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(54) **Process for preparing granular detergent compositions containing an intimately admixed anionic surfactant and an anionic polymer.**

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Description

Technical field

The present invention relates to a process for preparing granular detergent compositions containing an anionic surfactant and an anionic water-soluble polymer in intimate admixture. The compositons herein disperse and dissolve more rapidly in the laundering solution than similar compositions with surfactant alone.

The dispersibility and solubility of granular detergent compositions presents a challenge and dilemma to those who formulate and process such compositions. The spray-dried form of such compositions has provided generally satisfactory dispersibility and solubility if the individual components are soluble or dispersible in water. The spray-dried form, however requires acceptance of a relatively low density no higher than 0.4-0.5 grams per milliter to obtain substantial porosity. The porosity, of course provide a speed of solubility benefit. Higher density granular detergent compositions can be made by various mechanical mixing and agglomeration processes but solubility rate generally becomes less satisfactory. It is an object of this invention to improve the dispersibility and solubility of granular detergent compositions that are made by prrocesses that provide higher densities than are available from conventional spray-drying processes.

Background art

U.S. Patent 4,072,621, Rose, issued Feb. 7, 1978, discloses the addition of a water-soluble copolymer of a vinyl compound and maleic anhydride to granular detergents containing aluminosilicate builders.

British Patent 2,048,841, Burzio, published Dec. 17, 1980, discloses the use of polymeric acryl-amides to stabilize aqueous suspensions of zeolites. The suspensions are said to be suitable for spray-drying to obtain detergent compositions.

U.S. Patent 3,933,673. Davies, issued Jan. 20, 1976, describes the use of partial alkali metal salts of homo- or copolymers of unsaturated aliphatic mono- or polycarboxylic acids as builders which provide improved storage properties.

U.S. Patent 3.794,605, Diehl. issued Feb. 26, 1974, relates to the use of from 0,1% to 20% of a mixture of salts of cellulose sulfate esters and copolymers of a vinyl compound with maleic anhydride to provide whiteness maintenance benefits to detergent compositions.

U.S. Patent 3,380,922, Shields, issued Apr. 30, 1968, discloses film-forming resinous polymers useful as binders to improve mechanical properties of detergents.

U.S. Patent 3,803,285. Jensen, issued Apr. 9, 1974, describes granular detergents containing various starch derivatives. The granules are said to be free-flowing and cake resistant, and to dissolve rapidly in water.

U.S. Patent 3,922,230, Lamberti et al, issued.

November 25, 1975, discloses detergent compositions containing oligomeric polyacrylates.

U.S. Patent 4,031,022. Vogt et al, issued June 21, 1977, discloses detergent compositions containing copolymers of alphanydroxyacrylic acid and acrylic acid.

U.S. Patent 4.076.643. Brahm et al. issued February 28, 1978. discloses the preparation of free-flowing particulate premixes intended for use in detergent compositions. The premix contains one or more liquid or paste-like surfactants and a water-soluble hydroxy-carboxylic polymer or copolymer.

British Patent 1,333.915, published Oct. 17, 1973, discloses that polyacrylic acids of molecular weight greater than 1000 and having from 5-55% of its carboxyl groups neutralized as the sodium salt are free-flowing powders useful as detergent builders.

According to the present invention there is provided a process for making a granular detergent composition comprising :

(a) from 3% to 40% by weight of the composition of a non-soap anionic surfactant ;

(b) from 5% to 85% by weight of the composition of a water-soluble neutral or alkaline salt or mixtures thereof ; and

(c) from 1% to 50% by weight of the non-soap anionic surfactant of a water-soluble anionic polymer in substantially or completely neutralised salt form, having an average molecular weight of from 300 to 15,000 and at least 1 ionizable site per 200 units of molecular weight, wherein component (c) optionally forms part but not all of component (b) characterised in that the process includes the steps of (i) forming an intimate solid mixture of said surfactant, together with any accompanying non-surfactant sulfate impurity, and said polymer from an aqueous solution thereof in the absence of the water soluble neutral or alkaline salts other than the anionic polymer salt, or from a dispersion thereof in the absence of at least a major portion of said water soluble neutral or alkaline salts, and any other components of said granular detergent composition, provided that, where said solid intimate mixture is formed in the presence of a minor proportion of the water

soluble neutral or alkaline salt and any other components of said composition, a premix is made by adding the water soluble polymer (c) to an aqueous dispersion of the non-soap anionic surfactant, and any accompanying non-surfactant sulphate impurity, before the addition of any other material forming the minor proportion of the components of said composition ; and (ii) agglomerating or dry mixing said intimate solid mixture of said surfactant and polymer with the, or the major portion of the other components of said granular detergent composition.

Detailed description of the invention

The granular detergent compositions prepared by the process of the present invention contain the following essential components :

1) non-soap amonic surfactant,
2) water-soluble salts ; and
3) water-soluble anionic polymer.

