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3,649,569

TEXTILE TREATING COMPOUNDS, COMPOSITIONS AND PROCESSES FOR TREATING TEXTILES

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No Drawing. Continuation-in-part of application Ser. No. 648,527, June 5, 1967. This application May 29, 1969, Ser. No. 829,093

Int. Cl. D06m *13/30*

U.S. Cl. 252—543 17 Claims

ABSTRACT OF THE DISCLOSURE

Novel softening compounds having one long alkyl group containing 20 to 30 carbon atoms, i.e., zwitterionic, tertiary phosphine oxide and anionic sulfonate compounds; novel liquid and solid detergent softener compositions containing said novel softening compounds or ethoxylated alcohol, ethoxylated alcohol sulfate or tertiary amine oxide compounds having an alkyl group containing 20 to 30 carbon atoms. said compositions also containing either a conventional organic detergent, a brightening agent, alkaline detergency builder salts or mixtures thereof; processes for the softening of textiles during the wash or rinse cycle of the laundering process employing critical amounts of said softening compounds.

This application is a continuation-in-part of my copending application, Ser. No. 648,527, filed June 5, 1967 and now abandoned for Textile Treating Compounds, Composition and Processes for Treating Textiles.

BACKGROUND OF THE INVENTION

(1) Field of invention

This invention relates to novel softening compounds, detergent compositions containing these novel softening compounds, and processes for softening textile materials. Hereinafter the terms softening agents and softening compounds are used interchangeably.

The use of softening agents to improve the softness or "hand" of textile materials is well-known. Aside from imparting softness to textiles, softening agents generally prevent the accumulation of static electric charges and make the ironing of the textile easier. Only in the past decade have softening agents become generally known to the housewife. Prior to this time soap residues provided the same effect of "hand" or softness. With the advent of synthetic detergents which effectively remove fatty residues from the textile material this benefit disappeared. Obviously, if fatty materials were to be added to the laundering process to obtain softening, it would be necessary to add them during the rinse cycle or in the drying cycle where no synthetic detergent is present. However, such addition of fatty materials appeared impractical as a comparatively large amount (about 1% of the fabric weight) is required to produce an appreciable softening effect.

In the light of these problems, cationic surface active agents having at least one long alkyl radical, usually containing about 18 carbon atoms, were developed. They have proved to be effective softeners and can be used at very low concentrations in the rinse water, i.e., about 0.05% based on the weight of the textile. Most of the softeners used in home laundry situations today are cationics. Despite the effectiveness of these cationic softening agents, they do have certain drawbacks. For example, they are not compatible with anionic detergents which are used in most heavy-duty detergent compositions. When the cationic softening agent is used in the

presence of anionic detergents, a "scum" is formed due to the reaction between the cationic softening agent and the anionic detergent. Even if the cationic softening agents are used with a nonionic detergent, the cationics generally will not attach to the textile material during the laundering process in sufficient quantity to do much softening. Thus, the cationic softening agent must, to be effective, be added separately in the rinse cycle. Almost all of the softeners used under domestic conditions are so added, necessitating an extra step in the washing process which forces the housewife to return to the washing machine during the rinse cycle.

Another problem associated with the use of cationic softeners is their effect on the brightening effectiveness of brightener compounds used in conjunction with them. Because of yellowing associated with the use of cationic softening agents and that yellowing discoloration which inherently develops in cotton fabric on aging, it is desirable to add a brightening agent to softener formulations. Such brighteners counteract the yellow hue of the fabric by giving off a blue-white fluorescence. Addition of brighteners to softener formulations intended for household use is common and such formulations are greatly preferred by the average housewife. The best and most commonly used brighteners, however, are very inefficient when used in cationic formulations. The reasons for this are not entirely understood, but the brightness conferred to cotton by a given amount of such a brightener when it is applied to the cloth from a cationic softener solution is only one-quarter to one third as much as that brightness conferred to cotton by the same amount of brightener applied to the cloth from distilled water. Since the brightener compounds are extremely expensive, a softener formulation which would permit more efficient brightener usage would be highly desirable.

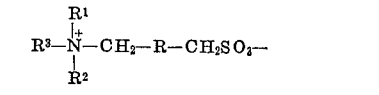
(2) Description of prior art

The lower homologs of the softening compounds which have been found to be useful in the present invention are well known as synthetic detergent compounds. The following patents disclose the lower homologs of the softening agents of this invention: DAS 1,162,966, Canadian 706,408, U.S. 3,227,749, U.S. 3,047,579, British 995,260, U.S. 3,178,370, U.S. 2,930,760 and U.S. 1,970,578. There is nothing in the art which indicates that the higher homologs of these detergent compounds would have softening characteristics.

SUMMARY

This invention provides a novel class of softening agents which contain substituents containing from 20 to 30 carbon atoms. The novel C_{20-30} substituent-containing softening agents of this invention comprise the following subclasses:

(1) Novel zwitterionic compounds having the formula

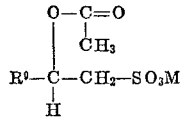


wherein R^1 and R^2 are selected from the group consisting of ethyl, methyl, n-propyl, isopropyl, 2-hydroxyethyl and 2-hydroxypropyl, R^3 is a carbon chain containing 20 to 30 carbon atoms selected from the group consisting of alkly and alkenyl groups and wherein said alkyl and alkenyl groups contain from 0–2 hydroxyl substituents, from 0–5 ether linkages and 0–1 amide linkage, and R is an alkylene group containing from 1 to 4 carbon atoms with 0–1 hydroxyl substituents;

(2) Novel tertiary phosphine oxide compounds having the formula $R^4R^5R^6P\rightarrow O$ wherein R^4 is selected from the group consisting of alkyl, alkenly and monohydroxy alkyl groups having a chain length from 20 to 30 carbon

atoms, and wherein R^5 and R^6 are each selected from a group consisting of alkyl and monohydroxy alkyl groups containing from 1 to 4 carbon atoms; and

(3) Novel anionic sulfonate compounds having the formula



wherein M is selected from a group consisting of alkali metal, ammonium and substituted ammonium cations, and R^9 is an alkyl group containing from 20 to 30 carbon atoms.

Also provided are the following compositions:

(a) Compositions comprising from about 1% to about 20% of a conventional water-soluble synthetic organic detergent having one long alkyl group containing less than 20 carbon atoms and from about 1% to about 25% of the novel softening agents of the invention or the ethoxylated alcohol, ethoxylated alcohol sulfate, or amine oxide softening agents described hereinafter;

(b) Compositions comprising from 1% to about 25% of the novel softening agents of the invention or the ethoxylated alcohol, ethoxylated alcohol sulfate, or amine oxide softening agents described hereinafter as the sole detergent and from about 1% to about 90% of a water-soluble alkaline detergency builder salts; and

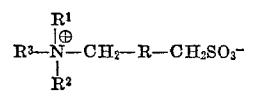
(c) Compositions comprising from 1% to about 25% of the novel softening agents of the invention or the ethoxylated alcohol, ethoxylated alcohol sulfate, or amine oxide softening agents described hereinafter, from about .01% to about 1% of brightener compounds and the balance water. This invention also provides processes for treating textile using, e.g., the above compositions and/or novel softening agents.

It has been discovered that the compounds of the present invention which are employed in the processes and compositions embodied in the invention have outstanding softening characteristics and are as effective as the most often used cationic softeners. The softening compounds of this invention neither interact with anionic detergents nor affect the brightening effectiveness of the best and most often used brightening agents as do cationic softening agents. Aside from their softening effectiveness, the softening compounds of this invention exhibit detergency characteristics. Thus, the compounds of this invention can be advantageously used in conjunction with detergents and brightening agents.

(A) NOVEL SOFTENING COMPOUNDS OF THE INVENTION

The novel compounds of the invention are characterized as follows:

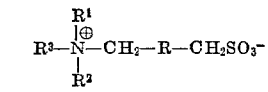
(1) Zwitterionic compounds having the formula



wherein R^1 and R^2 are each selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, 2-hydroxyethyl and 2-hydroxypropyl, R^3 is a carbon chain containing from 20 to 30 carbon atoms selected from the group consisting of alkyl and alkenyl groups and wherein said alkyl and alkenyl groups contain from 0–2 hydroxyl substituents, from 0–5 ether linkages, and 0–1 amide linkage and R is an alkylene group containing from 1 to 4 carbon atoms with 0 to 1 hydroxyl substituents.

(a) Preferred zwitterionic compounds

The preferred compounds of this class of softening agents are generically described as follows:



wherein R^1 and R^2 are each selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, 2-hydroxyethyl and 2-hydroxypropyl groups, R^3 is a carbon chain containing from 20 to 26 carbon atoms selected from the group consisting of alkyl and alkenyl groups and wherein said alkyl and alkenyl groups contain 0–2 hydroxyl substituents, and R is an alkylene group containing 1 to 4 carbon atoms with 0–1 hydroxyl substituent.

