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

Granulierte Reinigungsmittel mit Löslichkeit

Compositions détergentes granulées à solubilité

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EP 0 219 314 B2

DescriptionTechnical Field

5 **[0001]** The present invention relates to granular detergent compositions containing a specific mixture of alkylbenzene sulfonate surfactant, alkyl sulfate surfactant, alkali metal silicate and sodium sulfate. The compositions are prepared by drying, preferably by spray-drying, an aqueous slurry comprising the above components.

[0002] While a composition in accordance with the invention preferably also contains detergent builder materials, it should be substantially free of pyrophosphate and 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.

10 **[0003]** 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.

15 **[0004]** 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 2:1 to 4:1, sodium sulfate and substantially no pyrophosphate or anhydrous Form I 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 (eg., 137.9 kPa to 1379 kPa and optionally admixing additional builders and other ingredients to provide finished granular detergent compositions. Such a process is the subject of the commonly assigned European Patent Application Publication No 0220024.

25 Background Art

[0005] 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.

30 **[0006]** U.S. Patent 4,141,841, McDonald, issued February 27, 1979, discloses granular detergents containing particulate 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.

35 **[0007]** EP-A-0084657 discloses physically stable strongly foaming spray-dried granular detergent compositions comprising 35-50% C₁₀-C₁₄ alkylbenzene sulfonates, 0-15% C₁₀-C₂₀ alkyl sulfates, 5-20% sodium silicate, 0-10% sodium sulfate, 5-25% sodium tripolyphosphate and 5-25% sodium aluminosilicate zeolite.

[0008] AU-A-61106 discloses mixtures of linear C₁₀-C₁₅ alkyl benzene sulfonates and C₁₄-C₁₈ alkyl sulfates in a tripolyphosphate-built, silicate- and sulfate-containing spray-dried detergent composition having enhanced cleaning properties.

40 **[0009]** 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.

45 **[0010]** Japanese OPI 72998 and 72999, published April 25, 1985, discloses 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

50 **[0011]** According to the present invention, there is provided a granular detergent composition prepared by drying an aqueous slurry, said composition comprising:

(a) a mixture of C₁₁-C₁₃ alkylbenzene sulfonate surfactant and a C₁₂-C₁₆ alkyl sulfate surfactant in a weight ratio of sulfonate surfactant to sulfate surfactant of from 4:1 to 1:4;

55 (b) an alkali metal silicate having a molar ratio of SiO₂ to alkali metal oxide of from 1.0 to 3.2;

(c) from 10% to 60% by weight of sodium sulfate; and

(d) from 1-45% by weight of a water-soluble non phosphate detergent builder material,

wherein the composition contains less than 5% by weight of a pyrophosphate or anhydrous Form 1 tripolyphosphate detergent builder material; characterised in that said detergent composition comprises from 30% to 60% by weight of said surfactant mixture, wherein the weight ratio of (a) to (b) is from 2.0:1 to 4.0:1, to provide granules initially containing by weight from 1% to 3% water.

Detailed Description of the Invention

[0012] The granular detergent compositions of the present invention contain from 30% to 60%, preferably from 35% to 60%, more preferably from 40% to 50%, by weight of a mixture of C₁₁-C₁₃ alkylbenzene sulfonate surfactant and C₁₂-C₁₆ 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.

[0013] Sulfonate surfactants useful herein are the water-soluble 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.

[0014] Preferred are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from 12 to 13.

[0015] Useful alkyl sulfate surfactants are the water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium (e.g., monoethanolammonium or triethanolammonium) salts of C₁₂-C₁₆ linear or branched alkyl sulfates. Preferred are those containing a C₁₂-C₁₅, especially C₁₄-C₁₅, linear alkyl group.

[0016] 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.

[0017] The compositions of the present invention also contain an alkali metal silicate having a molar ratio of SiO₂ 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.

[0018] 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.

[0019] In addition, the weight ratio of the alkylbenzene sulfonate plus alkyl sulfate surfactants herein to the alkali metal silicate must be from 2:1 to 4:1, preferably from 2.5:1 to 3.5:1.

[0020] The present compositions further contain from 10% to 60%, preferably from 20% to 50%, by weight of 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.

[0021] The compositions herein are 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 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. Those 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).

[0022] 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 2:1 to 4:1 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 portion of the granular detergent obtained by drying an aqueous slurry of the essential components of the composition of the present invention should be free of substantially free of detergent pyrophosphate or anhydrous Form 1 tripolyphosphate builder.

[0023] For the purposes of the present invention, "substantially free" means less than 5%, preferably less than 3%, by weight of such builder material.

[0024] The composition contains from 1 % to 45% by weight of non-phosphate detergent builders including any of those described in US 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 phosphonates, polyphosphonates, carbonates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium salts of the above.

