferably is present in its hexahydrate form in the crutcher mix slurry.

The pyrophosphate salts useful herein can be obtained commercially or can be formed by neutralization of the corresponding pyrophosphoric acids or acid salts. The preferred material herein is sodium or potassium pyrophosphate.

Readily available commercially are tetrasodium pyrophosphate Na4P2O7 and its decahydrate Na4P2O7.10H2O, tetrapotassium pyrophosphate K4P2O7, sodium acid pyrophosphate or "acid pyro" Na2H2P2O7 and its hexahydrate Na2H2P2O7.6H2O, and pyrophosphoric acid H4P2O7. Monosodium pyrophosphate and trisodium pyrophosphate also exist, the latter as the anhydrous form or the mono- or nona-hydrate. The generic formula for the anhydrous forms of these compounds can be expressed as MxHyP2O7, where M is alkali metal and x and y are integers having the sum of 4.

Alkali Metal Silicate

For other compositions herein, the crutcher mix slurry contains from about 1% to about 50%, preferably from about 3% to about 30%, more preferably from about 5% to about 20%, by weight of an alkali metal silicate having a molar ratio of SiO2 to alkali metal oxide of from about 1.6 to about 3.2, preferably from about 1.6 to about 2.4. Sodium silicate, particularly having a molar ratio of from about 1.6 to about 2.2, is preferred.

The alkali metal silicates can be purchased in either liquid or granular form. Silicate solutions or slurries can conveniently be used to avoid having to dissolve the dried form in the aqueous crutcher mix slurry of the components herein.
Aluminosilicate Material

For certain preferred compositions herein containing the silicate in the crutcher mix slurry, the slurry also contains up to about 50%, preferably from about 5% to about 40%, more preferably from about 10% to about 30%, by weight of a finely divided water-insoluble aluminosilicate ion exchange material of the formula
\[ \text{Na}_2[(\text{AlO}_2)_z \cdot (\text{SiO}_2)_y] \cdot x\text{H}_2\text{O} \]
wherein \( z \) and \( y \) are at least about 6, the molar ratio of \( z \) to \( y \) is from about 1.0 to about 0.5 and \( x \) is from about 10 to about 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula
\[ M_z[(\text{AlO}_2)_z \cdot (\text{SiO}_2)_y] \]
wherein \( M \) is sodium, potassium, ammonium or substituted ammonium, \( z \) is from about 0.5 to about 2 and \( y \) is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO\(_3\) hardness per gram of anhydrous aluminosilicate.

The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from about 10% to about 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 about 18% to about 22% water in their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns. Amorphous materials are often smaller, e.g., down to less than about 0.01 micron. Preferred ion exchange materials have a particle size diameter of from about 0.2 micron to about 4 microns. 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, microscopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion exchange materials herein are usually further characterized by their calcium ion exchange capacity, which is at least about 200 mg equivalent of CaCO\(_3\) water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least about 2 grains Ca\(^{++}\)/gallon/minute/gram/gallon of aluminosilicate (anhydrous basis), and generally lies with the range of from about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/minute/gram/gallon, based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a calcium ion exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

The amorphous aluminosilicate ion exchange materials usually have a Mg\(^{++}\) exchange capacity of at least about 50 mg eq. CaCO\(_3\)/g (12 mg Mg\(^{++}\)/g) and a Mg\(^{++}\) exchange rate of at least about 1 grain/gallon/minute/gram/gallon. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units).

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, incorporated herein by reference. 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
\[ \text{Na}_{12}[(\text{AlO}_2)_{12} \cdot (\text{SiO}_2)_{12}] \cdot x\text{H}_2\text{O} \]
wherein \( x \) is from about 20 to about 30, especially about 27.

Neutral or Alkaline Salt

The crutcher mix slurry herein also contains from about 5% to about 65%, preferably from about 10% to about 50%, more preferably from about 15% to about 40%, by weight, of a water-soluble neutral or alkaline salt other than the tripolyphosphate, and pyrophosphate described above in compositions containing these ingredients, or other than the alkali metal silicate and aluminosilicate materials described above in compositions containing these ingredients. Other neutral or alkaline salts herein are described in U.S. Patent 4,379,060, Murphy, issued April 5, 1987, incorporated herein by reference. Such neutral or alkaline salts have a pH in solution of about seven or greater, and can be either organic or inorganic in nature. While some of the salts are inert, many of them also function as detergency builder materials in solution. Preferably, the salts are inorganic.
Examples of neutral water-soluble salts include the alkali metal, ammonium or substituted ammonium chlorides and sulfates. The alkali metal, and especially sodium, salts of the above are preferred. Sodium sulfate and sodium carbonate are typically found in detergent granules and are preferred salts herein.