Specific examples of the most preferred compounds of this class are as follows:

3-(N-eicosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-eicosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-[N-eicosyl-N,N-di(2-hydroxyethyl)ammonio]-2-hydroxypropane-1-sulfonate
3-(N-docosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-docosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-[N-docosyl-N,N-bis-(2-hydroxyethyl)ammonio]-2-hydroxypropane-1-sulfonate
3-(N-tetracosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-tetracosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-[N-tetracosyl-N,N-bis-(2-hydroxyethyl)ammonio]-2-hydroxypropane-1-sulfonate
3-(N-hexacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-hexacosyl-N,N-dimethylammonio)-propane-1-sulfonate

Examples of other preferred compounds of this class are as follows:

3-(N-eicosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulfonate
3-(N-docosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulfonate
3-(N-docosyl-N,N-diethylammonio)-propane-1-sulfonate
3-(N-tetracosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulfonate

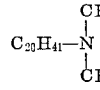
(b) Other zwitterionic compounds

Examples of other compounds within this class which are useful as softening agents are as follows:

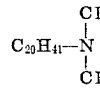
3-(N-heneicosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-heneicosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-(N-tricosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-tricosyl-N-ethyl-N-methylammonio)-2-hydroxypropane-1-sulfonate
3-(N-tricosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-(N-pentacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-pentacosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-[N-(2-methoxydocosyl)-N,N-dimethylammonio]-2-hydroxypropane-1-sulfonate
3-(N-heptacosyl-N,N-dimethylammonio)-propane-1-sulfonate
3-(N-octacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-nonacosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-triacontyl-N,N-dimethylammonio)-propane-1-sulfonate

3-[N-(2-steramidoethyl)-N-propyl-N-isopropyl]-butane-sulfonate
3-[N-(3,5-dioxatetracosyl)-N,N-dimethylammonio]-2-hydroxypropane-1-sulfonate
5-[N-(3-docosenyl)-N-(2-hydroxypropyl)-N-methyl-ammonio]pentane-1-sulfonate
6-[N-(2-hydroxydocos-4-enyl)-N,N-dimethylammonio] hexane-1-sulfonate
5-[N-(4-steramidobut-2-enyl)-N,N-diethylammonio]-2-hydroxypentane-1-sulfonate
4-[N-(3,5-dioxahexacos-10-enyl)-N,N-dimethylammonio]-3-hydroxybutane-1-sulfonate

The synthesis of the lower homologs of the novel softening compounds of this class is well known. See DAS 1,018,421 (Boehme Fettchemie G.m.b.H., Aug. 24, 1961) and Shell Bulletin IT–47–11/60. To simply illustrate such syntheses as applied to the compounds of this invention, consider the synthesis of two of the members of this class: (a) 3-(N-eicosyl-N,N-dimethylammonio) - 2 - hydroxypropane-1-sulfonate and (b) 3-(N-eicosyl-N,N-dimethylammonio)-propane - 1 - sulfonate. To form compound (a) the reaction product prepared by reacting epichlorohydrin with sodium bisulfite is reacted in turn with a tertiary amine having the following structure:



This type of quaternization reaction is described in Ralston, A. W., Fatty Acids and Their Derivatives, pp. 684–696 (1948). To form compound (b) the simplest synthesis is, generally, as follows: a tertiary amine having the following structure



is reacted with propane sultone.

(2) Tertiary phosphine oxide compounds having the formula $R^4R^5R^6P\rightarrow O$ wherein R^4 is selected from the group consisting of alkyl, alkenyl and monohydroxy alkyl groups having a chain length of from 20 to 30 carbon atoms, and wherein R^5 and R^6 are each selected from the group consisting of alkyl and monohydroxy alkyl groups containing from 1 to 4 carbon atoms.

(a) Preferred tertiary phosphine oxide compounds

Preferred compounds of this class are generically described as having the formula $R^4R^5R^6P\rightarrow O$ wherein R^4 is selected from the group consisting of alkyl, alkenyl and monohydroxy alkyl groups having a chain length of from 20 to 26 carbon atoms, and wherein R^5 and R^6 are each selected from a group consisting of methyl, ethyl and ethanol.

Specific examples of the most preferred compounds of this class are as follows:

Eicosyldimethylphosphine oxide
Eicosyldi(2-hydroxyethyl)phosphine oxide
Docosyldimethylphosphine oxide
Docosyldi(2-hydroxyethyl)phosphine oxide
Tetracosyldimethylphosphine oxide
Hexacosyldimethylphosphine oxide
Eicosyldiethylphosphine oxide
Docosyldiethylphosphine oxide
Tetracosyldi(2-hydroxyethyl)phosphine oxide

Other examples of the preferred compounds of this class are as follows:

Eicosylmethylethylphosphine oxide
Heneicosyldimethylphosphine oxide
β-Hydroxyeicosyldimethylphosphine oxide
β-Hydroxydocosyldimethylphosphine oxide
Heneicosylmethylethylphosphine oxide
Heneicosyldi(2-hydroxyethyl)phosphine oxide

Docosylmethylethylphosphine oxide
Tricosyldimethylphosphine oxide
Tricosylmethylethylphosphine oxide
Tetracosylmethylethylphosphine oxide
Tetracosyldi(2-hydroxyethyl)phosphine oxide
Pentacosyldimethylphosphine oxide
Hexacosyldi(2-hydroxyethyl)phosphine oxide

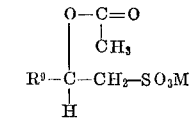
(b) Other tertiary phosphine oxide compounds

Other compounds of this class are as follows:

Eicosylmethyl-2-hydroxybutylphosphine oxide
Eicosyldibutylphosphine oxide
Eicosylmethyl-2-hydroxypropylphosphine oxide
Docosylmethyl-2-hydroxypropylphosphine oxide
Docosylmethyl-3-hydroxybutylphosphine oxide
2-tetracosenylmethylethylphosphine oxide
Heptacosyldimethylphosphine oxide
Heptacosyldiethylphosphine oxide
Octacosyldimethylphosphine oxide
Octacosyldiethylphosphine oxides
Nonacosyldimethylphosphine oxide
Nonacosyldiethylphosphine oxide
Triacontyldimethylphosphine oxide
Triacontyldiethylphosphine oxide

The lower homolog tertiary phosphine oxide of this class are prepared by methods such as those discussed by K. Darrell Berlin and G. B. Butler, "Chemical Review," vol. 60, pp. 243–259, June 1960. Using similar synthesis the tertiary phosphine oxides of this invention can be prepared by oxidizing the corresponding phosphine with, for example, hydrogen peroxide.

3. Anionic sulfonate compounds having the formula



wherein M is selected from a group consisting of alkali metal, and substituted ammonium cations, and R^9 is an alkyl group containing from 20 to 30 carbon atoms.

(a) Preferred anionic sulfonate compound

Examples of preferred softening compounds of this class are anionic sulfonate compounds having the structural formula above wherein R^9 is an alkyl group containing 20 to 26 carbon atoms, such as: sodium and potassium 2-acetoxydocosylsulfonate, ammonium 2-acetoxydocosylsulfonate, diethanolammonium 2 - acetoxydocosylsulfonate, sodium and potassium 2-acetoxytricosylsulfonate, sodium and potassium 2-acetoxytetracosylsulfonate, sodium and potassium 2-acetoxypentacosyl sulfonate, sodium and potassium 2-acetoxyhexacosylsulfonate, sodium and potassium 2-acetoxyheptacosylsulfonate, and sodium and potassium 2-acetoxyoctacosylsulfonate.

(b) Other anionic sulfonate compounds

Other suitable compounds of this class include sodium and potassium 2-acetoxynonacosylsulfonate, sodium and potassium 2-acetoxytriacontylsulfonate, sodium and potassium 2-acetoxyheneitriacontylsulfonate and sodium and potassium 2-acetoxydotriacontylsulfonate.

The following synthesis of the simplest compound of this class, sodium 2-acetoxydocosylsulfonate, is illustrative of the method by which the softening compounds of this class can be produced: Sodium 2-hydroxydocosylsulfonate (0.364 mole) is placed in a one-liter three-necked standard taper flask equipped with stirrer and condenser. A premixed solution of pyridine (1.36 moles) and acetic anhydride (7.35 moles) is added to this flask. The mixture is then heated on a steam bath for one week. Then, the mixture is evaporated to dryness and the solids dissolved in 1500 ml. of nearly boiling dioxane, treated with activated charcoal and filtered while hot. The product is then recrystallized from one liter of dioxane to produce 94.9% sodium 2-acetoxydocosylsulfonate.

(B) KNOWN COMPOUNDS USED AS SOFTENING COMPOUNDS IN THE INVENTION

(1) It has been discovered that certain known tertiary amine oxide compounds are useful as softening agents in the compositions and processes embodied in the present invention. Such tertiary amine oxide compounds have the formula $R^{10}R^{11}R^{12}N\rightarrow O$ wherein R^{10} is a straight or branched carbon chain containing from 20 to 30 carbon atoms selected from the group consisting of alkyl and alkenyl groups and wherein said alkyl and alkenyl groups contain from 0–2 hydroxyl substituents, from 0–5 ether linkages there being at least one moiety of at least 20 carbon atoms containing no ether linkages, and 0–1 amide linkage, and wherein R^{11} and R^{12} are each selected from the group consisting of alkyl and monohydroxy alkyl groups containing from 1 to 4 carbon atoms and wherein R^{11} and R^{12} can be joined to form a heterocyclic group containing from 4 to 6 atoms.

(a) Preferred tertiary amine oxide compounds

Preferred compounds of this class are generically described having the formula $R^{10}R^{11}R^{12}N\rightarrow O$ wherein R^{10} is a straight or branched carbon chain containing 20 to 26 carbon atoms selected from the group consisting of alkyl, alkenyl and monohydroxy alkyl groups and wherein R^{11} and R^{12} are each selected from a group consisting of methyl, ethyl and ethanol.

Specific examples of the softening compounds of this class which are preferably employed, alone or in combination, in the compositions and processes of this invention are as follows:

Eicosyl-bis-(β-hydroxyethyl)amine oxide
Eicosyldimethylamine oxide
Docosyldimethylamine oxide
Docosyl-bis-(β-hydroxyethyl)amine oxide
Tetracosyldimethylamine oxide
Tetracosyl-bis-(β-hydroxyethyl)amine oxide
Hexacosyldimethylamine oxide
Hexacosyl-bis-(β-hydroxyethyl)amine oxide

Examples of other preferred softening compounds of this class are as follows:

2-hydroxyeicosyldimethylamine oxide
Eicosylmethylethylamine oxide
Eicosyldiethylamine oxide
2-eicosyldiethylamine oxide
Heneicosyldimethylamine oxide
Heneicosyldiethylamine oxide
Docosylmethylethylamine oxide
Docosyldiethylamine oxide
Tricosyldimethylamine oxide
Tricosyldiethylamine oxide
Tetracosylmethylethylamine oxide
11-tetracosyldimethylamine oxide
Tetracosyldiethylamine oxide
β-Hydroxytetracosyldimethylamine oxide
Pentacosyldimethylamine oxide
Pentacosyldiethylamine oxide
Hexacosyldiethylamine oxide

(b) Other tertiary amine oxide compounds

Examples of other amine oxide softening compounds which are useful in the process of this invention, alone or in combination, are as follows:

Eicosylmethyl(2-hydroxypropyl)amine oxide
Eicosylmethylpropylamine oxide
Docosylbutylmethylamine oxide
2-docosenyldimethylamine oxide
2-methoxydocosyldimethylamine oxide
Heptacosyldimethylamine oxide
Heptacosyldiethylamine oxide
Octacosyldimethylamine oxide
Octacosylmethylethylamine oxide
Octacosyl-bis-(β-hydroxyethyl)amine oxide
Octacosyldiethylamine oxide
Nonacosyldiethylamine oxide
Nonacosyldimethylamine oxide
Triacontyldimethylamine oxide
Triacontyldiethylamine oxide
3,6-dioxaoctacosyldimethylamine oxide
2-hydroxy-4-oxatetracosyldimethylamine oxide
4-hydroxytetracos-2-enyldimethylamine oxide
4,8-triacont-2-enyldimethylamine oxide
4-stearamido-2-butenyldimethylamine oxide
N-eicosylmorpholine-N-oxide
N-docosylmorpholine-N-oxide
6-stearamidohexyldimethylamine oxide
β-Behenamidoethyldimethylamine oxide
Behenylglyceryl(β-hydroxyethyl)methylamine oxide
N-docosylpyrrolidine-N-oxide
N-eicosylpiperidine-N-oxide
N-tetracosylpyridine-N-oxide

The use of the foregoing tertiary amine oxide compounds as softening agents for the treatment of textiles during the rinse cycle is covered in the copending application of Warren I. Lyness, entitled "Softening of Textile Materials," Ser. No. 643,343, filed June 5, 1967 and now Pat. No. 3,554,784.

