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3,801,511

SPRAY-DRIED DETERGENT COMPOSITION
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No Drawing. Filed Apr. 17, 1972, Ser. No. 244,964
Int. Cl. C11d 3/10, 3/20, 17/06
U.S. Cl. 252-135

6 Claims

ABSTRACT OF THE DISCLOSURE

A spray-dried detergent composition is produced by a method whereby the resultant composition is in the form of crisp, free-flowing granules. The method comprises first forming an aqueous slurry of sodium carbonate, a water-soluble detergent, and as an anti-caking agent, a water-soluble compound having a greater solubility in water than does the sodium carbonate. The resultant slurry is thereafter spray dried to produce the crisp, free-flowing granules. The water-soluble compound when added to the slurry prior to spray drying imparts to the resultant composition the desired physical properties.

BACKGROUND OF THE INVENTION

This invention relates to a detergent composition. More particularly, it relates to a spray-dried detergent composition in the form of crisp, free-flowing granules.

Granular detergent compositions intended for the washing of soiled laundry are well known. Such compositions are referred to as built or heavy-duty detergent compositions. Generally, they contain a water-soluble detergent, a builder salt and, optionally, fluoescers, corrosion inhibitors, suds modifiers, etc.

The builder salt has the function of tying up, or sequestering, hardness ions found in wash water. Builder salts such as sodium tripolyphosphate perform their function of tying up hardness minerals by forming a soluble complex with the hardness ions. Other builder salts such as the alkali metal carbonates form a precipitate with the hardness ions thereby reducing the content of said ions in the wash water.

Built detergent compositions normally are in the form of granules and are packaged so as to be poured by the consumer into the wash water. An important attribute of these detergent compositions is that they possess the property of being easily pourable, i.e. free-flowing. This is a rather rigid requirement since it is preferable that a product be formulated so as to be transported throughout the country. Thus, any product intended for national distribution must be able to withstand the severest of humidity and temperature conditions (conditions which promote caking and reduce flowability).

Various known anti-caking agents have been added to built granular detergent compositions for the purpose of rendering the composition more crisp and free flowing. For example, magnesium sulfate is used, in part, for the anti-caking effect it has on built granular detergent compositions. Some agents though have disadvantages such as hindering the operation of the detergent or forming an insoluble complex and depositing onto the fabric.

Accordingly, there is a need for a built detergent composition in the form of granules that are free flowing and crisp.

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It is an object of this invention to produce a spray-dried detergent composition.

It is another object of this invention to produce a spray-dried detergent composition that is crisp and free flowing.

A still further object of this invention is to produce a crisp, free-flowing, built detergent composition that performs satisfactorily under a wide variety of washing conditions.

These and other objects will become apparent from the description to follow.

All percentages used hereinout are percentages by weight unless otherwise specified.

SUMMARY OF THE INVENTION

A process for producing crisp, free-flowing detergent granules and product so produced comprising the steps of:

- (a) forming an aqueous slurry containing from 4% to 35% of a water-soluble detergent selected from the group consisting of anionic, nonionic, zwitterionic and ampholytic detergents, from 7% to 55% of sodium carbonate, and from 0.7% to 15% of a water-soluble compound characterized in having a greater solubility in water than the sodium carbonate; and
- (b) spray drying the slurry to form crisp, free-flowing granules.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a spray-dried detergent composition. More particularly, the spray-dried, sodium carbonate-built detergent composition of this invention is in the form of crisp, free-flowing granules.

The spray-dried detergent compositions of this invention contain sodium carbonate as a builder salt, a water-soluble detergent and an anti-caking agent to be discussed hereinafter. The above composition is produced by a spray-drying operation whereby the resultant granules are crisp and free flowing.

Sodium carbonate has been used as a detergency builder salt previously. Similarly, many known water-soluble detergents have formed a part of detergent compositions. Hereinafter, examples of water-soluble detergents selected from the group consisting of anionic, nonionic, zwitterionic, and ampholytic detergents useful in the present invention are given.

