United States Patent [19]

Ohren

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[54] **DETERGENT COMPOSITIONS**

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[52] **U.S. Cl.** **252/110,** 252/109, 252/136, 252/526, 252/528, 252/530, 252/535, 252/536

[51] **Int. Cl.** **C11d 9/10,** C11d 3/065

[58] **Field of Search** 252/110, 109

[56] **References Cited**

UNITED STATES PATENTS

2,531,427	11/1950	Hauser	260/448
2,594,257	4/1952	Durgin	252/140
2,594,258	4/1952	Durgin	252/140
2,746,887	5/1956	O'Neil	117/139.5
3,407,144	10/1968	Bath	252/110 X
3,414,520	12/1968	McDonnell	252/110
3,583,923	6/1971	Cantrell et al.	252/110
3,625,905	12/1971	Weast	252/109

FOREIGN PATENTS OR APPLICATIONS

461,221	2/1937	Great Britain

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Attorney, Agent, or Firm—Julius P. Filcik; George W. Allen; Thomas H. O'Flaherty

[57] **ABSTRACT**

Granular laundering compositions comprising a curd-dispersant-containing, soap-based granule and a smectite-type clay. The soap and curd dispersant are formulated into the granule and the clay is attached to the surface of the granule. The resulting compositions exhibit enhanced solubility and provide through-the-wash fabric softening.

17 Claims, No Drawings

DETERGENT COMPOSITIONS

BACKGROUND OF THE INVENTION

The instant invention relates to granular laundering compositions which provide simultaneous laundering and softening of textiles during conventional fabric laundering operations. Such compositions employ a combination of a soap and a curd dispersent in granular form and certain smectite clay compounds having particular cation exchange characteristics.

Laundry soaps, i.e., the water-soluble salts of fatty acids, provide the user with good fabric cleansing coupled with product mildness. In addition, soaps deposit on many types of fabrics in the form of a "curd" and thereby provide desirable softening benefits. However, the buildup of heavy soap curd on fabrics eventually results in loss of fabric brightness. Furthermore, soap curd has been found to interfere with the flame retardant finishes commonly applied to children's chothing. That is to say, flame retardant fabrics coated with a heavy soap curd exhibit decreased levels of flame retardancy which, on removal of the soap curd, are restored to its original level.

From the foregoing, it can be seen that the use of soap-based laundering products presents a dilemma. The soap provides desirable fabric cleaning and through-the-wash fabric softening, but can eventually detract from fabric appearance and decrease the efficacy of the flame retardant finishes present on modern fabrics.

One method for preventing curd buildup on fabrics laundered with soap is to include a curd dispersant in the laundering bath. While this method achieves the desired result, the laundered fabrics no longer have the desirable softening benefits imparted by soap. More importantly, granular laundering compositions which contain both soap and significant amounts of curd dispersant are difficult to dissolve in aqueous laundering baths. When such products are added to water, the soap tends to undergo a phase transition and agglomerate as a gelatinous material which then deposits in an unsightly manner on the fabrics being laundered.

It has now been found that smectite-type clay material can be attached to the surface of soap-based detergent granules containing certain curd dispersants to substantially enhance the solubility of the granules. Furthermore, once the granules have dissolved, the clay is dispersed throughout the laundry liquor and deposits on the fabric surfaces to provide softening. Thus, the problem of excess curd buildup on fabrics is solved without losing the desirable softening benefits of soap-based compositions.

Various clay materials have been utilized in many different types of detergent systems for widely diverse purposes. Clays, for example, have been disclosed for use as builders (Schwartz and Perry, *Surface Active Agents*, Interscience Publishers, Inc., 1949, p. 233 and Schwartz, Perry and Berch, *Surface Active Agents and Detergents*, Vol. II, Interscience Publishers, Inc., 1958, pp. 297–300); as water-softeners (British Pat. No. 461,221); as anti-caking agents (U.S. Pat. Nos. 2,625,513 and 2,770,600); as suspending agents (U.S. Pat. Nos. 2,594,257, 2,594,258 and 2,920,045); and as fillers (U.S. Pat. No. 2,708,185).

It is also well known that some clay materials can be deposited on fabrics to impart softening and antistatic properties thereto. Such clay deposition is generally realized by contacting the fabrics to be so treated with aqueous clay suspensions (See, for example, U.S. Pat. No. 3,033,699 and 3,594,212). The co-pending application of Storm and Nirschl, entitled "Detergent Compositions"; Ser. No. 271,943, filed July 14, 1972, discloses the use of clay softeners in built, non-soap detegent compositions.

However, it has been heretofore unrecognized that clay minerals of the type used in the present invention can be attached to the surface of soap-based detergent granules, especially those containing curd dispersants, to enhance the solubility of the granules in water while concurrently providing fabric softening.

Accordingly, it is an object of the present invention to provide compositions which can be employed to yield simultaneous fabric laundering and fabric softening without interfering with flame retardancy.

It is a further object of the present invention to provide soap-based laundering and softening compositions containing curd dispersants in the form of granular formulations which can be easily dissolved in water over a wide temperature range.

It has surprisingly been discovered that by attaching smectite-type clays having particular cation exchange characteristics to the surface of curd-dispersant containing, soap-based detergent granules, the above objectives can be realized and granular fabric laundering and softening compositions can be obtained which are unexpectedly superior to similar compositions known to the prior art.

SUMMARY OF THE INVENTION

The present invention encompasses fabric laundering compositions comprising: (A) a granular particle which comprises: (i) from about 30% to about 80% by weight of said particle of a soap compound, and; (ii) from about 1% to about 30% by weight of said granular particle of a curd-dispersing agent; and (B) an impalpable smectite-type clay having an ion exchange capacity of at least about 50 meq/100 g. of clay, attached to the surface of said granular particle. The compositions have a weight ratio of granular particles to smectite clay in the range of from about 20:1 to about 3:1.

DETAILED DESCRIPTION OF THE INVENTION

The fabric laundering compositions of the present invention contain two essential components — granular soap-based particles and an impalpable smectite-type clay material attached to the surfaces of such particles. The composition of the granular particles and the nature of the clay material is described more fully as follows.

The Granular Particles

The granular particle component of the instant laundering composition comprises two essential ingredients (1) a soap compound and (2) a curd-dispersing agent.

Soap Compound

The granular particles of the instant invention comprise from about 30% to about 80%, preferably from about 40% to about 70%, by weight of the particles of a soap compound. Useful soap compounds include the ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkanolammonium salts of higher

fatty acids containing from about 8 to about 24 carbon atoms, preferably from about 10 to about 20 carbon atoms. Suitable fatty acids can be obtained from natural sources such as, for instance, 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 produced (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 tallow soap, sodium coconut soap, potassium tallow soap, potassium coconut soap and mixtures thereof.

The Curd Dispersing Agent

As noted above, it is well known that the use of soap in hard water results in the formation and precipitation of insoluble fatty acid salts, more commonly referred to as lime soaps. which have a tendency to coagulate and form a sticky curd. To prevent formation of such curd in laundering solutions containing the compositions of the instant invention, the granular particles in addition to the soap component contain from about 1% to about 30%, preferably from about 2% to about 20%, by weight of the particle of a curd-dispersing agent.

Such curd dispersing agents either prevent the formation of large particles of insoluble lime soaps or prevent such soaps from flocculating so that they are flushed away with the washing or rinsing liquid and do not adhere to fabrics or to surfaces of washing vessels.