The water-soluble salts herein preferably include the compounds commonly known as detergent builder materials. Such builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, phosphonates, polyphosphonates, carbonates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above.

Specific examples of inorganic phosphate builders are polymeric metaphosphate having a degree of polymerization of from about 6 to 21. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 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; 3,400,178; and 3,400,148, incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, and tetraborate decahydrate.

Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Salts of nitritotriacetic acid, such as sodium nitritotriacetate, are particularly preferred.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference. 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 methylenemalonic acid.

Other useful builders herein are sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentanetetracarboxylate, phloroglucinol 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 4,144,228, issued March 13, 1979 to Crutchfield et al, and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al, both incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polycetal carboxylate ester is then attached to chemically stable end groups to stabilize the polycetal carboxylate against rapid depolymerization in alkaline solution and converted to the corresponding salt. Preferred polycarboxylate builders herein are described in U.S. Patent 4,663,071, Bush et al, issued May 5, 1987, incorporated herein by reference.

The neutral or alkaline salt of the present invention is preferably selected from the alkali metal polycarboxylates, carbonates, sulfates, and silicates (in compositions containing tripolyphosphates and/or pyrophosphates), and mixtures thereof.

Water

The crutcher mix slurry herein also contains from about 25% to about 50%, preferably from about 30% to about 45%, more preferably from about 30% to about 40%, by weight, of water.

Spray Drying Tower

The aqueous crutcher mix slurry is spray dried in a spray drying tower at an inlet air temperature of at least about 200°C in a manner so that the bulk granule temperature does not exceed about 90°C to obtain base granules containing from about 5% to about 25% water. If there is more than about 5% alkali metal tripolyphosphate in the slurry, the base granules preferably contain from about 8% to about 20% by weight of water. Otherwise, the base granules preferably contain from about 7% to about 15% by weight of water.

Conventional spray drying towers, both co-current and counter-current, may be used to partially dry the aqueous slurry to the above specified degree. Preferably the hot air is supplied counter-currently to the spray tower. A preferred multilevel spray drying process and apparatus is described in U.S. Patents
3,629,951 and 3,629,955, both issued on December 28, 1971 to Davis et al, incorporated herein by reference.

The air inlet temperature is preferably at least about 230°C, more preferably at least about 260°C. It is also preferred that the granule temperature not be allowed to exceed about 85°C, and more preferably not exceed about 80°C, to minimize reversion of polyphosphates when present in the granules and also to minimize formation of silicate insolubles when silicate is present.

Secondary Dryer

The resulting base granules, which are generally free flowing agglomerates, are then further dried in a secondary dryer in a manner so that the granule temperature again does not exceed about 90°C to obtain granules containing from about 2% to about 8%, preferably from about 2% to about 8%, water. Preferably, the granule temperature does not exceed about 85°C. More preferably, it does not exceed about 80°C.

If there is more than about 5% alkali metal tripolyphosphate in the slurry, the granules should contain at least about 4% water, and preferably contain from about 8% to about 16% water, after drying in the secondary dryer.

In addition, if there is more than about 5% of alkali metal tripolyphosphate or pyrophosphate in the slurry, the drying should be accomplished so that no more than about 5% by weight of each of the tripolyphosphate and pyrophosphate is reverted to lower phosphates during the drying in the spray tower and in the secondary dryer. Preferably, less than about 3%, more preferably less than about 2%, most preferably less than about 1%, by weight, of each of the tripolyphosphate and pyrophosphate is reverted during these drying steps.

Any secondary dryer capable of drying the granules at the required temperature and moisture levels can be used in the practice of this invention. Suitable secondary dryers include rotary drum dryers, pneumatic conveying dryers, air lift dryers, conveyor and tray-type dryers, and the like. A fluid bed dryer is particularly preferred.

The resulting granular detergent compositions can be used as is as finished detergent compositions or as detergent additive compositions. The granules are preferably admixed with or agglomerated with other optional ingredients to provide finished detergent compositions.

Other ingredients commonly used in laundry or cleaning products can be included in the compositions of the present invention. These include auxiliary detergent surfactant and builder materials, bleaching agents and bleach activators, suds boosters or suds suppressors, anti-tarnish and anti-corrosion agents, soil suspending agents, soil release agents, fillers, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, smectite clays, enzymes, enzyme-stabilizing agents and perfumes. See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., incorporated herein by reference, for a description of these ingredients. Bleaching agents and activators are also described in U.S. Patent 4,412,934, Chung et al., issued November 1, 1983, and in U.S. Patent 4,483,871, Hartman, issued November 20, 1984, both of which are incorporated herein by reference.

