

[54] **CRYSTALLIZATION SEED-CONTAINING
DETERGENT COMPOSITION**

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References Cited

UNITED STATES PATENTS

3,755,180 8/1973 Austin 252/135 X

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Attorney, Agent, or Firm—Richard C. Witte; Julius P. Filcik; George W. Allen

[57] **ABSTRACT**

A detergent composition comprising a water-soluble alkali aluminate compound, a material capable of forming a water-insoluble reaction product with the free metal ions found in water, a water-soluble detergent, and preferably a crystallization seed capable of providing growth sites for the formation of water-insoluble reaction products. This detergent composition possesses the property of causing the rapid precipitation of the aforementioned water-insoluble reaction product which has the effect of rapidly reducing the free metal ion concentration of an aqueous solution.

13 Claims, No Drawings

CRYSTALLIZATION SEED-CONTAINING DETERGENT COMPOSITION

BACKGROUND OF THE INVENTION

This invention relates to detergent compositions capable of rapidly reducing the free polyvalent metal, especially calcium and magnesium, ion content of an aqueous solution.

It is known that many detergent compositions containing a water-soluble detergent perform satisfactorily when used in an aqueous wash solution containing a minimum of free polyvalent metal ions. When some water-soluble organic detergents come in contact with free polyvalent metal ions in the wash solution, there is formed a water-insoluble reaction product. The formation of this reaction product results in a poor performing detergent composition, i.e., part of the organic detergent is tied up thereby leaving less detergent to perform its cleaning function.

Another effect caused by free metal ions in an aqueous solution intended for the washing of soiled fabrics is that there is an interaction between the soil from the fabric and these free polyvalent metal ions. This interaction reduces the efficiency of the organic detergent by the making of soil on the fabrics more difficult to remove.

Because of the above-described considerations, many detergent compositions containing a water-soluble detergent intended for use in washing soiled fabrics in ordinary tap water have included therewith a material usually called "builder" capable of "tying up" or sequestering free metal ions. This "tying up" allows the detergent to perform its cleaning function unhindered by the free ions. Additionally, the tie up of free metal ions prevents a soil and free ion interaction to occur.

Some builders form a soluble complex with the free metal ions. Other builders, e.g. the water-soluble salts of carbonates, are of the precipitating type. Unfortunately, some of the precipitating builders used in detergent compositions do not reduce the free polyvalent metal ion content fast enough. That is, the builder competes with the organic detergent and the soil for the free ions. The result is that while some of the free calcium and magnesium ions are tied up or sequestered by the builders, some do react with the organic detergent and the soil. To the extent that the latter reactions occur, the cleaning performance of the detergent is decreased.

One means for preventing such interaction between free metal, particularly calcium and magnesium ions and detergents is to increase the rate of free polyvalent metal ion precipitation by employing seed crystals to stimulate formation of especially insoluble calcium and magnesium salts. Detergent compositions utilizing such seed crystals are described in the following copending U.S. Patent applications: Jacobsen and Uchtman, Ser. No. 248,443, filed Apr. 28, 1972; Benjamin, Saylor and Uchtman, Ser. No. 248,545, filed Apr. 28, 1972 and Benjamin, Ser. No. 248,546, filed Apr. 28, 1972.

Seed crystallization within detergent systems described by these applications is, however, impeded by many conventional organic detergent compounds, thereby necessitating selection of particular non-interfering detergents or provision of some means for delaying aqueous solubility of those detergent components which do interfere. In addition, a given detergent

composition employing one particular type of crystallization seed and precipitating builder is generally only effective for precipitation of only one particular type of free metal ion found in laundry solutions.

Accordingly, it is an object of the present invention to provide a detergent composition that allows the water-soluble detergent to perform its cleaning function unhindered by the presence of free metal ions.

It is a further object of the present invention to provide a detergent composition capable of simultaneously reducing the content of both free calcium and magnesium ions in laundry solutions.

It is a further object of the present invention to provide a detergent composition that reduces the free calcium and magnesium ion content of laundering solutions by providing growth sites for the growth thereon of water-insoluble salts of the said free calcium and magnesium ions even in the presence of conventional organic detergent compounds.

Another object of the present invention is to provide a detergent composition with improved precipitation characteristics for the water-insoluble salts of calcium and magnesium ions.