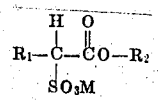
The effectiveness of particular materials as curd-dispersing agents can be ascertained by a simple procedure testing the ability of the test material to peptize lime soaps. Such a procedure is outlined in Schwartz and Perry, *Surface Active Agents*, Interscience Publishers, Inc., 1949 at pp. 326 and 327, and is summarized as follows.

The general method consists of preparing a series of mixtures containing varying proportions of sodium oleate and the curd dispersing agent being tested. These mixtures contain approximately 10% total soap-plus-curd dispersant in distilled water. Five milliliters of each mixture are then added to 45 milliliters of hard water (usually 200 ppm hardness as CaO). This is called the first dilution, and it usually results in a turbid but well-dispersed sol. Five milliliters of the first dilution are then added to 45 milliliters of hard water, forming the second dilution. This is a severe test since there is now more than enough lime present to precipitate all the soap. Furthermore, the total soap-plus-curd dispersant concentration is of the order of 0.1%. The results are expressed as the percentage of dispersant in the soap-curd dispersant mixture which is just sufficient to prevent flocculation on the second dilution. The more effective the curd dispersing agent, the lower is the percentage value. For purposes of the instant invention a "curd-dispersing agent" is any material which produces a percentage value in the above-described lime soap peptizing procedure of about 39% or less. A conventional non-curd dispersant surfactant for purposes of this invention is a surfactant providing a percentage value greater than 39% in the above-described lime soap peptizing procedure.

Examples of suitable curd-dispersing agents include certain anionic, semipolar nonionic, ampholytic and zwitterionic materials as well as certain amides and amines. Classes of these curd-dispersing agents are more fully described as follows.

1. Anionic organic detergents which are alkali metal, ammonium and substituted-ammonium salts of esters of α-sulfonated fatty acids in which the esters contain about 12 to about 25 carbon atoms.

These detergent compounds have the following structure:



wherein R_1 is an alkyl or alkenyl moiety of about 10 to about 20 carbon atoms (forming with the two carbon atoms a fatty acid group); R_2 is alkyl of 1 to about 10 carbon atoms; and M is a salt-forming moiety.

The salt-forming moiety 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-, trimethyl-ammonium and triethanolammonium 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.

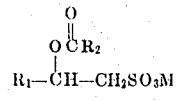
Specific examples of this class of compounds include the sodium and potassium salts of esters where R_2 is selected from methyl, ethyl, propyl, butyl, hexyl and octyl groups and the fatty acid group (R_1 plus the two carbon atoms in the structure above) is selected from lauric, myristic, palmitic, stearic, palmitoleic, oleic, linoleic acids and mixtures thereof. A preferred ester material herein is the sodium salt of the methyl ester of α-sulfonated tallow fatty acid, the term tallow indicating a carbon chain distribution approximately as follows: C_{14} - 2.5%, C_{16} - 28%, C_{18} - 23%, palmitoleic - 2%, oleic - 41.5%, and linoleic - 3% (the first three fatty acids listed are saturated).

Other examples of suitable salts of α-sulfonated fatty esters utilizable herein include the ammonium and tetramethylammonium salts of the hexyl, octyl, ethyl, and butyl esters of α-sulfonated tridecanoic acid; the potassium and sodium salts of the ethyl, butyl, hexyl, octyl, and decyl esters of α-sulfonated pentadecanoic acid; and the sodium and potassium salts of the butyl, hexyl, octyl, and decyl esters of α-sulfonated heptadecanoic acid; and the lithium and ammonium salts of the butyl, hexyl, octyl, and decyl esters of α-sulfonated nonadecanoic acid.

The salts of α-sulfonated fatty acid esters of the present invention are known compounds and are described in U.S. Pat. No. 3,223,645, issued Dec. 14, 1965 to Kalberg, this patent being hereby incorporated by reference.

2. Anionic organic detergents which are salts of 2-acyloxy-alkane-1-sulfonic acids.

These salts have the formula:



where R_1 is alkyl of about 9 to about 23 carbon atoms; R_2 is alkyl of 1 to about 8 carbon atoms; and M is a salt-forming moiety as hereinbefore described.

Specific examples of β-acyloxy-alkane-1-sulfonates, or alternatively, 2-acyloxy-alkane-1-sulfonates, utilizable herein to provide superior curd dispersion 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 ammonium salt of 2-hexanoyloxy-hexadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-hexadecane-1-sulfonic acid; the dimethylammonium salt of 2-heptanoyloxy-tridecane-1-sulfonic acid; the potassium salt of 2-octanoyloxy-tetradecane-1-sulfonic acid; the dimethylpiperidinium salt of 2-nonanoyloxytetradecane-1-sulfonic acid; the sodium salt of 2-acetoxyheptadecane-1-sulfonic acid; the lithium salt of 2-acetoxyoctadecane-1-sulfonic acid; the dimethylamine salt of 2-acetoxyoctadecane-1-sulfonic acid; the potassium salt of 2-acetoxynonadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-eicosane-1-sulfonic acid; the sodium salt of 2-propionyloxy-docosane-1-sulfonic acid; and isomers thereof.

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

Typical examples of the above described β-acetoxy alkanesulfonates are described in the literature: Belgian Pat. No. 650,323 issued July 9, 1963, discloses the preparation of certain 2-acyloxy alkanesulfonic acids. Similarly, U.S. Pat. Nos. 2,094,451 issued Sept. 28, 1937, to Guenther et al. and 2,086,215 issued July 6, 1937 to De Groote disclose certain salts off β-acetoxy alkanesulfonic acids. These patents are hereby incorporated by reference.

3. Anionic organic detergents which are alkyl ether sulfates.

These materials have the formula $RO(C_2H_4O)_xSO_3M$ wherein R is an alkyl or alkenyl moeity of about 10 to about 20 carbon atoms, x is 1 to 30, and M is a salt-forming cation as defined hereinbefore.

The alkyl ether sulfates useful in the present invention as curd dispersants 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 trialkylene glycol ether sulfate; sodium tallow alkyl hexaoxyethylene sulfate; and ammonium tetradecyl octaoxyethylene sulfate.

Preferred herein for reasons of excellent curd-dispersing properties and ready availability are the alkali metal coconut- and tallow-alkyl oxyethylene ether sulfates having an average of about 3 to about 10 oxyethylene moieties. The alkyl ether sulfates of the present invention are known compounds and are described in U.S. Pat. No. 3,322,876 to Walker (July 25, 1967) incorporated herein by reference.

4. Anionic organic detergents which 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 α-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture using 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.

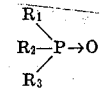
The α-olefins from which the olefin sulfates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

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 preferred embodiment herein are those olefin sulfonates which are described completely in U.S. Pat. No. 3,332,880 issued July 25, 1967, to Kessler et al., hereby incorporated by reference.

5. Nonionic organic detergents which are semipolar detergent compounds.

These include, for example, long chain tertiary phosphine oxides having the structure:



wherein R_1 is alkyl, alkenyl, or monohydroxyalkyl of about 8 to about 18 carbon atoms having from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety and R_2 and R_3 are each alkyl or monohydroxyalkyl groups containing from 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of the semi-polar bond.

