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(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
One Procter & Gamble Plaza
Cincinnati Ohio 45202 (US)

(72) Inventor: **Evans, Brett Alan**
6935 Lynnfield Ct.
Cincinnati Ohio 45243 (US)

Kaminsky, George John
1612 Peaslee Ave.
Cincinnati Ohio 45224 (US)

Hansen, Richard
9689 Sycamore Trace
Cincinnati Ohio 45242 (US)

(74) Representative: **Gibson, Tony Nicholas et al**
Procter & Gamble (NTC) Limited Whitley Road
Longbenton Newcastle upon Tyne NE12 9TS (GB)

(54) **Granular detergent compositions having improved solubility.**

(57) Spray dried granules containing high levels of certain surfactants dissolve rapidly.

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Description

GRANULAR DETERGENT COMPOSITIONS HAVING IMPROVED SOLUBILITY

Technical Field

The present invention relates to granular detergent compositions containing a specific mixture of alkylbenzene sulfonate surfactant, alkyl sulfate surfactant, alkali metal silicate and water-soluble sulfate. The compositions are prepared by drying, preferably by spray-drying, an aqueous slurry comprising the above components. While the compositions preferably also contain detergent builder materials, there should be relatively little or no pyrosphosphate or anhydrous Form 1 tripolyphosphate builder in that portion of the composition prepared by drying the slurry comprising the sulfonate and sulfate surfactants, silicate and sulfate.

Mixtures of alkylbenzene sulfonate and alkyl sulfate surfactants are desired for optimum detergency performance. However, such mixtures tend to gel on contact with water. This can result in poor solubility of granules having high levels of alkylbenzene sulfonate and alkyl sulfate surfactants, particularly when such granules are incorporated in dense detergent compositions.

It has now been found that very soluble granular detergent compositions containing high levels of alkylbenzene sulfonate and alkyl sulfate surfactants can be obtained by drying an aqueous slurry comprising the surfactants, silicate in a weight ratio of surfactant to silicate within the range of from 1.5:1 to 6:1, sulfate and relatively little or no pyrophosphate or anhydrous Form 1 tripolyphosphate detergent builder material. In preferred compositions, these soluble detergent granules are admixed or agglomerated with builders and other optional detergent ingredients. Particularly preferred compositions are obtained by admixing the soluble granules with builders, compacting the admix at relatively low pressures (e.g., 137.9 kPa to 1379 kPa and optionally admixing additional builders and other ingredients to provide finished granular detergent compositions.

Background Art

U.S. Patent 4,028,283, Murata et al, issued June 7, 1977, discloses granular detergents containing surfactants having a tendency to cake and an anticaking agent formed by reacting polyethylene glycol with an acid anhydride. The compositions can also contain 0-20% of other surfactants such as alkylbenzene sulfonates. Spray-dried detergents containing mixtures of alkylbenzene sulfonate and alkyl ethoxy sulfate surfactants, silicate and builders are exemplified.

U.S. Patent 4,141,841, McDanald, issued February 27, 1979, discloses granular detergents containing particulate and antistatic/softening additives. In Example 8, the particles are mixed with spray-dried base granule containing about 27% of a mixture of alkylbenzene sulfonate and alkyl ethoxy sulfate surfactants, 18% silicate and about 22% sodium tripolyphosphate.

Japanese OPI 106509, published August 21, 1979, discloses spray-dried granular detergents containing 15-40% surfactant, 5-20% silicate and no more than 12% phosphate. The compositions are said to have good physical properties and to cause less deposition of insolubles on clothes.

Japanese OPI 72998 and 72999, published April 25, 1985, disclose dense granular detergents formed by high shear mixing of alkylbenzene sulfuric acid and alkyl sulfuric acid with sodium carbonate and water to cause neutralization, admixing other ingredients such as builders, and then crushing and granulating the mixture.

Summary of the Invention

This invention relates to a granular detergent composition prepared by:

(1) forming base granules comprising, by weight:

(a) from 30% to % of a mixture of a C_{11}-C_{13} alkylbenzene sulfonate surfactant and a C_{12}-C_{16} alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from 4:1 to 1:4;

(b) an alkali metal silicate having a molar ratio of SiO_2 to alkali metal oxide of from 1.0 to 3.2; the weight ratio of (a) to (b) being from 1.5:1 to 6:1;

(c) from 15% to 60% of a water-soluble sulfate; and

(d) from 0% to 20% of a pyrophosphate or anhydrous Form 1 tripolyphosphate detergent builder material or mixtures thereof; said composition prepared by drying an aqueous slurry comprising the above components.