The intimate solid admixture is accomplished by drying a solution or slurry containing the polymer and surfactant or their precursors. Subsequent processing including incorporation of water-soluble salts and optional ingredients should avoid steps that result in appreciable solution of the polymer/surfactant mixture in the presence of other water-soluble components. An admixture of surfactant and polymer can be mixed with other components prior to spray-drying if the resultant paste or slurry contains no more than 52% water by weight. Under such conditions the intimate solid admixture of surfactant and polymer is maintened. Agglomeration and dry mixing techniques are used in the practise of the present invention for producing complete granular detergent compositions while maintaining an intimate admixture of surfactant and polymer.

While not bound by any particular theory, it is believed that the polymers which are useful in the present invention provide their benefit by eliminating or retarding the formation of a highly viscous "gum" phase of anionic surfactant and water which acts to retard granule dissolution.

Surfactant

The detergent compositions herein contain from 3% to 40% by weight of non-soap anionic surfactant, preferably from 4% to 35%, and more preferably from 5% to 30%. In relatively high sudsing detergent compositions the non-soap anionic surfactant generally represents from 10% to 35%, and preferably from 12% to 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 Dec. 30, 1975.

Useful non-soap anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 10 to 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl 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 9 to 15 carbon atoms, in straight chain or branched chain configuration. e.g., those of the type described in United States 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 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 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from 8 to 12 carbon atoms and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl group contains from 10 to 20 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of α-sulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group: water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety ; alkyl ether sulfates containing from 10 to 20 carbon atoms in the alkyl group and from 1 to 30 moles of ethylene oxide ; water-soluble salts of olefin sulfonates containing from 12 to 24 carbon atoms ; and β-alkyloxy alkane sulfonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety. Anionic sulfonate surfactants are particularly preferred in the compositions of the invention in that a very substantial solubility benefit is provided.

Particularly preferred anionic surfactants herein include linear alkylbenzene sulfonates containing an aver-

age of from 11 to 14 carbon atoms in the alkyl group ; tallowalkyl sulfates ; coconutalkyl glyceryl ether sulfonates ; alkyl ether sulfates wherein the alkyl moiety contains from 12 to 18 carbon atoms and wherein the average degree of ethoxylation is from 1 to 4 and olefin or paraffin sulfonates containing from 12 to 16 carbon atoms.

Specific prefered surfactants for use herein include sodium linear C_{12-13} alkylbenzene sulfonate and the sodium salt of a sulfated condensation product of a C_{12-18}, alcohol with 1 to 4 moles of ethylene oxide. The advantages obtained with the compositions and the process of the invention are particularly apparent when said compositions comprise a non-soap anionic surfactant selected from the group comprising alkyl benzene sulfonates, olefin sulfonates and paraffin sulfonates.

Water-soluble neutral or alkaline salt

The granular detergents of the present invention contain from 5% to 85%, preferably from 10% to 70%, and more preferably from 30% to 65%, by weight of water-soluble neutral or alkaline salts. The neutral or alkaline salt has a pH in solution of seven or greater, and can be either organic or inorganic in nature. The salt assists a providing the desired density and bulk to the detergent granules herein. While some of the salts are inert, many of them also function as a detergency builder.

The neutral or alkaline water-soluble salts useful in the practice of the invention are materials consistent with use in granular detergent compositions from such standpoints as biological safety, effect on environment, and physical and chemical properties. Sodium and potassium salts are particularly useful for reasons of cost and physical properties. Suitable salts may be inorganic or organic, monomeric or polymeric.

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 is typically used in detergent granules and is a particularly preferred salt herein.

Other useful water-soluble salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, 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, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from 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, tetraborate decahydrate, and silicates having a weight ratio of SiO_2 to alkali metal oxide of from 0,5 to 4,0, preferably from 1.0 to 2.4.

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. Salts of nitrilotriacetic acid, such as sodium nitrilotriacetate, are particularly preferred.

Polymeric polycarboxylate builders are set forth 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. Some of these materials are useful as the water-soluble anionic polymer as hereinafter described, but only if in intimate admixture with the non-soap anionic surfactant.

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 4,144,226, 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, converted to the corresponding salt, and added to a detergent composition.

Water-soluble silicate solids represented by the formula $SiO_2 \cdot M_2O$, M being an alkali metal, and having a $SiO_2 : M_2O$ weight ratio of from 0,5 to 4,0, are useful salts in the compositions of the inventions at levels of from 2% to 15% on an anhydrous weight basis, preferably from 3% to 8%. Anhydrous or hydrated particulate silicate can be utilized. In one embodiment of the invention, a silicate water solution containing from 35% to 55% silicate solids can be used as an agglomerating agent.

Water-soluble anionic polymer

The compositions of the present invention also contain in intimate admixture with the non-soap anionic detergent surfactant from 1% to 50%, preferably from 3% to 30%, and more preferably from 5% to 20%, by weight of the non-soap anionic detergent surfactant of a water-soluble anionic polymer with at least 1 ionizable site per 200 units of molecular weight, preferably at least about 1 ionizable site per 100 units of molecular weight. While some dispersion effect is obtained with average polymer molecular weights as high as 50,000, the average molecular weight of polymers useful in the present invention is from 300 to 15,000, and preferably is from 1000 to 5,000. Also, the water soluble anionic polymers are substantially or completely neutralized water soluble salts. As used herein, average molecular weight is on a polymer weight basis.