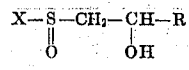
Examples of suitable phosphine oxides are:
dodecyldimethylphosphine oxide,
tetradecyldimethylphosphine oxide,
tetradecylmethylethylphosphine oxide,
3,6,9-trioxaoctadecyldimethylphosphine oxide,

cetyldimethylphosphine oxide,
3-dodecoxy-2-hydroxypropyldi(2-hydroxyethyl)-phosphine oxide,
stearyldimethylphosphine oxide,
cetylethylpropylphosphine oxide,
oleyldiethylphosphine oxide,
dodecyldiethylphosphine oxide,
tetradecyldiethylphosphine oxide,
dodecyldipropylphosphine oxide,
dodecyldi(hydroxymethyl)phosphine oxide,
dodecyldi(2-hydroxyethyl)phosphine oxide,
tetradecylmethyl-2-hydroxypropyl phosphine oxide,

oleyldimethylphosphine oxide, and
2-hydroxydodecyldimethylphosphine oxide.

6. Nonionic organic detergents which are certain organic sulfoxides.

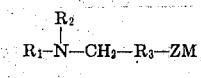
Such compounds have the general formula:



wherein R is an alkyl group of 8 to 16 carbon atoms and X is selected from the group consisting of methyl, ethyl and β-hydroxyethyl groups. Such compounds are described in U.S. Pat. No. 3,232,879 hereby incorporated by reference.

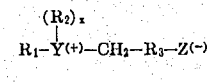
7. Ampholytic synthetic detergents which are derivatives of aliphatic secondary and tertiary amines in which the aliphatic group can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

These detergents have the formula



wherein R_1 is alkyl of about 8 to 18 carbon atoms, R_2 is alkyl of 1 to about 3 carbon atoms or is hydrogen, R_3 is alkylene of 1 to about 4 carbon atoms, Z is carboxy, sulfonate, sulfate, phosphate or phosphonate and M is a salt-forming cation, as hereinbefore described. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate; sodium 3-dodecylaminopropane sulfonate; N-alkyltaurines such as the ones prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072; sodium salts of N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091; and the products sold under the trade name "Miranol" and described in U.S. Pat. No. 2,528,378.

8. Zwitterionic synthetic detergents which are derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds, in which the aliphatic groups can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R_1 is an alkyl, alkenyl, hydroxyalkyl or alkylbenzyl group containing from about 8 to about 24 carbon atoms and having from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R_2 is an alkyl or monohydroxy alkyl group containing 1 to about 3 carbon atoms; x is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom, R_3 is an alkylene or hydroxy alkylene group of from 1 to about 4 carbon atoms and Z is a member selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples include:
4-[N,N-di(2-hydroxyethyl)-N-octadecyl-ammonio]-butane-1-carboxylate;
5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
3-[P,P-diethyl-P-3,6,9-trioxatetracosanephosphonio]-2-hydroxypropane-1-phosphate;
3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;

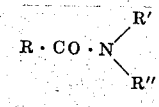
3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
3-(N,N-dimethyl-N-hexadecyl-ammonio)-2-hydroxypropane-1-sulfonate;
4-[N,N-di(2-hydroxyethyl-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;

3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate;
S-[N,N-di(3-hydroxypropyl)-N-hexadecyl-ammonio]-2-hydroxypentane-1-sulfate;
3-(dodecylbenzyldimethylammonio)propane-1-sulfonate; and
2-(dodecylbenzyldimethylammonio)ethane-1-sulphate.

Examples of compounds falling within this definition also include 3-(N,N-dimethyl-N-hexadecyl-ammonio)propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecyl-ammonio)-2-hydroxypropane-1-sulfonate which are especially preferred herein for their availability and curd dispersant characteristics. Some of the compounds of this type as well as their use as dispersing agents are more fully described in U.S. Pat. Nos. 2,699,991 and 3,660,470 herein incorporated by reference.

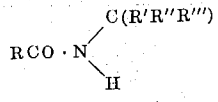
9. Organic carboxylic acid amides.

Such amide compounds include those aliphatic amides of the general formula:



wherein R is hydrogen, alkyl, or alkylol and R′ and R″ are hydrogen, alkyl, alkylol, or alkylene joined through an oxygen atom, the total number of carbon atoms in R, R′ and R″ being from about 9 to about 25.

Amides of this general type which are of special utility are those aliphatic carboxylic acid alkanolamides of the formula:



in which RCO is the acyl group of a soap-forming carboxylic acid having from about 10 to about 18 carbon atoms, R′ and R″ are each selected from the group consisting of hydrogen, alkyl, and alkylol substituents, and R‴ is an alkylol substituent, the total number of carbon atoms in R′, R″ and R‴ being from 1 to 7.

Some specific amides coming within the scope of the invention are:

lauric ethanolamide;
stearic ethanolamide;
dimethyl lauramide;
lauramide;
lauryl lauramide;
myristic N-methyl ethanolamide;
butyl capramide;
capric butanolamide;
dibutyl capramide;
dibutyl myristamide;
stearic acid amide of tris(hydroxymethyl)amino methane;
myristic glycerylamide;
N-lauroyl morpholine;
lauric glycerylamide;
palmitic acid amide of 2-amino-2-methyl-1,3-propanediol;
lauryl hydroxy-acetamide;
myristyl formamide;
lauric isopropanol amide; and
myristic acid amide of 3-amino-3-methyl-2,4-pentanediol.

Especially preferred is tallow acyl monoethanolamide.

Such amides, their preparation and use as dispersing agents are discussed more fully in U.S. Pat. No. 2,527,076, hereby incorporated by reference.

10. Organic alkyl and alkanol amines.

Such amine compounds include N-alkyl monoalkylolamines and N-alkyl dialkylolamines in which the alkyl group has from 10 to 16 carbon atoms and the alkanol group has 2 or 3 carbon atoms; N-alkyl morpholines in which the alkyl group has from 10 to 16 carbon atoms; and N-alkyl tris(hydroxymethyl)aminomethane in which the alkyl group has from 10 to 16 carbon atoms.

Specific examples of such compounds include N-dodecylmonoethanolamine, N-dodecyl-tris(hydroxymethyl)aminomethane, N-dodecyl isopropanolamine, N-tetradecyl monoethanolamine, N-dodecyl diethanolamine, N-tetradecyl diethanolamine and N-dodecyl morpholine. Compounds of this type and their use as curd-dispersing agents are described more fully in British Pat. No. 1,006,836, incorporated herein by reference.

Of all of the above-described types of curd-dispersing agents, the compounds preferred for use in the granular particles of the instant composition include the sodium salt of the methyl ester of α-sulfonated tallow fatty acid; the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 3 ethylene oxide groups per mole; the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 6 ethylene oxide groups per mole; sodium β-acetoxyhexadecane-1-sulfonate; sodium β-acetoxy tridecane-1-sulfonate; the sodium salt of sulfonated 1-hexadecene; dimethyldodecylphosphine oxide; sodium hexadecylmethylaminopropionate; 3(N,N-dimethyl-N-alkylammonio)-propane-1-sulfonate and 3(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate wherein in each propane sulfonate compound the alkyl group averages about 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-dodecylbenzene-N,N-dimethyl ammonio)-propane-1-sulfonate and tallow acyl monoethanolamide.

Highly preferred curd dispersing agents herein are the sodium salt of ethoxylated tallow alkyl sulfate averaging about 3 ethylene oxide groups per mole, the sodium salt of ethoxylated tallow alkyl sulfate averaging about 6 ethylene oxide groups per mole, and tallow acyl monoethanolamide.