(2) Ethoxylated alcohol compounds having the formula $R^7—O(C_2H_4O)_xH$ wherein x equals an integer of from 3 to 45 and R^7 is an alkyl group containing from 20 to 30 carbon atoms.

(a) Preferred ethoxylated alcohol compounds

Examples of preferred softening compounds of this class are as follows: the condensation product of reacting from 3 moles to 45 moles of ethylene oxide (e.g., 3, 9, 12, 15, 20 and 30 moles) with one mole of alcohol selected from the group consisting of eicosyl alcohol, heneicosyl alcohol, tricosyl alcohol, tetracosyl alcohol, pentacosyl alcohol and hexacosyl alcohol.

The ethoxylated alcohol softening compounds of this class can be generally prepared as follows: an alcohol containing 20 to 30 carbon atoms is mixed with NaOH, and ethylene oxide is bubbled into the mixture at elevated temperatures [see Weimer and Cooper, "Component Distribution of Alcohol, Ethylene Oxide Adducts," 43 J.A.O.C.S., pp. 440–5 (July 1966)].

(3) Ethoxylated alcohol sulfates having the formula $R^8—O(C_2H_4O)_xSO_3^-M$ wherein x equals an integer of from 1 to 20, M is selected from the group consisting of alkali metals, ammonium and substituted ammonium cations, and R^8 is an alkyl group containing from 20 to 30 carbon atoms.

(a) Preferred ethoxylated alcohol sulfate compounds

Examples of preferred softening compounds of this class are as follows: The alkali metal (e.g., sodium and potassium), ammonium and substituted ammonium cation (e.g., monoethanol and diethanol ammonium) salts of the sulfated condensation product of from 1 to 20 moles of ethylene oxide (e.g., 1, 3, 9, 12, 16 and 20 moles) with one mole of alcohol selected from the group consisting of eicosyl alcohol, heneicosyl alcohol, tricosyl alcohol, tetracosyl alcohol, pentacosyl alcohol and hexacosyl alcohol.

(b) Other ethoxylated sulfate compounds

Other suitable softening compounds of this class include the alkali metal (e.g., sodium and potassium), ammonium, and substituted ammonium cations (e.g., monoethanol and diethanol ammonium) salts of the sulfated condensation product of from 1 to 20 moles of ethylene oxide with one mole of alcohol selected from the group consisting of heptacosyl alcohol, octacosyl alcohol, nonacosyl alcohol, and triacontyl alcohol.

The ethoxylated alcohol sulfates of this class can be prepared, generally, by reacting the ethoxylated alcohol compounds of (3) above with sulfuric acid and then neu-

tralizing the product with an alkali metal or substituted ammonium base (e.g., sodium, potassium, and ammonium hydroxides or carbonates).

The limits defined above in delineating the carbon content in the long alkyl group of the softening compounds of this invention were determined on the basis of economic, solubility and softening considerations. Compounds containing long alkyl groups of more than 30 carbon atoms are usually too costly and too insoluble in water, while compounds containing alkyl groups of less than 20 carbon atoms are not effective softeners.

It was discovered that each of the foregoing classes of softening compounds were surprisingly more effective than their lower homologs, i.e., the C_{18} homologs. The reason for this unexpected increase in softening effectiveness is not known and was unpredictable. The unexpected softening effectiveness of the various novel compounds of the present invention are illustrated by Example II comparing the softening effectiveness of the novel compounds with the softening effectiveness of their lower homologs.

It was found that all of the foregoing softener compounds can be employed, alone or in combination, in novel liquid and solid detergent compositions. As pointed out above, the discovery that the softener compounds of the present invention can be used in conjunction with heavy-duty anionic detergents to form detergent compositions with excellent softening characteristics is particularly advantageous.

(C) COMPOSITIONS OF THE INVENTION

The compositions of this invention comprise three embodiments as set forth in detail hereinafter. In the first embodiment, the composition comprises as essential ingredients a conventional water-soluble synthetic organic detergent and certain softening agents. In the second embodiment, the composition comprises as essential ingredients certain softening agents which also act as the sole detergent active and water-soluble alkaline detergency builder salts. The third embodiment comprises as essential ingredients certain softening agents and brightener compounds.

(1) Compositions containing conventional organic synthetic detergent as an essential ingredient

This embodiment of the present invention relates to the novel combination of synthetic organic detergent compounds with the foregoing softening agents forming liquid and granular detergent compositions which exhibit effective softening properties. These detergent compositions can, if desired, be built with various water-soluble alkaline builder salts.

More specifically, this embodiment of the present invention relates to compositions consisting essentially of:

(a) from about 1% to about 20% of a conventional water-soluble synthetic organic detergent having one long alkyl group containing less than 20 carbon atoms,
(b) from 0% to about 90% of water-soluble alkaline detergency builder salts,
(c) from about 1% to about 25% of a softening agent selected from the group consisting of subclasses (1)–(3) of the novel softening agents described above in the "Summary" section, certain previously known compounds described above in Section B, and mixtures thereof, and
(d) the balance being water, all percentages by weight.

In the foregoing detergent compositions, whether liquid or granular, the amount of softening agent present is preferably from about 2.0% to 10% by weight and the amount of detergent present is preferably from about 2% to about 18% by weight.

The softening agents of the present invention exhibit excellent detergency characteristics and it has been found that formulations containing ratios of softener to synthetic organic detergent in the range of 4:1 to about 1:20 by weight have good detergency and softening characteristics. However, formulations containing ratios of softener to synthetic organic detergent in about a 1:1 ratio have been found to have preferred detergency and softening properties.

(2) Compositions containing detergency builder as an essential ingredient

This embodiment of the present invention relates to the novel combination of the softening agents of the present invention as the sole detergent active with water-soluble alkaline detergency builder salts. More specifically, this embodiment of the present invention relates to compositions consisting essentially of

(a) from about 1% to about 25% and more preferably from about 10% to about 20% of a softening agent selected from the group consisting of subclasses (1)–(3) of the novel softening agents described above in the "Summary" section, the previously known compounds described above in Section B and mixtures thereof,
(b) from about 1% to about 90% of a water-soluble alkaline detergency builder salt, and
(c) the balance being water, all percentages by weight.

It has been discovered that the foregoing compositions exhibit excellent detergency as well as softening characteristics at a level of 0.002%–1.5% in water.

In all detergent compositions, subsections (1) and (2), which contain water-soluble alkaline detergency builder salts as a component, the ratio of said detergent including said softening agents to said builder is in the range of 3:1 to about 1:10 by weight, and preferably in the range of 2:1 to about 1:5 by weight. Generally the balance of the detergent composition is water or moisture and desired detergent additives such as brightener compounds.

(3) Liquid compositions containing brightner compound as an essential ingredient

This embodiment of the present invention relates to the novel combination of the softening agents of the invention with certain brightener compounds in liquid softener formulations. More specifically, this embodiment of the present invention relates to compositions consisting essentially of

(a) from about 1% to about 25% and more preferably from about 1% to about 10% of a softening agent selected from the group consisting of (1)–(3) of the novel softening compounds described above in the "Summary" section, and the previously known compounds described in Section B and mixtures thereof,
(b) from about 0.01% to about 1% of a brightner compound and
(c) the balance being water, all percentages being by weight.

It has been discovered that the softening compounds of the present invention do not interfere with the brightening effectiveness of the brighteners generally preferred for domestic laundering operations. These brighteners will be discussed further below. Generally, brightening agents are employed in the foregoing detergent and liquid softener formulations in the amount of 0.01% to 1.0% by weight and most preferably from 0.1% to 0.8% by weight of the total composition.

The softening compounds which are preferred for use in the detergent compositions of this invention are those preferred compounds set out in Section A and Section B above. Softening agents (1)–(3) are the most preferred compounds. The preferred softening agents for the compositions of embodiment 3 are novel softening agents (2)–(3) and the known compounds of section B.

Water soluble synthetic organic detergents.—Among the synthetic organic detergents which can be employed in the foregoing detergent compositions and are within the contemplation of this invention are as follows:

(a) Anionic synthetic detergents: This class of synthetic detergents can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 18 carbon atoms, and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the synthetic detergents which form a part of the preferred compositions of the present invention are the sodium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8–C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkylbenzenesulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, especially those of the types described in United States Letters Patent Nos. 2,220,099 and 2,477,383; sodium alkylglyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium or potassium salts of alkylphenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 to about 12 carbon atoms; 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 amines of a methyltauride in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number being specifically set forth in United States Letters Patent Nos. 2,486,921; 2,486,922 and 2,396,278.

(b) Nonionic synthetic detergents: This class of synthetic detergents may be broadly defined as compounds, aliphatic or alkyl aromatic in nature, which do not ionize in water solution.

For example, a well-known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water-insolubility has a molecular weight of from about 1200 to 2500. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water-solubility of the molecule as a whole and the liquid character of the product is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include:

(1) The polyethylene oxide condensates of alkylphenols, e.g., the condensation products of alkylphenols or dialkylphenols wherein the alkyl groups contain 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 amount equal to 10 to 25 moles of ethylene oxide per mole of alkylphenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, n-octene, or n-nonene, for example.

(2) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylenediamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000, are satisfactory.