The forming of granular detergent compositions by a spray-drying operation is well practiced throughout the detergent industry. Generally, an aqueous slurry containing all or many of the total detergent composition components is formed and atomized into a spray-drying tower, the height of which can vary considerably. At the base of the tower, a source of hot air, i.e. air having a temperature of 300° F. to 800° F. is introduced. As the hot air rises, it contacts the aqueous slurry spray droplets, thereby driving off substantially all the water. The resultant granules are collected at the bottom of the tower while the water laden air exits at the top.

Surprisingly it has been found that when a compound possessing the property of being more soluble in water than the sodium carbonate (herein referred to as an anti-caking agent) is added to a carbonate-containing aqueous slurry prior to spray drying, the resultant spray-dried detergent composition is crisp and free flowing. Sodium carbonate as reported by Linke in "Solubilities of Inorganic and Metal Organic Compounds," 4th ed., has a solubility of 29.4 grams per 100 ml. of water at 25° C.

Preferably, the anti-caking agent has a solubility of greater than 100 grams per 100 ml. water at 25° C. Examples of materials more soluble than sodium carbonate are sodium acetate, sodium citrate and potassium carbonate. The above listing is not meant to be limiting, but is merely

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In accordance with this invention, an aqueous slurry containing from 7% to 55%, preferably 15% to 35% of sodium carbonate, from 4% to 35%, preferably from 10% to 20% of a water-soluble detergent selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic detergents, and from 0.7% to 15%, preferably 3.5% to 7% of the above-discussed anti-caking agents, is formed. This aqueous slurry is then spray dried by known spray-drying techniques. The resultant granular detergent composition is substantially dry, i.e. containing less than 10% of water and, more importantly, is crisp and free flowing.

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In the absence of adding the anti-caking agent to the aqueous slurry, the resultant composition is substantially sticky and not free flowing. Similarly, adding the agent as a dry component to a substantially dry spray-dried detergent composition does not result in a crisp, free-flowing detergent composition. Only when the anti-caking agent is added to the aqueous slurry and thereafter spray dried, are the fruits of this invention fully realized. It has been found that as the composition of this invention in the form of a droplet is being spray dried, the anti-caking agent migrates to the outer portions of the droplet. More specifically, during the drying of an individual droplet, water within the inner portions continually migrates to the surface of the droplet where it evaporates into the surrounding atmosphere. Since the anti-caking agent is more soluble in water than the sodium carbonate; it, in effect, is carried to the surface of the droplet along with the migrating water. When the water evaporates the anti-caking agent is left on or near the surface with the result that the sodium carbonate and detergent is left in the interior of the droplet. The ultimate result is that the granules formed from the droplets are crisp and free flowing. Additionally, in detergent compositions containing conventional ingredients such as sodium sulfate and/or sodium silicate, the anti-caking agent of this invention carries with it the aforementioned ingredients as it migrates to the droplet surface. This imparts an even greater anti-caking property to the spray-dried granule.

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The granules obtained from the spray drying operation are substantially dry, i.e. contain less than about 10% water, and are crisp and free flowing. They consist essentially of from 5% to 50%, preferably 15% to 30% of a water-soluble detergent as above described, from 10% to 80%, preferably 20% to 50% sodium carbonates, and from 1% to 20%, preferably 5% to 10% of an anti-caking agent as above-described and exemplified. In a preferred detergent composition, the anti-caking agent is selected from the group consisting of sodium acetate, sodium citrate and potassium carbonate.

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In addition to the sodium carbonate, water-soluble detergent and anti-caking agent, conventional built detergent composition components may be added to the composition of this invention either prior to or after the spray-drying step. Examples of such conventional components are the corrosion inhibitors, e.g. alkali metal silicates, fluorsceners, suds boosters, and sodium sulfate.

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An especially preferred composition of this invention contains from 3% to 25% on a finished product basis (2% to 17% on an aqueous slurry basis) of an alkali metal silicate having an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 3.2:1 to 1:2. Spray-dried granules containing the alkali metal silicate are especially crisp and free flowing.