Still another object of this invention is to provide a detergent composition with improved cleaning performance, particularly stain-removal properties.

By utilizing certain materials capable of forming water-insoluble reaction products with free polyvalent metal ions as well as water-soluble aluminate salts in combination with crystallization seeds, and conventional organic detergent compounds, these above-described objectives can be attained and detergent compositions formulated which have free polyvalent metal ion reduction, particularly free calcium and magnesium ion reduction, properties superior to those compositions known heretofore.

SUMMARY OF THE INVENTION

The instant invention provides detergent compositions which are capable of rapidly reducing the free polyvalent, especially calcium and magnesium, metal ion content of an aqueous solution when added thereto. Such compositions consist essentially of:

- from about 0.1% to 20% by weight of water-soluble alkali aluminates having an $\text{alkali}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of from about 10:1 to 1:10,
 - from about 10% to about 80% by weight of a material capable of forming, at a pH of 6 or above, a water-insoluble reaction product with free polyvalent metal ions; and
 - from about 5% by weight of a water-soluble organic detergent selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic detergents and mixtures thereof.
- d. up to about 50% by weight of a crystallization seed capable of providing growth sites in aqueous solution for the reaction products of (a) and (b), said crystallization seed having a particle size of less than about 20 microns.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to detergent compositions, particularly granular detergent compositions capable of rapidly reducing the free polyvalent metal ion content of water.

Detergent compositions of this invention contain (1) a water-soluble alkali metal aluminate; (2) a free metal

ion insolubilizing ingredient; (3) a water-soluble detergent; and (4) a crystallization seed that provides growth sites for the water-insoluble reaction products formed as a result of addition of this detergent composition to water. Each of these components is discussed in detail hereinafter.

Unless indicated to the contrary, the "%" indications used hereinafter stand for percent by weight.

The instant detergent compositions comprise from 0.1% to about 20% alkali metal aluminate having an alkali metal₂O/Al₂O₃ ratio of from about 10:1 to 1:10 especially from 2:1 to 1:2. Examples of alkali metal aluminates include lithium aluminate, potassium aluminate and sodium aluminate.

Alkali metal aluminates are crystalline solid materials described by various chemical formulas which are MAIO₂ or M₂O.Al₂O₃, wherein M is alkali metal. Such salts are available in either the hydrated or anhydrous form.

Alkali metal aluminates can have varying mole ratios of M₂O/Al₂O₃ within this crystalline structure. The preferred aluminates for use in the instant invention have a ratio of M₂O/Al₂O₃ from about 2:1 to 1:2 and are present in the instant compositions in an amount from 0.1% to about 10%. Highly preferred are aluminates having an M₂O/Al₂O₃ ratio of about 1:1 and are present in the instant compositions in an amount of from about 2% to about 10%.

Preferred for use in the composition of the present invention is sodium aluminate. Sodium aluminate is produced by one step of the Bayer process for the extraction of alumina hydrate from bauxite. Processes for the preparation of various forms of sodium aluminate are described in U.S. Pat. Nos. 2,018,607, 2,159,842 and 2,345,134.

The physical and chemical properties of the sodium aluminate component of the instant detergent compositions are described more fully in Kirk-Othmer, *Encyclopedia of Chemical Technology*, 2nd Edition, Volume 2, Interscience Publishers, 1963, pp. 6-11, incorporated herein by reference.

As discussed more fully below, alkali aluminates apparently contribute to the formation of complexes of free polyvalent metal ions, especially calcium and magnesium. Such complexes are susceptible to rapid precipitation from laundry solution in the presence of the other essential components of the instant detergent composition.

Another essential ingredient of the detergent compositions of this invention is a water-soluble material capable of forming a water-insoluble reaction product with free polyvalent metal ions, particularly calcium and magnesium ions. For purposes of the instant invention, a water-insoluble reaction product is a material having a solubility in water of less than 1.4×10^{-2} weight percent at 25°C., preferably less than 7.2×10^{-3} weight percent at 25°C.

