DETERGENT COMPOSITIONS CONTAINING A SMECTITE-TYPE CLAY SOFTENING AGENT

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Granular, built laundry detergent compositions containing particular smectite clay materials and quaternary ammonium anti-static agents. The compositions impart a soft hand and reduce the static charge of fabrics washed therein.

11 Claims, No Drawings
DETERGENT COMPOSITIONS CONTAINING A SMECTITE-TYPE CLAY SOFTENING AGENT

BACKGROUND OF THE INVENTION

The instant invention relates to granular built lye- dry detergent compositions which provide simulta neous laundering, softening and anti-static benefits on textiles during conventional fabric laundering operations. Such compositions employ a combination of synthetic detergent compounds, organic or inorganic detergent builders, particular smectite clay compounds having particular cation exchange characteristics and cationic anti-static agents.

Various clay materials have been utilized in many different types of detergent systems for widely diverse purposes. Clays, for example, have been disclosed for utilization as builders (Schwartz and Perry, Surface Active Agents, Interscience Publishers, Inc., 1949, pp. 232 and 299); as water-softeners (British Pat. No. 461,221); as anti-caking agents (U.S. Pat. Nos. 2,623,513 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 properties thereto. Such clay deposition is usually realized by contacting fabrics to be so treated with aqueous clay suspensions (see, for example, U.S. Pat. Nos. 3,033,699 and 3,594,221). The copending application of Storm and Nirschl, Ser. No. 271,943, filed July 14, 1972, and Ohren, Ser. No. 279,127, filed Aug. 9, 1972, relate to the use of clays as softeners in laundry compositions.

While the use of clays as fabric softeners is described in the cited art, such clay softeners are not entirely suitable for this purpose since they do not possess anti-static properties. Commercially acceptable softeners provide anti-static benefits, and such benefits have come to be expected by the user of such products. Indeed, fabrics coated with clays, while exhibiting a soft hand, tend to develop higher levels of static charge than the uncoated fabrics.

Various quaternary ammonium compounds known in the art possess anti-static properties, and the use of clays in combination with such cationic agents for various purposes has been taught in the prior art. For example, U.S. Pat. No. 3,594,212 teaches that quaternary ammonium compounds affixed to the surface of clay enhances clay deposition on fabrics; see, also, U.S. Pat. No. 3,625,505. However, as will be seen hereinafter, when quaternary compounds are chemically affixed to clay surfaces in the manner disclosed in the prior art, the desirable anti-static benefit of the quaternary compounds is lost. Furthermore, such quaternary ammonium compounds are not generally taught to be useful in combination with anionic surfactants in the manner disclosed herein.

U.S. Pat. No. 2,819,288 discloses clays in combination with cationic surfactants as dry emulsifiers; however, these compositions do not contain detergent compounds suitable for laundering fabrics.

Accordingly, while effective for their intended uses, the prior art compositions containing clay-plus-quaternary ammonium compounds are not suitable for laundering fabrics while concurrently imparting softness and anti-static benefits thereto.

The concurrently filed application of Nirschl and Gloss, entitled "Soap Compositions", Ser. No. 305,417, filed Nov. 10, 1972, discloses the use of clays and quaternary salts in soap compositions.

It is an object of the present invention to provide compositions which can be employed to concurrently launder, soften, and impart anti-static benefits to fabrics.

It is a further object of this invention to provide combined laundering, softening and anti-static compositions in the form of granular formulations which are readily dispersible in aqueous laundry baths.

These and the objects are obtained herein, as will be seen from the following disclosure.

SUMMARY OF THE INVENTION

The present invention encompasses granular built laundry detergent compositions comprising: (a) from about 2 to about 30 percent by weight of a non-soap synthetic detergent compound selected from the group consisting of anionic synthetic detergents, nonionic synthetic detergents, ampholytic synthetic detergents, and zwitterionic synthetic detergents and mixtures thereof; (b) from about 10 to about 60 percent by weight of an organic or inorganic detergent builder salt; (c) from about 1 to about 50 percent by weight of a smectite-type clay softening agent having an ion exchange capacity of at least about 50 meq/100 g; and (d) from about 0.5 to about 15 percent by weight of a substantially water-insoluble quaternary ammonium anti-static agent of the formula, $[\text{R}_3\text{N'}\text{R}']\text{X}^-$, wherein each $\text{R}$ is a hydrocarbyl group containing from about 10 to about 22 carbon atoms and each $\text{R'}$ is a hydrocarbyl group containing from about 1 to about 4 carbon atoms and wherein X is an anion, e.g., halide, hydroxide, sulfite, carbonate, phosphate, etc. In the above formula, the superscript n indicates the charge on the anion, $n$ can be 1 to 3 in the compounds herein. The weight ratio of smectite-type clay to quaternary ammonium compound in the compositions herein is from about 40:1 to about 1:1, and is preferably about 5:1. The quaternary ammonium compound is present in releasable combination with the compositions herein. By "releasable combination" is meant that, on admixture with water, the soluble components of the composition granules dissolve and the clay and quaternary compound are independently suspended in the aqueous medium.

The compositions herein preferably provide a solution pH of from about 7 to about 12 when dissolved in water at a concentration of about 0.12 percent by weight.

In a method aspect, the invention encompasses methods for concurrently cleansing, softening and providing antistatic effects on fibers and fabrics comprising laundering said fibers or fabrics in an aqueous laundry bath containing an effective amount (e.g., from about 0.02 to about 2 percent by weight) of a laundry detergent composition as described above.

DETAILED DESCRIPTION OF THE INVENTION

The compositions and processes of this invention employ four essential ingredients: the water-soluble detergent compound; the detergent builder; the clay softener; and the quaternary ammonium anti-static agent. The detergent compound functions in standard fashion to remove soil from fabrics being laundered. The detergent builder functions both to enhance the cleansing action of the detergent compound and to...
uniformly disperse the clay softener. The smectite-type clay functions to soften the laundered fabrics. The quaternary ammonium compound provides anti-static effects on the fabrics and adds an increment of softening benefits to the fabrics. These various components are described in greater detail hereinafter.

Anti-Static Agent

The quaternary ammonium anti-static agents are employed in the instant compositions at a concentration of from about 0.5 to about 15 percent, preferably from about 0.5 to about 5 percent by weight, and are therefore present in the laundering liquors at levels from about 5 ppm to about 150 ppm. In general, the quaternary anti-statics are used at a clay-to-quaternary weight ratio of from about 40:1 to about 1:1, preferably about 5:1.

The anti-static agents of this invention, are quaternary ammonium salts of the formula

$$[R_1N^+R_2^+X^-]$$

wherein each R group is a hydrocarbyl (i.e., alkyl or alkenyl) group containing from about 10 to about 22 carbon atoms and each R' group is a short-chain hydrocarbyl group containing from 1 to about 4 carbon atoms. X in the above compounds can be any salt-forming anion, e.g., halide, hydroxide, sulfate, carbonate, phosphate, etc. The charge on the anion is designated as n-, where n is 1–3. The number of cationic ammonium groups, n, will equal the charge, n, on the anion in order to provide electrical neutrality. Quaternary ammonium compounds wherein n=1 are commercially available and are preferred herein for this reason.

The quaternary ammonium anti-static agents herein are characterized by their limited solubility in water. That is to say, such quaternary salts are essentially insoluble in water, existing therein in what appears to be the mesomorphic liquid crystalline state. The insolubility of the quaternary salts used herein is a critical aspect of this invention inasmuch as water-soluble quaternary salts become chemically affixed to the surface of the clay or react with the preferred anionic surfactants. When the quaternary anti-static agent is affixed to the surface of the clay, or has reacted with the anionic surfactant, it does not provide the desired anti-static effects on fabrics.

The cause of the solubility properties of the particular class of quaternaries found to be useful herein is not known with certainty. While not intended to be limited by theory, it appears that the two extended hydrocarbyl chains (Co-Cn) present in the molecules serve to lower their solubility and probably account for their existence as liquid crystals. In any event, it has now been found the di-long chain quaternaries may be used in re-leasable combination with compositions containing clays. That is to say, the quaternary compound and the clay are independently suspended in the washing liquor and the quaternary compound does not appear to substantially affix itself to the clay surface by an ion exchange mechanism.

Quaternary ammonium compounds are not generally considered to be useful in combination with anionic surfactants since the opposite charges on these two types of compounds cause them to react and precipitate from solution. Yet, the anionics are a preferred class of surfactants for laundering fabrics. Surprisingly, it has now been found that the desirable anti-static effects of the insoluble quaternary ammonium compounds used herein are not negated when employed in combination with anionic surfactants. Apparently, the insoluble nature of the di-long chain quaternary compounds renders them somewhat compatible with anionics; whatever the reason, the quaternary ammonium anti-statics herein perform their anti-static function when used in combination with clays and anionic surfactants.

The quaternary ammonium anti-static agents used in this invention can be prepared in various ways well-known in the art. Many such materials are commercially available. The quaternaries are often made from alkyl halide mixtures corresponding to the mixed alkyl chain lengths in fatty acids. For example, the “di-tallow” quaternaries are made from alkyl halides having mixed C14-C16 chain lengths. Such mixed di-long chain quaternaries are useful herein and are preferred from a cost standpoint.

As noted above, essentially any anionic group can be the counter-ion in the quaternary compounds used herein. The anionic groups in the quaternary compounds can be exchanged, one for another, using standard anion exchange resins. Thus, quaternary ammonium salts having any desired anion are readily available. While the nature of such anions has no effect on the compositions and processes of this invention, chloride ion is the preferred counter-ion from a cost standpoint.

The following are representative examples of substantially water-insoluble quaternary ammonium anti-static agents suitable for use in the compositions and processes of the instant invention. All of the quaternary ammonium compounds listed can be formulated in re-leasable combination with the detergent compositions herein, but the compilation of suitable quaternary compounds hereinafter is only by way of example and is not intended to be limiting of such compounds. Ditallowdimethylammonium chloride is an especially preferred quaternary anti-static agent for use herein by virtue of its low cost, low solubility and high anti-static activity; other useful di-long chain quaternary compounds are dietyltrimethylammonium chloride; bis-docosyltrimethylammonium chloride; didecyldimethylammonium chloride; ditallowdimethylammonium bromide; dioleyldimethylammonium hydroxide; ditallowdimethylammonium chloride; ditallowdipropylammonium bromide; ditallowdibutylammonium fluoride, cetyldecylmethyltrimethylammonium chloride, bis-ditallowdimethylammoniumsulfate; tris-ditallowdimethylammonium phosphate; and the like.

Synthetic Detergent

From about 2 to about 30 percent by weight, preferably from about 5 to about 20 percent by weight, of the instant compositions comprise a non-soap synthetic detergent selected from the group consisting of anionic synthetic detergents, nonionic synthetic detergents, amphotolytic synthetic detergents, and zwitterionic synthetic detergents. Examples of synthetic detergents of these types are described as follows:

Anionic Detergents

Anionic synthetic detergents include water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 22 carbon atoms and a moiety selected from the group
consisting of sulfonic acid and sulfuric acid ester moieties. (Included in the term alkyl is the alkyl portion of higher acyl moieties.) Examples of this group of synthetic detergents which form a part of the preferred built detergent compositions of the present invention are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₆–C₁₈ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 20 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 11.8 carbon atoms and commonly abbreviated as C₁₂₄LAS); 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 and potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium and potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl groups contain from 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 oxide acid of phosphorus. The more common solubilizing groups, of course, are -SO₃H and -SO₂H. Alkyl phosphate esters such as (R-O)₂PO₃H and ROPO₃H in which R represents an alkyl chain containing from about 8 to about 20 carbon atoms are useful herein.

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

\[
\begin{align*}
\text{where } & \text{R}_1, \text{R}_2 \text{ is alkyl of about 9 to about 23 carbon atoms (forming with the two carbon atoms an alkane group); } \\
\text{R}_3 & \text{ is alkyl of 1 to about 8 carbon atoms; and M is a water-soluble cation. }
\end{align*}
\]

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

Specific examples of betacycloxy-alkane-1-sulfonates, or alternatively 2-acrcloyloxy-alkane-1-sulfonates, useful herein include the sodium salt of 2-acetoxy-tridecane-1-sulfonic acid; the potassium salt of 2-propionylxy-tetradecane-1-sulfonic acid; the lithium salt of 2-butanoyloxy-tetradecane-1-sulfonic acid; the sodium salt of 2-pentanoyloxyc10-undecane-1-sulfonic acid; the sodium salt of 2-acetoxy-hexadecane-1-sulfonic acid; the potassium salt of 2-ocanoyloxy-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-undecane-1-sulfonic acid; the sodium salt of 2-propionylxy-docosane-1-sulfonic acid; the isomers thereof.

Preferred beta-acrcloyloxy-alkane-1-sulfonate salts herein are the alkali metal salts of beta-acrcloyloxy-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 standpoint of their excellent cleaning properties and ready availability.


Another preferred class of anionic detergent compounds herein, both by virtue of superior cleaning properties and low sensitivity to water hardness (Ca⁺⁺ and Mg⁺⁺ ions) are the alkylated α-sulfocarboxylates, containing about 10 to about 23 carbon atoms, and having the formula

\[
\begin{align*}
\text{where } & \text{R} \text{ is C₄₋C₉ alkyl, M is a water-soluble cation as hereinbefore disclosed, preferably sodium ion, and } \\
\text{R'} & \text{ is short-chain alkyl, e.g., methyl, ethyl, propyl, and butyl. These compounds are prepared by the esterification of α-sulfonated carboxylic acids, which are commercially available, using standard techniques. Specific}
\end{align*}
\]
examples of the alkylated α-sulfocarboxylates preferred for use herein include:

- ammonium methyl-α-sulfopalmitate,
- triethanolammonium ethyl-α-sulfostearate,
- sodium methyl-α-sulfopalmidate,
- sodium ethyl-α-sulfopalmidate,
- sodium butyl-α-sulfostearate,
- potassium methyl-α-sulfolaurate,
- lithium methyl-α-sulfolaurate,

as well as mixtures thereof.

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

\[
\text{OR}_1 \quad \text{H} \\
\text{R}_2 - \text{C} - \text{C} - \text{SO}_3^- \\
\text{H} \quad \text{H}
\]

where \( R_1 \) is a straight chain alkyl group having from 6 to 20 carbon atoms, \( R_2 \) is a lower alkyl group having from 1 (preferred) to 3 carbon atoms, and \( M \) is a watersoluble cation as hereinbefore described.

Specific examples of β-alkyloxy alkane sulfonates, or alternatively 2-alkyloxy-1-alkanesulfonates, having low hardness (calcium ion) sensitivity useful herein to provide superior cleaning levels under household washing conditions include:

- potassium-β-methoxydecanesulfonate,
- sodium 2-methoxytridecanesulfonate,
- potassium 2-ethoxytetradecylsulfonate,
- sodium 2-isopropoxyhexadecylsulfonate,
- lithium 2-t-butoxytetradecylsulfonate,
- sodium β-methoxyoctadecylsulfonate, and
- ammonium β-n-propoxydodecylsulfonate.

Other synthetic anionic detergents useful herein are alkyl ether sulfates. These materials have the formula \( RO(C_2H_4O)_xSO_3^-M \) wherein \( R \) is alkyl or alkenyl of about 10 to about 20 carbon atoms, \( x \) is 1 to 30, and \( M \) is a watersoluble cation as defined hereinbefore. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having about 10 to about 20 carbon atoms. Preferably, \( R \) has 14 to 18 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols are reacted with 1 to 30, and especially 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 6 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

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

Preferred herein for reasons of excellent cleaning properties and ready availability are the alkali metal coproducts- and tallow-alkyl oxylethylene ether sulfates having an average of about 1 to about 10 oxylethylene 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 amides 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:

\[ R(SO_3)^2M_2, R(SO_3M_1M_2, R(SO_3)(SO_3)M_2 \]

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 \( C_{29} \) disodium 1,2-alkyldisulfates, \( C_{15} \) to \( C_{29} \) dipotassium-1,2-alkyldisulfonates or disulfates, disodium 1,9-hexadecyl disulfate, \( C_{15} \) to \( C_{29} \) disodium 1,2-alkyldisulfonates, disodium 1,9-stearyldisulfates and 6,10-octadecyldisulfonates.

The aliphatic portion of the disulfonates or disulfonates is generally substantially linear, thereby imparting 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 ammonium cations, as well as other metals in group II A, III A, III A, IV A and IV B of the Periodic Table except for boron. The preferred watersolubilizing cations are sodium or potassium. These di-anionic detergents are more fully described in British Letters Patent 1,151,392 which claims priority on an application made in the United States of America (No. 564,556) on July 12, 1966.

Still another anionic synthetic detergents include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfo succiniminate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfo-succiniminate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; diocetyl esters 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 α-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO₃, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO₃, etc., when used in the gaseous form.

The α-olefins from which the olefin sulfonates 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 sulfo-
nates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion 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 Adrian Kessler, issued July 25, 1967, titled "Detergent Composition", the disclosure of which is incorporated herein by reference.

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

Nonionic Synthetic Detergents

Most commonly, nonionic surfactants are compounds produced by the condensation of an alkylene oxide (hydrophilic in nature) with an organic hydrophobic compound which is usually aliphatic or alkyl aromatic in nature. The length of the hydrophilic of polyoxyalkylene moiety which is condensed with any particular hydrophobic compound can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Another type of nonionic surfactants are the so-called polar nonionics derived from amine oxides, phosphine oxides or sulfoxides. Examples of suitable nonionic surfactants 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, 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, for example, from polymerized propylene, disobutylene, octene, or none. 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-isooctylphenol condensed 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 may 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 tridecane, 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 Ter-gitol 15-S-9 marketed by the Union Carbide Corporation, Neodol 23-6.5 marketed by the Shell Chemical Company and Kyro EO8 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 1,500 to 1,800 and of course exhibits water insolubility. 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 ethylene diamine and excess propylene oxide, said base having a molecular weight of from about 2,500 to about 3,000. This base is condensed with ethylene oxide to the extent that the condensation product contains from about 40 to about 80 percent 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 Tetrone compounds marketed by the Wyandotte Chemicals Corporation.

5. Surfactants having the formula RR'RR"N → O (amine oxide surfactants) wherein R' 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" which is an alkyl group containing from about 10 to about 18 carbon atoms and no ether linkages, and each R° and R'° is selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms.

Specific examples of amine oxide surfactants include: dimethyldodecylamine oxide, dimethyltetradecylamine oxide, ethylenedimethyldodecylamine oxide, cetyldimethyldodecylamine oxide, dimethylestearlylamine oxide, cetylpropylamine oxide, diethyldodecylamine oxide, diethyldodecylamine oxide, dipropyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropylamine oxide, (2-hydroxypropyl)methyltetradecylamine oxide, dimethylethylamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, and the corresponding decyl, hexadecyl and octadecyl homologs of the above compounds.

6. Surfactants having the formula RR'RR"P → O (phosphate oxide surfactants) wherein R° 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 \( R' \) which is an alkyl group containing from about 10 to about 18 carbon atoms and no ether linkages, and each \( R^1 \) and \( R^2 \) is selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms.

Specific examples of the phosphine oxide detergents include: dimethyldecyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, cetyltrimethylphosphine oxide, dimethylstearylphosphine oxide, cetyltrimethylphosphine oxide, diethyldecyldodecylphosphine oxide, diethyltetradecylphosphine oxide, dipropyldecyldodecylphosphine oxide, bis-(hydroxymethyl)dodecylphosphine oxide, bis-(2-hydroxyethyl)dodecylphosphine oxide, (2-hydroxypropyl)methyltetradecylphosphine oxide, dimethylolpropyldodecylphosphine oxide, and dimethyl-(2-hydroxy-dodecyl)phosphine oxide and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds.

7. Surfactants having the formula

\[
R^1 - S - R^2
\]

(sulfoxide surfactants) wherein \( R^1 \) is an alkyl group containing from about 10 to about 28 carbon atoms, from 0 to about 5 ether linkages and from 0 to about 2 hydroxy substituents, at least one moiety of \( R' \) being an alkyl group containing no ether linkages and containing from about 10 to about 18 carbon atoms, and wherein \( R^2 \) is an alkyl group containing from 1 to 3 carbon atoms and from zero to two hydroxy groups. Specific examples of sulfoxide surfactants include octadecyl methyl sulfoxide, dodecyl methyl sulfoxide, tetradecyl methyl sulfoxide, 3-hydroxytetradeacyl methyl sulfoxide, 3-methoxytetradeacyl methyl sulfoxide, 3-hydroxy-4-dodecylbutyl methyl sulfoxide, octadecyl 2-hydroxyethyl sulf oxide, and dodecylethyl sulf oxide.

Of all 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 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.

**Amphoteric Synthetic Detergents**

Amphoteric synthetic detergents can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, for example, carboxy, sulfonate, sulfato. Examples of compounds falling within this definition are sodium 3-(dodecylamine)-propanoate, sodium 3-(dodecylamine)-propylene-sulfonate, sodium 2-(dodecylamine)ethyl sulfonate, sodium 2-(dimethylamino)octadecaneanoate, sodium 3-(N-carboxymethyldecylamine)-propylene-sulfonate, disodium octadecyl-iminodiacetate, sodium 1-carboxymethyl-2-undecylimidazole, and sodium N,N-bis(2-hydroxyethyl)-2-sulfato-3-dodecylammonio-pholamino. Sodium 3-(dodecylamine)-propano-sulfonate is preferred.

**Zwitterionic Synthetic Detergents**

Zwitterionic surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. The cati-onic atom in the quaternary compound can be part of a heterocyclic ring. In all of these compounds there is at least one aliphatic group, straight chain or branched, containing from about 3 to 18 carbon atoms and at least one aliphatic substituent containing an anionic water-solubilizing group, for example, carboxy, sulfonate, sulfate, phosphato, or phosphono. Examples of various classes of zwitterionic surfactants operable herein are described as follows:

1. Compounds corresponding to the general formula

\[
R_1 - \Theta_1 - R_2 - Z_\Theta^O
\]

wherein \( R_1 \) is alkyl, alkenyl or a hydroxylalkyl containing from about 8 to about 18 carbon atoms and containing if desired up to about 10 ethylene oxide moieties and/or a glyceryl moiety; \( Y_1 \) is nitrogen, phosphorus or sulfur, \( R_2 \) is alkyl or monohydroxyalkyl containing 1 to 3 carbon atoms; \( x \) is 1 when \( Y_1 \) is S, 2 when \( Y_1 \) is N or P; \( R_3 \) is alkyl or hydroxyalkylene containing from 1 to about 5 carbon atoms; and \( Z \) is a carboxy, sulfonate, sulfate, phosphate or phosphonate group. Examples of this class of zwitterionic surfactants include 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate; 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropene-1-sulfonate; 2-(N,N-dimethyl-N-dodecylammonio)acetate; 3-(N,N-dimethyl-N-dodecylammonio)propanoate; 2-(N,N-dimethyl-N-octadecylammonio)ethane-1-sulfate; 3-(P,P-dimethyl-P-dodecyldiphosphono)propane-1-sulfonate; 2-(S-methyl-S-tert-hexadecyldisulfonate)ethane-1-sulfonate; 3-(S-methyl-S-dodecylsulfonio)propionate; 4-(S-methyl-S-tetradecylsulfonio)butyrate; 3-(N,N-dimethyl-N-4-dodecylammonio)propane-1-sulfonate; 3-(N,N-dimethyl-N-2-diethoxyhexadecylammonio)propane-1-phosphate; and 3-(N,N-dimethyl-N-4-glyceryldodecylammonio)propanoate.

Preferred compounds of this class from a commercial standpoint are 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropene-1-sulfonate; 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropene-1-sulfonate; the alkyl group being derived from tallow fatty alcohol; 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate; 3-(N,N-dimethyl-N-tetradecylammonio)propane-1-sulfonate; 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropene-1-sulfonate, the alkyl group being derived from the middle cut of coconut fatty alcohol; 3-(N,N-dimethyldecylammonio)-2-hydroxypropene-1-sulfonate; 4-(N,N-dimethyl-tetradecylammonio)butane-1-sulfonate; 4-(N,N-dimethyl-N-hexadecylammonio)butane-1-sulfonate; 4-(N,N-dimethyl-hexadecylammonio)butyrate; 4-(N,N-dimethyl-N-octadecylammonio)hexanoate; 3-
**3,862,058**

(N,N-dimethyl-N-eicosylammonio)-3-methylpropane-1-sulfonate; and 6-(N,N-dimethyl-N-hexadecylammonio)hexanoate.

Means for preparing many of the surfactant compounds of this class are described in U.S. Pat. Nos. 2,129,264, 2,774,786, 2,813,898, 2,828,332 and 3,529,521 and; German Pat. No. 1,018,421 all incorporated herein by reference.

2. Compounds having the general formula:

\[ R_4 - M - R_5 - N - R_8 - COO^- \]

wherein \( R_4 \) is an alkyl, cycloalkyl, aryl, aralkyl or alkoxyalkyl group containing from 10 to 20 carbon atoms; \( M \) is a bivalent radical selected from the group consisting of aminocarboxyl, carboxylamino, carboxyloxy, aminocarboxyloxy, and the corresponding thio groupings and substituted amino derivatives; \( R_5 \) and \( R_8 \) are alkylene groups containing from 1 to 12 carbon atoms; \( R_6 \) is alkyl or hydroxyalkyl containing from 1 to 10 carbon atoms; \( R_7 \) is selected from the group consisting of \( R_8 \) groups, \(-M-\), \(-R_8\) COOMe wherein \( R_4 \), \( R_5 \), \( R_6 \) and \( R_7 \) are as defined above and \( Me \) is a monovalent salt-forming cation. Compounds of the type include \( N_4 \), \( N_2 \)-bis(oleamidopropyl)-N-methyl-N-carboxyethylammonium betaine; \( N_2 \)-bis(stearamidopropyl)-N-methyl-N-carboxylethylammonium betaine; \( N_4 \)-stearamidopropyl)-N-methyl-N-carboxymethyethylammonium betaine; \( N_4 \)-bis(oleamidopropyl)-N(2-hydroxyethyl)-N-carboxylethylammonium betaine; and \( N_2 \)-bis(stearamidopropyl)-N(2-hydroxyethyl)-N-carboxymethyethylammonium betaine.

Zwitterionic surfactants of this type are prepared in accordance with methods described in U.S. Pat. No. 3,265,719 and DAS 1,018,421.

3. Compounds having the general formula:

\[ R_9 - \text{CH} \backslash (\text{CH}_2) \_ n \text{CH} \backslash \text{SO}_3^- \]

wherein \( R_9 \) is an alkyl group, \( R_{10} \) is a hydrogen atom or an alkyl group, the total number of carbon atoms in \( R_9 \) and \( R_{10} \) being from 8 to 16 and

represents a quaternary ammonium group in which each group \( R_{11} \), \( R_{12} \) and \( R_{13} \) is an alkyl or hydroxyalkyl group or the groups \( R_{11} \), \( R_{12} \) and \( R_{13} \) are conjoined in a heterocyclic ring and \( n \) is 1 or 2. Examples of suitable zwitterionic surfactants of this type include the \( \gamma \) and \( \delta \) hexadecyl pyridino sulfobetaines, the \( \gamma \) and \( \delta \) hexadecyl \( \gamma \)-picolino sulfobetaines, the \( \gamma \) and \( \delta \) tetradecyl pyridino sulfobetaines and the hexadecyl trimethylammonio sulfobetaines. Preparation of such zwitterionic surfactants is described in South African patent application 69/5788.

4. Compounds having the general formula:

\[ R_{14} - M - R_{17} - Z_1 \]

wherein \( R_{14} \) is an alkylaryl group containing from about 8 to 24 carbon atoms in the alkyl chain; \( R_{16} \) is a hydrogen atom or an alkyl group or hydroxyalkyl group containing from 1 to 7 carbon atoms; \( R_{18} \) is alkyl or hydroxyalkyl containing from 1 to 7 carbon atoms; \( R_{16} \) is alkyne or hydroxyalkylene containing from 1 to 7 carbon atoms and \( Z_1 \) is selected from the group consisting of sulfonate, carboxy and sulfate. Examples of zwitterionic surfactants of this type include 3-(N-dodecylbenzyl)-N,N-dimethylammonio)propene-1-sulfonate; 4-(N-dodecylbenzyl-N,N-dimethylammonio)butane-1-sulfonate; 3-(N-hexadecylbenzyl)-N,N-dimethylammonio)propene-1-sulfonate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)propionate-4; (N-hexadecylbenzyl-N,N-dimethylammonio)butate; 3-(N-tetradecylbenzyl)-N,N-dimethylammonio)propene-1-sulfate; 3-(N,N-di(dodecylbenzyl))-N,N-dimethylammonio)propene-1-sulfonate; 4-[N,N-di(hexadecylbenzyl)]-N,N-dimethylammonio)butrate; and 3-[N,N-di(tetradecylbenzyl)-N,N-dimethylammonio)-2-hydroxypropene-1-sulfonate.

Zwitterionic surfactants of this type as well as methods for their preparation are described in U.S. Pat. Nos. 2,697,116; 2,697,656 and 2,669,991 and Canadian Pat. No. 883,864, all incorporated herein by reference.

5. Compounds having the general formula:

\[ R_{19} - (\text{CH}_2) \_ n \text{CH} \backslash \text{SO}_3^- \]

wherein \( R_{19} \) is an alkylphenyl cycloalkylphenyl or alkenylphenyl group containing from 8 to 20 carbon atoms, in the alkyl, cycloalkyl or alkenyl moiety; \( R_{19} \) and \( R_{20} \) are each aliphatic groups containing from 1 to 5 carbon atoms; \( R_{21} \) and \( R_{22} \) are each hydrogen atoms, hydroxy groups or aliphatic groups containing from 1 to 3 carbon atoms and \( R_{23} \) is an alkylene group containing from 2 to 4 carbon atoms.

Examples of zwitterionic surfactants of this type include 3-(N-dodecylbenzyl)-N,N-dimethylammonio)propene-1-sulfonate; 4-(N-hexadecylbenzyl-N,N-dimethylammonio)butane-1-sulfonate; 3-(N-tetradecylbenzyl)-N,N-dimethylammonio)propene-1-sulfonate; and 3-(N-dodecylbenzyl)-N,N-dimethylammonio)propene-1-sulfonate. Compounds of this type are described more fully in British Pat. Nos. 970,883 and 1,046,252, incorporated herein by reference.

Of all the above-described types of zwitterionic surfactants, preferred compounds include 3-(N,N-dimethyl-N-alkylammonio)propene-1-sulfonate and 3(N,N-dimethyl-N-alkylammonio)-2-hydroxypropene-1-sulfonate wherein in both compounds the alkyl group averages 14.3 carbon atoms in length; 3(N,N-dimethyl-N-hexadecylammonio)-propene-1-sulfonate; 3(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropene-1-sulfonate; and 3-(N-dodecylbenzyl)-N,N-
Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Pat. No. 755,038, e.g., a ternary mixture of sodium tripolyphosphate, trisodium nitroliotriacetate and trisodium ethane-1-hydroxy-1,1-diphosphonate.

While any of the foregoing alkaline poly-valent builder materials are useful herein, sodium tripolyphosphate, sodium nitroliotriacetate, sodium mellitate, sodium citrate and sodium carbonate are preferred herein for this builder use. Sodium tripolyphosphate is especially preferred herein as a builder both by virtue of its detergent builder activity and its ability to homogeneously and quickly disperse the smectite clays throughout the aqueous laundry media without interfering with clay deposition on the fabric surface. Sodium tripolyphosphate is also especially effective for suspending illite and kaolinite clay soils and retarding their redeposition on the fabric surface.

The detergent builders are used at concentrations of from about 10 percent to about 60 percent, preferably 20 percent to 50 percent, by weight of the detergent compositions of this invention.

Clay Compounds

The fourth essential component of the present compositions consists of particular smectite clay materials to provide fabric softening concurrently with fabric cleansing. These smectite clays are present in the detergent compositions at levels from about 1 percent to about 50 percent, preferably from 5 percent to 15 percent by weight, of the total compositions. The clays used herein are "impalpable," i.e., have a particle size which cannot be perceived tactiley. Impalpable clays have particle sizes below about 50 microns; the clays used herein have a particle size range of from about 5 microns to about 30 microns.

The clay minerals used to provide the softening properties of the instant compositions can be described as expandable, three-layer clays, i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100 g. of clay. 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_O)_{2-x}(OH)_x and Mg_2(Si_O)_4(OH)_2, for the aluminum and magnesium oxide type clays, 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 present 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 crystall 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:

\[ \text{smectite clay (Na)} + \text{NH}_4\text{OH} \rightarrow \text{smectite clay (H}_4\text{)} + \text{NaOH} \]

Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of millequivalents per 100 g. of clay (meg/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 Grishaw, "The Chemistry and Physics of Clays", pp. 264–265, Interscience (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, in 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 meg/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 meg/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, as noted above, are removed from fabric surfaces by means of the instant compositions. However, smectites, such as nontronite, having an ion exchange capacity of approximately 50 meg/100 g., saponite, which has an ion exchange capacity of 70 meg/100 g., and montmorillonite, which has an ion exchange capacity greater than 70 meg/100 g., have been found to be useful in the instant compositions in that they are deposited on the fabrics to provide the desired softening benefits. Accordingly, clay minerals useful herein can be characterized as expandable, three-layer smectite-type clays having an ion exchange capacity of at least about 50 meg/100 g. A smectite-type clay known as "foober clay," found in a relatively thin vein above the Black Hills, also has the requisite ion exchange characteristics of the clays useful herein and such fooler clay is also encompassed by the term "smectite-type clay," as used herein.

The smectite clays used in the compositions herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoiite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under various tradenames, for example, Thixogel No. 1 (also, "Thixo-Jell") and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC and Volclay No. 325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH450, from International Minerals and Chemicals; and Vegum Pro and Vegum F, from R. T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained under the foregoing tradenames can comprise mixtures of the various discreet mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

While any of the 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 is an extremely white form of smectite clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3 percent of iron (expressed as Fe$_2$O$_3$) 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 product performance. On the other hand, certain smectite clays 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, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type minerals for use in the granular detergent compositions disclosed herein.

Optional Components

The detergent compositions disclosed herein can contain other materials commonly used in such compositions. For example, various soil-suspending agents such as carboxymethylcellulose, corrosion inhibitors, dyes, fillers such as sodium sulfate and silica, optical brighteners, 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, can also be employed herein. Bound water can also be present in said detergent compositions.

Composition Preparation

The clay-containing detergent compositions of this invention are in granular form. The compositions can be conveniently prepared in standard fashion by admixing the detergent compound, clay and optional ingredients in a crutcher and spray-drying the mixture to form granules. Following this, the quaternary ammonium anti-static agent can be sprayed on the granules from a melt. It is a critical aspect of this invention to avoid affixing the quaternary compound to the surface of the clay by an ion exchange mechanism; accordingly, it is preferable to avoid spraying the detergent granules with an aqueous solution or suspension of the quaternary compound. The ion-exchange problem is avoided by employing a melt of the quaternary compound to
spray the granules. The compositions are then added to water to provide a laundering liquor containing the instant compositions to the extent of from about 0.02 percent to about 2 percent by weight. Soiled fabrics are added to the laundering liquor and cleansed in the usual manner. The effective amount of the detergent compositions to be used will depend to an extent on the weight of clothes being laundered and their degree of soiling. Aqueous laundering baths containing said compositions provide adequate cleaning, softening and anti-static benefits with soiled fabrics, especially cotton and cotton/polyester blends. The suspended clay material in the laundering liquor also serves to adsorb fugitive dyes in solution, thereby reducing or inhibiting dye transfer.

The granular built detergent compositions and processes of the instant invention are illustrated by the following examples. The following test is used to assess through-the-wash anti-static efficacy of the test products.

Anti-Static Test

A bundle of mixed fabrics (ca. 53% all-cotton; 12% 65/35 polyester/cotton blend; 17% nylon; 18% Da-cron®) is washed for 10 minutes in a miniature agitator containing two gallons of aqueous washing liquor containing the test laundry compositions (as set forth, below). The laundering temperature is 100°F; water hardness 7 gr/gal. artificial hardness. The bundle comprises 5% by weight of the washing liquor. The bundle is spun dry and rinsed for two minutes in two gallons of water at 100°F and 7 gr/gal. hardness. The fabrics are then dried in a commercial dryer for 50 minutes.

The static charge on each fabric is then measured by a standard electrostatic technique. The sum of the absolute values of the charges on all fabrics in the bundle, summed by the area of the fabric (yards²) of the total fabric surface (2 sides of the fabric) is then computed. This so-called “static value”, in volts/yd², correlates with gross observations of the effects of static charges on fabric surfaces, i.e., electrical shocks, fabric clinging, etc. Depending on the fabric bundle tested, no static cling is exhibited by fabrics having a static value of less than about 1.5 v/yd²; substantial static cling is noted in fabrics having a static value above about 4.5 v/yd².

EXAMPLE I

Composition A

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactant*</td>
<td>16.6</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>43.3</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>5.8</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>10.0</td>
</tr>
<tr>
<td>Gelwhite GP</td>
<td>9.8</td>
</tr>
<tr>
<td>Ditallowdimethylammonium chloride</td>
<td>2.0</td>
</tr>
<tr>
<td>Miscellaneous minors**</td>
<td>ex. 3.5</td>
</tr>
<tr>
<td>Moisture</td>
<td>Balance</td>
</tr>
</tbody>
</table>

*1.2:1 sodium tallow alkyl sulfate:sodium C₁₄₆ linear alkyl benzene sulfonate
**Including perfumes, carboxymethylcellulose, coconut alcohol ethoxide and perfume

Composition A is prepared by admixing all components except the ditallowdimethylammonium chloride in a crutcher and spray-drying to form granules consisting of the surfactant, builder, clay, etc. The granules are then uniformly sprayed with a melt of the ditallowdimethylammonium chloride.

Composition A is admixed with water at a concentration of 0.12 percent by weight and used to launder soiled fabrics in standard fashion. The fabrics are cleaned and softened and the static charge, as measured by the foregoing test, is substantially reduced.

The ditallowdimethylammonium chloride of Composition A is replaced by an equivalent amount of dioleoyldimethylammonium bromide, bis-[ditallowdimethylammonium] carbonate and tris-[ditallowdibutylammonium] phosphate, respectively, and equivalent cleansing, softening and anti-static results are secured.

EXAMPLE II

Composition B

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactant*</td>
<td>12.8</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>37.8</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>4.5</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>10.8</td>
</tr>
<tr>
<td>Voltclay BC</td>
<td>11.5</td>
</tr>
<tr>
<td>Ditallow dimethyl ammonium chloride</td>
<td>0.92</td>
</tr>
<tr>
<td>Miscellaneous minors**</td>
<td>4.2</td>
</tr>
<tr>
<td>Moisture</td>
<td>Balance</td>
</tr>
</tbody>
</table>

*1.2:1 sodium tallow alkyl sulfate:sodium C₁₄₆ linear alkyl benzene sulfonate
**Including perfume, brighteners, carboxymethylcellulose and coconut benzoxethoxylate ex. 0.6%

Composition B (prepared in the same manner as Composition A, above) was employed in the anti-static test set forth hereinabove. In this test, Composition B was used at a solution concentration of 0.131 percent by weight. Fabrics laundered in the aqueous bath containing Composition B were tested for static charge following each of two wash-rinse-drying cycles. After one cycle, fabrics laundered in Composition B had a static value of 1.2; after two cycles the static value was 1.7. As a point of comparison, fabrics laundered in a built, anionic detergent composition without clay or quaternary ammonium salt had a static value of 8.0 after the first cycle and 8.6 after the second cycle. Fabrics laundered in a built, anionic detergent composition containing a clay softener had a higher static value than fabrics laundered in liquors without clay.

As can be seen from the foregoing examples, the compositions herein provide substantial softening and anti-static benefits. Furthermore, the compositions herein overcome the problem associated with increased static charge buildup on fabrics laundered with detergents containing clay softeners, alone.

Compositions A and B of the instant invention also provide excellent cleaning and detergency when employed in washing solutions at the specified concentrations.

Substantially similar detergency, softening and anti-static results are obtained when the anionic surfactant mixture in Compositions A and B is replaced with an equivalent amount of 2-acetoxy-tridecane-1-sulfonic acid; sodium methyl-α-sultopalmitate; sodium α-methoxyoctadecylsulfonate; sodium coconut alkyl ethylene glycol ether sulfonate; and the sodium salt of the sulfuric acid ester of the reaction product of one mole of tallow fatty alcohol and three moles of ethylene oxide, respectively.

Substantially similar detergency, softening and anti-static benefits are obtained when the anionic surfactant...
mixture in Compositions A and B is replaced with an equivalent amount of 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 with about 11 moles 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, respectively.

Substantially similar detergent, softening and anti-static benefits are obtained when the anionic surfactant mixture in Compositions A and B is replaced with an equivalent amount of 3(N,N-dimethyl-N-alkylammonio)-propene-1-sulfonate or 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)-propene-1-sulfonate; 3(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)-propene-1-sulfonate; 3-(N-dodecylbenzyl-N,N-dimethylammonio)acetate; 3-(N-dodecylbenzyl-N,N-dimethylammonia)propionate; 6-(N-dodecylbenzyl-N,N-dimethylammonio)hexanoate; (N,N-dimethyl-N-hexadecylammonio)acetate; and sodium 3-(dodecylamino)-propene-1-sulfonate, respectively.

Substantially similar detergent, softening and anti-static benefits are obtained when the sodium tripolyphosphate builder in Compositions A and B is replaced with an equivalent amount of sodium nitritocitrate; sodium mellitate; sodium citrate; and sodium carbonate, respectively.

Substantially similar detergent, softening and anti-static benefits are obtained when the clay softening agent in Compositions A and B is replaced with an equivalent amount of volchonskoite; nontronite; hectorite; sauconite; and vermiculite, respectively, all such clays having an ion-exchange capacity at least about 50 meq/100 g.

Substantially similar detergent, softening and anti-static benefits are obtained when the quaternary ammonium anti-static agent in Compositions A and B is replaced by ditallowdimethylammonium bromide; ditallowdiheximmonium chloride; dioctadecyl dibutylnonmmonium chloride; and ditallowdimethylammonium hydroxide, respectively.

In addition to the fabric softening and anti-static benefits which the built laundry detergent compositions of this invention provide, the compositions provide still other advantages. For example, the dye-transfer inhibition noted above is a significant advantage not commonly shared by ordinary laundering and fabric softening compositions.

Moreover, the particular class of clays described herein which are deposited on the fabrics provide a soil-release benefit. The clays are adsorbed by the fabrics being washed providing an improved soil-release surface. The benefit from this treatment is that during subsequent washings, stains and soils are more easily removed from the fabrics as compared to a fabric which has not previously been exposed to a treatment by the clay-containing compositions of this invention. Furthermore, all of these benefits are enjoyed without impairing the water-absorbent qualities of the treated fabric. This is in marked contrast with ordinary quaternary ammonium fabric softeners which reduce the water-absorbent property of treated fabrics after several fabric treatments.

It is especially significant that each of the benefits described above in no way impairs or interferes with the general overall cleaning effectiveness of the detergent composition, even in compositions containing anionic surfactants. The fact that these benefits are attained during the relatively brief span of a short washing cycle, for example about 6 to about 15 minutes, is especially noteworthy.

What is claimed is:

1. A granular, built laundry detergent composition, comprising:

   a. from about 2 percent to about 30 percent by weight of a non-soap synthetic detergent compound selected from the group consisting of anionic synthetic detergents, nonionic synthetic detergents, ampholytic synthetic detergents, zwitterionic synthetic detergents and mixtures thereof;

   b. from about 10 percent to about 60 percent by weight of an organic or inorganic detergent builder salt;

   c. from about 1 percent to about 50 percent by weight of a smectite-type clay softening agent having an ion exchange capacity of at least about 50 meq/100 g.; and

   d. from about 0.5 percent to about 15 percent of a substantially water-insoluble quaternary ammonium anti-static agent of the formula

\[ R_{n}N^{+}R_{m}^{+}X^{-} \]

wherein each R is a hydrocarbyl group containing from about 10 to about 22 carbon atoms, each R' is a hydrocarbyl group containing from 1 to about 4 carbon atoms, X is an anion and n and m is an integer from 1 to 3, at a weight ratio of said smectite-type clay to quaternary ammonium anti-static agent of from about 40:1 to about 1:1;

said quaternary ammonium compound being in releasable combination in said composition.

2. A composition according to claim 1 wherein

   a. wherein the synthetic detergent compound is an anionic synthetic detergent and is present at from about 5 percent to about 20 percent by weight;

   b. wherein the builder salt is selected from the group consisting of alkali metal carbonates, alkali metal borates, alkali metal phosphates, alkali metal polyphosphates, alkali metal tripolyphosphates, alkali metal bicarbonates, alkali metal sulfates, water-soluble amino polyacetates, water-soluble salts of phytic acid, and water-soluble polyphosphonates, and is present at from about 20 percent to about 50 by weight;

   c. wherein the smectite-type clay softening agent is selected from the group consisting of dioctadecyl expandable three-layer aluminosilicates and trioctadecyl expandable three-layer magnesium silicates and is present at from about 5 percent to about 15 percent by weight; and

   d. wherein the quaternary ammonium anti-static agent is present at a concentration of from about 0.5 percent to about 5 percent of the total composition.

3. A composition according to claim 1 wherein the smectite clay softening agent is selected from the group consisting of montmorillonites, volchonskoites, nontronites, hectorites, sauconites and vermiculites.
4. A composition according to claim 1 wherein the anionic surfactant is a water-soluble salt of an organic sulfuric reaction product containing an alkyl group of from about 8 to about 22 carbon atoms and a moiety selected from the group of sulfuric acid ester moieties and sulfuric acid ester moieties.

5. A composition according to claim 1 wherein the builder salt is selected from the group consisting of sodium tripolyphosphate, sodium nitrolothiacetate, sodium mellitate, sodium citrate and sodium carbonate.

6. A composition according to claim 1 wherein the anti-static agent is ditallowdimethylammonium chloride.

7. A composition according to claim 6 wherein the smectite-type clay softening agent is montmorillonite.

8. A composition according to claim 6 wherein the smectite-type clay softening agent is Gelwhite GP.

9. A composition according to claim 6 wherein the smectite-type softening agent is Volclay BC.

10. A granular, built laundry detergent composition, comprising:

\[ a. \] from about 5 percent to about 20 percent of a mixture, in a 1.22:1 weight ratio, of sodium tallow alkyl sulfate and sodium linear alkyl benzene sulfonate wherein the alkyl chain of the sulfonate averages about 12 carbon atoms in length;

\[ b. \] from about 20 percent to about 50 percent of a sodium tripolyphosphate builder salt;

\[ c. \] from about 5 percent to about 15 percent of a member selected from the group consisting of Gelwhite GP and Volclay BC clay softening agents; and

\[ d. \] from about 0.5 to about 5 percent by weight of ditallowdimethylammonium chloride.

11. A process for simultaneous laundering softening, and providing anti-static benefits to fabrics comprising contacting said fabrics with an aqueous medium containing from about 0.02 percent by weight to about 2 percent by weight of a composition in accordance with claim 1.