Examples of detergents useful in the present invention follow:

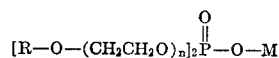
(A) Anionic soap and non-soap synthetic detergents

This class of detergents includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Suitable fatty acids can be obtained from natural sources such as, for instance, from plant or animal esters (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale and fish oils, grease, lard, and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Naphthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. 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.

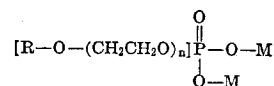
This class of detergents also includes water-soluble salts, particularly the alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a sulfonic acid or sulfuric acid ester radical. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Examples of this group of synthetic detergents which form a part of the preferred built detergent compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols ($\text{C}_8\text{--C}_{18}$ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in U.S. Letters Pats. No. 2,220,099 and 2,477,383 (especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 13 carbon atoms abbreviated hereinafter as C_{13}LAS); 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 sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 8 to about 12 carbon atoms.

Anionic phosphate surfactants are also useful in the present invention. These are surface active materials having substantial detergent capability in which the anionic solubilizing group connecting hydrophobic moieties is an oxy acid of phosphorus. The more common solubilizing groups, of course, are $\text{--SO}_4\text{H}$, $\text{--SO}_3\text{H}$, and $\text{--CO}_2\text{H}$. Alkyl phosphate esters such as $(\text{R--O})_2\text{PO}_2\text{H}$ and ROPO_3H_2 in which R represents an alkyl chain containing from about 8 to about 20 carbon atoms are useful.

These esters can be modified by including in the molecule from one to about 40 alkylene oxide units, e.g., ethylene oxide units. Formulae for these modified phosphate anionic detergents are



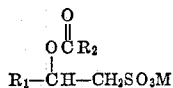
or



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in which R represents an alkyl group containing from about 8 to 20 carbon atoms, or an alkylphenyl group in which the alkyl group contains from about 8 to 20 carbon

atoms, and M represents a soluble cation such as hydrogen, sodium, potassium, ammonium or substituted ammonium; and in which n is an integer from 1 to about 40.

Another class of suitable anionic organic detergents particularly useful in this invention includes salts of 2-acyloxyalkane-1-sulfonic acids. These salts have the formula



where R_1 is alkyl of about 9 to about 23 carbon atoms (forming with the two carbon atoms an alkane group); R_2 is alkyl of 1 to about 8 carbon atoms; and M is a salt-forming radical.

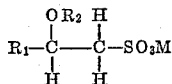
The salt-forming radical M in the hereinbefore described structural formula is a water-solubilizing cation and can be, for example, an alkali metal cation (e.g. sodium, potassium, lithium), ammonium or substituted-ammonium cation. Specific examples of substituted ammonium cations include methyl-, dimethyl-, and trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like.

Specific examples of beta-acyloxy-alkane-1-sulfonates, or alternatively 2-acyloxy-alkane-1-sulfonates, utilizable herein to provide superior cleaning levels under substantially neutral washing conditions include the sodium salt of 2-acetoxy-tridecane-1-sulfonic acid; the potassium salt of 2-propionyloxy-tetradecane-1-sulfonic acid; the lithium salt of 2-butanoyloxy-tetradecane-1-sulfonic acid; the sodium salt of 2-pentanyloxy-pentadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-hexadecane-1-sulfonic acid; the potassium salt of 2-octanyloxy-tetradecane-1-sulfonic acid; the sodium salt of 2-acetoxy-heptadecane-1-sulfonic acid; the lithium salt of 2-acetoxy-octadecane-1-sulfonic acid; the potassium salt of 2-acetoxy-nonadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-uncosane-1-sulfonic acid; the sodium salt of 2-propionyloxy-docosane-1-sulfonic acid; the isomers thereof.

Preferred beta-acyloxy-alkane-1-sulfonate salts therein are the alkali metal salts of beta-acetoxy-alkane-1-sulfonic acids corresponding to the above formula wherein R_1 is an alkyl of about 12 to about 16 carbon atoms, these salts being preferred from the standpoints of their excellent cleaning properties and ready availability.