For the preferred laundry detergent compositions of the invention, typical laundry wash water solutions comprise from about 0.1% to about 2% by weight of the composition. Fabrics to be laundered are agitated in these solutions to effect cleaning, stain removal, and optional fabric care benefits. The pH of a 0.1% by weight aqueous solution of this composition will be in the range of from about 7.0 to about 11.0, preferably from about 8.0 to about 11.0, and most preferably from about 9.0 to about 10.5.

The following nonlimiting examples illustrate the compositions of the present invention.

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

EXAMPLE I

A crutcher slurry is prepared containing the following components.
The crutcher slurry is held approximately 5-10 minutes so that 30-80% of the tripolyphosphate hydrates to the hexahydrate form. The slurry is spray dried by atomizing with swirl nozzles at 35-84 kg/cm² pressure into a counter-current spray drying tower having an inlet air temperature of about 332°C. A slip stream sample of partially dried granules having a temperature of less than about 55°C and containing about 18.8% water is captured from within the spray tower and continuously fed to a fluidized bed, having a cross-sectional area of 0.14 m². Fluid bed air is heated to about 165°C and pumped through a perforated distribution plate at sufficient rate to fluidize the bed of granules. Dried granules are continuously withdrawn from the bed at about 72.7 kg/hr. and contain 10.4% water. The temperature of the sample is about 86°C. Less than about 3% of the tripolyphosphate has reverted to pyrophosphate and orthophosphate during the drying process. This compares to about 15% reversion in a sample taken from the bottom of the spray tower at the same time and having a temperature of about 104°C. This demonstrates the lower tripolyphosphate reversion that can be obtained using the two stage drying operation of the present invention versus a conventional spray drying process and the importance of maintaining the granule temperature under 90°C during the two stage drying operation.

The black-fabric solubility grade for the above fluid bed sample is 9.5 (on a 0-10 scale, where 10 equals no insolubles) versus a grade of 7.5 for the totally spray dried sample taken from the bottom of the spray drying tower. Further, the cake grade for the fluid bed sample is 1.5 (kg force to break a 6.35 cm diameter x 6.35 cm long cylindrical plug formed under a 9.1 kg weight for one minute) versus a grade of 3.3 for the totally spray dried sample.

EXAMPLE II

A crutcher slurry is prepared containing the following components.

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<tr>
<th>Component</th>
<th>Wt. %</th>
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<tr>
<td>Sodium C₁₂ linear alkylbenzene sulfonate</td>
<td>3.3</td>
</tr>
<tr>
<td>Sodium tallowalkyl sulfate</td>
<td>5.3</td>
</tr>
<tr>
<td>Sodium C₁₄₋₁₅ alkyl sulfate</td>
<td>5.3</td>
</tr>
<tr>
<td>Sodium toluene sulfonate</td>
<td>0.8</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>4.5</td>
</tr>
<tr>
<td>Tetrasodium pyrophosphate</td>
<td>18.2</td>
</tr>
<tr>
<td>Sodium silicate (1.6 ratio)</td>
<td>4.5</td>
</tr>
<tr>
<td>Sodium polyacrylate (MW 4500)</td>
<td>1.0</td>
</tr>
<tr>
<td>Sodium sulfate and minors</td>
<td>24.6</td>
</tr>
<tr>
<td>Water</td>
<td>32.5</td>
</tr>
</tbody>
</table>

The slurry is dried in two stages as described in Example I to provide a composition of the present invention.

EXAMPLE III
A crutcher slurry is prepared containing the following components.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium C_{13} linear alkylbenzene sulfonate</td>
<td>7.3</td>
</tr>
<tr>
<td>Sodium C_{14-15} alkyl sulfate</td>
<td>7.3</td>
</tr>
<tr>
<td>Tallow fatty acid</td>
<td>0.7</td>
</tr>
<tr>
<td>Sodium Zeolite A (hydrated, avg. dia. 3 microns)</td>
<td>17.9</td>
</tr>
<tr>
<td>Sodium silicate (1.6 ratio)</td>
<td>1.4</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>3.7</td>
</tr>
<tr>
<td>Sodium polyacrylate (MW 4500)</td>
<td>1.1</td>
</tr>
<tr>
<td>Polyethene glycol (MW 8000)</td>
<td>1.1</td>
</tr>
<tr>
<td>Sodium sulfate and minors</td>
<td>26.1</td>
</tr>
<tr>
<td>Water</td>
<td>33.4</td>
</tr>
</tbody>
</table>