[0025] 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 US Patents 3,159,581; 3,213,030; 3,422,021; 3,422,1137; 3,400,176; and 3,400,148.

[0026] Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, and tetraborate decahydrate.

[0027] 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.

[0028] 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 methylenemalononic acid.

[0029] Other useful builders herein are sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanhexacarboxylate, cis-cyclopentanetetra-carboxylate, phloroglucinol trisulfonate, and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

[0030] 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.

[0031] 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.

[0032] A preferred builder for use in compositions that are substantially free of phosphorus-containing builders is sodium citrate.

[0033] The above granular detergent compositions can be used 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. When admixed, the builders herein should have the same particle size as the remainder of the composition, as described hereinafter.

[0034] The detergent builder materials that are admixed can include any of those described above and may also include phosphate materials such as sodium and potassium tripolyphosphate, polymeric metaphosphate having a degree of polymerisation of from 6 to 21 and orthophosphate. The tripolyphosphate is preferably present as Form II or hydrated Form I and for best solubility, the amount of pyrophosphate and anhydrous Form I 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.

[0035] 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.

[0036] 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.

[0037] 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).

[0038] 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 micrometers, more preferably from 100 to 800 micrometers.

[0039] The above compaction step is preferably accomplished by using equipment that applies a relatively uniform

EP 0 219 314 B2

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.

[0040] The following nonlimiting examples illustrate the detergent compositions of the present invention.

[0041] All percentages, parts and ratios are by weight unless otherwise specified.

Example I

[0042] The following granular detergent composition was prepared.

	Base Granules	
	Weight %	Grams Final Composition per use
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
		<u>23.122</u>
Preblend		
Base granules		23.122
Sodium tripolyphosphate hexahydrate (powdered)		20.576
		<u>43.698</u>
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
		<u>71.490</u>
Spray-On		
Admix		71.490
Mineral oil		0.710
		<u>72.200</u>

[0043] 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 deaerantants. 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%.

[0044] The base granules were then admixed with powdered STP hexahydrate to form the preblend. The preblend was compacted at 344.8kPa roll pressure on a 10 cm by 25 cm chilsonator, and screened to select a - 14(1168 micrometers)/ + 65(208 micrometers) particle size cut (Tyler mesh). Oversized particles were collected and granulated on a

Fitzmill using a 1168 micrometers screen and low rpm's. This was screened to select a -20(833 micrometers)/+ 48(205 micrometers) particle size cut. Both materials were dedusted by blowing off fines in a fluid bed dryer using ambient air.

[0045] 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.

[0046] 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.

[0047] The tissue had good air permeability as set forth in U.S. Patent 4,170,565, Flesher et al, issued October 9, 1979,

[0048] There are 12 cups, having 20 cc capacity each and at least 8 of the cups are filled with about 9 mg (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.

[0049] When the composition of Example 1 is incorporated in said laminated laundry product, it exhibits superior solubility.

Example II

[0050] 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
		<u>43.23</u>
Preblend		
Base granules		43.23
Sodium aluminosilicate		
(hydrated Zeolite A, avg. dia 3 microns)		14.90
Sodium carbonate		3.00
		<u>61.13</u>
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
		<u>63.57</u>

Claims

1. A granular detergent composition prepared by drying an aqueous slurry, said composition comprising,
 - (a) a mixture of C₁₁-C₁₃ alkylbenzene sulfonate surfactant and a C₁₂-C₁₆ 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 SiO₂ to alkali metal oxide of from 1.0 to 3.2;
 - (c) from 10% to 60% by weight of sodium sulfate; and
 - (d) from 1% to 45% by weight of a water-soluble non phosphate detergent builder material,
 wherein the composition contains less than 5% by weight of a pyrophosphate or anhydrous Form 1 tripolyphosphate detergent builder material; characterised in that said detergent composition comprises from 30% to 60% by weight of said surfactant mixture, wherein the weight ratio of (a) to (b) is from 2.0:1 to 4.0:1, to provide granules initially containing by weight from 1% to 3% water.
2. A composition according to Claim 1 comprising from 35% to 60% by weight of the sulfonate and sulfate surfactant mixture.
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 C₁₂-C₁₃ linear-alkylbenzene sulfonate and the sulfate surfactant is sodium C₁₄-C₁₅ linear alkyl sulfate.
5. A composition according to any one of claims 1-4 wherein the builder is sodium citrate.
6. 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 1-5.