Typical examples of the above described beta-acetoxy alkanesulfonates are described in the literature: Belgium Pat. 650,323 issued July 9, 1963, discloses the preparation of certain 2-acyloxy alkanesulfonic acids. Similarly, U.S. Pats. 2,094,451 issued Sept. 28, 1937, to Guenther et al. and 2,086,215 issued July 6, 1937, to DeGroote disclose certain salts of beta-acetoxy alkanesulfonic acids. These references are hereby incorporated by reference.

A preferred class of anionic organic detergents are the beta-alkyloxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from 6 to 20 carbon atoms, R_2 is a lower alkyl group having from 1 to 3 carbon atoms, and M is a salt-forming radical hereinbefore described.

Specific examples of beta-alkyloxy alkane sulfonates or alternatively 2-alkyloxy-alkane-1-sulfonates, utilizable herein to provide superior cleaning and whitening levels under household washing conditions include:

potassium beta-methoxydecane-sulfonate, sodium beta-methoxy-tridecane-sulfonate, potassium beta-ethoxytetradecylsulfonate, sodium beta-isopropoxyhexadecylsulfonate, lithium beta-tertbutoxytetradecylsulfonate, sodium beta-methoxyoctadecylsulfonate, and ammonium beta-n-propoxydodecylsulfonate.

Other synthetic anionic detergents useful herein are alkyl ether sulfates. These materials have the formula $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ wherein R is alkyl or alkenyl of about 10 to about 20 carbon atoms, x is 1 to 30, and M is a salt-forming cation defined hereinbefore.

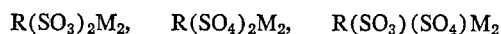
The alkyl ether sulfates of the present invention are condensation products of ethylene oxide and monohydric alcohols having about 10 to about 20 carbon atoms. Preferably, R has 14 to 18 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols are reacted with 1 to 30, and especially 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 6 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates of the present invention are sodium coconut alkyl ethylene glycol ether sulfate; lithium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate.

Preferred herein for reasons of excellent cleaning properties and ready availability are the alkali metal coconut and tallow-alkyl oxyethylene ether sulfates having an average of about 1 to about 10 oxyethylene moieties. The alkyl ether sulfates of the present invention are known compounds and are described in U.S. Pat. 3,332,876 to Walker (July 25, 1967) incorporated herein by reference.

Additional examples of anionic non-soap synthetic detergents which come within the terms of the present invention are the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic detergents of this variety are set forth in U.S. Letters Pats. 2,486,921; 2,486,922; and 2,396,278.

Additional examples of anionic, non-soap, synthetic detergents, which come within the terms of the present invention, are the compounds which contain two anionic functional groups. These are referred to as di-anionic detergents. Suitable di-anionic detergents are the disulfonates, disulfates, or mixtures thereof which may be represented by the following formulae:



where R is an acyclic aliphatic hydrocarbyl group having 15 to 20 carbon atoms and M is a water-solubilizing cation, for example, the C_{15} to C_{20} disodium 1,2-alkyldisulfates, C_{15} to C_{20} dipotassium-1,2-alkyldisulfonates or disulfates, disodium 1,9-hexadecyl disulfates, C_{15} to C_{20} disodium-1,2-alkyldisulfonates, disodium 1,9-stearyl disulfates and 6,10-octadecyldisulfates.

The aliphatic portion of the disulfates or disulfonates is generally substantially linear, desirable, among other reasons, because it imparts desirable biodegradable properties to the detergent compound.

The water-solubilizing cations include the customary cations known in the detergent art, i.e., the alkali metals, and the alkaline earth metals, as well as other metals in group II-A, II-B, III-A, IV-A and IV-B of the Periodic Table except for boron. The preferred water-solubilizing cations are sodium or potassium. These di-anionic detergents are more fully described in British Letters Patent 1,151,392 which claims priority on an application made

in the United States of America (No. 564,566) on July 12, 1966.

