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(54) **Granular detergents containing pyrophosphate and polyacrylate polymer.**

(57) Granular detergents containing organic surfactant, pyrophosphate builder, low levels of alkali metal silicate and polyacrylate polymer are disclosed. The compositions are prepared by drying an aqueous slurry of the components, and are preferably substantially free of orthophosphates.

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GRANULAR DETERGENTS CONTAINING PYROPHOSPHATE AND POLYACRYLATE POLYMER

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Technical Field

The present invention relates to granular detergents containing organic surfactant, pyrophosphate builder, low levels of alkali metal silicate, and a polyacrylate polymer. The compositions herein are prepared by drying an aqueous slurry comprising the components. While the compositions are preferably substantially free of orthophosphates, they can contain minor amounts of such material provided the weight ratio of pyrophosphate to orthophosphate is at least about 5:1.

Pyrophosphates are known to be potentially more efficient builders than the tripolyphosphates commonly used in detergents due to their ability to remove more calcium and magnesium ions from the laundering solution per unit of P_2O_5. They do so, however, by precipitating these ions as insoluble phosphates (e.g., dicalcium pyrophosphate) whereas the tripolyphosphates retain them in solution as complex ions. These precipitates can build up on fabrics over a period of time and cause undesirable effects, such as greyness and harshness of feel, unless antiredeposition agents are added to detergents containing pyrophosphates.

Pyrophosphate-built granular detergents have often contained high levels (e.g., 10% by weight) of alkali metal silicates to provide optimum granule structure and processing. It is believed that when a crutcher mix containing silicate is spray-dried, the silicate dries to a tough film capable of cementing finely crystalline granule walls together. This results in granules having very desirable physical properties, i.e, crisp, durable and free-flowing granules. Silicates having lower SiO_2 to alkali metal oxide molar ratios (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, reducing silicate

solubility and resulting in detergent granules which do not completely disintegrate in the laundering solution. High levels of silicate in detergents can thus cause an unacceptably high level of insoluble material being deposited on fabrics. It is apparent that there is a continuing need for the development of pyrophosphate-built granular detergents having acceptable granule structure and solubility, and capable of maintaining fabric whiteness.

Background Art

British Patent 1,551,239, Bailey et al, published August 30, 1979, discloses various polycarboxylate materials, including polyacrylates, as antiredeposition agents for detergents containing orthophosphate and pyrophosphate in a weight ratio of from about 9:2 to 3:7.

U.S. Patent 4,019,998, Benson et al, issued April 26, 1977, discloses granular detergents containing pyrophosphate and difficulty soluble silicates.

British Patent 1,460,893, Foster, published January 6, 1977, discloses granular detergents containing orthophosphate and/or pyrophosphate, and polyacrylates as antiredeposition agents.

European patent application 82200458.6 discloses the use of film-forming polymers, including polyacrylates, as structural aids to replace all or part of the silicate in low-phosphate granular detergents containing aluminosilicates.

Summary of the Invention

The present invention encompasses a granular detergent composition comprising:

(a) from about 5% to about 50% by weight of an organic surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof;

(b) from about 5% to about 80% by weight of an alkali metal pyrophosphate builder;

(c) from about 0.5% to about 6% by weight of an alkali metal silicate having a molar ratio of SiO_2 to alkali metal oxide of from about 1.0 to about 3.2; and

(d) from about 0.1% to about 5% by weight of a polyacrylate polymer soluble in an aqueous slurry comprising the above components and having a weight average molecular weight of from about 2,000 to about 200,000;

said composition prepared by drying an aqueous slurry comprising the above components, and the amount of orthophosphate in said composition being limited such that the weight ratio of pyrophosphate to orthophosphate is at least about 5:1.

Detailed Description of the Invention

The granular detergent compositions of the present invention contain, as essential components, an organic surfactant, a pyrophosphate builder, an alkali metal silicate and a polyacrylate polymer. The polyacrylate polymer acts as both a highly effective antiredeposition agent and structural aid, allowing for the formulation of granular detergents having desirable structure, solubility and whiteness maintenance characteristics. The amount of orthophosphate in the compositions should be limited such that the weight ratio of pyrophosphate to orthophosphate is at least about 5:1, preferably at least about 10:1, and more preferably at least about 20:1. The compositions are most preferably substantially free of orthophosphates because they tend to form coarse precipitates which more readily deposit on fabrics than the pyrophosphate precipitates.