Suitable polymers herein include homopolymers and copolymers of unsaturated aliphatic mono- or polycarboxylic acids. Preferred carboxylic acids are acrylic acid, hydroxyacrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, aconitic acid, crotonic acid, and citraconic acid. The polycarboxylic acids (e.g. maleic acid) can be polymerized in the form of their anhydrides and subsequently hydrolyzed. The copolymers can be formed of mixtures of the unsaturated carboxylic acids with or without other copolymerizable monomers, or they can be formed from single unsaturated carboxylic acids with other copolymerizable monomers. In either case, the percentage by weight of the polymer units derived from noncarboxylic acids is preferably less than 50%. Suitable copolymerizable monomers include, for example, vinyl chloride, vinyl alcohol, furan, acrylonitrile, vinyl acetate, methyl acrylate, methyl methacrylate, styrene, vinyl methyl ether, vinyl ethyl ether, vinyl propyl ether, acrylamide, ethylene, propylene and 3-butenoic acid.

Homo- and copolymers of sulfonates, sulfates and phosphates of suitable monomers such as styrene, vinyl alcohol, vinyl chloride, etc., are particularly useful in the practice of the invention. Polystyrene sulfonate with a molecular weight in the range of from 2000 to 6000 is particularly useful in the practice of the invention.

Other preferred polymers are the homopolymers and copolymers of acrylic acid, hydroxyacrylic acid, or methacrylic acid, and salts thereof, which in the case of the copolymers contain at least 50%, and preferably at least 80%, by weight of units derived from the acid. Particularly preferred polymers are sodium polyacrylate and sodium polyhydroxyacrylate. The most preferred is sodium polyacrylate. Other specific preferred polymers are the homopolymers and copolymers of maleic anhydride, especially the copolymers with ethylene, styrene and vinyl methyl ether.

The polymerization of acrylic acid homo- and copolymers can be accomplished using freeradical initiators, such as alkali metal persulfates, acyl and aryl peroxides, acyl and aryl peresters and aliphatic azo compounds. The reaction can be carried out in situ or in aqueous or non-aqueous solutions or suspensions. Chain-terminating agents can be added to control the molecular weight. The copolymers of maleic anhydride can be synthesized using any of the types of freeradical initiators mentioned above in suitable solvents such as benzene or acetone, or in the absence of a solvent, under an inert atmosphere. These polymerization techniques are well known in the art. It will be appreciated that instead of using a single polymeric aliphatic carboxylic acid, mixtures of two or more polymeric aliphatic carboxylic acids can be used to prepare the above polymers.

In general, natural polymers such as pectin, alginic acid, gum arabic and carragheenan and cellulose derivatives such as cellulose sulfate, carboxymethyl cellulose, hydroxypropyl cellulose and hydroxybutyl cellulose are not effective in the practice of the invention. Vinyl polymers without sufficient ionizable sites are likewise not effective.

In general, these deficiencies appear to be a result of a low ratio of ionizable sites to molecular weight or too high a molecular weight.

Optional ingredients

Nonionic surfactants may be present 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 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 con-

densation products of alkyl phenols having an alkyl group containing from 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from 3 to 12 moles of ethylene oxide par 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 9 to 15 carbon atoms with from 4 to 8 moles of ethylene oxide per mole of alcohol.

Suitable semi-polar nonionic surfactants include : (1) water-soluble amine oxides containing one alkyl moiety of from 10 to 18 carbon atoms and 2 moieties selected from alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms, (2) water-soluble phosphine oxides containing one alkyl moiety of 10 to 18 carbon atoms and 2 moieties selected from alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms and (3) water-soluble sulfoxides containing one alkyl moiety of from 10 to 18 carbon atoms and a moiety selected from alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

Water-soluble salts of the higher fatty acids, i.e., "soaps", can be used in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from 8 to 24 carbon atoms, and preferably from 12 to 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.

Cationic surfactants can be utilized in compositions of the present invention. A preferred cationic surfactant is a quaternary ammonium compound with one long chain alkyl and three short chain alkyl groups such as dodecyltrimethylammonium chloride.

Optional surfactants are preferably separated from the intimate admixture of non-soap anionic surfactant and polymer but may be present in the admixture in non-interfering amounts such that the overall anionic character of the admixture is maintained.

The detergent compositions of the invention can optionally contain water-insoluble aluminosilicate ion exchange material of the formula

$$Na_z[(AlO_2)_z \cdot (SiO_2)_y] \cdot xH_2O$$

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. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula

$$M_z(zAlO_2 \cdot ySiO_2)$$

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.