Revendications

1. Composition détergente granulaire préparée par séchage d'une suspension aqueuse, ladite composition comprenant:
 - (a) un mélange de tensioactif alkyl(en C₁₁-C₁₃)benzènesulfonate et de tensioactif alkyl(en C₁₂-C₁₆)sulfate, dans un rapport pondéral du tensioactif sulfonate au tensioactif sulfate de 4:1 à 1:4;
 - (b) un silicate de métal alcalin présentant un rapport molaire de SiO₂ à l'oxyde de métal alcalin de 1,0 à 3,2;
 - (c) de 10% à 60% en poids de sulfate de sodium; et
 - (d) de 1% à 45% en poids d'un adjuvant de détergence sans phosphate soluble dans l'eau, où la composition contient moins de 5% en poids d'un adjuvant de détergence pyrophosphate ou tripolyphosphate de forme 1 anhydre,
 caractérisée en ce que ladite composition détergente comprend de 30% à 60% en poids dudit mélange de tensioactifs où le rapport pondéral de (a) à (b) est de 2,0:1 à 4,0:1 pour avoir des granulés contenant initialement en poids de 1% à 3% d'eau.
2. Composition selon la revendication 1, comprenant de 35% à 60% en poids du mélange des tensioactifs sulfonate et sulfate.
3. Composition selon l'une quelconque des revendications 1 et 2, dans laquelle le rapport pondéral du tensioactif sulfonate au tensioactif sulfate est de 2:1 à 1:2.

4. Composition selon l'une quelconque des revendications 1-3, dans laquelle le tensioactif sulfonate est un alkyl (linéaire en C_{12} - C_{13})benzènesulfonate de sodium et le tensioactif sulfate est un alkyl(linéaire en C_{14} - C_{15})sulfate de sodium.

5. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle l'adjuvant est le citrate de sodium.

6. Produit pour la lessive stratifié, comprenant deux couches de tissu insoluble dans l'eau, dans lequel :

(1) au moins une couche est perméable à l'eau;

(2) au moins une couche définit plus d'un godet, chaque godet étant entouré d'un rebord de cette couche;

(3) la deuxième couche est soudée à la première couche au moins au niveau des rebords des godets, pour séparer physiquement les godets de manière à ce que le contenu des godets reste en place; et plus d'un godet contient une composition selon l'une quelconque des revendications 1-5.

Patentansprüche

1. Durch Trocknen einer wäßrigen Aufschlämmung hergestellte, granuliertte Waschmittelzusammensetzung, wobei die Zusammensetzung

(a) eine Mischung aus einem C_{11} - C_{13} -Alkylbenzolsulfonat-Tensid und einem C_{12} - C_{16} -Alkylsulfat-Tensid in einem Gewichtsverhältnis von Sulfonat-Tensid zu Sulfat-Tensid von 4:1 bis 1:4;

(b) ein Alkalimetallsilicat mit einem Molverhältnis von SiO_2 zu Alkalimetalloxid von 1,0 bis 3,2,

(c) 10 bis 60 Gew.-% Natriumsulfat; und

(d) 1 bis 45 Gew.-% eines wasserlöslichen phosphatfreien Waschmittelbuildermaterials

umfaßt, wobei die Zusammensetzung weniger als 5 Gew.-% eines Pyrophosphat- oder Triphosphat-Waschmittelbuildermaterials der wasserfreien Form 1 enthält, dadurch gekennzeichnet, daß die Waschmittelzusammensetzung 30 bis 60 Gew.-% der Tensidmischung umfaßt, wobei das Gewichtsverhältnis von (a) zu (b) 2.0:1 bis 4.0:1 beträgt, um Granulate vorzusehen, welche anfänglich 1 bis 3 Gew.-% Wasser enthalten.

2. Zusammensetzung nach Anspruch 1, umfassend 35 bis 60 Gew.-% der Sulfonat- und Sulfat-Tensidmischung.

3. Zusammensetzung nach Anspruch 1 und/oder 2, wobei das Gewichtsverhältnis von Sulfonat-Tensid zu Sulfat-Tensid 2:1 bis 1:2 beträgt.

4. Zusammensetzung nach mindestens einem der Ansprüche 1 bis 3, wobei das Sulfonat-Tensid ein Natrium- C_{12} - C_{13} -lineares -lineares Alkylbenzolsulfonat und das Sulfat-Tensid ein Natrium- C_{14} - C_{15} -lineares Alkylsulfat ist.

5. Zusammensetzung nach mindestens einem der Ansprüche 1 bis 4, wobei der Builder Natriumcitrat ist.

6. Laminiertes Wäscheprodukt, umfassend zwei Lagen aus wasserunlöslichem Gewebe, wobei:

(1) mindestens eine Lage wasserdurchlässig ist;

(2) mindestens eine Lage mehr als einen Becher definiert, wobei jeder Becher von einem Rand dieser Lage umgeben ist;

(3) die zweite Lage an der ersten Lage zumindest an den Rändern der Becher befestigt ist, um die Becher physikalisch voneinander zu trennen, so daß die Inhalte der Becher in Position bleiben; und wobei mehr als ein Becher eine Zusammensetzung nach mindestens einer der Ansprüche 1 bis 5 enthält.