(3) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(4) Long chain tertiary amine oxides corresponding to the following general formula, $RR'R''N\rightarrow O$, wherein R is an alkyl radical of from about 8 to 18 carbon atoms, and R' and R'' are each methyl or ethyl radicals. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, dimethyloctylamine oxide, dimethyldecylamine oxide, dimethyltetradecylamine oxide, dimethylhexadecylamine oxide.

(5) Long chain tertiary phosphine oxides corresponding to the following general formula, $RR'R''P\rightarrow O$ wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging from 10 to 18 carbon atoms in chain length and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond. Examples of suitable phosphine oxides are:

Dimethyldodecylphosphine oxide
Dimethyltetradecylphosphine oxide
Ethylmethyltetradecylphosphine oxide
Cetyldimethylphosphine oxide
Dimethylstearylphosphine oxide
Cetylethylpropylphosphine oxide
Diethyldodecylphosphine oxide
Diethyltetradecylphosphine oxide
Dipropyldodecylphosphine oxide
Bis-(hydroxymethyl)dodecylphosphine oxide
Bis-(2-hydroxyethyl)dodecylphosphine oxide
(2-hydroxypropyl)methyltetradecylphosphine oxide
Dimethyloleylphosphine oxide, and
Dimethyl-(2-hydroxydodecyl)phosphine oxide.

(c) Ampholytic synthetic detergents: This class of synthetic detergents can be broadly described as derivatives of aliphatic amines which contain a long chain of about 8 to 18 carbon atoms, and an anionic water-solubilizing group, e.g., carboxy, sulfo, or sulfato. Examples of compounds falling within this definition are sodium-3-dodecylaminopropionate and sodium - 3 - dodecylaminopropanesulfonate.

(d) Zwitterionic synthetic detergents: This class of synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium compounds, 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 one contains an anionic water-solubilizing group, e.g., carboxy, sulfo or sulfato. Examples of compounds falling within this definition are 3-(N,N - dimethyl - N - hexadecylammonio)-propane - 1 - sulfonate and 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate.

The anionic, nonionic, ampholytic and zwitterionic organic synthetic detergents mentioned above can be used singly or in combination in the practice of the present invention. The above examples are merely specific illustrations of the numerous detergents which can find application within the scope of this invention.

Alkaline builder salts.—Water-soluble inorganic alkaline builder salts which can be used alone with the detergent compound or in admixture with other builders are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates. (Ammonium or substituted ammonium salts can also be used.) Specific examples of such salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium pyrophosphate, potassium pyrophosphate, sodium bicarbonate, potassium tripolyphosphate, sodium hexametaphosphate, sodium

sesquicarbonate, sodium mono- and diorthophosphate, and potassium bicarbonate. Potassium pyrophosphate finds wide application especially in built liquid detergent compositions.

Examples of organic alkaline sequestrant builder salts which can be used alone with the detergent or in admixture with other organic and inorganic builders are alkali metal, ammonium or substituted ammonium, aminopolycarboxylates, e.g., sodium and potassium ethylene diaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylenediaminetriacetates, sodium and potassium nitrilotriacetates and sodium, potassium and triethanolammonium N-(2-hydroxyethyl)-nitrilodiacetates. Mixed salts of these polycarboxylates are also suitable. The alkali metal salts of phytic acid, e.g., sodium phytate are also suitable as organic alkaline sequestrant builder salts (see U.S. Pat. 2,739,942).

Examples of other suitable organic alkaline sequestrant builder salts include: water-soluble salts of ethane-1-hydroxy-1,1-diphosphonate (e.g., the trisodium and tripotassium salts—see U.S. Pat. 3,159,581); water-soluble salts of methylene diphosphonic acid (e.g., trisodium and tripotassium methylene diphosphonate and the other salts described in U.S. Pat. 3,213,030); water-soluble salts of substituted methylene diphosphonic acids (e.g., trisodium and tripotassium ethylidene, isopropylidene, benzylmethylidene, and halomethylidene diphosphonates and the other substituted methylenediphosphonates disclosed in British Pat. 1,026,366); water-soluble salts of polycarboxylate polymers and copolymers as described in the patent of Francis L. Diehl, U.S. 3,308,067 of Mar. 7, 1967 (e.g., polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid; fumaric acid; methylene malonic acid; and citraconic acid and copolymers with themselves and other compatible monomers such as ethylene); and mixtures thereof.

The detergent softener compositions of this invention can contain any of the usual adjuvants, diluents and additives, for example, water, sodium sulfate, perfumes, antitarnishing agents, antiredeposition agents, bacteriostatic agents, dyes, fluorescers, suds builders, suds depressors and the like, without detracting from the advantageous properties of the composition.

The foregoing synthetic organic detergent softener compositions can be formulated into any of the several commercially desirable composition forms, for example, granular, flake, liquid and tablet form.

According to another embodiment of this invention, all of the foregoing described softener compounds (Sections A and B) can be employed, alone or in combination, in novel processes to soften textile material.

(D) PROCESSES OF THIS INVENTION

In the practice of this embodiment of the present invention, the textile material is treated with a solution or dispersion of a softener compound, or a mixture of softener compounds of the invention during either the wash or rinse cycle of the laundering process. The detergency builders and synthetic organic detergents useful in this embodiment are the same as those described above in Section C. The softening compounds which are preferred for use in the following processes are those preferred compounds set out above in Sections A and B.

(1) Process of treating textiles during the wash cycle of the laundering process.—This embodiment of the present invention relates to a process of treating textile materials with a solution containing a softening compound of the invention. More particularly, this embodiment relates to a process comprising the step of treating said textile materials with an aqueous solution consisting essentially of

(a) from 0.001% to about 0.1% of a water-soluble synthetic organic detergent,
(b) from 0% to about 0.35% of a water-soluble alkaline detergency builder salt,
(c) from 0.001% to about 0.1% of a softener compound selected from the group consisting of subclasses (1)–(3) of the novel softening agents described above in the "Summary" section, the previously known compounds described above in Section B and mixtures thereof, and
(d) the balance being water, all percentages being by weight.

(2) *Processes of treating textiles during the rinse cycle of the laundering process.*—This embodiment of the present invention relates to a process of treating textile materials during the rinse cycle with the softening agents of the present invention. More particularly, this embodiment relates to a process of treating textiles with an aqueous solution consisting essentially of

(a) from 0.001% to about 0.1% of a softener compound selected from the group consisting of subclasses (1)–(3) described above in the "SUMMARY" section and mixtures thereof,
(b) the balance water, all percentages by weight.

(3) *Processes of treating textiles during the drying cycle of the laundering process.*—This embodiment of the present invention relates to a process of treating textile materials during the drying cycle with the softening agents of the present invention. For this embodiment, the softener compounds of this invention, including the known compounds of Section B, are attached to a flexible substrate and used in processes similar to those of U.S. Pat. 3,442,692, i.e., the flexible substrate carrying the fabric softener is placed in a conventional rotary drum clothes dryer together with clothes to be dried, thereby softening the clothes while they are dried and tumbled. It is preferred that the compositions be prepared according to the teachings of the following copending U.S. patent applications: David Russell Morton, Ser. No. 788,102, filed Dec. 30, 1968 entitled Textile Softening Agents Impregnated Into Absorbent Materials; Howard W. Krueger, Jr., Ser. No. 788,103, filed Dec. 30, 1968, entitled Fabric Softening Compositions; and especially Pablo O. Perez-Zamora, Ser. No. 819,965, filed Apr. 28, 1969, entitled Dryer Added Fabric Softening Compositions. As disclosed in these applications, preferred softeners for use in this type of composition and the method of using these compositions to soften clothes in a dryer are the novel zwitterionic compounds disclosed hereinbefore. They are preferred because they do not stain the fabrics being softened and the compositions can be used in the washing, rinsing and drying cycles. Particularly preferred are 3(N,N-dimethyl-N - eicosylammonio) - 2 - hydroxypropane-1-sulfonate; 3(N,N - dimethyl - N - docosylammonio) - 2 - hydroxypropane-1-sulfonate; and mixtures thereof.

The textile materials which are effectively softened by the treatment with the softening compounds of the present invention include artificial fibers and fabrics, either synthetic such as nylons, acrylics and polyesters, or cellulosic such as cotton, viscose rayon, cellulose acetate, and like materials. It has also been discovered that when nonwoven fabrics such as papers, e.g., tissues, napkins, etc., are treated with small amounts of the softening agents of this invention that they also become softened.

Other compatible softening agents

In the practice of all the foregoing embodiments of the present invention other softening agents, as well as additives such as perfumes, anticorrosion inhibitors and brightener compounds, can be used in conjunction with the softening compounds of the present invention. Examples of other softening agents which can be employed in combination with the softening agents of this invention appear in Chwala, "Textilhilfsmittel," Vienna 1939, particularly pages 61 to 64; March "An Introduction to Textile Finishing," London, 1948, particularly Chapter X; and Schwartz-Perry, "Surface Active Agents," New York, 1949, particularly pages 435–437. Other softening agents which can be used in conjunction with the softening com-

pounds of the present invention are characterized as follows: Ester, ether- or amide-like condensation products containing polyalcohol, polyglycol, polyglycerol radicals and suitable higher molecular, preferably long-chain aliphatic radicals with 12 to 18 carbon atoms, such as for instance fatty acid or fatty alcohol condensation products of the general formula $R—(C_2H_2O)_nH$ wherein R stands for the monovalent radical of an aliphatic alcohol or an aliphatic acid or amide with 12 to 18 carbon atoms and *n* for a number from 5 to 10; sulfated or sulfonated long-chain aliphatic alcohols; condensation products of long-chain fatty acids with hydroxy- or amino-sulfonic acids, such as compounds of the formula

$$C_{17}H_{33}COOCH_2CH_2CH_2SO_3Na$$

$$C_{17}H_{33}CONHCH_2CH_2SO_3Na$$

or

$$C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na$$

acylated or alkylated alkyl polyamines; and quaternary ammonium compounds such as ditallowalkyldimethylammonium chloride, cetylpyridinium chloride, cetyltrimethylammonium bromide and tetradecyldimethylbenzylammonium chloride; and mono- or polyesters of long-chain fatty acids with mono- or polyoxyamines.