Examples of materials capable of forming such a reaction product are the water-soluble salts of carbonates, bicarbonates, sesquicarbonates, oxalates, and fatty acids having 12 to 22 carbon atoms. Water-soluble cations of such materials are sodium, potassium, ammonium, substituted ammonium, and substituted amine, e.g. triethanolamine. Specific examples of such salts include sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, sodium sesquicarbonate, potassium sesquicarbonate,

sodium oxalate, ammonium oxalate, sodium oleate, palmitate, triethanolamine oleate and monoethanolamine stearate. Sodium carbonate is highly preferred. The contribution in part provided by these precipitate formation agents is that they provide an anion capable of reacting with free alkaline earth metal ions (which cause the water hardness), aluminate ions (discussed above), and the crystallization seeds (discussed hereinafter) so as to produce a complex water-insoluble reaction product. This reaction product is effectively and rapidly removed from solution as hereinafter discussed. The net effect is that the free ion content, particularly the free calcium and magnesium ion content of the water is rapidly lowered. The precipitate formation agent, i.e., material capable of forming a water-insoluble reaction product with free alkaline earth metal ions is present in the instant detergent compositions to the extent of from about 10% to 80%, preferably sodium carbonate in an amount from about 10% to 50%.

Another essential ingredient in the detergent compositions of this invention is a water-soluble detergent selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic detergents and mixtures thereof. Said detergent components are present in an amount from about 5% to about 50%, preferably from about 5% to about 35% of the detergent composition. Examples of ingredients suitable for being used as detergent actives in the instant compositions are as follows:

A. Anionic Soap and Non-Soap Synthetic Detergents

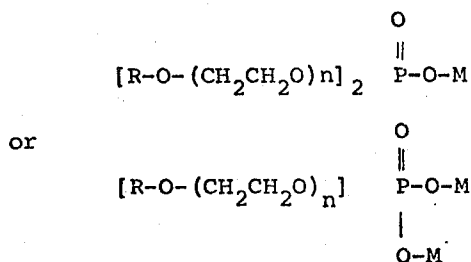
This class of detergents includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkylammonium salts of higher fatty acids containing from about eight to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Suitable fatty acids can be obtained from natural 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 eight 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 (C₈ - C₁₈ 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 nine to about 15 carbon atoms, in

straight chain or branched chain configuration, e.g., those of the type described in U.S. Pat. Nos. 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 C₁₃LAS); 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 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.

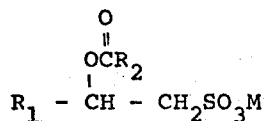
Anionic phosphate surfactants are also useful in the present invention. These are surface active materials having substantial detergent capability in which the anionic solubilizing group connecting hydrophobic moieties is an oxy acid of phosphorus. The more common solubilizing groups, of course, are —SO₃H, —SO₃H, and —CO₂H. Alkyl phosphate esters such as (R—O)₂PO₂H and ROPO₃H₂ in which R represents an alkyl chain containing from about eight 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



in which R represents an alkyl group containing from about eight to 20 carbon atoms, or an alkylphenyl group in which the alkyl group contains from about eight 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 R₁ is alkyl of about nine to about 23 carbon atoms (forming with the two carbon atoms an alkane group); R₂ is alkyl of one to about eight 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

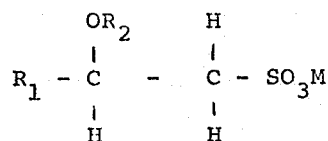
ammonium cations include methyl-, dimethyl-, and trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like.

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-pentanoyloxy-pentadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-hexadecane-1-sulfonic acid; the potassium salt of 2-octanoyloxy-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 R₁ 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. No. 650,323 issued July 9, 1963, discloses the preparation of certain 2-acyloxy alkanesulfonic acids. Similarly, U.S. Pat. No. 2,094,451 issued Sept. 28, 1937, to Guenther et al. and U.S. Pat. No. 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 R₁ is a straight chain alkyl group having from six to 20 carbon atoms, R₂ is a lower alkyl group having from one to three 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-tert-butoxytetradecylsulfonate, sodium beta-methoxyoctadecylsulfonate, and ammonium beta-n-propoxydodecylsulfonate.

Other synthetic anionic detergents useful herein are alkyl ether sulfates. These materials have the formula $RO(C_2H_4O)_xSO_3M$ 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.