Optional Granule Components

Besides the above-described soap and curd-dispersing components, the granular particles of the instant compositions can contain a wide variety of optional components generally found in conventional fabric laundering formulations. Such optional components include, for example, conventional anionic or nonionic surfactants which are not particularly useful as curd dispersants and alkaline builder salts. Such non-curd-dispersing surfactants are those having a percentage value in the above-described lime soap peptizing test greater than 39% and include the sodium salts of linear alkyl benzene sulfonic acid wherein the alkyl group average about 10 to 18 carbon atoms in length, sodium tallow alkyl sulfate, the condensation product of coconut fatty alcohol with about 6 moles of ethylene oxide per mole of 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 alcohol. When employed, such conventional non-curd-dispersing surfactants generally comprise from about 1% to 30% by weight of the granular particle.

Typical alkaline builders include sodium tripolyphosphate, sodium citrate, sodium nitrilotriacetate, sodium carbonate and sodium mellitate. When employed, such conventional builders generally comprise from about 1% to 30% by weight of the granular particle.

Other optional granule components include the various soil-suspending agents such as carboxymethylcellulose, corrosion inhibitors, dyes, fillers such as sodium sulfate and silica, optical brighteners, bleaches such as sodium perborate, suds boosters, suds depressants, germicides, anti-tarnishing agents, pH adjusting agents such as sodium silicate, enzymes, and the like, well known in the art for use in detergent compositions. Bound water can also be present in said compositions.

The soap-based granules herein can be prepared in standard fashion, e.g., by blending the soap, curd dispersant and optional ingredients of the granules in a crutcher, and subsequently blowing the mix in standard spray-drying equipment.

Clay Compounds

The present compositions contain, as an essential ingredient, particulate smectite-type clay materials which increase the solubility of the combined soap-curd dispersant granules and provide fabric softening concurrently with fabric cleansing. These smectite clays are present in the detergent compositions at concentrations from about 4% to about 25%, preferably from 5% to 15% by weight, of the total composition. The weight ratio of clay to the soap-based granules is from about 20:1 to about 3:1 by weight.

The clay minerals used to provide the solubility and softening properties of the instant compositions can be described as impalpable, expandable, three-layer clays, i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least about 50 meq/100 g. of clay. The term "impalpable" as used to describe the clays employed herein means that the individual clay particles are of a size that they cannot be perceived tactilely. Such particle sizes are within the range below about 50 microns. In general, the clays herein will have a particle size within the range of from about 5 microns to about 25 microns. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

There are two distinct classes of smectite-type clays. In the first, aluminum oxide is present in the silicate crystal lattice; in the second class of smectites, magnesium oxide is present in the silicate crystal lattice. The general formulas of these smectites are $Al_2(Si_2O_5)_2(OH)_2$ and $Mg_3(Si_2O_5)(OH)_2$, for the aluminum and magnesium oxide type clay, respectively. It is to be recognized that the range of the water of hydration in the above formulas can vary with the processing to which the clay has been subjected. This is immaterial to the use of the smectite clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as Na+, Ca++, as well as H+, can be copresent in the water of hydration to provide electrical neutrality. Except as noted hereinafter, such cation substitutions are immaterial to the use of the clays herein since the desirable physical properties of the clays are not substantially altered thereby.

The three-layer, expandable alumino-silicates useful herein are further characterized by a dioctahedral crystal lattice, while the expandable three-layer magnesium silicates have a trioctahedral crystal lattice.

As noted hereinabove, the clays employed in the compositions of the instant invention contain cationic counterions such as protons, sodium ions, potassium ions, calcium ion, magnesium ion, and the like. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation:

$$\text{smectite clay (Na)} + NH_4OH \rightleftarrows \text{smectite clay } (NH_4) + NaOH \text{ Clays,}$$

Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure clay cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq/100 g.). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration, or by a methylene blue procedure, all as fully set forth in Grimshaw, *The Chemistry and Physics of Clays*, Interscience Publishers, Inc. pp. 264–265 (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which, in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. for kaolinites to about 150 meg/100 g., and greater, for certain clays of the montmorillonite variety. Illite clays have an ion exchange capacity somewhere in the lower portion of the range, i.e., around 26 meq/100 g. for an average illite clay.

It has been determined that illite and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the instant compositions. Indeed, such illite and kaolinite clays constitute a major component of clay soils and, are, in fact, removed from fabric surfaces by means of the instant compositions. However, smectites, such as nontronite, having an ion exchange capacity of approximately 50 meq/100 g., saponite, which has an ion exchange capacity of around 70 meq/100 g., and montmorillonite, which has an ion exchange capacity greater than 70 meq/100 g., have been found to be useful in the instant compositions. This is so since such smectites, if attached to the granule surface, increase composition solubility while, once added to laundering liquor, deposit on the fabrics to provide softening. Accordingly, clay minerals useful herein can be characterized as impalpable, expandable, three-layer smectite-type clays having an ion exchange capacity of at least about 50 meq/100 g.

While it is not intended that the instant invention be limited by theory, it appears that the advantageous solubility, softening (and potentially dye scavenging) benefits of the instant compositions are ascribable to the physical characteristics and ion exchange properties of the clays used herein. That is to say, experiments have shown that non-expandable clays such as the kaolinites and the illities, which are both classes of clays having ion exchange capacities below 50 meq/100 g., do not provide the beneficial aspects of the clays employed in the instant compositions.

Furthermore, the unique physical and electrochemical properties of the smectite clays apparently cause their interaction with, and dispersion of, the mixture of soap and curd dispersant used in the instant compositions. Thus, it has now been found that, rather than agglomerating to form viscous gels when contacted by water, the soap-plus-curd dispersant granules having the smectite-clay attached thereto used herein can be added to aqueous laundry baths over a broad temperature range to yield homogeneous soap solutions containing homogeneous, stable clay suspensions. The problems of gelling and agglomeration usually encoun-

tered when such non-clay containing, soap-curd dispersant granules are added to aqueous media in solid form are alleviated by the presence of the clay. Apparently, the negative electrical charges on the clay particles serve to repulse the aggregates which tend to form when the granular compositions herein are contacted by water thereby providing the desired homogeneous soap solution. whatever the reason for the advantageous co-action of the soap-based granules and smectite clay used herein, the attachment of the expandable, three-layer, dioctadedral alumino-silicates and expandable, three-layer, trioctahedral magnesium silicates to the surface of the granules in the manner of this invention provides a means whereby the water solubility of the granules is greatly improved while additionally providing a homogeneous clay dispersion which provides effective fabric softening.

The smectite clays used in the compositions herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under commercial names such as "fooler clay" (clay found in a relatively thin vein above the main bentonite or montmorillonite veins in the Black Hills) and various tradenames such as Thixogel No. 1 and Gelwhite GP from Georgia Kaolin Co., Elizabeth, N.J. Volclay BC and Volclay No. 325, from American Colloid Co., Skokie, Ill; Black Hills Bentonite BH 450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R. T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained under the foregoing commercial and tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

While any of the impalpable smectite-type clays having a cation exchange capacity of at least about 50 meg/100 g. are useful herein, certain clays are preferred. For example, Gelwhite GP and fooler clay are extremely white forms of smectite clays and are therefore preferred when formulating white, granular compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% of iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in laundry compositions and is preferred from the standpoint of fabric softening performance. Likewise, Thixogel No. 1, is a preferred clay herein from the standpoint of both product solubility and through-the-wash fabric softening performance. On the other hand, certain smectite clays, such as those marketed under the name "bentonite", are sufficiently contaminated by other silicate minerals that their ion exchange capacity falls below the requisite range, and such clays are of no use in the instant compositions.

Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14A X-ray diffraction pattern. This characteristic pattern, together with exchange capacity measurements performed in the manner noted above, provides a basis for selecting suitable impalpable semctite-type clay minerals for use in the granular detergent compositions disclosed herein.