The slurry is spray dried by atomizing with swirl nozzles at 77 kg/cm² pressure into a counter-current spray drying tower having an inlet air temperature of about 254°C. A sample of partially dried granules having a temperature of less than about 55°C and containing about 18.8% water is captured from within the spray tower and charged to a batch fluidized bed having a cross-sectional area of 0.14 m². Fluid bed air is heated to about 163°C and pumped through a perforated distribution plate at sufficient rate to fluidize the bed of partially dried granules. At the end of 7 minutes, a sample of dried granules is withdrawn from the bed and contains 8.8% water. The temperature of the sample is about 47°C. The black-fabric solubility grade for the fluid bed sample is 9.0 (on a 0-10 scale, where 10 equals no insolubles) versus a grade of 7.5 for a sample taken at the exit of the spray tower during the same time period.

EXAMPLE IV

A crutcher slurry is prepared containing the following components.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium C_{13} linear alkylbenzene sulfonate</td>
<td>9.5</td>
</tr>
<tr>
<td>Sodium C_{14-15} alkyl polyethoxy (2.25) sulfate</td>
<td>4.1</td>
</tr>
<tr>
<td>Tallow fatty acid</td>
<td>0.1</td>
</tr>
<tr>
<td>Sodium silicate (2.4 ratio)</td>
<td>13.2</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>13.8</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>23.7</td>
</tr>
<tr>
<td>Minors</td>
<td>0.8</td>
</tr>
<tr>
<td>Water</td>
<td>35.0</td>
</tr>
</tbody>
</table>

The slurry is spray dried by atomizing with swirl nozzles at 28-84 kg/cm² pressure into a counter-current spray drying tower having an inlet air temperature of about 343°C. A 13.6 kg sample of partially dried granules having a temperature of less than about 55°C and containing about 9.2% water is captured from within the spray tower and charged to a batch fluidized bed having a cross-sectional area of 0.14 m². The fluid bed inlet air is heated to about 152°C and pumped through a perforated distribution plate at sufficient rate to thoroughly fluidize the bed of partially dried granules. At the end four minutes, a sample of dried granules is withdrawn from the bed and contains 5.6% water. The temperature of the sample is about 84°C. The black-fabric solubility grade for the fluid bed sample is 7.0 (on a 0-10 scale, where 10 equals no insolubles) versus a grade of 3.5 for a sample taken at the exit of the spray tower during the same time period and having a temperature of 123°C.

Claims

1. A granular detergent composition characterized in that it is prepared by:
(a) forming an aqueous slurry comprising, by weight:

(1) from 0% to 50% of a detergent surfactant, preferably from 10% to 30% of an anionic synthetic surfactant;
(2) from 5% to 55%, preferably from 15% to 30%, of an alkali metal tripolyphosphate or pyrophosphate, or mixtures thereof, preferably sodium tripolyphosphate;
(3) from 5% to 65% of a water-soluble neutral or alkaline salt other than the tripolyphosphate and pyrophosphate in (2); and
(4) from 25% to 50%, preferably from 30% to 45%, water;

(b) spray drying the aqueous slurry in a spray tower at an inlet air temperature of at least 200°C while not exceeding a granule temperature of 90°C to obtain base granules comprising from 5% to 25% by weight of water; and

(c) drying the base granules in a secondary dryer while not exceeding a granule temperature of 90°C to obtain granules comprising from 2% to 20% by weight of water, but at least 4% water when the slurry comprises more than 5% tripolyphosphate, and wherein no more than 5% by weight of each of any tripolyphosphate and pyrophosphate present in the slurry is reverted to pyrophosphate, orthophosphate, and mixtures thereof, during steps (b) and (c).

2. A composition according to Claim 1 wherein the anionic surfactant is selected from the group consisting of C_{11-13} alkylbenzene sulfonates, C_{12-18} alkyl sulfates, C_{12-16} alkyl sulfates ethoxylated with an average of up to 4 ethylene oxide units, and mixtures thereof.

3. A composition according to Claims 1 or 2 wherein the inlet air temperature of the tower is at least 230°C, preferably at least 260°C, the temperature of the base granules does not exceed 85°C, and the base granules comprise from 8% to 20% by weight of water.