Additional examples of anionic non-soap synthetic detergents which come within the terms of the present invention are the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic detergents of this variety are set forth in U.S. Letters Pats. 2,486,921, 2,486,922, and 2,396,278.

Still other anionic synthetic detergents include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfo succinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfo-succinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl ester of sodium sulfosuccinic acid.

Other suitable anionic detergents utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefin by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide may be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example, by liquid SO₂, chlorinated hydrocarbon, etc., when used in the liquid form, or by air, nitrogen, gaseous SO₂, etc., when used in the gaseous form.

The alpha-olefins from which the olefin sulfonates are derived from mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportions of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific anionic detergent which has also been found excellent for use in the present invention is described more fully in the U.S. Pat. 3,332,880 of Philip F. Pflaumer and Adriaan Kessler, issued July 25, 1967, titled Detergent Composition, the disclosure of which is herein incorporated by reference.

(B) Nonionic synthetic detergents

Nonionic synthetic detergents may be broadly defined as 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 hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

For example, a well known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility, has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is re-

tained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include:

(1) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene, or nonene, for example.

(2) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 and 3,000, are satisfactory.

(3) The condensation product of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(4) Nonionic detergents include nonyl phenol condensed with either about 10 or about 30 moles of ethylene oxide per mole of phenol and the condensation products of coconut alcohol with an average of either about 5.5 or about 15 moles of ethylene oxide per mole of alcohol and the condensation product of about 15 moles of ethylene oxide with one mole of tridecanol.

Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; dodecyl mercaptan condensed with 10 moles of ethylene oxide per mole of mercaptan; bis-(N-2-hydroxyethyl) lauramide; nonyl phenol condensed with 20 moles of ethylene oxide per mole of nonyl phenol; myristyl alcohol condensed with 10 moles of ethylene oxide per mole of myristyl alcohol; lauramide condensed with 15 moles of ethylene oxide per mole of lauramide; and di-isooctylphenol condensed with 15 moles of ethylene oxide.

(5) A detergent having the formula R¹R²R³N→O (amine oxide detergent) wherein R¹ is an alkyl group containing from about 10 to about 28 carbon atoms, from 0 to about 2 hydroxy groups and from 0 to about 5 ether linkages, there being at least one moiety of R¹ which is an alkyl group containing from about 10 to about 18 carbon atoms and 0 ether linkages, and each R² and R³ are selected from the group consisting of alkyl radicals and hydroxyalkyl radicals containing from 1 to about 3 carbon atoms;

Specific examples of amine oxide detergents include: dimethyldodecylamine oxide, dimethyltetradecylamine oxide, ethylmethyltetradecylamine oxide, cetyldimethylamine oxide, dimethylstearylamine oxide, cetylpropylamine oxide, diethyldodecylamine oxide, diethyltetradecylamine oxide, dipropyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, bis-(2-hydroxymethyl)-3-dodecoxy - 1 - hydroxypropylamine oxide, (2-hydroxypropyl)methyltetradecylamine oxide, dimethyloleyamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, and the corresponding decyl, hexadecyl and octadecyl homologs of the above compounds.

(6) A detergent having the formula R¹R²R³P→O (phosphine oxide detergent) wherein R¹ is an alkyl group containing from about 10 to about 28 carbon atoms, from

0 to about 2 hydroxy groups and from 0 to about 5 ether linkages, there being at least one moiety of R¹ which is an alkyl group containing from about 10 to about 18 carbon atoms and 0 ether linkages, and each of R² and R³ are selected from the group consisting of alkyl radicals and hydroxyalkyl radicals containing from 1 to about 3 carbon atoms.

Specific examples of the phosphine oxide detergents include: dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, cetyldimethylphosphine oxide, dimethylstearylphosphine oxide, cetylethylpropylphosphine oxide, diethyldodecylphosphine oxide, diethyltetradecylphosphine oxide, dipropyldodecylphosphine oxide, bis-(hydroxymethyl)dodecylphosphine oxide, bis-(2-hydroxyethyl)dodecylphosphine oxide, (2-hydroxypropyl)methyltetradecylphosphine oxide, dimethylolelylphosphine oxide, and dimethyl-(2-hydroxydodecyl)phosphine oxide and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds.