Composition Preparation

The compositions herein are formulated by simply preparing granules comprising the soap, curd dispersant, and any of the optional ingredients mentioned hereinabove, and then contacting the granules with the smectite-type clay. The clay can then be simply admixed with the soap-based granules and blended. In this precedure, the clay is attached to the soap-based granules mainly by electrostatic surface forces between the clay and soap granules.

In a preferred method for attaching the clay to the granules, the soap-based granules are coated with a material of the type hereinafter disclosed which promotes adhesion of the clay particles to the surface of the granules. When an adhesion-promoting material is used, the substantially dry soap-based granules can be first sprayed with said material in liquid form and then admixed with the clay. The clay and sprayed granules are then thoroughly blended to provide good contact and optimum coating of the granules with the clay. In an alternate procedure, the clay and granules are concurrently admixed and sprayed with the adhesion-promoting material. Mixing of the clay and granules can be achieved using a standard drum mixer.

The materials used herein to promote adhesion of the clays to the surface of the granules can be any water-soluble or water-dispersable organic materials, preferably those which are liquids or are liquifiable at convenient temperatures for spraying, i.e., at temperatures from about 60°F to about 150°F. Of course, the adhesion-promoting materials used herein should not be toxic or deleterious to fabrics. Since most soap compositions are desirably white in color, colorless organic materials are preferred herein for attaching the clay to the soap-based granules. Preferably, the materials used herein have sufficient hydrophilic character that they are easily dissolved or dispersed in water, but they are preferably not hydroscopic.

A variety of liquid and liquifiable organic compounds are useful herein for attaching the clay to the surface of the soap-based granules. For example, all manner of common ethoxylated nonionic surfactants can be used for this purpose. Nonionic surfactants produced by the condensation of an alkylene oxide moiety (hydrophilic in nature) with an organic hydrophobic compound which is usually aliphatic or alkyl aromatic in nature can be used. The length of the hydrophilic or polyoxyalkylene moiety which is condensed with any particular hydrophobic compound can be readily adjusted to yield colorless, liquid or liquifiable, water dispensable, organic, nonionic surfactants which are useful adhesion promoters herein. Examples of nonionic surfactants which can be used as the adhesion-promoting materials herein include:

1. The polyethylene oxide condensates of alkyl phenols. These compounds include 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, 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 can be derived, for example, from polymerized propylene, diisobutylene, octene, or nonene. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol, dodecyl phenol condensed with about 12 moles of ethylene oxide per mole of phenol, dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol, di-isooctyl-phenol con-

densed with about 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-610 marketed by the GAF Corporation; and Triton X-45, X-114, X-100 and X-102, all marketed by the Rohm and Haas Company.

2. The condensation products of aliphatic alcohols with ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched and generally contains from about 8 to about 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of about 6 moles of ethylene oxide with 1 mole of tridecanol, myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of myristyl alcohol, the condensation product of ethylene oxide with coconut fatty alcohol wherein the coconut alcohol is a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms and wherein the condensate contains about 6 moles of ethylene oxide per mole of alcohol, and the condensation product of about 9 moles of ethylene oxide with the above-described coconut alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol 15-S-9 marketed by the Union Carbide Corporation, Neodol 23-6.5 marketed by the Shell Chemical Company, and Kyro EOB marketed by The Procter & Gamble Company.

3. The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene moieties 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 the polyoxyethylene content is about 50% of the total weight of the condensation product. Examples of compounds of this type include certain of the commercially available Pluronic surfactants marketed by the Wyandotte Chemicals Corporation.

4. The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. The hydrophobic base of these products consists of the reaction product of ethylenediamine and excess propylene oxide, said base having a molecular weight of from about 2500 to about 3000. This base is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic compounds marketed by the Wyandotte Chemicals Corporation.

The fatty acids are another class of materials which can be used to promote the attachment of the clays to the surface of the granules. Fatty acids useful herein are those C_{10} to C_{22} straight chain and branched chain aliphatic carboxylic acids which can be obtained, for example, by the saponification of triglycerides. Both saturated and unsaturated fatty acids are useful herein. Mixtures of fatty acids obtainable from certain designated fats, e.g., tallow fatty acids, obtainable from tallow; coconut fatty acids, obtainable from coconut oil and; palm fatty acids, obtainable from palm oil, are also useful herein. The C_{12} to C_{20} aliphatic fatty acids, and mixtures thereof, are preferred members of this class of adhesion-promoting materials herein.

Exemplary fatty acids which can be employed herein to affix the clay to the soap-based granules include lauric, myristic, palmitic, stearic, elaidic, oleic and eicosanoic acids, and mixtures thereof.

The fatty alcohols having C_{10} to C_{22} hydrocarbon chains are also useful herein as adhesion promoters. These materials can be obtained in a variety of ways well known in the art, e.g., from various triglyceride oils such as palm oil and coconut oil. Exemplary alcohols useful herein include 1-dodecanol, 1-tetradecanol, 1-hexadecanol and 1-octadecanol.

Preferred materials which can be used herein to attach the smectite clays to the surfaces of the soap-plus-curd dispersant granules include; coconut alcohol ethoxylate containing 6 ethylene oxide units per molecule; tallow alcohol ethoxylate containing 11 ethylene oxide units per molecule, i.e., tallow ethylene oxide (**11**); coconut fatty acid mixtures; tallow fatty acid mixtures, the condensate of one mole of ethylene oxide with 1-dodecanol; and the condensate of one mole of 1-dodecanol with ethylene oxide hexamer. Especially preferred adhesion promoters herein include coconut fatty acids and tallow ethylene oxide (**11**).

In addition to providing good attachment of the smectite-type clays to the surface of the soap-based granules herein, the optionally employed adhesion-promoting materials serve the additional function of providing an unexpected additional increment of solubility to the compositions. That is to say, while the soap-plus-curd dispersant granules herein exhibit poor solubility in laundering baths on the range of from about 60°F. to 120°F., the surface coating of the adhesion-promoting materials enhances this solubility. while the soap-plus-curd dispersant granules coated with the adhesion-promoting materials are not rendered sufficiently soluble to be optimally useful for cool water washing (i.e., at about 80°F), the added increment of solubility imparted by the adhesion-promoting materials complements the substantial increase in solubility afforded by the smectite-type clays. Accordingly, the soap-based granules coated with the adhesion promoter and having the smectite-type clays attached to the surface have a water solubility comparable to that of the better commercial synthetic detergent compositions over a wide temperature range.

In addition to providing optimal attachment of the smectite clays to the soap-based granules and enhancing the water solubility of the compositions herein, the optionally-employed, adhesion-promoting materials serve to decrease product dust levels. The decreased product dust levels afforded by the adhesion promoters aids in processing and provides a more acceptable product for the consumer.

When the adhesion-promoting materials herein are employed to attach the smectite-type clays to the surface of the soap-based granules, they are preferably used in an amount sufficient to provide said granules with at least a monolayer coating of said materials. For most purposes, the adhesion-promoting material can comprise from about 0.5% to about 8%, preferably 1% to about 4%, by weight of the total composition. Of course, higher proportions of the adhesion promoters can be employed, but this represents an economic waste in that such increased proportions are not required to affix the clay to the granules and do not fur-

ther increase product solubility to any substantial degree.