BRIGHTENER COMPOUNDS

Examples of brightener compounds which can be used in conjunction with the softening agents of the present invention include those disclosed in Stensby, "Optical Brighteners in Fabric Softeners," Soap Chem. Specialties, 41, No. 5, 85–8 (May 1965), Netherlands Pat. 64/08162 (Unilever Jan. 1, 1965), U.S. Pat. 2,950,253 (Boehme Fettchemie G.m.b.H. Aug. 23, 1960) and Kirk et al., "Optical Brighteners," Encyclopedia Chem. Tech. 3,737–50 (1964). Specific examples of brightener compounds are cotton brighteners of the bis-triazinylstilbene type as

4,4'-bis[4-anilino-6-di(hydroxyethyl)amino-sym-triazin-2-ylamino]-2,2'-stilbenedisulfonic acid,
disodium 4,4'-bis(4-anilino-6-morpholino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,
disodium 4,4'-bis-(4,6-dianilino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,
disodium 4,4'-bis-(4-anilino-6-ethylamino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate and
disodium 4,4'-bis-(4-anilino-6-N-methylethanolamino-symtriazin-2-ylamino)-2,2'-stilbenedisulfonate;

the bis-N-acylstilbene type such as bis-benzoyl-, bis-p-aminobenzoyl- and bis-dimethoxybenzoyl- derivatives of 4,4'-diaminostilbene-2,2'-disulfonic acids; the stilbene-triazole type such as sodium-4(2H-naphtho[1,2-d]triazol-2-yl)-2-stilbenesulfonate; and the dibenzothiophenedioxide type such as 3,7-bis(p-methoxybenzoylamido)-dibenzothiophene-2,8-disulfonic acid-5,5-dioxide.

Other brightener compounds which can be used are those which are especially suitable for brightening synthetic fibers. Examples of these brighteners include the bis-azoles such as 1,2-bis(5-methyl-2-benzoxazolyl)ethylene, bis(5-methyl-2-benzoxazolyl) thiophene and N-hydroxyethyl - 1,2-bis(benzimidazolyl)ethylene; monoazole types such as 2-(m-chlorostyryl)-naphtho-[1,2-d]-oxazole and 2-styryl-benzoxazole; the pyrazoline type such as 1-p-sulfonamidophenyl-3-p-chlorophenyl-2-pyrazoline; and the coumarin type such as 4 - methyl-7-dimethylaminocoumarin and 3-phenyl-7(diamino-sym-triazinylamino)-coumarin.

When the foregoing brightener compounds are employed in the processes of the present invention, it has been found that good results are obtained when the brightener is present in the aqueous solution in the amount of about .0001% to about 0.001% by weight of the solution and most preferably from about .0002% to about 0.0005% by weight. When said brightener compounds are employed in the detergent compositions of the invention, it has been found that good results are obtained when the brightener is present in the composition in the amount of from 0.01% to about 1% and most preferably from about 0.1% to about 0.8% by weight of the total composition. Generally, these brightener compounds are used in combination for best brightening results.

The following laboratory procedures were used in connection with the examples below.

PROCEDURES USED IN EXAMPLES

(A) Preparation of test cloths

The test cloths are commercial 14" x 14" terry cloth towels (Style 600 from Cannon) which are washed three times with a typical heavy-duty built anionic detergent (described hereinafter) in a standard automatic washing machine. After having been washed they are rinsed four times in water (2 parts water per 1 part of cloth). Thereafter the cloths are dried in a standard automatic dryer. At this point the test cloths are ready for use in the tests appearing in the following examples.

(B) Laundering procedures

In the tests requiring washing or rinsing of the test cloths the following procedures and equipment are used. In all washing and rinsing operations a one-gallon Dexter washing machine is employed. The wash cycle in all instances lasts for 10 minutes and is conducted at a temperature of 130° F. The rinsing step is carried out in two stages; first, the test cloths undergo a pre-rinse which lasts for one minute and then the cloths are given a final rinse which lasts for 2 minutes. Both steps are conducted at a temperature of 100° F. The drying step is carried out in a standard automatic dryer.

The water used in the laundering process is of 7 grain hardness except in the few instances where distilled water is used (these instances are pointed out in the examples). The heavy-duty anionic detergent used in connection with the washing steps consists essentially of about 17.5% of a 50/50 mixture of sodium tallow alkyl sulfates and sodium straight-chain alkylbenzenesulfonates having an average chain length of 13.5 carbon atoms, about 50% sodium tripolyphosphate, about 6% silicate, about 14% sodium sulfate and the balance water.

(C) Determination of softener effectiveness

To determine the effectiveness of the softening compounds of the present invention the following comparisons are made: (1) to demonstrate the effectiveness of the softening agents of the present invention when used in conjunction with anionic detergents, test cloths (as described in Procedure A) are treated with the softeners of the present invention in the presence of a heavy-duty anionic detergent; and then are compared with separate sets of similar cloths which are treated with a popular cationic softener (described below) added during the rinse cycle; and (2) to demonstrate the effectiveness of the softening compounds of the present invention when added during the rinse cycle, test cloths (described in Procedure A) treated during the rinse cycle with the various softening compounds of this invention are compared with test cloths treated with the foregoing cationic softener.

The comparisons of softening effectiveness between the various softening agents are made by a panel of three experts. Each expert is presented with three pairs (one treated with softening compounds of the present invention and the other with the cationic softener) of the treated Cannon terry cloths and asked to handle each pair and select the softer of the two cloths if a difference can be discerned.

The cationic softening agent which is used is a quaternary ammonium chloride. This quaternary cationic softener has two alkyl groups containing 16–18 carbon atoms and is commercially available under the trade name of "Arquad 2HT–75" and "Aliquat H–226." This cationic

softener is employed in the following tests during the rinse cycle at a level of at least 25 parts per million (0.15 g.) which represents the normal usage level.

EXAMPLE I

(A) Synthesis of novel compounds

(1) 3 - (N-eicosyl-N,N-dimethylammonio)-2-hydroxypropane - 1 - sulfonate.—The following materials are admixed in a two gallon stirred autoclave (a pressure vessel with heating means):

Sodium metabisulfite ($Na_2S_2O_5$)—278 g. (1.39 moles)
Methanol (CH_3OH—128 g. (4.0 moles)
Sodium hydroxide (NaOH—6 g. (0.15 mole)
Water (H_2O)—464 g.

This mixture is heated for a period of 6 minutes while 259 g. or 2.8 moles of epichlorohydrin ($CH_2ClCHOCH_2$) is added. The resultant temperature after the addition of the epichlorohydrin is 200° C. At this point 12 g. of NaOH (0.3 mole) is added and the temperature maintained at 200° C. After waiting another 12 minutes 1045 g. of methanol (32.7 moles) along with 800 g. or 2.48 moles of eicosyl dimethylamine ($C_{20}H_{41}N(CH_3)_2$) are added. The temperature of the resulting mixture is then increased to 250° C. and the pressure brought to 50 p.s.i.g. After allowing the mixture to remain under these conditions for 45 minutes a sample was taken and analyzed. It was found that 31% of this mixture was 3-(N-eicosyl-N,N - dimethylammonio)-2-hydroxypropane-1-sulfonate. This compound is isolated by extracting the unreacted materials with petroleum ether and then dried in vacuo.

(2) 3 - (N-eicosyl-N,N-dimethylammonio)propane-1-sulfonate.—The following materials are admixed in a 5 liter 3-necked flask equipped with a mechanical stirrer, condenser and drying tube:

Dimethyleicosylamine—325.6 g. (1 mole)
Propane sultone—122 g. (1 mole)
Dry acetone—2 liters

The propane sultone and acetone are added simultaneously to the dimethyleicosylamine. This solution is heated and refluxed for 5 hours. After cooling to room temperature, the precipitate which forms is filtered out by a suction filtering device. The filtrate is then added to a 5 liter flask containing 2 liters of dry acetone and refluxed. During the refluxing, 500 ml. of ethanol is added at which point all of the filtrate is dissolved in the solution. This solution is cooled to 34° C. and left for 12 hours. The precipitate which forms is filtered out and air dried. It is found to be 86% yield (based on the amine starting material) of 3-(N-eicosyl-N,N-dimethylammonio)-propane-1-sulfonate.

(3) Eicosyldimethylphosphine oxide.—800 ml. of a 3 molar methyl magnesium chloride in tetrahydrofuran solution (contains 2.4 moles methyl magnesium chloride) is placed in a 3 liter 3-necked glass flask. The flask is equipped with a methanical stirring condenser, dropping funnel, thermometer, nitrogen inlet, and an outlet through a drying tube containing "Drierite." To this solution, 110 g. (0.8 mole) of diethyl hydrogen phosphite is added dropwise, while maintaining the temperature at 20–25° C. using an ice bath. After addition of the phosphite the ice bath is removed and the solution stirred one-half hour. In a separate flask 320 g. or 0.88 mole of eicosyl bromide is melted and dissolved in 100 ml. of dry tetrahydrofuran. The temperature of the reaction is raised to 40° C. The eicosyl bromide solution is then added dropwise to the foregoing mixture. The resulting mixture is stirred and refluxed for 18 hours. Thereafter the solution is cooled to 30–35° C. and poured into a beaker containing 180 ml. of water, 1200 ml. of ice and 220 ml. of concentrated HCl and; then, immediately poured into a separatory funnel where the layers are separated by extracting the water layer with 200 ml. of diethylether. The remaining solvents are evaporated on a flask evaporator and the residue dissolved in 600 ml. of $CHCl_3$. This solution is washed with 220 ml. of 10% HCl and then with 150 ml. of 15% Na_2CO_3. The solution is dried and the $MgSO_4$ filtered from the filtrate on a flash evaporator. The residue is distilled through a large-bore, short-path condenser to produce 0.4 g. of (30%) eicosyldimethylphosphine oxide.

(4) Ethoxylated alcohol compounds.—600 g. or 2.0 moles of eicosyl alcohol are admixed with 0.8 g. of sodium hydroxide (anhydrous pellets) in a two gallon stirred autoclave and the temperature of the mixture increased to about 300° C. 265 g. or 6.0 moles of ethylene oxide (liquid form) is then added to the mixture over a period of about 10 minutes with the temperature maintained at about 300° C. The reaction mixture is then cooled to a temperature below 150° C. and the pressure is vented to 40 p.s.i.g. The product is then removed by blowing it out of the autoclave vessel. The product is essentially free from impurities, and is found to have a molecular weight of 430. This is determined by "hydroxyl-value" analysis (titrating with a 0.1 N potassium hydroxide solution).