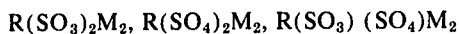
The alkyl ether sulfates of the present invention are condensation products of ethylene oxide and monohydric alcohols having about 10 to about 20 carbon atoms. Preferably, R has 14 to 18 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols are reacted with 1 to 30, and especially 3 or 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 or 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. No. 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. Pat. Nos. 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 IIA, IIB, IIIA, IVA and IVB 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

Pat. No. 1,151,392 which claims priority on an application made in the United States of America (Ser. 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. Pat. Nos. 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-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl-sulfosuccinamate; 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 SO_2 , chlorinated hydrocarbon, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2 , 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. No. 3,332,880 of Phillip F. Pflaumer and Adriaan Kessler, issued July 25, 1967, titled Detergent Composition, the disclosure of which is herein incorporated by reference.

Specific preferred anionic surfactants include sodium linear alkyl benzene sulfonate wherein the alkyl chain averages from about 10 to 18, more preferably about 12, carbon atoms in length; sodium tallow alkyl sulfate; sodium 2-acetoxy-tridecane-1-sulfonic acid; sodium methyl- α -sulfopalmitate; sodium β -methoxyoctadecyl-sulfonate; sodium coconut alkyl ethylene glycol ether sulfonate; the sodium salt of the sulfuric acid ester of the reaction product of one mole of tallow alcohol and three moles of ethylene oxide; and mixtures thereof.

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 1,500 to 1,800. 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 retained 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 six 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 eight 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.

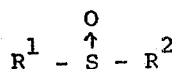
5. A detergent having the formula $R^1R^2R^3N \rightarrow O$ (amine oxide detergent) wherein R^1 is an alkyl group containing from about 10 to about 28 carbon atoms, from 0 to about 2 hydroxy groups and from 0 to about 5 ether linkages, there being at least one moiety of R^1 which is an alkyl group containing from about 10 to about 18 carbon atoms and 0 ether linkages, and each R^2 and R^3 are selected from the group consisting of alkyl radicals and hydroxyalkyl radicals containing from one to about three carbon atoms;

Specific examples of amine oxide detergents include: dimethyldodecylamine oxide, dimethyltetradecylamine oxide, ethylmethyltetradecylamine oxide, cetyldimethylamine oxide, dimethylstearylamine oxide, cetyl-ethylpropylamine oxide, diethyldodecylamine oxide, diethyltetradecylamine oxide, dipropyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, bis-(2-hydroxyethyl)-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 $R^1R^2R^3P \rightarrow O$ (phosphine oxide detergent) wherein R^1 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 R^1 which is an alkyl group containing from about 10 to about 18 carbon atoms and 0 ether linkages, and each of R^2 and R^3 are selected from the group consisting of alkyl radicals and hydroxyalkyl radicals containing from one to about three carbon atoms.

Specific examples of the phosphine oxide detergents include: dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, cetyldimethylphosphine oxide, dimethylstearylphosphine oxide, cetyl-ethylpropylphosphine oxide, diethyldodecylphosphine oxide, diethyltetradecylphosphine oxide, dipropyldodecylphosphine oxide, bis-(hydroxymethyl)dodecylphosphine oxide, bis-(2-hydroxyethyl)-dodecylphosphine oxide, (2-hydroxypropyl)methyltetradecylphosphine oxide, dimethyloleylphosphine 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 R^1 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 R^1 being an alkyl radical containing 0 ether linkages and containing from about 10 to about 18 carbon atoms, and wherein R^2 is an alkyl radical containing from one to three carbon atoms and from one to two hydroxyl groups: octadecyl methyl sulfoxide, dodecyl methyl sul-

foxide, tetradecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide, octadecyl 2-hydroxyethyl sulfoxide, dodecylethyl sulfoxide.

Of all of the above-described types of nonionic surfactants, preferred nonionic surfactants include the condensation product of nonyl phenol with about 9.5 moles of ethylene oxide per mole of nonyl phenol, the condensation product of coconut fatty alcohol with about 6 moles of ethylene oxide per mole of coconut fatty alcohol, the condensation product of tallow fatty alcohol and with about 11 moles of ethylene oxide per mole of tallow fatty alcohol and the condensation product of a secondary fatty alcohol containing about 15 carbon atoms with about 9 moles of ethylene oxide per mole of fatty alcohol.

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 eight 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-iminodiacetate, 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 three 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-hexadecylammonio)-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-tetradecyl-sulfonio)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. Pat. Nos.

2,129,264; 2,178,353; 2,774,786; 2,813,898; and 2,828,332.

Of all of the above-described types of zwitterionic surfactants, preferred compounds include 3(N,N-dimethyl-N-alkylammonio)-propane-1-sulfonate and 3(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate wherein in both compounds the alkyl group averages 14.8 carbon atoms in length; 3(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate; 3(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)-propane-1-sulfonate; (N-dodecylbenzyl-N,N-dimethylammonio)propionate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)(propionate), 6-(N-dodecylbenzyl-N,N-dimethylammonio)hexanoate; and (N,N-dimethyl-N-hexadecylammonio)acetate.

In highly preferred granular detergent compositions of this invention, from about 10% to about 25% of anionic sulfated reaction product of tallow alcohol with from about 3 to 10 moles of ethylene oxide is used if the detergent composition is intended to provide a medium to high suds pattern. Combinations of nonionic detergents and anionic sulfated reaction products of tallow alcohols with from about 3 to about 10 moles of ethylene oxide are preferred if the detergent composition is intended to provide reduced suds levels. If this anionic-nonionic surfactant mixture is employed, the weight ratio of nonionic to anionic varies between about 2:1 to 1:2.

An other essential component for use in the granular detergent compositions of the present invention is a crystallization seed which is capable of providing growth sites for the reaction product of the various aforementioned precipitate-forming ionic species in solution. The presence of this crystallization seed improves the rapid precipitation of the complex water-insoluble reaction product and, hence, rapid reduction of free calcium and magnesium ion content. For purposes of the instant invention, "rapid reduction of free ion concentration" means the reduction of the content in solution of free polyvalent metal ions to a concentration of less than 0.5 grains per gallon of water within 120 seconds after the addition of the instant detergent compositions to water. Preferably, free ion concentration is "rapidly reduced" to less than 0.1 grain per gallon within 30 seconds. Typically, from 5 to 9 grains of free calcium and/or magnesium ions (expressed herein as the number of grains equivalent to calcium carbonate per gallon) is found in tap water.

Any crystallization seed is suitable so long as it provides a growth site for the reaction product of the various ionic components present in aqueous solution of the instant compositions. The seed material need not provide the same anion or cation as the aluminate or material capable of forming a water-insoluble reaction product with the free calcium ions. Examples of such crystallization seed are sparingly soluble compounds, i.e., those compounds that are not completely dissolved in water within 120 seconds at 25° C. Illustrative of such materials are calcium carbonate, calcium and magnesium oxalate, barium sulfate, calcium, magnesium and aluminum silicates, calcium and magnesium oxide, calcium and magnesium salts of fatty acids having 12 to 22 carbon atoms, calcium and magnesium hydroxide, calcium fluoride, barium carbonate and mixed salts such as calcium-magnesium silicates and calcium-

aluminum silicates and cellulose derivatives, e.g. cellulose linters. This listing is exemplary of the crystallization seeds suitable for use. A preferred crystallization seed is calcium carbonate.

An essential characteristic of the crystallization seed is that it must have a maximum particle dimension of less than 20 microns, preferably from 0.01 micron to 5 microns. Crystallization seeds must have a particle size less than 20 microns because it is essential to maximize seed surface area per unit weight of seed material for the most beneficial performance of the total composition. That is, if the seed particle size is too large, the growth of the complex water-insoluble reaction product will be too slow with the result being that the free metal ion content reduction will not be rapid enough. In addition, there must be a sufficiently large crystallization seed surface area in solution be present for crystal growth to occur thereon. The crystallization seed is used in an amount of up to about 50% of the compositions of this invention. Preferably, the crystallization seed is present in the instant compositions to the extent of from about 5% to about 35%.

The following examples are illustrative of the composition of the instant invention.

EXAMPLE I

A detergent composition having the following formula was prepared:

Ingredient	Composition %
Sodium salt of sulfated C ₁₆ fatty alcohol ethoxylated with 3 moles of ethylene oxide	15
Sodium carbonate	30
Calcium carbonate	30
Sodium aluminate-mole ratio of Na ₂ O/Al ₂ O ₃ = 1:1	5
Sodium sulfate + minors	balance to 100

This composition was compared in water hardness depletion performance with an identical composition having the sodium aluminate components eliminated and replaced with an additional 5% of sodium sulfate. These compositions were added, under continuous stirring, to an 18 liter beaker filled with water in such an amount that 0.12% of the detergent composition was present in solution. Ten milliliters of wash solution was removed at various time intervals and analyzed for calcium and magnesium hardness ions using the technique of atomic absorption. The results are expressed as % of free Ca⁺⁺ or Mg⁺⁺ ions originally present which remained in solution (i.e., the % of these ions not precipitated from solution). The initial hardness concentrations at time 0 expressed in grains/gallon were

Ca⁺⁺ 4.5 grains/gallon
Mg⁺⁺ 2.5 grains/gallon

Results of such testing of these two compositions are set forth in Table I.

TABLE I

Time in Minutes	NaAlO ₂ Concentration			
	0%		5% (Ex. I composition)	
	% remaining		% remaining	
	Calcium	Magnesium	Calcium	Magnesium
0	100	100	100	100

TABLE I-Continued

Time in Minutes	NaAlO ₂ Concentration			
	0%		5% (Ex. I composition)	
	% remaining		% remaining	
	Calcium	Magnesium	Calcium	Magnesium
1/2	45.5	90.6	30.7	40.9
1	34.6	85.3	15.9	13.6
1 1/2	28.1	82.8	11.2	9.1
2	22.7	84.1	9.9	6.7
3	19.5	82.7	8.9	6.1
5	16.4	82.3	7.4	5.4
8	14.3	81.5	6.3	4.8

The above test demonstrates the marked and rapid removal of calcium and magnesium ions resulting from the addition of a composition of this invention to an aqueous medium. A substantially similar composition not containing the essential sodium aluminate of the instant invention provided Ca⁺⁺ and Mg⁺⁺ removal to a much lesser extent.

The demonstrated superior Ca⁺⁺ and Mg⁺⁺ depletion provided by the composition of the instant invention, in turn, contributed to the detergency performance advantages derived from the instant compositions. Such advantages are demonstrated by the following examples:

Detergent compositions having the formulas given hereinafter are prepared:

Ingredient — Wt. %	Example or Composition No.			
	II	A	III	B
Sodium salt of sulfated C ₁₆ alcohol ethoxylated with 3 moles of ethylene oxide	15	15	15	15
Sodium carbonate	30	30	40	40
Sodium sulfate	15	15	15	15
Calcium carbonate	10	10	22	22
Sodium silicate solids ratio: SiO ₂ /Na ₂ O=1.6	10	10	—	—
Sodium aluminate ratio: Na ₂ O/Al ₂ O ₃ =1.1	5	0	5	0
Minor additives and water	balance to 100			

Example II and Composition A compositions are used for carrying out stain removal performance tests using the conditions given hereinafter. An upright top-loading washing machine is used for the comparative cleaning treatment of polyester/cotton stained with facial soil swatches. The washing temperature is 100° F. and the detergent product is used at a concentration of 0.12% in solution. The water hardness is 7 U.S. grains/U.S. gallon (Ca/Mg = 2/1). Each set of swatches is washed for 10 minutes in a solution of the compositions being tested. At the end of the wash cycle, the swatches are rinsed and dried. The facial soil removal performance is measured with a Hunter Color Difference Meter. Testing results are obtained by measuring Hunter whiteness readings calculated with the following formula:

$$\text{Hunter Whiteness} = 7L^2 - 40Lb/700;$$

L and b being respectively the whiteness and greenness/yellowness readings. The Example II composition

of the instant invention provide significantly better facial soil removal than the silimar Composition A composition which does not contain the essential sodium aluminate of the Example II composition.

Example III and Composition B were used for stain removal performance tests using the conditions given for Example II and Composition A hereinbefore. Cotton muslin swatches stained with clay and tea served for evaluating the comparative stain removal performance. The testing results were measured and expressed as Hunter Whiteness readings.

TABLE II

Swatches:	Example or Composition	
	B	III
	Stain Removal	
Cotton muslin		
clay	19.9	22.2
tea	2.4	3.8

The Example III composition of the instant invention provides superior clay and tea stain removal from cotton muslin swatches by reference to what is obtained from the use of the Composition A composition which does not contain the essential sodium aluminate component of the Example III composition. This performance superiority is significant and apparent to the consumer.

Additional examples illustrative of this invention are:

	Example of Composition No.			
	C	IV	D	V
	Composition			
Sodium salt of sulfated C ₁₆ alcohol ethoxylated with 3 moles of ethylene oxide	15	15	15	15
Sodium carbonate	30	30	40	40
Sodium sulfate	26	26	18	18
Calcium carbonate	30	30	20	20
Sodium aluminate ratio: ratio: Na ₂ O/Al ₂ O ₃ = 1	0	5	0	5
Minor ingredients and water	balance to 100			

The test carried out with compositions of the instant invention containing sodium aluminate (Examples IV and V) provide significantly better cleaning performance to what is obtained in comparative tests using compositions which do not contain the essential sodium aluminate ingredient (Compositions C and D).

Substantially similar results are obtained from the use of the above compositions in the event sodium carbonate is replaced by an equivalent amount of the water-soluble sodium salt of bicarbonate, sesquicarbonate, silicate, oxalate or fatty acids having from 12 to 22 carbon atoms.

Substantially similar results are also obtained in the event the sodium salt of sulfated C₁₆ alcohol ethoxylated with 3 moles of ethylene oxide is substituted with an equivalent amount of any of the following organic surface-active agents: sodium linear C₁₀₋₁₈ alkyl benzene sulfonate; sodium tallow alkyl sulfate; sodium 2-

acetoxo-tridecane-1-sulfonate; sodium methyl- α -sulfolpalmite; sodium β -methoxyoctadecyl sulfonate; sodium coconut alkyl ethylene glycol ether sulfonate; the sodium salt of the sulfated condensation product of tallow alcohol with from about 3 to about 10 moles of ethylene oxide; the condensation product of nonylphenol with about 9 moles of ethylene oxide per mole of nonyl phenol; the condensation product of coconut fatty alcohol with about 6 moles of ethylene oxide per mole of coconut fatty alcohol; the condensation product of tallow fatty alcohol with about 11 moles of ethylene oxide per mole of tallow fatty alcohol; the condensation product of a secondary fatty alcohol containing about 15 carbon atoms with about 9 moles of ethylene oxide per mole of secondary fatty alcohol; sodium 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate; sodium 3-(N,N-dimethyl-N-alkylammonio)-propane-1-sulfonate whereby for these two compounds the alkyl group averages 14.8 carbon atoms in length; sodium 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate; sodium 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; sodium 3-(N-dodecylbenzyl-N,N-dimethylammonio)acetate; sodium 3-(N-dodecylbenzyl-N,N-dimethylammonio)propionate; 6-(N-dodecylbenzyl-N,N-dimethylammonio)hexanoate; sodium (N,N-dimethyl-N-hexadecylammonio)acetate; and mixtures thereof.

Substantially similar results are as well obtained if calcium carbonate is replaced by an equivalent amount of any of the following crystallization seeds: calcium and magnesium oxalate, barium sulfate, calcium, magnesium and aluminum silicates, calcium and magnesium oxide, calcium and magnesium salts of fatty acids having 12 to 22 carbon atoms, calcium and magnesium hydroxide, calcium fluoride, barium carbonate or cellulose derivatives.

Substantially similar results are also obtained in the event the sodium aluminate is substituted with an equivalent amount of potassium aluminate having a molar ratio of K₂O/Al₂O₃ of about 1.

What is claimed is:

1. Detergent compositions capable of rapidly reducing the free polyvalent metal ion content of an aqueous solution when added thereto, said compositions consisting essentially of:

- from 0.1% to about 10% by weight of alkali metal aluminates having an alkali metal₂O/Al₂O₃ mole ratio of from about 2:1 to 1:2;
- from about 10% to about 80% by weight of a material capable of forming, at a pH of 6 or above, a water-insoluble reaction product with free polyvalent metal ions, said water-insoluble reaction product having a solubility in water of less than 1.4×10^{-2} weight percent at 25° C.;
- from about 5% to about 50% by weight of a water-soluble organic detergent selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic detergents and mixtures thereof; and
- from about 5% to about 35% by weight of a crystallization seed capable of providing growth sites in aqueous silution for the reaction products of (a) and (b), said crystallization seed having a particle size of from 0.01 micron to 5.0 microns.

2. The detergent compositions of claim 1 wherein the aluminate component is sodium aluminate having a mole ratio of Na₂O/Al₂O₃ of about 1:1 and is present in

an amount of from about 2% to about 10% by weight.