Detailed Description of the Invention

The granular detergent compositions of the present invention contain from 30% to 85%, preferably from 35% to 60 %, more preferably from 40% to 50%, by weight of a mixture of C_{11}-C_{13} alkylbenzene sulfonate surfactant and C_{12}-C_{16} alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from 4:1 to 1:4, preferably from 3:1 to 1:3, more preferably from 2:1 to 1:2.

Sulfonate surfactants useful herein are the watersoluble salts, particularly the alkali metal, ammonium and alkanolammonium (e.g., monoethanolammonium or triethanolammonium) salts of alkylbenzene sulfonates in which the alkyl group contains from 11 to 13 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.

Preferred are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from 12 to 13.

Useful alkyl sulfate surfactants are the water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium (e.g., monoethanolammonium or triethanolammonium) salts of C_{12}-C_{16} linear or branched alkyl sulfates. Preferred are those containing a C_{12}-C_{15}, especially C_{14}-C_{15}, linear alkyl group.

The compositions herein can also contain minor amounts (generally less than about 30%, but preferably less than about 15%, by weight of the above sulfonate and sulfate surfactants) of other detergent surfactants known in the art. These can include anionic, nonionic, cationic, ampholytic and zwitterionic surfactants, such as those disclosed in U.S. Patent 3,919,678, Laughlin, et al, issued December 30, 1975.

The compositions of the present invention also contain an alkali metal silicate having a molar ratio of SiO_2 to alkali metal oxide of from 1.0 to 3.2, preferably from 1.6 to 2.4. Sodium silicate, particularly having a molar ratio of from 1.6 to 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 slurry (e.g., crutcher mix) of the components herein.

In addition, the weight ratio of the alkylbenzene sulfonate plus alkyl sulfate surfactants herein to the alkali metal silicate should be from 1.5:1 to 6:1, preferably from 2:1 to 4:1, more preferably from 2:5:1 to 3.5:1.

The present compositions further contain from 10% to 60%, preferably from 20% to 50%, by weight of a water-soluble (preferably sodium) sulfate. Sodium sulfate is usually formed during the sulfation/sulfonation and neutralization steps in the production of the alkylbenzene sulfonate and alkyl sulfate surfactants herein.

The compositions herein prepared by drying an aqueous slurry comprising the components. The slurry generally contains from 25% to 70%, preferably from 40% to 60%, water, whereas the dried granules initially contain from 1% to 10%, preferably from 1% to 3%, 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).

The granular detergents herein are very soluble in the wash water even though they contain high levels of alkylbenzene sulfonate and alkyl sulfate surfactants. Good solubility is obtained when the weight ratio of total sulfonate plus sulfate surfactant to silicate is within the 1.5:1 to 6:1 range specified above. While not intending to be limited by theory, it is believed that this relatively high level of silicate provides structure and helps to maintain integrity of the high surfactant granules and that this minimizes gelling when the surfactants contact the wash water. However, if the silicate level becomes too high (e.g., a surfactant to silicate ratio of 1:1), overall solubility can suffer due to the formation of silicate insolubles. On the other hand, granules having a surfactant to silicate ratio of, for example, 8:1, have insufficient structure and tend to be too mushy at these high surfactant levels.

For good solubility, the amount of detergent pyrophosphate or anhydrous Form 1 tripolyphosphate builder material in the portion of the granular detergent obtained by drying an aqueous slurry of the essential components herein should also be minimized. Thus the compositions can contain from 0% to 20%, preferably from 0% to 15%, more preferably from 0% to material in the portion of the granular detergent obtained by drying an aqueous slurry of the essential components herein should also be minimized. Thus the compositions can contain from 0% to 20%, preferably from 0% to 15%, more preferably from 0% to 10%, by weight of such detergent builder material or mixtures thereof. Most preferably, the compositions are substantially free of such detergent builder (e.g., they contain less than 5%, preferably less than 3%, by weight of such builder).

The compositions can contain up to 60% preferably from 1% to 45% by weight of other detergent builders including any of those described in U.S. Patent 3,925,262, Laughlin et al, issued December 9, 1975. Builders are generally selected from the various water-soluble alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, 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 sodium and potassium tripolyphosphate, (Form 11 or hydrated Form 1), polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176; and 3,400,148.

Examples of 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 polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Polymeric polycarboxylate builders are also described in U.S. Patent 3,308, 067. Diehl, issued March 7, 1967.

Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and 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 are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al, and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al.

These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution and converted to the corresponding salt.

A preferred phosphate builder is Form 11 sodium tripolyphosphate preferably anhydrous. A preferred builder for use in compositions that are substantially free of phosphate builders is sodium citrate.

When admixed, the builders herein should have the same particle size as the remainder of the composition, as described hereinafter.