The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from 10% to 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 18% to 22% water in their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from 0.1 micrometers to 10 micrometers. Amorphous materials are often smaller, e.g., down to less than 0.01 micrometers. Preferred ion exchange materials have a particle size diameter of from 0.2 micrometers to 4 micrometers. 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 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 300 mg. eq./g. to 352 mg. eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least 0.129 g/min/g of aluminosilicate (anhydrous basis), and generally lies within the range of from 0.129 g/min/g to 0.387 g/min/g based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a calcium ion exchange rate of at least 0.258 g/min/g.

The amorphous aluminosilicate ion exchange materials usually have a Mg^{--} exchange capacity of at least 50 mg. eq. $CaCO_3$/g. (112 mg. Mg^{--}/g.) and a Mg^{--} exchange rate of at least 0.064 g/min/g. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54×10^{-10}m).

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 structufe and can be naturally-occurring aluminosilicates or synthetically derived. A method of producing aluminosilicate ion exchange materials is discussed in U.S. Patent 3,985,669, Krummel, et al., issued October 12, 1976.

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

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$$

wherein x is from 20 to 30, especially 27.

Other ingredients commonly used in detergent compositions can be included in the compositions of the present invention. These include color speckles, bleaching agents such as perborates and percarbonates and bleach activators, suds boosters or suds suppressors, anti-tarnish and anti-corrosion agents, soil suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, pH adjusting agents, non-builder alkalinity sources, hydrotopes such as toluene sulfonates and xylene sulfonates, enzymes, enzyme-stabilizing agents, perfumes and water.

The detergent compositions of the present invention can comprise a portion of compositions containing a wide variety of materials suitable for detergent or other uses.

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

A slurry was prepared containing 30% of the sodium salt of linear C_{13} alkyl benzene sulfonate (sodium C_{13}LAS). 3% of a copolymer of acrylamide and acrylate having a molecular weight of approximately 15,000 and an acrylamide content of 12%, 15% sodium sulfate and 52% water. The slurry was spray dried to produce a granule containing an intimate admixture of the sodium C_{13} LAS and the copolymer of acrylamide and acrylate. Water content was reduced to less than 10% by weight.

A granular detergent composition was prepared containing the following components :

	%
Sodium nitrilotriacetate (NTA)	44
Sodium carbonate	9
Sodium silicate (SiO_2:Na_2O=2.4)	5
C_{12-13} alcohol ethoxylated with 6.5 moles of ethylene oxide per mole of alcohol	6
Sodium C_{13} LAS	15
Acrylamide/Acrylate copolymer	1.5
Sodium sulfate	8
Water	7
Hydrous silica (Zeosyl 200)	3.0
Miscellaneous	Balance

The NTA, sodium carbonate and sodium silicate in dry particulate form were placed in a Marion Mixer Model 2030. After 1 minute of mixing, the C_{12-13} alcohol-6.5 ethoxylate was added as a spray and acted as an agglomerating agent. An appropriate quantity of the granular mixture of sodium C_{13} LAS, polymer and sodium sulfate was then added followed by the hydrous silica. The resultant granular detergent product is screened to remove large lumps, if any. The final product had a density of 0.67 grams per milliliter.

Entrapment test

This method is used to determine the entrapment potential of a granular detergent product relative to another comparison product, the comparison product being a pre-established standard which preferably has a consumer validated entrapment profile. The test is designed with conditions of high stress (low agitation, low temperature, high product-to-fabric ratio) in order to maximize visual differences between products.

The entrapment test measures the ability or inability of a granular detergent to dissolve and disperse out of an enclosed fabric pocket during the course of a gentle wash cycle in a full scale washer.

Equipment

Full scale washer-Kenmore or G.E.
Black fabric-10 cm × 15 cm rectangles
Stapler

Procedure

The entrapment test is carried out in a full-scale washer (66 litres fill) in 15°C city water over a 10 minutes gentle wash cycle (Kenmore = 48 48 RPM, GE = 60 RPM).

1. Four fabric pockets are to be constructed-Two 10 cm × 15 cm rectangles of the black fabric are stapled together along three sides to form an open pocket.
2. One-fourth of the recommended usage of the product to be tested is placed in each of the four fabric pockets.
3. Each of the fabric pockets is stapled shut along the fourth side to form a closed pocket.
4. The washer is filled with 15°C city water and the four pockets are added to the washer as agitation begins.
5. Two pockets are removed from the washer at the end of the wash-spin cycle ; the other two pockets are removed at the end of the rinsespin cycle.
6. Pockets are squeezed lightly to remove excess water and are blotted between paper towels to remove additional water.
7. The pockets are opened along 3 sides and spread open to air dry. Comparisons between products are made after the pockets have dried completely.

Using the entrapment test, visual comparisons can be made between products to determine relative dissolution and solubility.

The composition of Example 1 was compared to a composition made by the same procedure but without the inclusion of the acrylamid/acrylate copolymer. The composition of Example 1 had a substantial advantage as measured by the entfapment test.