3. The detergent compositions of claim 1 wherein the material capable of forming a water-insoluble reaction product with free polyvalent metal ions provides a water-insoluble reaction product having a solubility in water of less than 7.2×10^{-3} weight percent at 25° C.

4. The detergent compositions of claim 3 wherein said material capable of forming a water-insoluble reaction product is present to the extent of from about 10% to 50% by weight and is selected from the group consisting of the water-soluble salts of carbonates, bicarbonates, sesquicarbonates, silicates, oxalates, and fatty acids having from 12 to 22 carbon atoms.

5. The detergent compositions of claim 4 wherein the crystallization seed is a material that will not completely dissolve in water within 120 seconds at 25° C.

6. The detergent compositions of claim 5 wherein the crystallization seed is selected from calcium carbonate, calcium and magnesium oxalate, barium sulfate, calcium, magnesium and aluminum silicates, calcium and magnesium oxide, calcium and magnesium salts of fatty acids having 12 to 22 carbon atoms, calcium and magnesium hydroxide, calcium fluoride, barium carbonate and cellulose derivatives.

7. The detergent composition of claim 6 wherein the water-soluble organic detergent is selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic detergents and mixtures thereof and is present in an amount of from about 5% to about 35% by weight.

8. The detergent composition of claim 7 wherein the aluminate component is sodium aluminate having a ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of about 1:1 and is present in an amount of from about 2% to about 10% by weight.

9. The detergent composition of claim 7 wherein the material capable of forming a water-insoluble reaction product with free polyvalent metal ions is sodium carbonate.

10. The detergent composition of claim 7 wherein the crystallization seed is calcium carbonate.

11. Detergent compositions capable of rapidly reducing the free polyvalent metal ion content of an aqueous solution when added thereto, said composition consisting essentially of:

- a. from about 2% to about 10% by weight of sodium aluminate having a mole ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of about 1:1;
- b. from about 10% to about 50% by weight of sodium carbonate;
- c. from about 5% to about 35% by weight of calcium carbonate having a particle size of from 0.01 mi-

cron to 5.0 microns; and

d. from about 5% to about 35% by weight of a water-soluble organic detergent selected from the group consisting of sodium linear C_{10-18} alkyl benzene sulfonate; sodium tallow alkyl sulfate; sodium 2-acetoxytridecane-1-sulfonate; sodium methyl- α -sulfopalmitate; sodium β -methoxyoctadecyl sulfonate; sodium coconut alkyl ethylene glycol ether sulfonate; the sodium salt of the sulfated condensation product of tallow alcohol with from about 3 to about 10 moles of ethylene oxide; the condensation product of nonylphenol with about 9 moles of ethylene oxide per mole of nonylphenol; the condensation product of coconut fatty alcohol with about 6 moles of ethylene oxide per mole of coconut fatty alcohol; the condensation product of tallow fatty alcohol with about 11 moles of ethylene oxide per mole of tallow fatty alcohol; the condensation product of a secondary fatty alcohol containing about 15 carbon atoms with about 9 moles of ethylene oxide per mole of secondary fatty alcohol; sodium 3(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate; sodium 3(N,N-dimethyl-N-alkylammonio)-propane-1-sulfonate whereby for these two compounds the alkyl group averages 14.8 carbon atoms in length; sodium 3(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate; sodium 3(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; sodium 3-(N-dodecylbenzyl-N,N-dimethylammonio)acetate; sodium 3-(N-dodecylbenzyl-N,N-dimethylammonio)propionate; 6-(N-dodecylbenzyl-N,N-dimethylammonio)-hexanoate; sodium(N,N-dimethyl-N-hexadecylammonio)acetate; and mixtures thereof.

12. The detergent composition of claim 11 wherein the water-soluble organic detergent is the sodium salt of the sulfated reaction product of tallow alcohol with from about 3 to about 10 moles of ethylene oxide per mole of tallow alcohol and is present in an amount from about 10% to about 25% by weight.

13. The detergent composition of claim 11 wherein the water-soluble organic detergent is a mixture of the sodium salt of the sulfated reaction product of tallow alcohol with from about 3 to about 10 moles of ethylene oxide per mole of tallow alcohol in combination with nonionic water-soluble organic detergents whereby the weight ratio of said nonionics to said anionics is from 2:1 to 1:2 and the total surfactant concentration is from about 10% to about 25% by weight.

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