By replacing the amount of ethylene oxide in the foregoing reaction with either 880 g. (20 moles) or 1760 g. (40 moles) of ethylene oxide, it is found that the resulting products have excellent softening characteristics.

Also, the 600 g. or 2.0 moles of eicosyl alcohol in the foregoing reaction could equally be replaced with 2.0 moles of heneicosyl alcohol, tricosyl alcohol, tetracosyl alcohol, pentacosyl alcohol, or hexacosyl alcohol to produce reaction products which have excellent softening characteristics.

(5) Sulfated ethoxylated alcohol compounds.—300 grams (or 0.87 mole) of the condensation product of reacting one mole of eicosyl alcohol with one mole of ethylene oxide [as shown in the preceding synthesis (4)] is reacted with 106 g. or 0.9 mole of chlorosulfonic acid in a 500 ml. glass beaker having an agitator connected thereto. This reaction takes place at 150° to 160° C. After about 5 minutes the mixture is added to a 1500 ml. glass beaker containing 875 g. of water and 25 g. of sodium chloride. To this solution, 50 g. of a 50% sodium hydroxide solution is added. By analysis the resulting product has a molecular weight of 415 which is found by analytically determining the SO_3^- content of the product (titrating with hexadecyltrimethylammonium bromide).

(6) Sodium-2-acetoxydocosyl-1-sulfonate.—324.5 g. of 1.0 mole of docosanyl-1-oxide is mixed in a 5 liter glass flask with 104.0 g. or 1.0 mole of sodium bisulfite and 2.0 liters of a 50% solution of isopropanol. This mixture is refluxed for 1 week in a steam bath (100° C.). The mixture is then cooled to room temperature and the precipitate filtered out using a Buckner suction funnel. The precipitate is washed 3 times with pentane and then dried in vacuo. The resultant product is a 75% yield of sodium-2-hydroxydocosyl-1-sulfonate, based on the epoxide starting material. In a separate 5 liter glass flask 380.5 g. or 3.73 moles of acetic anhydride and 1592 g. or 20.15 moles of pyridine are mixed and stirred with an electric stirring device for a period of 30 minutes. To this mixture 428.6 g. or 1 mole of the foregoing reaction product (sodium-2-hydroxydocosyl-1-sulfonate) is added. This mixture is then heated to a temperature of 45–50° C. on an electric heating mantle for 12 hours. The temperature is then raised to 100-105° C. and the mixture refluxed for 10 days. At the end of the 10-day period the mixture is poured into glass beakers and the solvents evaporated on a steam bath (100° C.). The solid residue is dissolved in 3800 ml. of dioxane containing about 5 g. of charcoal and the solution warmed in a steam bath for 12 hours. The solution is filtered out and the filtrate cooled to room temperature. The precipitate is filtered out and dried in vacuo. The resultant material represented a 50% yield of sodium-2-acetoxydocosyl-1-sulfonate based on the hydroxysulfonate starting material.

EXAMPLE II

To illustrate the surprising increase in softening effectiveness between the softening compounds of the present invention and their lower homologs the following tests are conducted.

Test cloths treated in accordance with procedure A are exposed to solutions of known concentrations of the softening compounds of this invention having an alkyl radical containing 20 carbon atoms, and their corresponding lower homologs having alkyl radicals containing either 16 or 18 carbon atoms respectively. Such treatments are carried out during a normal rinse cycle using procedure B. After drying the test cloths, they are compared using procedure C for softness. The results of this comparison are shown in the following table.

Compound	No. of carbons in long alkyl carbon chain	Percent of compound by weight of solution	Softness
(A) Lower homologs:			
3-(N-hexadecyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate.	16	0.1	Fair.
3-(N-hexadecyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate.	16	0.1	Do.
Hexadecyldimethylphosphine oxide.	16	0.1	Do.
Reaction product of reacting 1 mole of hexadecyl alcohol with 3 moles of ethylene oxide.	16	0.1	Do.
Sulfated reaction product of reacting 1 mole of hexadecyl alcohol with 1 mole of ethylene oxide (sodium salt).	16	0.1	Do.
Sodium-2-acetoxyoctadeyel-1-sulfonate.	16	0.1	Do.
3-(N-octadecyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate.	18	0.05	Do.
3-(N-octadecyl-N,N-dimethylammonio)-propane-1-sulfonate.	18	0.05	Do.
Octadecyldimethylphosphine oxide.	18	0.05	Do.
Reaction product of reacting 1 mole of octadecyl alcohol with 3 moles of ethylene oxide.	18	0.05	Do.
Sulfated reaction product of 1 mole of octadecyl alcohol with 1 mole of ethylene oxide (sodium salt).	18	0.05	Do.
Sodium-2-acetoxyeicosyl-1-sulfonate.	18	0.05	Do.
(B) Novel compounds of this invention:			
3-(N-eicosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate	20	0.015	Good.
3-(N-eicosyl-N,N-dimethylammonio)-propane-1-sulfonate.	20	0.015	Do.
Reaction product of 1 mole of eicosyl alcohol with 3 moles of ethylene oxide.	20	0.015	Do.
Sulfated reaction product of reacting 1 mole of eicosyl alcohol with 1 mole of ethylene oxide (sodium salt).	20	0.015	Do.
Sodium-2-acetoxydocosyl-1-sulfonate.	20	0.015	Do.

It can be seen that it requires twice as much of the compound having an alkyl radical of 16 carbon atoms (0.1%) to achieve the same degree of softening as achieved by the compound (higher homolog) having an alkyl radical of 18 carbon atoms (0.05%). However, even more surprising is the observation that using over three times as much of compound having an alkyl radical of 18 carbon atoms (0.05%) does not soften cloths to the softness obtained using the softening compounds of this invention which have an alkyl radical of 20 carbon atoms (0.015%). No reason is known for this unexpected increase in softening effectiveness between the C_{18} and C_{20} homologs. This observation is particularly surprising in view of the fact that there is a difference in molecular structure of only 2 methylene groups between the C_{18} and C_{20} compounds.

EXAMPLE III

The following tests are made to illustrate the surprising softening effectiveness of the softening compounds of the present invention when added during the wash cycle. Four separate wash cycles per softening compound are performed according to procedure B, each wash cycle containing 6 g. of the heavy-duty built anionic detergent (described previously), and respectively. 0.075 g., 0.15 g., 0.3 g. and 0.6 g. of each of the following softening compounds:

3-(N-eicosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-eicosyl-N,N-dimethylammonio)-propane-1-sulfonate
Eicosyldimethylphosphine oxide
Reaction product of 1 mole of eicosyl alcohol with 3 moles of ethylene oxide
Sulfated reaction product of 1 mole of eicosyl alcohol with 1 mole of ethylene oxide (sodium salt)
Sodium 2-acetoxydocosyl-1-sulfonate
Eicosyldimethylamine oxide

The wash load of each cycle contains a cloth load of 5% by weight of test cloths treated according to procedure A. After washing the test cloths, each set is rinsed and dried using standard techniques. It is observed that all the dried test cloths are softened to an equal degree. To a separate set of test cloths treated in accordance with procedure A comprising a 5% by weight cloth load in a rinse cycle, 0.15 g. of the cationic softener described in procedure C is added. These cloths are subsequently dried and compared to the towels treated with the foregoing softening compounds. It is found that the softness or "hand" of all the compared cloths is substantially equal and that no degree of difference in softness is discernible.

Results similar to the foregoing are obtained in that cloths similarly treated are softened if the above described softening agents are replaced by any of the specific softening compounds found above at Section A(1)(a) "preferred zwitterionic compound." Section A(2)(a) "preferred tertiary phosphine oxide compounds"; Section B(1)(a) "preferred ethoxylated alcohol compounds." Section B(3)(a) "preferred ethoxylated alcohol sulfate compounds"; Section A(3)(a) "preferred anionic sulfonate compounds"; and Section B(1)(a) "preferred tertiary amine oxide compounds."

EXAMPLE IV

The following test illustrates the softening effectiveness of the softening compounds of this invention when employed in the rinse cycle. Test cloths treated according to procedure A (each test load containing a cloth load of 5% by weight) are washed for 10 minutes in an aqueous solution containing 6 g. of the heavy-duty anionic detergent described in procedure B. After the washing step the cloths are either rinsed in an aqueous solution containing 0.15 g. of the cationic softener described in procedure C for 0.15 g. of one of the following softening compounds:

3-(N-eicosyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate
3-(N-eicosyl-N,N-dimethylammonio)-propane-1-sulfonate
Eicosyldimethylphosphine oxide
Reaction product of reacting 1 mole of eicosyl alcohol with 3 moles of ethylene oxide
Sulfated reaction product of reacting 1 mole of eicosyl alcohol with 1 mole of ethylene oxide (sodium salt)
Sodium 2-acetoxydocosyl-1-sulfonate

After drying all test cloths treated with the softening compounds of this invention are compared with the cloth treated with the cationic softener using procedure C. It is found that those test cloths treated with the foregoing softening agents are substantially softer than those treated with the cationic softener.

Similar results can be obtained in that cloths similarly treated are softened by replacing the foregoing softening agent with any of the specific softening compounds found at Section A(1)(a) "preferred zwitterionic compound." Section A(2)(a) "preferred tertiary phosphine oxide compounds"; Section B(2)(a) "preferred ethoxylated alcohol compounds." Section B(3)(a) "preferred ethoxylated alcohol sulfate compounds"; and Section A(3)(a) "preferred anionic sulfonate compounds."

EXAMPLE V

This example shows that the brightening efficiency of a typical cotton brightener in a softening composition is much better when the softening agents of the present invention are used as the softening compounds in a softener/brightener formulation than when a typical cationic compound is used. In this test, test cloths described in procedure A are treated with aqueous dispersions consisting of about 0.005% by weight of one of the softening agents found in the following table and about 0.0002% by weight of a bis-triazinylstilbene type cotton brightener [4,4' - bis-(4-anilino-6-di[hydroxyethyl]amino-sym - triazin-2-ylamino)-2,2'-stilbenesulfonic acid]. To each solution (dispersion) a set of test cloths is added in sufficient amount to reach a cloth load of 5% by weight. After ten minutes exposure time, followed by rinsing in distilled water and drying, the test cloths are placed in a fluorimeter to determine the extent of fluorescence conferred to the fabric. The following results are obtained:

Formulation:	Fluorimeter reading
A 50–50 mixture of a eicosyldimethylamine oxide and docosyldimethylamine oxide+the above brightener	85
Eicosyldimethylphosphine oxide+the above brightener	101
A 50–50 mixture of the reaction products of reacting one mole of eicosyl alcohol and one mole of docosyl alcohol with 10 moles of ethylene oxide	100
The above described cationic softener+the above brightener	32
When no softener is added to the brightener solution	101

Thus, the interference with brightening by the softening agents of the present invention is very slight while the interference given by the cationic softener is very extensive.