Example II

The composition of Example 1 was produced on an Aeromatic Spray Granulator Fluid Bed.

The slurry of Example 1 containing the Sodium C_{13} LAS and acrylamide/acrylate copolymer was sprayed on a fluidized bed of the NTA and sodium carbonate suspended with heated air. The bed was allowed to cool and the remaining ingredients were added.

The resultant granular detergent composition has physical properties, including rate of dissolution and density equivalent to the composition of Example 1 and a substantial advantage solubility over a product made without inclusion of the polymer.

Surfactant dispersibility test

Samples of spray-dried C_{13} LAS with its accompanying sodium sulfate, both with (10%) and without the acrylamide/acrylate copolymer of Example 1 were tested by adding 1 gram of granules into 400 ml of room temperature water which was stirred slowly with a magnetic stirrer. The time required to dissolve the sample without the polymer was twice as long (25 minutes) as the sample with the polymer (12 minutes). Additional evaluations using the same procedure showed the following results :

TABLE I
C_{13}LAS

% Polyacrylic acid (MW=2000)	Dispersion time (min)
0	19
13.2	11
26.4	5

TABLE II
30% tallow alkyl sulfate
40% C_{12}LAS
30% C_{12-15} alkyl 2.25 ethoxy ether sulfate

% Polymer of Example I	Dispersion time (min.)
0	11
16.8	7.5
40.9	2

TABLE III
30% tallow alkyl sulfate
40% C_{12} LAS
30% C_{12-15} alkyl 2.25 ethoxy ether sulfate

% Polyacrylic acid (MW=2000)	Dispersion time (min.)
0	11
7.8	7.5
15.6	0.67
31	0.33
48	0.17

At a concentration of 40.7% of polymer in the paste, the following molecular weight dependence of the dispersibility of sodium C_{13} LAS with polyacrylic acid was observed.

MW of polyacrylic acid	Dispersion time (min.)
1000	less than ½
2000	1/2
5000	4-1/2
104,000	28
1,250,000	75

Example III

The following composition was prepared by spray-drying an aqueous crutcher mixture of the components listed. Water content of the crutcher mix was approximately 38% and reduced to approximately 8% by spray drying. The sodium polyacrylate with a molecular weight of 2000 was mixed with the anionic surfactant paste prior to adding the balance of the components to the crutcher.

Component	Parts
Sodium C_{12} alkylbenzene sulfonate	13.86
Sodium C_{14-15} alkyl polyethoxy (2.25) sulfate	5.94
Sodium polyacrylate (avg. m.w. 2000)	0.52
Tetrasodium pyrophosphate	7.81
Sodium silicate (2.0 weight ratio-SiO_2/Na_2O)	5.21
Sodium sulfate	13.34
Sodium polyacrylate[1] (avg. m.w. 50,000—70,000)	1.04
Water & miscellaneous	4.38
	52.1

Added to improve physical properties and retard deposition of calcium pyrophosphate.
The resulting spray dried granules were dry mixed with the following components :

Component	Parts
Tetrasodium pyrophosphate	41.26
Sodium carbonate	5.21
Perfume, enzymes, dust control agents	1.43
	47.9

The water dispersibility of the resulting composition was substantially superior to a composition containing the same ingredients except no sodium polyacrylate (avg. m.w. 2000) and to a composition containing the same ingredients in which the sodium polyacrylate (avg. m.w. 2000) was not admixed with the anionic surfactant paste prior to mixture with other ingredients.

Example IV
The following composition was prepared:

	%
Sodium linear C_{12} alkylbenzene sulfonate, sodium polyacrylate, and sodium sulfate flake (LAS/SPA)	7.10
C_{14-15} primary alcohol hepta ethoxylate (7)	12.97
Sodium tripolyphosphate (anhydrous)	24.00
Sodium carboxymethylcellulose (CMC)	1.22
Sodium silicate	7.41
Maleic anhydride methyl vinyl ether copolymer (Mwt 250,000)	1.33
Sodium perborate tetrahydrate	28.8
Magnesium sulphate	0.74
Fluorescer	0.34
Enzyme	1.33
Suds suppressor (15% silica/85% silicone)	0.34
Water & miscellaneous	Balance

The sodium silicate, sodium tripolyphosphate, maleic anhydride copolymer, CMC, magnesium sulphate and fluorescer, were first formed into a crutcher mix of moisture content 42% and spray dried to give a granular powder of density 650-670 g/litre and moisture content of 7%.

This granular base powder was fed into a 76 mm diameter Patterson-Kelley zig-zag blender and the nonionic surfactant sprayed on at a temperature of 40°C over a period of two minutes. Mixing was allowed to continue for a further 8 minutes after which the powder density was 800-830 g/litre.

The sodium perborate, suds suppressor ingredients and enzyme were then dry mixed into the nonionic containing powder by means of a Vertomix in-line mixer (made by Babcock Gardner ltd., Middleway, St, Blazey, Cornwall, England) resulting in a powder of density 790-800 g/litre. The product was passed through a sieve of opening 0.853 mm and the oversize recycled for further size reduction. The LAS/SPA flake was made from an aqueous slurry of solids content 50% by weight, in which the solids comprise 90% LAS paste, 10% sodium polyacrylate (Goodrite K-759, a sodium polyacrylate of molecular wt. 2100 made by Goodrich Chemical Group, Cleveland, Ohio, USA).

This slurry was dried on rollers heated by 24.5 N/Cm^2 steam and removed as a flake of thickness 0.25 mm comprising 80% LAS, 10% sodium polyacrylate, 7% sodium sulfate, 3% moisture. The flake was broken up by 10 minutes agitation in a cube mixer and the portion passing through a sieve of opening 0.853 mm was used as a dry additive in the product. Addition of the LAS/SPA flake to the remainder of the product was carried out in a Vertomix, using the same procedure as for the dry mixing of the other ingredients, to give a finished product density of 750 grams/liter.

The finished product had a particle size distribution as follows :

>1.204 mm	0%
>0.853 mm	2.8%
>0.422 mm	18.5%
>0.211 mm	39.2%
>0.152 mm	14.1%
>0.104 mm	18.4%
<0.104 mm	7.0%

Dispersion and solubility of the finished product in water was excellent.

The product of Example IV is prepared with a LAS/SPA flake thickness of 0.10 mm and a LAS/SPA flake thickness of 0,50 mm. Comparable dispersion and solubility is obtained.

The present invention is also helpful in reducing product loss in the sump or drain plug connection of front loading washing machines. In such machines, the sump comprises the drain plug which is located at the lowest point of the machine and a short length of piping which connects the plug either to the external casing or to part of the wash water recirculation system. Product is added to the washing machine via a dispenser, the contents of which are flushed by a stream of cold water into the external casing of the machine at the start of the cycle. Any component of the product having a low rate of solubility in cold water tends to collect in the sump and this tendency is enhanced by the formation of viscous surfactant phases which cause aggregation of other components. The tendency is particularly noticeable when anionic surfactant is dry mixed with the remainder of the formulation and compositions in accordance with the present invention can be shown to overcome this problem.

The following compositions were prepared :

(a) A flaked composition comprising
88,9% NaLAS
7.8% Na_2SO_4 + miscellaneous
3,3% H_2O

(b) A flaked composition comprising
80% NaLAS
10% Sodium polyacrylate Mw = 2000
7% Na_2SO_4 + miscellaneous
3% H_2O

Both flake compositions were prepared as in Example IV above. In a model test using a funnel fitted with a length of tubing to simulate a washing machine sump and adapted to trap undissolved material, the percentage of the initial formulation remaining as a residue in the sump was :

Sample (a) 17.1%
Sample (b) 4,5%

Claims

1. A process for making a granular detergent composition comprising :
(a) from 3% to 40% by weight of the composition of a non-soap anionic surfactant ;
(b) from 5% to 85% by weight of the composition of a water-soluble neutral or alkaline salt or mixtures thereof ; and
(c) from 1% to 50% by weight of the non-soap anionic surfactant of a water-soluble anionic polymer in substantially or completely neutralised salt form, having an average molecular weight of from 300 to 15,000 and at least 1 ionizable site per 200 units of molecular weight, wherein component (c) optionally forms part but not all of component (b) characterised in that the process includes the steps of (i) forming an intimate solid mixture of said surfactant, together with any accompanying non-surfactant sulfate impurity, and said polymer from an aqueous solution thereof in the absence of the water soluble neutral or alkaline salts other than the anionic polymer salt, or from a dispersion thereof in the absence of at least a major portion of said

water soluble neutral or alkaline salts, and any other components of said granular detergent composition, provided that, where said solid intimate mixture is formed in the presence of a minor proportion of the water soluble neutral or alkaline salt and any other components of said composition, a premix is made by adding the water soluble polymer (c) to an aqueous dispersion of the non-soap anionic surfactant, and any accompanying non-surfactant sulphate impurity, before the addition of any other material forming the minor proportion of the components of said composition ; and (ii) agglomerating or dry mixing said intimate solid mixture of said surfactant and polymer with the, or the major portion of the other components of said granular detergent composition.

2. A process according to claim 1 wherein an intimate solid mixture comprising either a C_{13} alkyl benzene sulfonate and a water-soluble acrylate/acrylamide copolymer of molecular weight MWt 15,000 and acrylamide content of 12%, or mixtures of C_{12} alkyl benzene sulfonate and C_{14-15} alkyl ether sulfate and an acrylate homopolymer of molecular weight MWt 2,000, is spray-dried from an aqueous slurry also containing a minor portion of said water-soluble netural or alkaline salt or mixtures thereof, provided that said slurry contains no more than 52% water by weight.

3. A process according to claim 1 wherein the non-soap anionic surfactant comprises an alkali metal salt of a C_{11-13} alkyl benzene sulfonate.