(7) A detergent having the formula



(sulfoxide detergent) wherein R¹ is an alkyl radical containing from about 10 to about 28 carbon atoms, from 0 to about 5 ether linkages and from 0 to about 2 hydroxyl substituents at least one moiety of R¹ being an alkyl radical containing 0 ether linkages and containing from about 10 to about 18 carbon atoms, and wherein R² is an alkyl radical containing from 1 to 3 carbon atoms and from one to two hydroxyl groups: octadecyl methyl sulfoxide, dodecyl methyl sulfoxide, tetradecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide, octadecyl 2-hydroxyethyl sulfoxide, dodecyl-ethyl sulfoxide.

(C) Ampholytic synthetic detergents

Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato.

Examples of compounds falling within this definition are

sodium 3-(dodecylamino)-propionate,
sodium 3-(dodecylamino)propane-1-sulfonate,
sodium 2-(dodecylamino)ethyl sulfate,
sodium 2-(dimethylamino)octadecanoate,
disodium 3-(N-carboxymethyl)dodecylamino)propane-1-sulfonate,
disodium octadecyl-iminodiazetate,
sodium 1-carboxymethyl-2-undecylimidazole, and
sodium N,N-bis(2-hydroxyethyl)-2-sulfato-3-dodecoxypropylamine.

(D) Zwitterionic synthetic detergents

Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium and phosphonium or tertiary sulfonium compounds, in which the cationic atom may be part of a heterocyclic ring, and in which the aliphatic radical may be straight chain or branched, and wherein one of the aliphatic substituents contains from about 3 to 18 carbon atoms, and at least one aliphatic substituent contains an anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are

3-(N,N-dimethyl-N-hexadecyl-ammonio)-2-hydroxypropane-1-sulfonate,
3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate,
2-(N,N-dimethyl-N-dodecylammonio)acetate,
3-(N,N-dimethyl-N-dodecylammonio)propionate,
2-(N,N-dimethyl-N-octadecylammonio)-ethyl sulfate,
2-(trimethylammonio)ethyl dodecylphosphonate,
ethyl 3-(N,N-dimethyl-N-dodecylammonio)propylphosphonate,
3-(P,P-dimethyl-P-dodecylphosphonio)-propane-1-sulfonate,
2-(S-methyl-S-tert.hexadecylsulfonio)ethane-1-sulfonate,
3-(S-methyl-S-dodecylsulfonio)propionate,
sodium 2-(N,N-dimethyl-N-dodecylammonio)ethyl phosphonate,
4-(S-methyl-S-tetradecylsulfonio)butyrate,
1-(2-hydroxyethyl)-2-undecylimidazolium-1-acetate,
2-(trimethylammonio)octadecanoate, and
3-(N,N-bis-(2-hydroxyethyl)-N-octadecylammonio)-2-hydroxypropane-1-sulfonate.

Some of these detergents are described in the following U.S. Pats. 2,129,264, 2,178,353, 2,774,786, 2,813,898, and 2,828,332.

The following examples are illustrative of this invention.

EXAMPLE I

The following aqueous slurries were prepared:

	Percent	
	A	B
Sodium carbonate	11.5	11.5
Sodium salt of linear C-alkyl benzene sulfonate (LAS)	6.5	6.5
Sodium salt of sulfate ester of tallow alcohol ethoxylated with 3 moles of ethylene oxide	2.80	2.80
Toluene sulfonate	0.6	0.6
Sodium silicate (SiO ₂ :Na ₂ O=2.4)	11.5	11.5
Sodium sulfate	16.5	19.4
Sodium acetate	2.9	-----
Water	44.0	44.0
Balance (dye, fluorescers, carboxymethyl cellulose)	3.7	3.7

Slurry A was pumped to a spray nozzle of a spray-drying tower. The tower was about 110 feet in height and 23 feet in diameter. The spray nozzle had an orifice diameter of 0.188 inch and was located at the top of the tower. Air having a temperature of 650° F. was introduced at the bottom of the tower and exited at the top of the tower.