Use of the clay-to-soap-based granules ratio noted hereinabove results in compositions wherein a substantial proportion of the surface of the granules are coated with the clay. Of course, when the adhesion-promoting materials are additionally employed, greater coverage of the granules is more easily achieved. While soap-based granules having about 10%, and greater, of their surfaces coated with the clay exhibit the desirable solubility properties disclosed herein, it is preferred that the clay coat at least about 40% of the granule surface. Such higher degrees of surface coating are most readily achieved by use of the adhesion-promoting materials disclosed above.

For fabric laundering and softening purposes, compositions of the instant invention are added to aqueous laundering liquor to the extent of from about 0.02% to about 2% by weight, preferably form about 0.1% to about 1% by weight. Addition of such compositions provide a laundering liquor pH of from about 7 to 12.

The detergent compositions of the instant invention are illustrated by the following examples

EXAMPLE I

A soap-based laundry granule is prepared having the following composition:

Component	Wt.%
Sodium soap[1]	42.6
Potassium soap[1]	11.2
TAE_3S[2]	10.7
$C_{11.8}LAS$[3]	8.8
Sodium silicate	8.9
Sodium sulfate	11.9
Brightener	0.57
Perfume	0.17
Water	3.4
Miscellaneous	Balance

[1]Soap mixtures comprising 90% tallow and 10% coconut soaps
[2]Sodium salt of ethoxylated tallow alkyl sulfate having an average of about 3 ethylene oxide units per molecule.
[3]Sodium salt of liner alkyl benzene sulfonate having an average alkyl chain length of about 12 carbon atoms.

The foregoing ingredients are mixed in a crutcher and spray-dried to provide a granular, soap-based composition.

Eighty-eight and four-tenths parts by weight of the soap-based granules prepared above are admixed with 11.6 parts by weight of an impalpable sodium montmorillonite clay having an ion exchange capacity greater than 50 meq/100 g. marketed under the tradename Thixogel No. 1. Such admixture provides a composition comprising the soap-plus-curd dispersant granules having the clay attached to the surface of the granules.

such a composition is a stable laundry detergent formulation providing excellent fabric laundering and as noted below also has desirable solubility and fabric softening characteristics when added to laundering liquor to the extent of about 0.12% by weight.

EXAMPLE II

A soap-based laundry granule is prepared having the following composition:

Component	Wt. %
Sodium soap[1]	42.6
Potassium soap[1]	11.2
TAE_3S[2]	10.7
$C_{11.8}LAS$[3]	8.8
Sodium silicate	8.9
Sodium sulfate	11.9
Brightener	0.57
Perfume	0.17
Water	3.4
Miscellaneous	Balance

[1]Soap mixtures comprising 90% tallow and 10% coconut soaps
[2]Sodium salt of ethoxylated tallow alkyl sulfate having an average of about 3 ethylene oxide units per molecule.
[3]Sodium salt of linear alkyl benzene sulfonate having an average alkyl chain length of about 12 carbon atoms.

The foregoing ingredients are mixed in a crutcher and spray-dried to provide a granular, soap-based composition.

Eighty-eight and four-tenths parts by weight of the soap-based granules above are admixed with 8.6 parts by weight of impalpable sodium montmorillonite clay having an ion exchange capacity greater than 50 meq/100 g., marketed under the tradename, Thixogel No. 1. Such admixture of clay and soap-based granules is sprayed with liquid coconut fatty acid and mixing is continued to provide uniform soap-plus-curd dispersant granules having the clay attached to the surface of the granules. Enough coconut fatty acid is employed to provide about 3% by weight of the total composition.

Such a composition is a stable laundery detergent formulation providing excellent fabric laundering and, as noted in greater detail below, also has desirable solubility and fabric softening characteristics when added to laundering liquor to the extent of about 0.12% by weight.

EXAMPLE III

A soap-based laundry granule is prepared having the following composition:

Component	Wt. %
Sodium soap[1]	51.8
Tallow monoethanolamide	2.5
Sodium tripolyphosphate	11.5
Sodium ethylenediamine tetraacetate	0.21
Sodium silicate	5.50
Carboxymethylcellulose	0.33
Sodium perborate	15.6
Perfume, brightener, moisture & misc.	Balance

[1]A mixture of tallow and coconut soaps comprising 80% tallow soap and 20% coconut soap.

The foregoing ingredients are mixed in a crutcher and spray-dried to provide a granular, soap-based composition.

Ninety-five parts by weight of the soap-based granules prepared above are admixed with 5 parts by weight of an impalpable sodium montmorillonite clay having an ion exchange capacity of about 85–100 meq/100 g. marketed under the tradename Volclay BC. Such admixture provides a composition comprising the soap-plus-curd dispersant granules having the clay attached to the surface of the granules.

Such a composition is a stable laundry detergent formulation providing excellent fabric laundering and as

noted below also has desirable solubility and fabric softening characteristics when added to laundering liquor to the extent of about 0.7% by weight.

EXAMPLE IV

A soap-based laundry granule is prepared having the following composition:

Component	Wt. %
Soap[1]	53.5
Tallow monoethanolamide	2.6
Sodium tripolyphosphate	11.8
Sodium ethylenediamine tetraacetate	0.22
Sodium silicate	5.7
Carboxymethylcellulose	0.34
Sodium perborate	16.0
Perfume, brightener, moisture and miscellaneous	Balance

[1]A mixture of tallow and coconut soaps comprising 80% tallow soap and 20% coconut soap.

The foregoing ingredients are mixed in a crutcher and spray dried to provide a granular, soap-based composition.

Ninety-two parts by weight of the soap-based granules prepared above are admixed with 5 parts by weight of an impalpable sodium montmorillonite clay having an ion exchange capacity of about 85–100 meg./100 g. marketed under the tradename Volclay BC and 3 parts by weight of a liquid coconut fatty acid. Mixing is continued to provide uniform soap-plus-curd dispersant granule having the clay attached to the surface of such granules.

Such a composition is a stable, laundry detergent formulation providing excellent fabric laundering and, as noted in greater detail below, also has desirable solubility and fabric softening characteristics when added to laundering liquor to the extent of about 0.7% by weight.

Solubility Test

The water solubilitiy of foregoing compositions is assessed, as follows

Automatic mini-washers each containing about 1–½ gallons of water (7 gr/gal. hardness) and loaded with 6 blue cotton terry towels (14 × 14 inches; ca. 250 grams) are employed in the tests. Machine settings are "wash-wear", i.e., gentle agitation. After the water and terry towels are in the machines, test product is poured uniformly into the machine in an amount equivalent to 1 cup per 17–19 gallons, and agitation is begun. After 15 seconds agitation, the machine is stopped and a product lumping grade is assigned. This grade is a visual assessment of the tendency of the product to coagulate or to form large particles. Small particles are not considered when assigning a lumping grade. Using this visual procedure, a grade of 1 indicates many large lumps; a grade of 10 indicates no large lumps.

A second measurement is then taken which measures the length of time unitl all product is dissolved, up to a maximum time of 4 minutes. One unit is substracted from the grade if the time for dissolution of the product is greater than one minute.

Lumping is assessed at temperatures of 80°F., 100°F. and 120°F. A TOTAL SOLUBILITY INDEX is then assigned as follows: Lumping Grade at 80°F. × 0.2 + **Lumping Grade at** 100°F. × 0.4 + Lumping Grade at 120°F. × 0.4 = TOTAL SOLUBILITY INDEX.

In the above test, the TOTAL SOLUBILITY INDEX of the compositions of Examples I, II, III and IV above, is substantially greater than that of compositions comprising soap-plus-curd dispersant granules without the attached clay.