4. A process according to either one of claims 1 and 3 wherein the water-soluble anionic polymer is selected from water-soluble salts of polyacrylic acid, copolymers of an acryl amide and an acrylate, polystyrene sulfonate polymers and mixtures thereof.

5. A process according to any one of claims 1, 3 and 4 wherein the water-soluble anionic polymer is at a level of from 5% to 20% by weight of the non-soap anionic surfactant.

6. A process according to any one of claims 1-4 wherein the water-soluble anionic polymer has a molecular weight of from 1000 to 5000.

7. A process according to any one of claims 1-6 wherein the non-soap anionic surfactant is at a level of from 12% to 30% by weight of the granular detergent composition.

8. A process according to any one of claims 1-7 wherein the water-soluble neutral or alkaline salt comprises a material selected from alkali metal polyphosphates, alkali metal nitrilo-triacetates, alkali metal sulfates and mixtures thereof.

Ansprüche

1. Ein Verfahren zur Herstellung einer granulierten Detergenszusammensetzung, enthaltend

(a) 3 Gew.-% bis 40 Gew.-% der Zusammensetzung eines anionischen Nicht-Seifen-oberflächenaktiven Mittels ;

(b) 5 Gew.-% bis 85 Gew.-% der Zusammensetzung eines wasserlöslichen, neutralen oder alkalischen Salzes oder Mischungen davon ; und

(c) 1 Gew.-% bis 50 Gew.-% des anionischen Nicht-Seifenoberflächenaktiven Mittels eines wasserlöslichen, anionischen Polymers in im wesentlichen oder vollständig neutralisierter Salzform mit einem mittleren Molekulargewicht von 300 bis 15.000 und wenigstens einer ionisierbaren Stelle je 200 Einheiten des Molekulargewichts, wobei die Komponente (c) gegebenenfalls einen Teil der, jedoch nicht die gesamte Komponente (b) bildet, dadurch gekennzeichnet, daß das Verfahren die Stufen

(i) der Bildung eines innigen festen Gemisches des genannten oberflächenaktiven Mittels, zusammen mit etwaigen begleitenden Nicht-surfactant-Sulfatverunreinigungen, und des genannten Polymers aus einer wässerigen Lösung hievon in Abwesenheit der wasserlöslichen neutralen oder alkalischen Salze, die von dem anionischen Polymersalz verschieden sind, oder aus einer Dispersion hievon in Abwesenheit wenigstens eines größeren Teiles dieser wasserlöslichen neutralen oder alkalischen Salze, und etwaiger weiterer Komponenten der genannten granulierten Detergenszusammensetzung, mit der Maßgabe, daß dann, wenn dieses feste innige Gemisch in Anwesenheit eines kleineren Anteiles der wasserlöslichen neutralen oder alkalischen Salze und etwaiger anderer Komponenten der genannten Zusammensetzung gebildet wird, ein Vorgemisch hergestellt wird durch Zusetzen des wasserlöslichen Polymers (c) zu einer wässerigen Dispersion des anionischen Nicht-Seifen-oberflächenaktiven Mittels, und etwaiger begleitender Nicht-surfactant-Sulfatverunreinigungen, vor der Zugabe etwaiger weiterer, den kleineren Anteil der Komponenten der genannten Zusammensetzung bildender Materialien ; und

(ii) Agglomerieren oder Trockenvermischen des innigen festen Gemisches aus dem oberflächenaktiven Mittel und dem Polymer mit den, oder dem größeren Teil der, anderen Komponenten der genannten granulierten Detergenszusammensetzung umfaßt.

2. Ein Verfahren nach Anspruch 1, worin ein inniges festes Gemisch, umfassend entweder ein C_{13}-Alkyl-

benzolsulfonat und ein wasserlösliches Acrylat/Acrylamid-Copolymer vom Molekulargewicht 15.000 und einem Acrylamidgehalt von 12% oder Gemische aus C_{12}-Alkylbenzolsulfonat und C_{14-15}-Alkylethersulfat und einem Acrylathomopolymer vom Molekulargewicht 2.000, aus einer wässerigen Aufschlämmung sprühgetrocknet wird, die auch einen kleineren Anteil an den genannten wasserlöslichen neutralen oder alkalischen Salzen oder Gemischen hievon enthält, mit der Maßgabe, daß diese Aufschlämmung nicht mehr als 52 Gew.-% Wasser enthält.

3. Ein Verfahren nach Anspruch 1, wobei das anionische NichtSeifen-oberflächenaktive Mittel ein Alkalimetallsalz eines C_{11-13}-Alkylbenzolsulfonats umfaßt.

4. Ein Verfahren nach einem der Ansprüche 1 und 3, wobei das wasserlösliche, anionische Polymer aus wasserlöslichen Salzen der Polyacrylsäure, Copolymeren eines Acrylamids und eines Acrylats, Polystyrolsulfonatpolymeren und Mischungen davon ausgewählt ist.

5. Ein Verfahren nach einem der Ansprüche 1, 3 und 4, wobei das wasserlösliche, anionische Polymer in einer Menge von 5 Gew.-% bis 20 Gew.-% des anionischen Nicht-Seifen-oberflächenaktiven Mittels vorliegt.

6. Ein Verfahren nach einem der Ansprüche 1 bis 4, wobei das wasserlösliche, anionische Polymer ein Molekulargewicht von 1.000 bis 5.000 hat.

7. Ein Verfahren nach einem der Ansprüche 1 bis 6, wobei das anionische Nicht-Seifen-oberflächenaktive Mittel in einer Menge von 12 Gew.-% bis 30 Gew.-% der granulierten Detergenszusammensetzung vorliegt.

8. Ein Verfahren nach einem der Ansprüche 1 bis 7, wobei das wasserlösliche, neutrale oder alkalische Salz ein Material umfaßt, das aus Alkalimetallpolyphosphaten, Alkalimetallnitrilotriacetaten, Alkalimetallsulfaten und Mischungen davon ausgewählt ist.

Revendications

1. Procédé pour préparer une composition détergente granulaire comprenant :
(a) de 3 à 40% en poids, par rapport à la composition, d'un tensioactif anionique qui n'est pas un savon ;
(b) de 5 à 85% en poids, par rapport à la composition, d'un sel neutre ou alcalin soluble dans l'eau ou des mélanges de tels sels, et
(c) de 1% à 50% en poids, par rapport au tensioactif anionique qui n'est pas un savon, d'un polymère anionique, soluble dans l'eau, sous forme d'un sel quasi-totalement ou totalement neutralisé, ayant un poids moléculaire moyen de 300 à 15.000 et au moins un site ionisable par 200 unités de poids moléculaire, le constituant (c) formant facultativement une partie mais non la totalité du constituant (b), caractérisé en ce que le procédé comprend les étapes consistant (i) à former un mélange solide intime dudit tensioactif, avec n'importe quelle impureté d'accompagnement de type sulfate non tensioactif, et dudit polymère à partir de sa solution aqueuse, en l'absence de sels hydrosolubles, neutres ou alcalins, autres que le sel de polymère anionique, ou à partir d'une dispersion du polymère, en l'absence d'au moins une partie principale ou majeure desdits sels hydrosolubles neutres ou alcalins, et de tous autres constituants de ladite composition détergente granulaire, à la condition que, lorsque ledit mélange solide intime est formé en présence d'une proportion mineure du sel neutre ou alcalin soluble dans l'eau et de tous autres constituants de ladite composition, on prépare un mélange préliminaire en ajoutant le polymère soluble dans l'eau (c) à une dispersion aqueuse du tensioactif anionique qui n'est pas un savon, et de toute impureté éventuelle de type sulfate non tensioactif, avant l'addition de toute autre matière éventuelle formant la proportion mineure des constituants de ladite composition ; et (ii) à agglomérer ou mélanger à sec ledit mélange solide intime dudit tensioactif et du polymère avec les, ou avec la majeure partie des autres constituants de ladite composition granulaire.

2. Procédé selon la revendication 1, dans lequel un mélange solide intime comprenant un alkyl (en C_{13}) benzène sulfonate et un copolymère acrylate/acrylamide soluble dans l'eau, de poids moléculaire égal à 15.000 et contenant 12% d'acrylamide, ou comprenant des mélanges d'un alkyl (en C_{12}) benzène sulfonate et d'un (éther oxyde d'alkyle en C_{14-15}) sulfate et d'un homopolymère d'acrylate de poids moléculaire égal à 2000, est séché par atomisation à partir d'une suspension aqueuse contenant aussi une proportion mineure dudit sel hydrosoluble neutre ou alcalin, ou de leurs mélanges, à la condition que ladite suspension ne contienne pas plus de 52% d'eau en poids.

3. Procédé selon la revendication 1 dans lequel le tensioactif anionique qui n'est pas un savon comprend un sel de métal alcalin d'un (alkyl en C_{11-13})-benzènesulfonate.

4. Procédé selon l'une ou l'autre des revendications 1 et 3, dans lequel le polymère anionique soluble dans l'eau est choisi entre les sels solubles dans l'eau d'un acide polyacrylique, les copolymères d'un acrylamide et d'un acrylate, les polymères poly(styrènesulfonates) et leurs mélanges.

5. Procédé selon l'une quelconque des revendications 1, 3 et 4, dans lequel le polymère anionique soluble

dans l'eau est à une concentration de 5 à 20% en poids par rapport au tensioactif anionique qui n'est pas un savon.

6. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le polymère anionique soluble dans l'eau a une masse moléculaire de 1000 à 5000.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel le tensioactif anionique qui n'est pas un savon est présent en une concentration de 12 à 30% en poids par rapport à la composition détergente granulaire.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel le sel neutre ou alcalin soluble dans l'eau comprend une substance choisie parmi les polyphosphates de métaux alcalins, les nitrilotriacétates de métaux alcalins, les sulfates de métaux alcalins et leurs mélanges.