The above granular detergent compositions can be used as is as finished detergent compositions or as detergent additive compositions. However, they are preferably used as (and hereinafter referred to as) detergent base granules which are then admixed or agglomerated with builder material and with other optional ingredients to provide finished detergent compositions exhibiting good solubility. Such finished compositions can comprise by weight from 5% to 50%, preferably from 10% to 40%, more preferably from 12% to 25%, of the alkylbenzene sulfonate and alkyl sulfate surfactants herein and from 5% to 95%, preferably from 10% to 85%, more preferably from 15% to 75%, of detergent builder material, such as described above. However, for best solubility, the amount of pyrophosphate and anhydrous Form 1 tripolyphosphate should be minimised i.e. the finished compositions preferably contain from 0% to 20% preferably from 0% to 10% of such material or mixtures thereof.

The compositions can also contain minor amounts, generally less than 30%, preferably less than 20%, by weight of other ingredients usually included in detergent compositions. These include auxiliary detergent surfactants, color speckles, bleaching agents, and bleach activators, suds boosters or suds suppressors, antitarnish and anticorrosion agents, soil suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, pH adjusting agents, nonbuilder alkalinity sources, enzymes, enzyme-stabilizing agents and perfumes.

Agglomeration can be accomplished by agitating in the presence of a suitable binder (e.g., in a fluidized bed, tumble mixer, or a rotating drum or pan) or by mechanically mixing under pressure (e.g., extruding, pressing, milling, compacting or pelletizing). Final sizing can then be achieved by grinding and screening.

In a preferred embodiment, the detergent base granules are admixed with from 0% to 300%, preferably from 25% to 200%, more preferably from 50% to 150%, by weight of the base granules, of a detergent builder material such as described above. The resulting admix is then preferably compacted at a relatively low pressure of from 137.9 to 1379 preferably from 275.8 to 1034 more preferably from 344.8 to 689.4 kilo Pascals (kPa).

The composition is then preferably admixed with an additional 0% to 300%, preferably from 25% to 200%, more preferably from 50% to 150%, by weight of the base granules, of a detergent builder material. The above levels and types of builder material and compaction pressure are preferably selected so that the final detergent composition has a bulk density of from 0.55 to 1.2, preferably from 0.65 to 1.1, more preferably from 0.70 to 0.9 g/cc and an average particle size of from 20 to 1500 microns, preferably from 50 to 1200 microns, more preferably from 100 to 800 microns.

The above compaction step is preferably accomplished by using equipment that applies a relatively uniform compaction pressure, for example, by using compaction rollers with smooth (i.e., noncorrugated) surfaces. After compaction, the composition is preferably granulated and screened to provide an average particle size similar to that desired for the final composition.

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

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

Example I

The following granular detergent composition was prepared.

	Weight %	Grams Final Composition per use
Base Granules		
Sodium C_{13} linear alkylbenzene sulfonate	22.1	5.110
Sodium C_{14-15} alkyl sulfate	22.1	5.110
Sodium silicate (1.6 ratio)	13.7	3.172
Sodium sulfate	32.2	7.455
Polyethylene glycol (m. wt. 8000)	1.5	0.340
Sodium polyacrylate (m. wt. 4500)	2.0	0.453
C_{12-13} alcohol polyethoxylate (6)	3.0	0.680
Sodium diethylenetriamine pentaacetate	1.5	0.340
Moisture	2.0	0.462
		23.122
Preblend		
Base granules		23.122
Sodium tripolyphosphate hexahydrate (powdered)		20.576
		43.698
Admix		
Preblend		43.698
Sodium tripolyphosphate hexahydrate (granular)		19.429
Dye		0.003
Brightener		0.613
Suds suppressor prill comprising dimethylsilicone, silica, sodium tripolyphosphate and polyethylene glycol (MW = 8000)		1.703
Protease		2.044

Sodium carbonate	4.000
	71.490
Spray-On	
Admix	71.490
Mineral oil	0.710
	72.200

The base granules were produced by spray-drying an aqueous crutcher mix of the components on a 305 cm tower using a crutcher temperature of 93 C a size 3-1/2 nozzle to make fine granules, and silicone deaeratants. If the base granules contained more than 2% moisture, a second drying stage on a continuous fluid bed was performed to reduce moisture to 2%.

The base granules were then admixed with powdered STP hexahydrate to form the preblend. The preblend was compacted at 344.8 kPa roll pressure on a 10 cm by 25 cm chilsonator, and screened to select a -14(1168 microns)/+65(208 microns) particle size cut (Tyler mesh). Oversized particles were collected and granulated on a Fitzmill using a 1168 microns screen and low rpm's. This was screened to select a -20(833 microns)/+48(295 microns) particle size cut. Both materials were dedusted by blowing off fines in a fluid bed dryer using ambient air.