Substantially similar solubility results are obtained when, in the above-described tests, the ethoxylated tallow alkyl sulfate curd dispersing agent of the Example I and II compositions or the tallow monoethanolamide curd-dispersing agent of the Example III and IV compositions is replaced with equivalent amounts of the sodium salt of the methyl ester of α-sulfonated tallow fatty acid; the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 6 ethylene oxide groups per mole; sodium β-acetoxy-hexadecane-1-sulfonate; sodium β-acetoxy tridecane-1-sulfonate; the sodium salt of sulfonated 1-hexadecene; dimethyldodecylphosphine oxide; sodium hexadecylmethylaminopropionate; 3(N,N-dimethyl-N-alkylammonio)-propane-1-sulfonate and 3(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate wherein 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-hyroxypropane-1-sulfonate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)-propane-1-sulfonate; methyl-β-hydroxydodecyl sulfoxide; stearic ethanolamide or N-dodecymonethanolamine.

Substantially similar solubility results are obtained, when in the above-described tests, the Thixogel No. 1 clay of the Example I and II compositions or the Volclay BC of the Example III and IV compositions is replaced with an equivalent amount of fooler clay, Gelwhite GP, Volclay No. 325, Black Hills Bentonite BH 450, Veegum Pro or Veegum F.

Substantially similar solubility results are obtained when, in the above-described tests, the sodium linear alkyl benzene sulfonate non-curd-dispersing surfactant of the Example I and II compositions is replaced with an equivalent amount of sodium tallow alkyl sulfate, the condensation product of coconut fatty alcohol with about 6 moles of ethylene oxide per mole of alcohol or the condensation product of a secondary fatty alcohol containing about 15 carbon atoms with about 9 moles of ethylene oxide per mole of alcohol.

Substantially similar solubility results are obtained when, in the above-described tests, the sodium tripolyphosphate builder of the Example III and IV compositions is replaced with an equivalent amount of sodium citrate, sodium carbonate, sodium mellitate or sodium nitrilotriacetate.

Substantially similar solubility results are obtained when, in the above-described tests, the coconut fatty acid adhesion-promoting agent of the Example II and Example IV compositions is replaced with an equivalent amount of coconut alcohol ethoxylate containing 6 ethylene oxide units per mole; tallow alcohol ethoxylate containing 11 ethylene oxide units per mole; tallow fatty acid mixtures, the condensate of one of ethylene oxide with 1-dodecanol; the condensate of one mole of 1-dodecanol with ethylene oxide hexamer; or the condensate of 9.5 moles of ethylene oxide with nonyl phenol.

Softness Test

The through-the-wash fabric softening performance

of the laundering compositions herein is assessed by laundering cotton and cotton/polyester swatches in aqueous laundry baths containing 0.1% by weight of the compositions of Examples I and II, and 0.7% by weight of the compositions of Example III and IV above. After two complete laundering cycles and drying in an automatic dryer, fabric softness is assessed tactilely by experienced graders. Fabric softness of products laundered in the compositions herein is comparable to that of fabrics laundered in a commerical laundry detergent employing a commercial fabric softener in the rinse cycle. Microscopic examination of the swatches indicates that substantial amounts of the clay are deposited on the fabric, but no substantial amount of curd is found on the fabric surface.

Substantially similar fabric softening results are obtained in the above-described tests when the ethoxylated tallow alkyl sulfate curd-dispersing agent of the Example I and II compositions or the tallow monoethanolamide curd-dispersing agent of the Example III and IV compositions is replaced with an equivalent amount of the sodium salt of the methyl ester of α-sulfonated tallow fatty acid; the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 6 ethylene oxide groups per mole; sodium β-acetoxy-hexadecane-1-sulfonate; sodium β-acetoxy tridecane-1-sulfonate; the sodium salt of sulfonated 1-hexadecene; dimethyldodecylphosphine oxide; sodium hexadecylmethylaminopropionate; 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; methyl-β-hydroxydodecyl sulfoxide; stearic ethanolamide or N-dodecylmonoethanolamine.

Substantially similar fabric softening results are obtained, when in the above-described tests, the Thixogel No. 1 clay of the Example I and II compositions or the Volclay BC of the Example III and IV compositions is replaced with an equivalent amount of fooler clay, Gelwhite GP, Volclay No. 325, Black Hills Bentonite BH 450, Veegum Pro or Veegum F.

Substantially similar fabric-softening results are obtained when, in the above-described tests, the sodium linear alkyl benzene sulfonate non-curd-dispersing surfactant of the Example I and II compositions is replaced with an equivalent amount of sodium tallow alkyl sulfate, the condensation product of coconut fatty alcohol with about 6 moles of ethylene oxide per mole of alcohol or the condensation product of a secondary fatty alcohol containing about 15 carbon atoms with about 9 moles of ethylene oxide per mole of alcohol.

Substantially similar fabric-softening results are obtained when, in the above-described tests, the sodium tripolyphosphate builder of the Example III and IV compositions is replaced with an equivalent amount of sodium citrate, sodium carbonate, sodium mellitate or sodium nitrilotriacetate.

Substantially similar fabric softening results are obtained when, in the above-described tests, the coconut fatty acid adhesion-promoting agent of the Example II and IV compositions is replaced with an equivalent amount of coconut alcohol ethoxylate containing 6 ethylene oxide units per mole; tallow alcohol ethoxylate containing 11 ethylene oxide units per mole; tallow fatty acid mixtures, the condensate of one mole of ethylene oxide with 1-dodecanol; the condensate of one mole of 1-dodecanol with ethylene oxide hexamer; or the condensate of 9.5 moles of ethylene oxide with nonyl phenol.

What is claimed is:

1. A fabric laundering composition comprising

A. granular particles which comprise

i. from about 30% to about 80% by weight of said granular particles of a soap compound, and

ii. from about 1% to about 30% by weight of said granular particles of a soap-curd-dispersing agent; and

b. an impalpable smectite clay having an ion exchange capacity of at least about 50 meq/100 grams, attached to the surface of said granular particles;

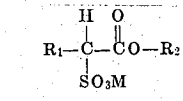
said composition having a weight ratio of granular particles to impalpable smectite clay of from about 20:1 to 3:1.

2. A composition in accordance with claim **1**

A. wherein the soap compound is a salt of a higher fatty acid containing from about 8 to about 24 carbon atoms and is present in said granular particles to the extent of from about 40% to about 70% by weight of the granular particles;

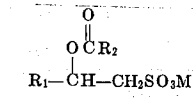
B. wherein the soap-curd-dispersing agent is selected from the group consisting of

i. compounds of the formula



wherein R_1 is alkyl or alkenyl of about 10 to 20 carbon atoms, R_2 is alkyl of 1 to about 10 carbon atoms and M is a salt-forming cation;

ii. compounds of the formula



wherein R_1 is alkyl of about 9 to about 23 carbon atoms, R_2 is alkyl of 1 to about 8 carbon atoms and M is a salt-forming cation;

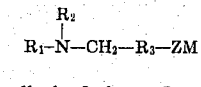
iii. compounds of the formula

$$RO(C_2H_4O)_xSO_3M$$

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;

iv. olefin sulfonates containing from about 12 to 24 carbon atoms;

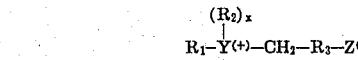
v. compounds of the formula



wherein R_1 is alkyl of about 8 to 18 carbon atoms, R_2 is selected from the group consisting of alkyl of 1 to about 3 carbon atoms and hydrogen, R_3 is alkylene of 1 to about 4 carbon atoms, Z is se-

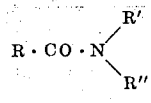
lected from the group consisting of carboxy, sulfonate, sulfate, phosphate and phosphonate, and M is a salt-forming cation;

vi. compounds of the formula



wherein R_1 is selected from the group consisting of alkyl, alkenyl, hydroxyalkyl and alkylbenzene groups, all groups containing from about 8 to about 24 carbon atoms and having from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R_2 is an alkyl or monohydroxyl alkyl group containing 1 to about 3 carbon atoms; x is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom, R_3 is alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a group selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups; and

vii. compounds of the formula



wherein R is hydrogen, alkyl or alkylol and R′ and R″ are each hydrogen, alkyl, alkylol, or alkylene joined through an oxygen atom, the total number of carbon atoms in R, R′ and R″ being from about 9 to about 25;

and wherein said soap-curd-dispersing agent is present in said granular particles to the extent of from about 2% to about 20% by weight of said granular particles; and

C. wherein said impalpable smectite clay is selected from the group consisting of dioctahedral expandable three-layer aluminum-silicates and trioctahedral expandable three-layer magnesium silicates, and is present to the extent of from about 4% to about 25% by weight of the total composition.

3. A composition in accordance with claim **2**

A. wherein the soap is selected from the group consisting of sodium tallow soap, sodium coconut soap, potassium tallow soap, potassium coconut soap and mixtures thereof;

B. wherein the soap-curd-dispersing agent is selected from the group consisting of the sodium salt of the methyl ester of α-sulfonated tallow fatty acid; the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 3 ethylene oxide groups per mole; the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 6 ethylene oxide groups per mole; sodium β-acetoxy-hexadecane-1-sulfonate; sodium β-acetoxy tridecane-1-sulfonate; the sodium salt of sulfonated 1-hexadecane; sodium hexadecylmethylaminopropionate; 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 about 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; and tallow acyl monoethanolamide; and

C. wherein the smectite clay is selected from the group consisting of montmorillonites, volchonskoites, nontronites, hectorites, sauconites and vermiculites.

4. A composition in accordance with claim **3**

A. wherein the soap-curd-dispersing agent is selected from the group consisting of the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 3 ethylene oxide groups per mole; the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 6 ethylene oxide groups per mole; and tallow acyl monoethanolamide; and

B. wherein the smectite clay is a montmorillonite.

5. A composition in accordance with claim **4** wherein the soap-curd-dispersing agent is the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 3 ethylene oxide groups per mole and the smectite clay is a sodium montmorillonite.

6. A composition in accordance with claim **2** wherein the granular particles contain, in addition to the soap and soap-curd-dispersing agent, from 1% to 30% by weight of the particle of a conventional, non-soap-curd-dispersing surfactant and wherein the composition in addition to the granule particles and impalpable smectite clay, contains an adhesion-promoting material comprising from about 0.5% to about 8% by weight of the total composition.

7. A composition in accordance with claim **6**

A. wherein the soap is selected from the group consisting of sodium tallow soap, sodium coconut soap, potassium tallow soap, potassium coconut soap and mixtures thereof;

wherein the soap-curd-dispersing agent is selected from the group consisting of the sodium salt of the methyl ester of α-sulfonated tallow fatty acid; the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 3 ethylene oxide groups per mole; the sodium salt of ethoxylated tallow alkyl sulfate having an average of about 6 ethylene oxide groups per mole; sodium β-acetoxy-hexadecane-1-sulfonate; sodium β-acetoxy tridecane-1-sulfonate; the sodium salt of sulfonated 1-hexadecene; sodium hexadecylmethylaminopropionate; 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 about 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; and 3-(N-dodecylbenzyl-N,N-dimethylammonio)-propane- 1-sulfonate and tallow acyl monoethanolamide; and

C. wherein the smectite clay is selected from the group consisting of montmorillonites, volchonskoites, nontronites, hectorites, sauconites, saponites, and vermiculites.

8. A composition in accordance with claim **7**

A. wherein the conventional non-soap-curd-dispersing surfactant is selected from the group consisting of sodium linear alkyl benzene sulfonate wherein the alkyl group averages from about 10 to

18 carbon atoms in length, sodium tallow alkyl sulfate, and

B. wherein the adhesion-promoting material is selected from the group consisting of non-ionic surfactants produced by the condensation of an alkylene oxide moiety with an organic hydrophobic compound, fatty acids containing from about 10 to about 22 carbon atoms and fatty alcohols containing from about 10 to 22 carbon atoms.

9. A composition in accordance with claim **8**

A. wherein the soap-curd-dispersing agent is selected from the group consisting of the sodium salt of ethoxylated tallow alkyl sulfate averaging about 3 ethylene oxide groups per mole; the sodium salt of ethoxylated tallow alkyl sulfate averaging about 6 ethylene oxide groups per mole; and tallow acyl monoethanolamide;

B. wherein the smectite clay is a montmorillonite;

C. wherein the conventional non-soap-curd-dispersing surfactant is sodium linear alkyl benzene sulfonate wherein the alkyl group averages about 12 carbon atoms in length; and

D. wherein the adhesion-promoting material is selected from the group consisting of coconut alcohol ethoxylate containing 6 ethylene oxide units per molecule; tallow alcohol ethoxylate containing 11 ethylene oxide units per molecule; coconut fatty acid mixtures; tallow fatty acid mixtures, the condensate of one mole of ethylene oxide with 1-dodecanol; and the condensate of one mole of 1-dodecanol with ethylene oxide hexamer, said adhesion-promoting material being present to the extent of from about 1% to about 4% by weight of the total composition.

10. A composition in accordance with claim **9** wherein the adhesion-promoting material is selected from the group consisting of tallow alcohol ethoxylate containing 11 ethylene oxide units per molecule and coconut fatty acid mixtures.

11. A composition in accordance with claim **10** wherein the soap-curd-dispersing agent is the sodium salt of ethoxylated tallow alkyl sulfate averaging about 3 ethylene oxide groups per mole and the smectite clay is a sodium montmorillonite.

12. A composition in accordance with claim **4** wherein the granular particles, in addition to the soap and soap-curd-dispersing agent, contain from about 1% to about 30% by weight of the granular particles of an alkaline builder salt.

13. A composition in accordance with claim **12** wherein the alkaline builder salt is sodium tripolyphosphate.

14. A composition in accordance with claim **13** wherein the soap-curd-dispersing agent is tallow acyl monoethanolamide and the smectite clay is a sodium montmorillonite.

15. A composition in accordance with claim **12** which, in addition to the granular particles and impalpable smectite clay, contains an adhesion-promoting material comprising from about 0.5% to about 8% by weight of the total composition.

16. A composition in accordance with claim **15** wherein the alkaline builder salt is sodium tripolyphosphate and the adhesion-promoting material is selected from the group consisting of coconut alcohol ethoxylate containing 6 ethylene oxide units per molecule; tallow alcohol ethoxylate containing 11 ethylene oxide units per molecule; coconut fatty acid mixtures; tallow fatty acid mixtures, the condensate of one mole of ethylene oxide with 1-dodecanol; and the condensate of one mole of 1-dodecanol with ethylene oxide hexamer, said adhesion-promoting material being present to the extent of from about 1% to about 4% by weight of the total composition.

17. A composition in accordance with claim **16** wherein the soap-curd-dispersing agent is tallow acyl monoethanolamide and the smectite clay is a sodium montmorillonite.

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