4. A composition according to any one of the preceding Claims wherein the base granules are dried in a secondary dryer, preferably a fluid bed dryer, while not exceeding a granule temperature of 85°C to obtain granules comprising from 8% to 16% by weight of water.

5. A composition according to Claims 1, 2 or 3 wherein the base granules are dried in a secondary dryer, preferably a fluid bed dryer, while not exceeding a granule temperature of 85°C to obtain granules comprising from 2% to 8% by weight of water and wherein no more than 2% by weight of each of any tripolyphosphate and pyrophosphate present in the slurry is reverted to pyrophosphate, orthophosphate, and mixtures thereof, during steps (b) and (c).

6. A granular detergent composition characterized in that it is prepared by:

(a) forming an aqueous slurry comprising, by weight:

(1) from 0% to 50% of a detergent surfactant, preferably from 10% to 30% of an anionic synthetic surfactant;
(2) from 1% to 50%, preferably from 3% to 30%, of an alkali metal silicate having a molar ratio of SiO_2 to alkali metal oxide of from 1.6 to 3.2, preferably sodium silicate having a molar ratio of SiO_2 to sodium oxide of from 1.6 to 2.4;
(3) from 0% to 50% of a finely divided aluminosilicate ion exchange material selected from the group consisting of:

(i) crystalline aluminosilicate material of the formula:
\[ \text{Na}_z[\text{AlO}_2]_y[\text{SiO}_2]_z\times\text{H}_2\text{O} \]
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 250, said material having a particle size diameter of from 0.1 micron to 10 microns, a calcium ion exchange capacity of at least 200 mg CaCO_3 eq./g and a calcium ion exchange rate of at least 2 grains Ca^+ /gallon/minute/gram/gallon;

(ii) amorphous hydrated aluminosilicate material of the empirical formula:
\[ \text{M}_z[\text{zAlO}_2]_y[\text{SiO}_2]_z \]
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 CaCO_3 hardness per gram of anhydrous aluminosilicate and a Mg^++ exchange rate of at least 1 grain/gallon/minute/gram/gallon; and

(iii) mixtures thereof;

(4) from 5% to 65% of a water-soluble neutral or alkaline salt other than the silicate and aluminosilicate in (2) and (3); and

(5) from 25% to 50%, preferably from 30% to 45%, water;

(b) spray drying the aqueous slurry in a spray tower at an inlet air temperature of at least 200°C while not exceeding a granule temperature of 90°C to obtain base granules comprising from 5% to 25% by weight of water; and
(c) drying the base granules in a secondary dryer while not exceeding a granule temperature of 90°C to obtain granules comprising from 2% to 20% by weight of water.

7. A composition according to Claim 6 wherein the anionic synthetic surfactant is selected from the group consisting of C_{11-13} alkylbenzene sulfonates, C_{12-18} alkyl sulfates, C_{12-16} alkyl sulfates ethoxylated with an average of up to 4 ethylene oxide units, and mixtures thereof.

8. A composition according to Claims 6 or 7 wherein the slurry comprises from 5% to 40%, preferably from 10% to 30%, by weight of aluminosilicate ion exchange material of the formula 

\[ \text{Na}_{12}[(\text{AlO}_2)_{12}:(\text{SiO}_2)_{12}].x\text{H}_2\text{O} \]

wherein \( x \) is from 20 to 30.

9. A composition according to Claims 6, 7 or 8 wherein the slurry is spray dried at a tower inlet air temperature of at least 260°C while not exceeding a granule temperature of 85°C to obtain base granules comprising from 7% to 15% by weight of water.

10. A composition according to Claims 6, 7, 8, or 9 wherein the base granules are dried in a secondary dryer, preferably a fluid bed dryer, while not exceeding a granule temperature of 85°C to obtain granules comprising from 2% to 8% by weight of water.
### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. Cls)</th>
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<tr>
<td>Y</td>
<td>GB-A-1 237 084 (UNILEVER LTD.) * whole document *</td>
<td>1-10</td>
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<td>C 11 D 1/02</td>
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<td>C 11 D 3/08</td>
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<td>A</td>
<td>FR-A-1 481 514 (KNAPSACK AG) * claims *</td>
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**TECHNICAL FIELDS SEARCHED (Int. Cls)**

C 11 D

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

**Place of search**

BERLIN

**Date of completion of the search**

19-09-1989

**Examiner**

PELLI-WABLAT B

**CATEGORY OF CITED DOCUMENTS**

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
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P: intermediate document

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E: earlier patent document, but published on, or after the filing date
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L: document cited for other reasons
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