The admix was prepared at 181.5 kg per batch in a drum mixer. Carbonate, granular STP (with dye sprayed-on), brightener, enzymes, and suds suppressor prills were blended with the compacted mainstream product cut and regranulated overs. The ratio of mainstream product cut to overs was 7 to 1. Mineral oil was sprayed on the final admix in 13.6 to 18.1 kg batches at a 1% level using a Forberg Mixer.

The composition of Example 1 is preferably incorporated into a laminated laundry product formed from two plies of water insoluble tissues, at least one of which is water permeable, which are laminated together. At least one of the plies has cup like depressions, surrounded by rims and the other ply being attached to the first ply at the rims to physically separate the cups. In one embodiment the laminate is made with plies of the tissue paper described by Trokhan in U.S. Patent 4,529,480, issued July 16, 1985.

The tissue had good air permeability as set forth in U.S. Patent 4,170,565, Flesher et al, issued October 9, 1979.

There are 12 cups, having 20 cc capacity each and at least 8 of the cups are filled with about 9 gm (11 cc) of the detergent composition and the other cups are filled with at least one detergent adjuvant. Other materials which can be used to form suitable laminates and processes for forming suitable laminates are disclosed in Bahrani US Patent No. 4571924 and European Patent Application Publication No. 0184261.

When the composition of Example 1 is incorporated in said laminated laundry product, it exhibits superior solubility.

Example II

The following granular detergent composition can be prepared and used according to Example I.

	Base Granules	
	Weight %	Grams Final Composition per use
Sodium C_{13} linear alkylbenzene sulfonate	15.75	6.81
Sodium C_{14-15} alkyl sulfate	15.75	6.81
Sodium silicate (1.6 ratio)	7.88	3.41
Sodium sulfate	23.01	9.95
Polyethylene glycol (m. wt. 8000)	0.78	0.34
Sodium polyacrylate (m. wt. 4500)	1.05	0.46
C_{12-13} alcohol polyethoxylate (6)	1.57	0.68
Sodium citrate	32.15	13.90
Unreacted	0.35	0.15
Moisture	1.7	0.73
		43.23

Preblend	
Base granules	43.23
Sodium aluminosilicate (hydrated Zeolite A, avg. dia 3 microns)	14.90
Sodium carbonate	3.00
	61.13

Admix	
Preblend	61.13
Brightener	0.53
Suds suppressor prill comprising dimethylsilicone, silica, sodium tripolyphosphate and polyethylene glycol (MW = 8000)	0.91
Protease	1.00
	63.57

Claims

1. A granular detergent composition comprising, by weight:
(a) from 30% to 85% of a mixture of a C_{12}-C_{13} alkylbenzene sulfonate surfactant and a C_{12}-C_{16} alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from 4:1 to 1:4;
(b) an alkali metal silicate having a molar ratio of SiO_2 to alkali metal oxide of from 1.0 to 3.2;
the weight ratio of (a) to (b) being from 1.5:1 to 6:1;
(c) from 10% to 60% of a water-soluble sulfate; and
(d) from 0% to 20% of a pyrophosphate or anhydrous Form 1 tripolyphosphate detergent builder material or mixtures thereof;
said composition prepared by drying an aqueous slurry comprising the above components.

2. A composition according to Claim 1 comprising from 35% to 60% preferably from 35% to 60% of the sulfonate and sulfate surfactants.

3. A composition according to either one of Claims 1 and 2 wherein the weight ratio of sulfonate surfactant to sulfate surfactant is from 2:1 to 1:2.

4. A composition according to any one of Claims 1-3 wherein the sulfonate surfactant is sodium C_{12}-C_{13} linear alkylbenzene sulfonate and the sulfate surfactant is sodium C_{14}-C_{15} linear alkyl sulfate.

5. A composition according to any one of Claims 1-4 wherein the weight ratio of (a) to (b) is from 2.0:1 to 4.0:1.

6. A composition according to any one of Claims 1-5 wherein the alkali metal silicate is sodium silicate having a molar ratio of SiO_2 to alkali metal oxide of from 1.6 to 2.4.

7. A composition according to any one of Claims 1-6 being substantially free of pyrophosphate or anhydrous Form 1 tripolyphosphate detergent builder material.

8. A composition according to any one of claims 1-7 further comprising from 1% to 45% by weight of detergent builder, other than pyrophosphate or anhydrous Form 1 tripolyphosphate builders.

9. A composition according to claim 8 when dependent on claim 7 wherein the builder comprises sodium citrate.

10. A laminated laundry product comprising two plies of water insoluble tissue in which:
(1) at least one ply is water permeable;
(2) at least one ply defines more than one cup, each cup being surrounded by a rim of that ply;
(3) the second ply is sealed to the first ply at least at the rims of the cups to physically separate the cups so that the contents of the cups remain in place; and more than one cup contains a composition according to any one of Claims 1-9.