Excellent softening with no interference with brightening is obtained when any of the above listed softening agents are replaced by any of the softening compounds found at Section A(1)(a) "preferred zwitterionic compound." Section A(2)(a) "preferred tertiary phosphine oxide compounds"; Section B(2)(a) "preferred ethoxylated alcohol compounds." Section B(3)(a) "preferred ethoxylated alcohol sulfate compounds"; Section A(3)(a) "preferred anionic sulfonate compounds"; and Section B(1)(a) "preferred tertiary amine oxide compounds."

Results similar to those above are observed when the brightener used in the foregoing test is replaced with any of the brighteners found at Summary D(2) "Brightener Compounds."

COMPOSITIONS

The softening compounds of the present invention can be beneficially employed in granular detergent compositions containing brighteners.

The following table sets forth examples of such formulations. These formulations are found to have excellent detergency and brightening as well as excellent softening characteristics.

TABLE I

Component	Examples (percent by weight of the composition) 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
(a) Softening agent:																	
3-(N-eicosyl-N,N-dimethylammonio)-2-hydroxy-propane-1-sulfonate	10													22		10	
3-(N-docosyl-N,N-dimethylammonio)-2-hydroxy-propane-1-sulfonate		10															
3-(N-eicosyl-N,N-dimethylammonio)-propane-1-sulfonate			7														
Eicosyldimethylphosphine oxide				10											10		10
Docosyldimethylphosphine oxide					10												
Eicosyl alcohol ethylene oxide (3 moles) reaction product						10											
Eicosyl alcohol ethylene oxide (5 moles) reaction product							10										
Sulfated reaction product of 1 mole ethylene oxide and 1 mole eicosyl alcohol (sodium salt)								10									
Eicosyldimethylamine oxide									10	10		10	25				
Sodium 2-acetoxydocosyl sulfonate											10						
(b) Builder material:																	
Sodium tripolyphosphate	30	20	30	30	35					45	55	30	40	50	35	30	20
Potassium ethane-1-hydroxy-1,1,2-triphosphonate			20	20									20			20	
Sodium nitrilotriacetate	10	20			5					8		10			5		20
Sodium ethane-1-hydroxy-1,1-diphosphonate	10	20			10							10			10		20
(c) Detergent:																	
Sodium straight chain alkyl (Av. $C_{13.5}$) benzene sulfonate	6		8		9												8
Sodium tallow alkyl sulfate			4		5												4
3-(N,N-dimethyl-N-tallow-alkylammonio)-2-hydroxypropane-1-sulfonate	5	5		5												12	
Reaction product of SO_3 and C_{18} alpha-olefin neutralized with NaOH										14	13						
Tallow alcohol ethylene oxide (5 moles) reaction product			5	3													
Tallow alkyldimethyl phosphine oxide					5										10		
Tallow alkyl di (2-hydroxy ethyl)-amine oxide												14					
(d) Brightener:																	
[4,4'-bis(4-anilino-6-dihydroxyethylamino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonic acid]	0.15	0.16		0.17	0.16					0.16	0.16			0.16	0.17		0.16
4,4'-bis(4-anilino-6-dimorpholino-sym-triazin-2-ylamino)-2,2'-stilbene disulfonate	0.14		0.16	0.13						0.15	0.16		0.16	0.16	0.13	0.16	0.17
Disodium 4,4'-bis(4,6-dianilino-sym-triazin-2-ylamino)-2,2'-stilbene disulfonate		0.14	0.14			0.16							0.14			0.16	
(e) Miscellaneous:																	
Sodium silicate (SiO_2:Na_2O=1.6)	6	5	6	5	6					5	6	6	6	6	5	6	6
Benzotriazole			.02		.02					.02	.02	.02	.02	.02		.02	
Sodium perborate	5	5		5								5		5	5		5
Sodium sulfate	10		13	10	8					13	15	10	5	7	12	13	
Coconut ammonia amide			2	2											2		
Sodium carboxymethyl cellulose	1.6	1.6	1.6	1.2	1.6					1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Sodium random octadecyl phosphonate	0.2	0.3	0.1	0.2	0.3					0.1		0.2	0.2		0.3	0.1	0.3
Water										Balance							
Form										Granular							

The softening compounds of the present invention can also be employed beneficially in homogeneous liquid formulations comprised of either (1) softening agents, synthetic detergents, brightening agents and water, or (2) softening agents, brightener and water. Liquid formulation (1) is found to have excellent detergency and brightening as well as softening characteristics. Liquid formulation (2) is found to have excellent softening and brightening characteristics. The latter formulation can be employed beneficially as either a wash or rinse additive. Examples of these liquid formulations are set forth in the following table.

TABLE II

Component	Examples (percent by weight of the composition)												
	18	19	20	21	22	23	24	25	26	27	28	29	30
(a) Softening agent:													
3-(N-eicosyl-N, N-dimethyl ammonio)-2-hydroxy propane-1-sulfonate	10												
Eicosyldimethylphosphine oxide				5	10								10
Docosyldimethylphosphine oxide						5							
Eicosyl alcohol ethylene oxide (20 moles) reaction product							10						
Docosyl alcohol ethylene oxide (20 moles) reaction product								5					
Sulfated reaction product of 3 moles ethylene oxide and 1 mole eicosyl alcohol (sodium salt)									5				
Eicosyldimethylamine oxide		5	10							10	10		
Sodium 2-acetoxyeicosyl sulfonate											5	5	
(b) Builder material: Sodium nitrilotriacetate										5			5
(c) Detergent: Ammonium straight chain alkyl (Avg. $C_{13.5}$) benzene sulfonate					2.5		2.5			2.5	2.5		2.5
(d) Brightener:													
[4, 4'-bis (4-anilino-6-dihydroxyethylamino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonic acid]	0.17	0.26		0.24	0.07		0.07		0.13	0.07	0.07		0.13
4,4'-bis (4-anilino-6-dimorpholino-sym-triazin-2-ylamino)-2,2'-stilbene disulfonate	0.07	0.04	0.34			0.13	0.07	0.06			0.07	0.07	
Disodium 4,4'-bis (4,6-dianilino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate			0.07		0.06			0.08		0.07		0.07	
(e) Miscellaneous:													
NaCl	10		10										
Ethanol	20		20										
Water							Balance						
Form							Liquid						

EXAMPLE VI

A non-woven cloth substrate, Stock A, is wrapped about a hollow, tubular cardboard core, and a rod is passed through the core and held so as to allow the substrate to easily unroll. More particularly, Stock A is a dry-laid, non-woven cloth comprising about 70% regenerated cellulose (American Viscose Corporation) and about 30% hydrophobic binder-resins (Rhoplex HA–8 on one side of the cloth, Rhoplex HA–16 on the other; Rohm & Haas, Inc.). The cloth has a thickness of about 4 to 5 mills, a basis weight of about 26 grams per square yard, and weighs about 2 grams per 100 square inches. The fibers are about ¼ inch in length, about 1.5 denier and are oriented substantially haphazardly. The fibers were lubricated with sodium oleate.

A nonionic substrate coating, having a melting point of about 114° F., is prepared by melting 200 grams of substantially solid, waxy, polymer of ethylene glycol (Carbowax 1540; M.P. about 114° F.) in a container set into a water bath heated to 150° F.

The substrate coating is applied to the substrate by means of a padding machine. This machine, "Atlas Laboratory Wringer" (Model No. LW–391, Type 11W–1) made by Atlas Electrical Devices Company, Chicago, Ill., is commercially available and is especially adaptable to small scale use. The machine basically comprises two hard rubber rollers mounted so that their surfaces touch (fit flush together). Pressure can be exerted onto the rollers and adjusted by means of weights. A trough-like pan under the rollers is so constructed as to provide guiding members along its length for feeding or leading the substrate into the rollers. The liquidified substrate coating is then placed into the pan, and the pan is heated to about 150° F. to keep the substrate coating in a liquid state. The substrate is unrolled and passed submersed through the substrate coating in the pan. The substrate, traveling at a rate of 5 to 6 feet per minute, is then directed upward and through the turning rollers onto which no weights are exerted and which squeezes off excess substrate coating. The turning rollers continuously pull the substrate through the rollers and, after solidifying (or substantially slidifying) the treated substrate, provides a substrate having its fibers substantially completely coated and its free space substantially completely filled and having about 2 grams of Carbowax 1540 per 100 square inches of the substrate.

The substrate, containing the solidified substrate coating, is then passed through a pair of transfer rollers which consists essentially of a pair of hard rubber rollers, the bottom roller sitting in a trough which contains the liquified outer coating which is a formulation (M.P. 155° F.) consisting of:

	Percent
3 - [N,N - dimethyl-N-alkyl(C_{20}–C_{22})ammonio]-2-hydroxypropane - 1 - sulfonate	60
Nonionic anti-static agent trade named "J–S Antistat"	15
Isopropyl alcohol	23.5
Perfume	1.5

As the treated substrate passes through the turning rollers, the outer coating formulation adheres to the bottom roller and is brought into contact with the face-down side of the passing substrate, thereby achieving a fabric softening composition having an outer coating on only one of its sides. After solidifying, the opposite side of substrate is then passed face-down through a second pair of transfer rollers and solidified to achieve a fabric softening composition having an outer coating on both sides.

This latter composition is substantially solid, stable to decomposition, not "runny" or dripping, and which, although waxy to the touch, does not cause the composito stick together when folded. The fabric softening composition has an outer coating of about 6 grams per 100 square inches of substrate. The total amount of inner and outer coatings is about 8 grams per 100 square inches of substrate, and results in a weight ratio of 4:1 by weight of the substrate.

Prior to rerolling, the fabric softening composition can be perforated at desired uniform lengths, or instead of rerolling, the composition can be cut at desired lengths and packaged as individual sheets.