The compositions herein are prepared by drying an aqueous slurry comprising the components. The slurry generally contains from about 25% to about 50% water, whereas the dried granules initially contain from about 2% to about 10%, preferably from about 2% to about 5%, water. The drying operation can be accomplished by any convenient means, such as by using spray-drying towers, both counter-current and co-current, fluid beds, flash-drying equipment, or industrial microwave or oven-drying equipment. These are more fully described in U.S. Patent 4,019,998, Benson et al, issued April 26, 1977 (particularly from Column 14, line 19 to Column 15, line 9), incorporated herein by reference.

While not intending to be limited by theory, it is believed

that the granular detergents herein exhibit superior structure and physical properties because the polyacrylate polymer dries to a tough, non-sticky, non-hygroscopic film which cements the granule walls together much in the same manner as do the silicates. The polymer film is readily water-soluble so that the granules quickly disintegrate in the laundering solution and leave little or no insoluble residue on fabrics. Moreover, the low level of silicate in the compositions contributes to the desired granule structure, and also aids processing and inhibits metal corrosion, without causing excessive insoluble silicate deposition. Finally, the polyacrylate polymer is also highly effective at suspending the insoluble dicalcium pyrophosphate salts, preventing their deposition and build-up on fabrics.

Organic Surfactant

The detergent compositions herein contain from about 5% to about 50% 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 about 10% to about 30% 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, both incorporated herein by reference. 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, 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.

Useful anionic surfactants also 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 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_8-C_{18} 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. Patents 2,220,099 and 2,477,383. 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 C_{11-13}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 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 salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and from about 10 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 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; 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 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing

from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 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 alkylene 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 about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to 12 moles of ethylene oxide per mole of alkyl phenol.

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 about 9 to 15 carbon atoms with from about 4 to 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 18 carbon atoms and two 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 about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and

hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 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 about 8 to 18 carbon atoms and at least one aliphatic 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 about 8 to 18 carbon atoms.

Particularly preferred surfactants herein are anionic surfactants selected from the group consisting of the alkali metal salts of C_{11-13} alkylbenzene sulfonates, C_{14-18} alkyl sulfates, C_{14-18} alkyl linear polyethoxy sulfates containing from about 1 to about 4 moles of ethylene oxide, and mixtures thereof.

Pyrophosphate Builders

The compositions of the present invention also contain from about 5% to about 80%, preferably from about 10% to about 70%, and most preferably from about 15% to about 60%, by weight of an alkali metal pyrophosphate builder. Sodium and potassium, particularly sodium, pyrophosphates are preferred. The pyrophosphate salts useful herein can be obtained commercially or can be formed by neutralization of the corresponding pyrophosphoric acids or acid salts. The pyrophosphates can be anhydrous or hydrated, although anhydrous pyrophosphates in finely divided form are preferred for rapid dissolution in the wash.

Readily available commercially are tetrasodium pyrophosphate $Na_4P_2O_7$ and its decahydrate $Na_4P_2O_7.10H_2O$, tetrapotassium pyrophosphate $K_4P_2O_7$, sodium acid pyrophosphate or "acid pyro" $Na_2H_2P_2O_7$ and its hexahydrate $Na_2H_2P_2O_7.6H_2O$, and pyrophosphoric acid $H_4P_2O_7$. 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 $M_xH_yP_2O_7$, where M is alkali metal and x and y are integers having the sum of 4.

Alkali Metal Silicate

The compositions herein contain from about 0.5% to about 6%, preferably from about 1% to about 5%, more preferably from about 1.5% to about 4%, and most preferably from about 1.5% to about 3%, by weight of an alkali metal silicate having a molar ratio of SiO_2 to alkali metal oxide of from about 1.0 to about 3.2, preferably from about 1.6 to about 2.4. Sodium silicate, particularly having a molar ratio of from about 1.8 to about 2.2, is preferred.

The alkali metal silicates can be purchased in either liquid or granular form. Silicate slurries can conveniently be used to avoid having to dissolve the dried form in the aqueous slurry (e.g., crutcher mix) of the components herein.

Polyacrylate Polymer

The compositions of the present invention contain from about 0.1% to about 5%, preferably from about 0.3% to about 3%, and more preferably from about 0.5% to about 2%, by weight of a polyacrylate polymer soluble in an aqueous slurry comprising the essential components herein. The polymer should have a molecular weight of from about 2,000 to about 200,000, preferably from about 25,000 to about 150,000, and more preferably from about 40,000 to about 100,000.

It will be appreciated that the polymer must be at least partially soluble in the slurry of the components for it to dry to a film capable of cementing the granule walls together as the slurry is dried. For optimum granule structure and physical properties, the polymer should be substantially soluble in the slurry, and it is preferably completely soluble in the slurry. Since the slurry will generally be a strong electrolyte solution due to the presence of the pyrophosphate and silicate salts, and, when present, anionic surfactants and other neutral or alkaline

salts, optimum solubility of the polymer is obtained when it is in the form of an at least partially neutralized alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanol ammonium) salt. The alkali metal, especially sodium, salts are most preferred.

Suitable polymers herein are the at least partially neutralized salts of homopolymers and copolymers of acrylic acid, hydroxyacrylic acid and methacrylic acid. The copolymers can be formed of mixtures of these unsaturated carboxylic acids with or without other copolymerisable monomers, or they can be formed from single acids with other copolymerisable monomers. In either case, the percentage by weight of the polymer units derived from the acids is preferably greater than about 50%. Suitable copolymerisable monomers include, for example, vinyl chloride, vinyl alcohol, furan, acrylonitrile, methacrylonitile, vinyl acetate, methyl acrylate, methyl methacrylate, styrene, alpha-methylstyrene, vinyl methyl ether, vinyl ethyl ether, vinyl propyl ether, acrylamide, ethylene, propylene and 3-butenoic acid.

Preferred polymers of the above group are salts of homopolymers of acrylic acid, hydroxyacrylic acid, or methacrylic acid, or copolymers of these acids containing at least about 80% by weight of units derived from the acid. Particularly preferred is sodium polyacrylate, especially when it has an average molecular weight of from about 50,000 to about 70,000.

Optional Components

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

Preferred cobuilders for use herein are disclosed in U.S. Patent 4,019,998, Benson et al, issued April 26, 1977 (particularly from Column 11, line 40 to Column 13, line 5), incorporated

herein by reference. Particularly preferred are the aluminosilicates, tripolyphosphates, carbonates and nitrilotriacetates, and mixtures thereof.

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.

EXAMPLE I

The following composition, intended for usage at a level of 1½ cups (129 g) in a normal capacity, top-loading washing machine, was prepared by spray-drying an aqueous crutcher-mix slurry of the components.

Component	Wt %
Sodium C_{12} alkylbenzene sulfonate	3.5
Sodium tallow alkyl sulfate	5.5
Sodium C_{14-15} alkyl polyethoxy(2.25) sulfate	5.5
Tetrasodium pyrophosphate	24.0
Sodium carbonate	10.0
Sodium silicate (2.0r)	2.0
Sodium sulfate	42.0
Polyethylene glycol 8000	1.0
Sodium polyacrylate (avg. m.w. 50,000-70,000)	1.0
Water + minors	Balance to 100

Other compositions of the present invention are obtained when the pyrophosphate in the above composition is replaced with a mixture of 21% pyrophosphate and 5% of either hydrated sodium aluminosilicate Zeolite A (avg. dia. 3 microns), sodium tripolyphosphate or sodium nitrilotriacetate, or when the silicate level is increased to 4%.

Other compositions herein are obtained when the polyacrylate is replaced with sodium polyhydroxyacrylate of m.w. 80,000, with a sodium polyacrylate polymer containing about 5-15% by weight of acrylamide and having a m.w. of about 20,000 or 40,000, or with sodium polyacrylate having a m.w. of 120,000.

Particularly preferred compositions are obtained by drying an aqueous slurry comprising the essential components herein and alkali metal tripolyphosphates, wherein the weight ratio of pyrophosphate to tripolyphosphate is from about 50:1 to about 1:1, preferably from about 20:1 to about 2:1, and more preferably from about 10:1 to about 4:1. The tripolyphosphate contributes to the formation of granules having very desirable structure and physical properties, including improved structural integrity and free-flowing characteristics, and reduced caking tendencies. The tripolyphosphates also contribute to improved whiteness maintenance performance.

EXAMPLE II

The following composition, intended for usage at a level of ⅓ cup (51.9 g) in a normal capacity, top-loading washing machine, was prepared by spray-drying an aqueous crutcher-mix slurry of the components.

Component	Wt %
Sodium C_{12} alkylbenzene sulfonate	16.6
Sodium C_{14-15} alkyl polyethoxy(2.25) sulfate	7.1
Tetrasodium pyrophosphate	58.8
Sodium carbonate	6.3
Sodium silicate (2.0r)	1.9
Sodium sulfate	1.9
Polyethylene glycol 8000	1.6
Sodium polyacrylate (avg. m.w. 50,000-70,000)	1.8
Water + minors	Balance to 100

The dispersibility of the above granular composition can be improved by intimately mixing about 1% by weight of sodium polyacrylate of m.w. 2000 with the anionic surfactant paste prior to adding the balance of the components to the crutcher, as described in European patent application 82201390.0.

EXAMPLE III

The following composition is prepared by first intimately mixing the 2000 m.w. polyacrylic acid with the anionic surfactant paste, and then spray-drying an aqueous crutcher-mix slurry of the components.

Component	Wt. %
Socium C_{13} alkylbenzene sulfonate	10.8
Sodium C_{14-15} alkyl polyethoxy (1.0) sulfate	27.2
Tetrasodium pyrophosphate	10.0
Sodium tripolyphosphate	5.0
Sodium silicate (2.0r)	6.0
Sodium sulfate	29.6
Sodium polyacrylate (avg. m.w. 50,000-70,000)	2.0
Polyacrylic acid (avg. m.w. 2000)	1.0
Water + minors	Balance to 100

The base granules obtained are then admixed, at a level of 52.1 parts, with 41.3 parts of tetrasodium pyrophosphate, 5.2 parts of sodium carbonate, 0.6 parts of polyethylene glycol 6000, and minors to provide a finished granular detergent intended for usage at a level of ½ cup (51.9g) in a normal capacity, top-loading washing machine.

CLAIMS

1. A granular detergent composition comprising:

(a) from about 5% to about 50% by weight of an organic surfactant selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof;

(b) from about 5% to about 80% by weight of an alkali metal pyrophosphate builder;

(c) from about 0.5% to about 6% by weight of an alkali metal silicate having a molar ratio of SiO_2 to alkali metal oxide of from about 1.0 to about 3.2; and

(d) from about 0.1% to about 5% by weight of a polyacrylate polymer soluble in an aqueous slurry comprising the above components and having a weight average molecular weight of from about 2,000 to about 200,000;

said composition prepared by drying an aqueous slurry comprising the above components, and the amount of orthophosphate in said composition being limited such that the weight ratio of pyrophosphate to orthophosphate is at least about 5:1.

2. The composition of Claim 1 wherein the organic surfactant comprises an anionic surfactant selected from the group consisting of alkali metal salts of C_{11-13} alkylbenzene sulfonates, C_{14-18} alkyl sulfates, C_{14-18} alkyl polyethoxy sulfates containing from about 1 to about 4 moles of ethylene oxide, and mixtures thereof.

3. The composition of Claim 2 wherein the pyrophosphate builder is sodium or potassium pyrophosphate.

4. The composition of Claim 3 wherein the silicate is sodium silicate having a molar ratio of from about 1.6 to about 2.4.

5. The composition of Claim 4 comprising from about 10% to about 30% by weight of the organic surfactant, from about 15% to about 60% by weight of the pyrophosphate builder, and from about 1.5% to about 4% by weight of the silicate.

6. The composition of Claim 1 wherein the polymer has a weight average molecular weight of from about 25,000 to about 150,000.

7. The composition of Claim 6 wherein the polymer has a weight average molecular weight of from about 40,000 to about 100,000.

8. The composition of Claim 7 wherein the polymer is a salt of a homopolymer of acrylic acid, hydroxyacrylic acid or methacrylic acid, or a copolymer thereof containing at least about 80% by weight of units derived from the acid.

9. The composition of Claim 8 wherein the polymer is sodium polyacrylate.

10. The composition of Claim 5 wherein the polymer is sodium polyacrylate having a weight average molecular weight of from about 40,000 to about 100,000 and represents from about 0.5% to about 2% by weight of the composition.

11. The composition of Claim 10 prepared by spray-drying an aqueous slurry of the components.

DEH:sp

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 83 20 1275

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	DE-A-2 403 894 (UNILEVER N.V.) * Pages 7, 8; example 1; claims 1-3 *	1	C 11 D 3/06 C 11 D 3/37
A		3,5,8	
D,A	US-A-4 019 998 (R.W. BENSON et al.)		
A	DE-A-2 744 569 (LION FAT & OIL CO.) * Claims 1-4 *		
A	US-A-3 579 455 (P.M. SABATELLI) * Claims 1-4 *		

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 11 D 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	30-12-1983	SCHULTZE D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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