Spray-dried granules collected at the bottom of the tower had the following composition:

	Percent
Sodium carbonate	20
LAS	14
Sodium salt of sulfate ester of ethoxylated tallow alcohol	6
Toluene sulfonate	1
Sodium silicate	20
Sodium sulfate	30
Sodium acetate	5
Water	3
Balance	1

The identical procedure as above was repeated with Slurry B.

Granules resulting from each spray drying operation were then tested for flowability. Sealed cardboard containers containing the granules to be tested were stored in a room at a temperature of 80° F. and 60% relative humidity. At the end of 14 days, 28 days, 42 days, 56 days containers containing composition A and B were opened. Flowability of the contents within each container was

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tested by pouring the contents out and assigning a pour grade number based on visual observation. A grade of 5.0 indicates the contents flowed rapidly out of the container. A grade of 0 indicates that the contents did not flow at all, i.e. were completely caked.

Results of the above tests are as follows:

Days.....	0	14	28	42	56
Composition A.....	5.0	4.0	4.3	4.0	4.3
Composition B.....	5.0	4.0	4.0	4.0	3.7

The above results indicate that the composition of this invention, i.e. Composition A, was more free-flowing over a period of time than the prior art composition, i.e. Composition B.

EXAMPLE II

When Example I was repeated substituting sodium citrate for sodium acetate at the same weight level, the following pour results were obtained:

Days:	
0	5.0
14	4.5
28	4.5
42	4.5
56	4.3

EXAMPLE III

Potassium carbonate when substituted for the sodium acetate in the slurry of Example I followed by the same spray drying operation resulted in granules that had substantially the same free-flowing characteristics.

The following examples of spray-dried detergent composition are illustrative of this invention:

EXAMPLE IV

	Percent
Sodium carbonate	10
Sodium salt of sulfate tallow alcohol	50
Sodium citrate	1
Sodium silicate (SiO ₂ :Na ₂ O=1.6)	10
Sodium sulfate	24
Balance (water)	5

EXAMPLE V

	Percent
Sodium carbonate	70
Coconut alcohol ethoxylated with six moles of ethylene oxide	10
Potassium carbonate	15
Sodium sulfate	4
Balance (water)	1

What is claimed is:

1. In a process for producing crisp, free-flowing detergent granules comprising the steps of:

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- (a) forming an aqueous slurry containing from 15% to 35% of sodium carbonate and from 10% to 20% of a water-soluble detergent selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic detergents, the balance comprising water; and
- (b) spray-drying the slurry to form crisp, free-flowing detergent granules;

the improvement which comprises, in step (a), adding from 0.7% to 15% of an anti-caking agent selected from the group consisting of sodium acetate, sodium citrate and potassium carbonate to the aqueous slurry.

2. The process of claim 1 wherein the crisp, free-flowing detergent granules have a water content of less than 10%.

3. The process of claim 1 wherein the anti-caking agent forms from 3.5% to 7% of the aqueous slurry.

4. The process of claim 1 wherein the aqueous slurry contains from 2% to 17% of an alkali metal silicate having an SiO₂:Na₂O ratio of 3.6:1 to 2:1.

5. A spray-dried detergent composition prepared in the manner of claim 1 and in the form of crisp, free-flowing granules consisting essentially of:

- (a) from 5% to 50% of a water-soluble detergent selected from the group consisting of anionic, nonionic, zwitterionic and ampholytic detergents;
- (b) from 10% to 80% of sodium carbonate; and
- (c) from 1% to 20% of an anti-caking agent selected from the group consisting of sodium acetate, sodium citrate and potassium carbonate.

6. The spray-dried detergent composition of claim 5 additionally containing from 3% to 25% of an alkali metal silicate having a SiO₂:Na₂O ratio of from 3.6:1 to 1:2.

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U.S. Cl. X.R.

252-89, 109, 132, 383, 384, 385, 531, 532, 539