A 12 inch by 8⅓ inch sheet of this composition is tested for softening performance in an automatic "Kenmore 800," electric clothes dryer; satisfactory fabric softening and fabric softener release are achieved and there is no staining of the fabrics, which are left with a pleasant perfume odor and no static cling.

A similar fabric softening composition is obtained when dimethylditallowalkylammonium chloride is substituted for the outer coating formulation used above and results in a fabric softening composition having an outer coating with a melting point of about 140° F.

Compositions with similar softening effectiveness result if any of the foregoing softener compounds are replaced with any of the specific compounds found at Section A(1)(a) "preferred zwitterionic compound". Section A(2)(a) "preferred tertiary phosphine oxide compounds"; Section B(2)(a) "preferred ethoxylated alcohol compounds"; Section B(3)(a) "preferred ethoxylated alcohol sulfate compounds"; Section A(3)(a) preferred anionic sulfonate compounds"; and Section B(1)(a) preferred tertiary amine oxide compounds".

Compositions with similar brightening effectiveness result if any of the foregoing brightening compounds are replaced with any of the specific brighteners found at Summary D(2) "Brightener Compounds."

The foregoing description and examples of this invention have been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of the invention.

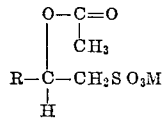
What is claimed is:

1. A detergent composition with softening properties consisting essentially of:

(a) from about 1% to about 20% of a water-soluble synthetic organic detergent selected from the group consisting of anionic detergents, nonionic detergents, ampholytic detergents and zwitterionic detergents, said detergents having one long alkyl group containing less than 20 carbon atoms,

(b) from 0% to about 90% of water-soluble alkaline detergency builder salts,

(c) from about 1% to about 25% of a softening agent having the formula

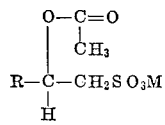


wherein M is selected from a group consisting of alkali metal, ammonium and substituted ammonium cations, and R is an alkyl group containing from 20 to 30 carbon atoms; and

(d) the balance being water, all percentages by weight.

2. The detergent composition of claim 1 wherein the amount of softening agent (c) present is from about 2.1% to about 10%.

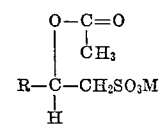
3. The detergent composition of claim 1 wherein the softening agent (c) is an anionic sulfonate compound of the formula



wherein M is selected from the group consisting of alkali metal, ammonium and substituted-ammonium and where R is an alkyl group containing from 20 to 26 carbon atoms.

4. A detergent composition with softening properties consisting essentially of:

(a) from 1% to 25% of a softening agent having the formula



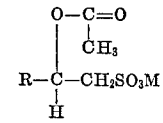
wherein M is selected from a group consisting of alkali metal, ammonium and substituted ammonium cation, and R is an alkyl group containing from 20 to 30 carbon atoms;

(b) from about 1% to about 90% of a water-soluble alkaline detergency builder salt, and

(c) the balance being water, all percentages by weight,

5. The detergent composition of claim 4 wherein the amount of softening agent (a) present is in the amount of from about 10% to about 20%.

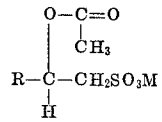
6. The detergent composition of claim 4 wherein the softening agent (a) is an anionic sulfonate compound of the formula



wherein R is an alkyl group containing from 20 to 26 carbon atoms.

7. A liquid softener composition consisting essentially of:

(a) from about 1% to about 25% of a softening agent having the formula



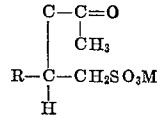
wherein M is selected from a group consisting of alkali metal, ammonium and substituted ammonium cations, and R is an alkyl group containing from 20 to 30 carbon atoms;

(b) from about 0.01% to about 1% of a brightener compound, and

(c) the balance being water, all percentages by weight.

8. The liquid softener composition of claim 7 wherein the amount of softening agent (a) is present in the amount of from 1% to about 10% and the brightener compound (b) is present in the amount of about 0.1% to about 0.8%.

9. The liquid softener composition of claim 7 wherein the softening agent (a) is an anionic sulfonate compound of the formula



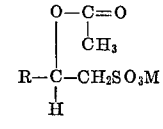
wherein R is an alkyl group containing from 20 to 26 carbon atoms.

10. The process of simultaneously washing and softening textile materials comprising the step of treating said textile materials by contacting them with an aqueous solution consisting essentially of

(a) from 0.001% to about 0.1% of a water-soluble synthetic organic detergent selected from the group consisting of anionic detergents, nonionic detergents, ampholytic detergents and zwitterionic detergents, said detergents having one long alkyl group containing less than 20 carbon atoms,

(b) from 0% to about 0.35% of a water-soluble alkaline detergency builder salt,

(c) from 0.001% to about 0.1% of a softening agent having the formula

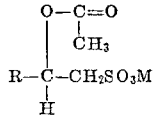


wherein M is selected from a group consisting of alkali metal, ammonium and substituted ammonium cations, and R is an alkyl group containing from 20 to 30 carbon atoms; and

(d) the balance water, all percentages by weight.

11. The process of claim 10 wherein the aqueous solution contains from about 0.002% to about 0.01% softening agent.

12. The process of claim 10 wherein the softening agent is an anionic sulfonate compound of the formula



wherein M is selected from the group consisting of alkali metal, ammonium and substituted ammonium and wherein R is an alkyl group containing from 20 to 26 carbon atoms.

13. The process of claim 10 wherein the aqueous solution also contains from about 0.0001% to about 0.001% by weight of a brightening agent selected from the group consisting of

4,4'-bis-[4-anilino-6-di(hydroxyethyl)amino-sym-triazin-2-ylamino]-2,2'-stilbenedisulfonic acid,

disodium 4,4'-bis(4-anilino-6-morpholino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,

disodium 4,4'-bis(4,6-dianilino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,

disodium 4,4'-bis(4-anilino-6-ethylamino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,

disodium 4,4'-bis(4-anilino-6-methylethanolamino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,

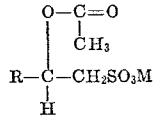
sodium-4(2H-naphtho[1,2-d]triazol-2-yl)-2-stilbenesulfonate,

2-(m-chlorostyryl)-naphth-[1,2-d]oxazole,1-p-sulfonamidophenyl-3-p-chlorophenyl-2-pyrazoline, and

1,2-bis(5-methyl-2-benzoxazolyl)ethylene, and mixtures thereof.

14. The process of softening textile materials comprising the step of treating said textile materials by contacting them with an aqueous solution consisting essentially of

(a) from 0.001% to about 0.1% of a softener compound having the formula

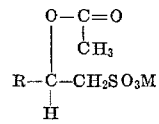


wherein M is selected from a group consisting of alkali metal, ammonium and substituted ammonium cations, and R is an alkyl group containing from 20 to 30 carbon atoms; and

(b) the balance being water, all percentages by weight.

15. The process of claim 14 wherein the aqueous solution contains from about 0.002% to about 0.01% softening agent.

16. The process of claim 14 wherein the softening agent is an anionic sulfonate compound of the formula



wherein M is selected from the group consisting of alkali metal, ammonium and substituted ammonium and wherein R is an alkyl group containing from 20 to 26 carbon atoms.

17. The process of claim 14 wherein the aqueous solution also contains from about 0.0001% to about 0.001% by weight of a brightening agent selected from the group consisting of

4,4'-bis-[4-anilino-6-di(hydroxyethyl)amino-sym-triazin-2-ylamino]-2,2'-stilbenedisulfonic acid,

disodium 4,4'-bis(4-anilino-6-morpholino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,

disodium 4,4'-bis(4,6-dianilino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,

disodium 4,4'-bis(4-anilino-6-ethylamino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,

disodium 4,4'-bis(4-anilino-6-methylethanolamino-sym-triazin-2-ylamino)-2,2'-stilbenedisulfonate,

sodium-4(2H-naphtho[1,2-d]triazol-2-yl)-2-stilbenesulfonate,

2-(m-chlorostyryl)-naphth-[1,2-d]-oxazole,

1-p-sulfonamidophenyl-3-p-chlorophenyl-2-pyrazoline, and

1,2-bis(5-methyl-2-benzoxazolyl)ethylene, and mixtures thereof.

References Cited

UNITED STATES PATENTS

2,061,617	11/1936	Downing et al.	252—8.7 X
2,061,618	11/1936	Downing et al.	252—8.7 X
2,061,619	11/1936	Downing et al.	252—353 X
2,061,620	11/1936	Downing et al.	252—353 X
2,086,215	7/1937	De Groote	260—513 R
2,094,451	9/1937	Guenther et al.	260—458 X
3,332,880	7/1967	Kessler et al.	252—161
3,014,042	12/1961	Mantz	260—309.7
3,296,145	1/1967	Findlan et al.	252—8.8 X
3,318,817	5/1967	Smith	252—152
3,329,609	7/1967	Blomfield	252—8.75 X
3,351,557	11/1967	Almstead et al.	252—152 X
3,400,148	9/1968	Quimby	252—152 X
3,454,494	7/1969	Clark et al.	252—8.8

OTHER REFERENCES

Jungermann et al., "Fatty Amine Oxides," Soap and Chemical Specialties, September 1964, pp. 59–62.

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U.S. Cl. X.R.

252—8.6, 8.7, 8.75, 8.8, 8.9, 89, 301.3, 523, 526, 528, 535, 538, 541, 545, 547, 554, 557; 260—400

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,649,569 Dated March 14, 1972

Inventor(s) Charles Bruce McCarty

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 15, line 32, "(Unilever Jan. 1, 1965)" should be -- (Unilever Jan. 18, 1965) --.
Column 15, line 36, after "type" insert -- such --.
Column 17, line 59, "methanical" should be -- mechanical --.
Columns 21 and 22, Table I, "5" and "3" adjacent "Tallow alcohol ethylene oxide (5 moles) reaction product" under Examples 3 and 4, respectively, should be under Examples 2 and 3, respectively.
Columns 21 and 22, Table I, "5" adjacent "Tallow alkyldimethyl phosphine oxide" and under Example 5 should be under Example 4.
Column 24, line 1, "slidifying" should be -- solidifying --.
Column 24, line 48, before "substrate" insert -- the --.
Column 26, line 3, Claim 4, after "weight" delete -- , -- and insert -- . --.

Signed and sealed this 7th day of November 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents