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3,630,894

**DETERGENT COMPOSITIONS**

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19 Claims

**ABSTRACT OF THE DISCLOSURE**

A detergent composition which also softens textiles and which is non-yellowing and, further, does not render the textile water repellent, comprising a surface active detergent component and a *sulfolanyl (or sulfolenyl) ester of a long chain carboxylic acid*.

The present invention relates to a detergent composition which imparts to textiles laundered therewith an outstanding and superior degree of softness and, more particularly, to detergent compositions containing an organic surface active agent as the deterative component which agent may be anionic, cationic, non-ionic, ampholytic or zwitterionic, and preferably anionic, in combination with a *sulfolanyl ester of a long chain carboxylic acid*.

The employment of various compounds and compositions, and particularly cationic quaternary ammonium compounds as softeners is very well known and conventional in the art. It is also well known to employ these materials for their softening effect during a laundering operation, and particularly in the rinse cycle of the laundering process. This technique has been necessitated by the fact that such cationic compounds as heretofore used, are not compatible with the major type of detergent presently used in the washing cycle of the laundering operation.

By far the predominating type of detergent used in home laundering, as well as in commercial and industrial laundering processes is of the anionic type and, more particularly, is of the alkali metal higher-alkyl benzene sulphonate type. The use of a cationic substance in conjunction with anionic detergent materials results in a precipitate, which is completely ineffective as a fabric softener. This manifestation of incompatibility is also undesirable, because it requires more detergent in order to accomplish the necessary and desirable degree of washing efficacy. As a consequence of these difficulties, it is generally necessary and conventional to add the presently available cationic softeners to the clothes in the absence of any anionic detergent, and obviously where this is done during washing, it must be accomplished during the rinsing cycle.

Even when the cationic softeners are used in the rinse cycle or, indeed, as a treatment for textiles generally apart from a laundering operation, there arises still another grave disadvantage due to the fact that the quaternary ammonium softeners have a tendency to build up water repellency in the treated materials, and this effect is cumulative, producing, after many treatments, a water repellent textile which becomes difficultly launderable when soiled. Still another known disadvantage of the cationic softners lies in their tendency to yellow fabrics when the latter are treated with such compounds, whether in a laundering operation at any stage, or, again, as a general treatment for textiles to soften them.

It is, therefore, an object of this invention to provide a detergent composition which is not only highly efficaceous for washing clothes, but is also outstanding for softening them as well.

It is another object of this invention to provide both liquid and solid detergent compositions wherein the active detergent ingredient may be any of the conventional detergents such as anionic, cationic, non-ionic, ampholytic or zwitterionic in combination with sulfolane esters of long chain carboxylic acids whereby there is obtained a co-action between the two components to impart to the textiles laundered with such components an outstanding degree of cleanliness, together with a remarkable degree of softness.

It is still another, further, object of this invention to provide a detergent composition, in any suitable physical form from liquid to solid state, including gels, pastes, powders, tablets, etc., which is outstanding in both cleaning and softening textiles laundered therewith, and which does not produce a noticeable yellowing of the textile material.

Still another object of this invention lies in the provision of detergent compositions which are characterized as "built" detergents, and which are not only outstanding in their laundering performance, but are also superior and unique in producing a non-yellowing, non-water repellent, soft finish on laundered goods.

Still another object of this invention lies in providing processes for making and using the detergent composition of this invention, and particularly for using such compositions in a laundering process.

Other objects will appear hereinafter as the description proceeds.

The detergent compositions of this invention comprise (1) any of the conventional surface active, deterative agents selected from the general classes of anionic, non-ionic, cationic, ampholytic and zwitterionic agents in combination with (2) a higher fatty acid ester of a sulfolanyl alcohol.

The surface active detergent compound of the compositions of this invention may as noted above, be selected from any one of the five (5) major classes of detergents, which include the anionic, cationic, non-ionic, ampholytic and zwitterionic types.

The anionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and an anionic solubilizing group. Typical examples of anionic solubilizing groups are sulfonate, sulfate, carboxylate, phosphonate and phosphate. Examples of suitable anionic detergents which fall within the scope of the invention include the soaps, such as the water-soluble salts of higher fatty acids or rosin acids, such as may be derived from fats, oils and waxes of animal, vegetable or marine origin, e.g., the sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and the sulfates and sulfonated synthetic detergents, particularly those having at least 8 and about 8 to 30, and preferably about 12 to 22, carbon atoms in the molecular structure.

As examples of suitable synthetic anionic detergents there may be cited the higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the alkyl group in a straight or branched chain, e.g., the sodium salts of higher alkyl benzene sulfonates or of the higher alkyl toluene, xylene and phenol sulfonates; alkyl naphthalene sulfonate, ammonium diamyl naphthalene sulfonate, and sodium dinonyl naphthalene sulfonate. Mixed long chain alkyls derived from coconut oil fatty acids and tallow fatty acids can also be used along with cracked paraffin wax olefins and polymers of lower mono-olefins. In one preferred type of composition there is used a linear alkyl benzene sulfonate having a high content of 3- (or higher) phenyl isomers and a correspondingly low content (well below 50%) of 2- (or lower) phenyl isomers; in other

terminology, the benzene ring is preferably attached in large part at the 3 or higher (e.g. 4, 5, 6 or 7) position of the alkyl group and the content of isomers in which the benzene ring is attached at the 2 or 1 position is correspondingly low. Particularly preferred materials are set forth in U.S. Pat. 3,320,174, May 16, 1967, of J. Rubinfeld.

Other anionic detergents are the olefin sulfonates, including long chain alkene sulfonates, long chain hydroxyalkane sulfonates or mixtures of alkenesulfonates and hydroxyalkanesulfonates. These olefin sulfonate detergents may be prepared, in known manner, by the reaction of  $\text{SO}_3$  with long chain olefins (of 8–25, preferably 12–21 carbon atoms) of the formula  $\text{RCH}=\text{CHR}_1$ , where R is alkyl and  $\text{R}_1$  is alkyl or hydrogen, to produce a mixture of sultones and alkenesulfonic acids, which mixture is then treated to convert the sultones to sulfonates. Especially good characteristics are obtained by the use of a foodstock containing a major proportion i.e. above 70% and preferably at 90%, of  $\alpha$ -olefins. Examples of such products are  $\text{C}_{14}$   $\alpha$ -olefin sulfonate,  $\text{C}_{16}$   $\alpha$ -olefin sulfonate, etc. Examples of other sulfate or sulfonate detergents are paraffin sulfonates, such as the reaction products of alpha olefins and bisulfites (e.g. sodium bisulfite), e.g. primary paraffin sulfonates of about 10–20, preferably about 15–20, carbon atoms; e.g. sodium n-pentadecane sulfonate, sodium n-octadecyl sulfonate sulfates of higher alcohols; salts of  $\alpha$ -sulfofatty esters (e.g. of about 10 to 20 carbon atoms, such as methyl  $\alpha$ -sulfomyristate or  $\alpha$ -sulfotallowate).

Examples of sulfates of higher alcohols are sodium lauryl sulfate, sodium tallow alcohol sulfate; Turkey red oil or other sulfated oils, or sulfates of mono- or di-glycerides of fatty acids (e.g. stearic monoglyceride monosulfate), alkyl poly (ethenoxy) ether sulfates such as the sulfates of the condensation products of ethylene oxide and lauryl alcohol, e.g. with 1 to 20 ethenoxy groups per molecule; lauryl or other higher alkyl glyceryl ether sulfonates; aromatic poly (ethenoxy) ether sulfates such as the sulfates of the condensation products of ethylene oxide and nonyl phenol (e.g. having 1 to 10 oxyethylene groups per molecule and usually from 2 to 10 such groups).

The suitable anionic detergents include also the acyl sarcosinates (e.g. sodium lauroylsarcosinate) the acyl esters (e.g. oleic acid ester) of isethionates, and the acyl N-methyl taurides (e.g. potassium N-methyl lauroyl- or oleyl tauride). In each instance the acyl moieties usually vary from fatty  $\text{C}_{10}$  to  $\text{C}_{20}$  to preferably  $\text{C}_{12}$  to  $\text{C}_{16}$ .

The most highly preferred water soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono-, di and triethanolamine), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of the higher alkyl benzene sulfonates, olefin sulfonates, the higher alkyl sulfates, and the higher fatty acid monoglyceride sulfates. The particular salt will be suitably selected depending upon the particular formulation and the proportions therein. Mixtures of various cations can also be used.

Nonionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and a hydrophilic group which is a reaction product of a solubilizing group such as carboxylate, hydroxyl, amido or amino with an alkylene oxide, e.g. ethylene oxide or with the polyhydration product thereof, e.g. polyethylene glycol.

As examples of such nonionic surface active agents there may be noted the condensation products of alkyl phenols with ethylene oxide, e.g., the reaction product of isooctyl phenol with about 6 to 30 ethylene oxide units; condensation products of alkyl thiophenols with 10 to 15 ethylene oxide units; condensation products of higher fatty alcohols such as tridecyl alcohol with ethylene oxide; ethylene oxide addends of monoesters of hexahy-

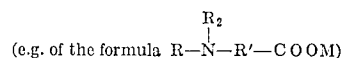
dric alcohols and inner ethers thereof such as sorbitan monolaurate, sorbitol mono-oleate and mannitan monopalmitate, and the condensation products of polypropylene glycol with ethylene oxide.

Other non-ionics include the alkylolamine condensates of higher fatty acids such as lauric and migristic mono and di-ethanolamide; the higher alkyl amine oxides such as lauryl dimethyl amine oxide, lauryl bis (hydroxyethyl) amine oxide; higher alkyl mono and di-sulfoxides, phosphine oxides and the like.

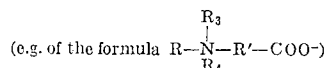
Cationic surface active agents may also be employed. Such agents are those surface active detergent compounds which contain an organic hydrophobic group and a cationic solubilizing group. Typical cationic solubilizing groups are amine and quaternary groups.

As examples of suitable synthetic cationic detergents there may be noted the diamines such as those of the type  $\text{RNHC}_2\text{H}_4\text{NH}_2$  wherein R is an alkyl group of about 12 to 22 carbon atoms, such as N-2-aminoethyl stearyl amine and N-2-aminoethyl myristyl amine; amide-linked amines such as those of the type  $\text{R}^1\text{CONHC}_2\text{H}_4\text{NH}_2$  wherein  $\text{R}^1$  is an alkyl group of about 9 to 20 carbon atoms, such as N-2-amino ethylstearyl amide and N-amino ethyl myristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom is an alkyl group of about 12 to 18 carbon atoms and three of the groups linked to the nitrogen atom are alkyl groups which contain 1 to 3 carbon atoms, including such 1 to 3 carbon alkyl groups bearing inert substituents, such as benzyl group, and there is present an anion such as halogen, acetate, methosulfate, etc. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium bromide, trimethyl stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, dimethyl-ethyl lauryl ammonium chloride, dimethyl-propyl-myristyl ammonium chloride, and the corresponding methosulfates, acetates, etc.

Examples of suitable amphoteric detergents are those containing both an anionic and a cationic group and a hydrophobic organic group, which is advantageously a higher aliphatic radical, e.g. of 10–20 carbon atoms. Among these are the N-long chain alkyl aminocarboxylic acids



the N-long chain alkyl iminodicarboxylic acids (e.g. of the formula  $\text{RN}(\text{R}'\text{COOM})_2$ ) and the N-long chain alkyl betaines



where R is a long chain alkyl group, e.g. of about 10–20 carbons,  $\text{R}'$  is a divalent radical joining the amino and carboxyl portions of an amino acid (e.g. an alkylene radical of 1–4 carbon atoms), M is hydrogen or a salt-forming metal,  $\text{R}^2$  is a hydrogen or another monovalent substituent (e.g. methyl or other lower alkyl), and  $\text{R}^3$  and  $\text{R}^4$  are monovalent substituents joined to the nitrogen by carbon-to-nitrogen bonds (e.g. methyl or other lower alkyl substituents). Examples of specific amphoteric detergents are N-alkyl-beta-aminopropionic acid; N-alkyl-beta-iminodipropionic acid, and N-alkyl, N,N-dimethyl glycine; the alkyl group may be, for example, that derived from coco fatty alcohol, lauryl alcohol, myristyl alcohol (or a lauryl-myristyl mixture), hydrogenated tallow alcohol, cetyl, stearyl, or blends of such alcohols. The substituted aminopropionic and iminodipropionic acids are often supplied in the sodium or other salt forms, which may likewise be used in the practice of this invention. Examples of other amphoteric detergents are the fatty imidazolines such as those made by reacting a long

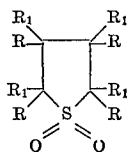
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chain fatty acid (e.g. of 10 to 20 carbon atoms) with diethylene triamine and monohalocarboxylic acids having 2 to 6 carbon atoms, e.g. 1 - coco - 5 - hydroxy - ethyl - 5-carboxymethylimidazoline; betaines containing a sulfonic group instead of the carboxylic group; betaines in which the long chain substituent is joined to the carboxylic group without an intervening nitrogen atom, e.g. inner salts of 2-trimethylamino fatty acids such as 2-trimethylaminolauric acid, and compounds of any of the previously mentioned types but in which the nitrogen atom is replaced by phosphorus.

The preferred anionic detergent compounds are selected from the general class of the linear alkyl benzene sulphonates, and olefin sulphonates, and particularly those characterized by a linear alkyl or alkenyl chain of from  $C_{10}$  to  $C_{22}$ . It is, of course, understood that the carbon chain length represents, in general, an average chain length since the methods for producing such products usually employ reagents of mixed chain lengths. Substantially, pure olefins as well as alkylating compounds used in other techniques can be employed to give alkylated benzenes, wherein the alkyl moiety is substantially (i.e. at least 99%) of one chain length, i.e.  $C_{12}$ ,  $C_{13}$ ,  $C_{14}$ , etc. Still further, it is preferred that the linear alkyl benzene sulphonate contain a low content of 2-phenyl isomers and preferably a high percentage of 5-phenyl or higher isomers thereof. The most preferred isomers are those which contain below about 35% of the 2-phenyl material. In producing olefin sulphonates, a similar situation obtains, i.e. use of mixed olefin chain length feed stock. However, again olefins of substantially one chain length are available and may be used to make the sulphonate detergent.

Water-soluble builder salts may also be present, in the usual proportions, in the detergent formulations when heavy duty cleaning is desired. These salts include phosphates and particularly condensed phosphates (e.g. pyrophosphates or tripolyphosphates), silicates, borates and carbonates (including bicarbonates), as well as organic builders such as salts of nitrilotriacetic acid or ethylene diamine tetracetic acid. Sodium and potassium salts are preferred, although alkaline earth metals, amine, alkylolamine and ammonium are contemplated. Specific examples are sodium tripolyphosphate, potassium pyrophosphate, sodium hexametaphosphate, sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, sodium tetraborate, sodium silicate, salts (e.g. Na salt) of methylene diphosphonic acid, trisodium nitrilotriacetate, or mixtures of such builders, including mixtures of pentasodium tripolyphosphate and trisodium nitrilotriacetate in a ratio, of these two builders, of 1:10 to 10:1, e.g. 1:1. The proportions of builder salt may be, for example, 50 parts or more (e.g. 50 to 1000 parts) per 100 parts of detergent.

The sulfolanyl esters useful in the present invention are characterized by the formula:

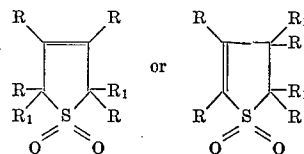


wherein one R is a higher fatty acyloxy radical and the other R's are independently hydrogen, lower alkyl ( $C_1$  to  $C_8$ ); lower acyloxy ( $C_1$  to  $C_8$ ); halogen; hydroxy; lower alkyl ( $C_1$  to  $C_8$ ) sulfonyl; carboxamide ( $CON<$ ); sulfonamide ( $SO_2N<$ ); substituted alkyl ( $C_1$  to  $C_8$ )—e.g. hydroxyalkyl, haloalkyl, cyanoalkyl, etc.; aryl, e.g. phenyl, substituted phenyl, naphthyl, substituted naphthyl, etc.

The  $R_1$ 's may be the same as R or represent no sub-

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stituent and thereby produce a double bond to yield compounds of the type:



The higher fatty acid acyloxy groups encompassed herein are those of from  $C_{10}$  to  $C_{20}$ , saturated or unsaturated. Simple oxy, oxo, halo, cyano, etc. substituents are contemplated in the acyloxy radical.

The esters used in the invention are generally known and may be prepared from the sulfolane (or sulfolene) alcohol and the selected fatty acid or fatty acid halide.

Illustrative sulfolane and sulfolene alcohols include:

- 3-sulfolanol
- 2-sulfolanol
- 3-sulfolen-2-ol
- 2-sulfolen-4-ol
- sulfolan-3,4-diol
- sulfolan-2,3-diol
- 2-sulfolene-5-ol
- 2-sulfolene-4,5-diol
- 3-methyl-3-sulfolanol
- 2-ethyl-3-sulfolanol
- 3-methyl-2-sulfolanol
- 2-methyl-3-ethyl-3-sulfolanol
- 2-methyl-sulfolan-3,4-diol
- 2,4-dimethyl-3-sulfolanol
- 4-bromo-3,5-dimethyl-2-sulfolanol
- 4-bromo-3,5-dimethyl-3-sulfolanol
- 4-allyl-3-sulfolanol
- 3-chloro-2,4-dimethyl-3-sulfolanol
- 4-chloro-3,5-diethyl-3-sulfolanol
- 2-bromo-3-sulfolanol
- 3-carboxamido-2-sulfolanol
- 4-sulfonamido-3-sulfolanol
- 4-carboethoxy-3-sulfolanol
- 3-carboethoxy-3-sulfolanol
- 4-hydroxyethyl-3-sulfolanol

Illustrative sulfolanyl or sulfolenyl esters useful in the present invention are as follows:

- 3-sulfolanyl decylate
- 3-sulfolanyl undecylate
- 3-sulfolanyl laurate
- 3-sulfolanyl stearate
- 3-ethyl-3-sulfolanyl decylate
- 3-methyl-3-sulfolanyl decylate
- 3-methyl-3-sulfolanyl hexadecanoate
- 2-hydroxy-3-sulfolanyl dodecanoate
- 3-hydroxy-4-sulfolanyl dodecanoate
- 3-ethyl-4-sulfolanyl dodecanoate
- 3-methyl-4-sulfolanyl dodecanoate
- 2-methyl-3-ethyl-3-sulfolanyl dodecanoate
- 3-methoxy-4-sulfolanyl tetradecanoate
- 3-acetoxy-4-sulfolanyl tetradecanoate
- 3-propionoxy-4-sulfolanyl tetradecanoate
- 3-methyl-sulfonyl-4-sulfolanyl tetradecanoate
- 3-cyano-4-sulfolanyl tetradecanoate
- 3-hydroxyethyl-4-sulfolanyl tetradecanoate
- 3-cyanoethyl-4-sulfolanyl tetradecanoate
- 3-ethoxyethyl-4-sulfolanyl tetradecanoate
- 2,4-dimethyl-3-sulfolanyl tetradecanoate
- 2,4-diethyl-3-sulfolanyl dodecanoate
- 3,4-dimethyl-2-sulfolanyl dodecanoate
- 2-sulfolanyl dodecanoate
- 2-methyl-2-sulfolanyl dodecanoate
- 3-methyl-2-sulfolanyl dodecanoate
- 4-(2-sulfolenyl) dodecanoate
- 4-(2-sulfolenyl) octadecanoate
- 3-(2-sulfolenyl) dodecanoate

4-bromo-3,5-dimethyl-2-sulfolanyl dodecanoate  
 2-bromo-3-sulfolanyl dodecanoate  
 4-carboethoxy-3-sulfolanyl dodecanoate  
 2-sulfolanyl tetradecanoate  
 2-sulfolanyl hexadecanoate  
 2-sulfolanyl octadecanoate  
 2-sulfolanyl eicosanate  
 4-(2-sulfolenyl) tetradecanoate  
 4-(2-sulfolenyl) hexadecanoate  
 4-(2-sulfolenyl) eicosanate  
 3-(2-sulfolenyl) decanoate  
 3-(2-sulfolenyl) tetradecanoate  
 3-(2-sulfoenyl) octadecanoate  
 3-(2-sulfolenyl) eicosanate  
 5-(2-sulfolenyl) tetradecanoate  
 5-(2-sulfolenyl) octadecanoate  
 4-hydroxy-5-(2-sulfolenyl) tetradecanoate  
 4-hydroxy-5-(2-sulfolenyl) eicosanate  
 2,4-dimethyl-3-(4-sulfolenyl) tetradecanoate  
 2,4-diethyl-3-(4-sulfolenyl) tetradecanoate

The quantity of sulfolanyl ester may vary considerably in the compositions of the invention. Generally, the ester should comprise from about 1% to about 20% by weight of the detergent formulation with a preferred range being from 2 to 10% by weight.

In "built" detergents, the organic cleaning agent, i.e. the anionic, non-ionic, etc., compound, may comprise from about 5% to upwards of 75% by weight of the total formulation, and usually varies from 5 to 35% by weight. In liquid compositions, the amount of water used is relatively high in order to obtain pourable and generally stable systems. In these liquids, total solids may vary from a few percent, i.e. 2-10%, upwards of about 60% with the organic detergent present, usually in amounts from about 2 to 25% and preferably 5 to 15%. In solid formulations, i.e. powders etc., total solids may run as high as 90% or more and here the organic detergent may be used at the high concentrations above indicated but usually the range is 5 to 25%. The second major component of the "built" or heavy duty liquids, and this is true of the solid (i.e. powdered or tableted types) formulations also, is the alkaline builder salt, and the amount thereof, again, may vary considerably, e.g. from 5 to 75% of the total composition. In the solid formulations larger percentages are generally employed, e.g. 15 to 50%, whereas in the liquid types the salts are used in lesser amounts e.g. 5 to 25% by weight of the total composition.

In any of the contemplated systems the amount of ester softener will be governed primarily by economic considerations since as pointed out above as little as 1% thereof based on the total detergent formulation used gives noticeable and marked softening effects. It is, of course, understood that to obtain a significant degree of softening based on the above figures one is expected to employ the detergent composition in its usual amount which based on the wash water is about 0.15% and based on the "load" is about 2.5%. From these figures it is evident that significant softening is obtained where the softener is used at extremely low concentrations e.g. 0.02% by weight based on the clothing load and in the neighborhood of 0.001% when calculated on the basis of the treating bath e.g. wash water or the like.

In view of the wide latitude in the concentrations of the components of detergent compositions it is convenient to suggest the amount of softener to be used in terms of the organic detergent present. A useful and operative range of detergent to softener is 40:1 to 1:10, preferably 15:1 to 1:2 and most preferred is a range of 5:1 to 1:1.

In formulating the aqueous, liquid, pourable, detergent compositions of this invention it is desirable to have present adjuvants for improving if necessary and/or desired the homogeneity and pourability (i.e. viscosity) thereof. Particularly useful are the non-detergent alkali metal benzene sulfonates, such as sodium toluene sulfonate, sodium xylene sulfonate and sodium cumene sulfonate,

and water soluble alcohols preferably unsaturated, aliphatic, monohydric alcohols such as ethanol and isopropanol. Such additives are especially advantageous in heavy duty formulations containing large amounts of builder salts. These compounds may be used singly or in admixture and in amounts from about 1% to about 20% by weight based on the total weight of the aqueous composition.

The following examples will serve to illustrate the present invention without being deemed limitative thereof. Parts are by weight unless otherwise indicated.

#### EXAMPLE I

A composition of the following is formulated:

	G.
Linear dodecyl benzene sulfonate -----	10
3-sulfolanyl dodecanoate -----	5
Sodium tripolyphosphate -----	40

The above is added to terry cloth towels in a washing machine during the wash cycle and carried through the normal sequence of spin, rinse, and spin cycles. After drying the towels are rated as to softness on a scale of 1 to 10. A rating of 1 corresponds to the results obtained with sulfonate and phosphate alone, and such a rating indicates that the towels are quite harsh. A rating of 10 is considered excellent insofar as softness and fluffiness are concerned. A rating of 5, generally, cannot be distinguished by the layman from a rating of 1. Ratings of 8 to 10 are notably and outstandingly soft. In the instant example, the towels are rated as having a softness of 8.

The concentration of the above formulation in the wash water is about 0.09% by weight based on the weight of water present during the wash cycle.

#### EXAMPLE II

Example I is repeated to provide, however, a wash water concentration of 0.17%. The same results are obtained.

#### EXAMPLE III

Example I is repeated except that the formulation is made up by dispersing the ester in concentrated (50%) aqueous solution of the sulfonate and this is added with the phosphate to the washing machine. Similar results are obtained.

#### EXAMPLE IV

Example III is repeated using an equal weight of 3-sulfolanyl tetradecanoate.

#### EXAMPLE V

Example III is again repeated using an equal amount of 3-sulfolanyl hexadecanoate.

The results of Examples IV and V are even superior to the previous ones. The softness ratings of the towels are 10.

#### EXAMPLE VI

Example III is once again repeated using equal amounts (i.e. 5 g.) of the following esters:

- (A) 3-sulfolanyl octadecanoate
- (B) 4-hydroxy-3-sulfolanyl hexadecanoate
- (C) 3-sulfolanyl phenyl stearate
- (D) 2-sulfolanyl dodecanoate
- (E) 3-methyl-3-sulfolanyl octadecanoate
- (F) 4-hydroxy-2-sulfolanyl tetradecanoate

The results are outstanding giving excellent softness in each instance.

#### EXAMPLE VII

Example I is repeated except that an equal weight of the following anionic detergents are used in place of the dodecyl benzene sulfonate:

- (A) sodium lauryl sulfate

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- (B) sodium alkenyl sulfonate ( $C_{15}$ —20%;  $C_{16}$ —29%;  $C_{17}$ —28%,  $C_{18}$ —14%;  $C_{19}$ —1%)  
 (C) sodium m-tetradecane sulfonate  
 (D) ammonium alkenyl sulfonate ( $C_{16}$  alkenyl).

## EXAMPLE VIII

Example III is repeated using the following ester softeners in the amounts indicated in lieu of the 5 g. of ester softener of Example III:

- (a) 1 g. 3-sulfolanyl dodecanoate  
 (b) 3 g. 3-sulfolanyl dodecanoate  
 (c) 3 g. 3-sulfolanyl hexadecanoate  
 (d) 4 g. 3-sulfolanyl hexadecen-1-oate  
 (e) 2 g. 3-sulfolanyl octadecen-1-oate  
 (f) 2 g. 2-sulfolanyl dodecanoate  
 (g) 3 g. 4-(2-sulfolanyl) tetradecanoate  
 (h) 5 g. 4-(2-sulfolanyl) octadecen-1-oate  
 (i) 5 g. 3-methyl-3-sulfolanyl phenyl stearate  
 (j) 5 g. 3-sulfolanyl-(p-hydroxyphenyl) stearate.

## EXAMPLE IX

A heavy duty liquid formulation is prepared containing:

	Percent
Nonyl phenol+10 moles of ethylene oxide condensate (non-ionic detergent) -----	10.0
Potassium xylene sulfonate -----	8.0
3-sulfolanyl hexadecanoate -----	4.0
Sodium carboxymethyl cellulose -----	0.8
Tetra potassium pyrophosphate -----	15.0
Water -----	Balance to 100

In a towel test (at 120° F.) using tap water, excellent softening is obtained.

## EXAMPLE X

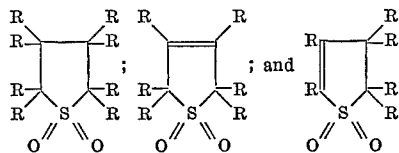
A heavy duty powdered detergent is formulated containing

	Percent
Sodium linear tridecyl benzene sulfonate -----	12
Pentasodium tripolyphosphate -----	40
Sodium sulfate -----	27
Sodium silicate ( $Na_2O:S:O_2=1:2.35$ ) -----	3
3-sulfolanylhexadecanoate -----	6
Brighteners, perfume -----	2
Moisture -----	10

In a terry cloth towel test in an automatic washing machine using tap water (hardness=100 p.p.m.) at 120° F. and 100 g. of the formulation, the results are outstanding yielding towels exhibiting superior wet and dry softness.

What is claimed is:

1. A method for softening textile material which comprises applying to said textile material from an aqueous bath, an amount sufficient to soften the textile material of an ester of the formula selected from the following formulas



wherein one R is  $C_{10}$  to  $C_{20}$  fatty acyloxy radical and the other R's are selected from the group consisting of hydrogen, halogen, hydroxy,  $C_1$  to  $C_8$  alkyl,  $C_1$  to  $C_8$  hydroxyalkyl,  $C_1$  to  $C_8$  haloalkyl,  $C_1$  to  $C_8$  cyanoalkyl,  $C_1$  to  $C_8$  alkyl sulfonyl, phenyl and naphthyl.

2. A method as defined in claim 1 wherein the ester softener is present in the bath in an amount from about 0.001% to about 10% by weight based on the weight of the bath.

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3. A method as defined in claim 2 wherein the amount is from 0.001% to about 1%.

4. A method as defined in claim 1 wherein the bath additionally contains an organic detergent selected from the group consisting of anionic, nonionic, cationic, ampholytic and zwitterionic detergent materials.

5. A method as defined in claim 4 wherein the detergent is anionic.

6. A method as defined in claim 4 wherein the detergent is non-ionic.

7. A method as defined in claim 5, wherein the anionic detergent is a linear higher alkyl benzene sulfonate.

8. A method as defined in claim 5, wherein the anionic detergent is a linear higher olefin sulfonate.

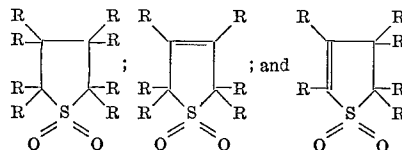
9. A method as defined in claim 7, wherein the anionic detergent is a linear  $C_{10}$  to  $C_{16}$  alkyl benzene sulfonate.

10. A method as defined in claim 2 wherein the application to textile occurs during the rinse cycle of a laundering process.

11. A detergent composition characterized by softening properties when used to clean textiles in an aqueous bath consisting essentially of

(A) an organic detergent selected from the group consisting of anionic, nonionic, cationic, ampholytic and zwitterionic detergent materials, and

(B) a compound of the formula selected from the following formulas



wherein one R is  $C_{10}$  to  $C_{20}$  fatty acyloxy radical and the other R's are selected from the group consisting of hydrogen, halogen, hydroxy,  $C_1$  to  $C_8$  alkyl,  $C_1$  to  $C_8$  hydroxyalkyl,  $C_1$  to  $C_8$  haloalkyl,  $C_1$  to  $C_8$  cyanoalkyl,  $C_1$  to  $C_8$  alkyl sulfonyl, phenyl and naphthyl, said (A) and (B) being in the ratio of 40:1 to 1:10.

12. A composition as defined in claim 11 wherein (A) is an anionic compound.

13. A composition as defined in claim 12 wherein (A) is a sulfonate.

14. A composition as defined in claim 13 wherein (A) is a linear higher alkyl benzene sulfonate and (B) is a  $C_{10}$  to  $C_{20}$  fatty acid ester of a sulfolanol.

15. A composition as defined in claim 14 wherein (B) is a  $C_{10}$  to  $C_{20}$  fatty acid ester of 3-sulfolanol.

16. A composition as defined in claim 15 wherein (B) is 3-sulfolanyl dodecanoate.

17. A composition as defined in claim 15 wherein (B) is 3-sulfolanyl hexadecanoate.

18. A composition as defined in claim 15 wherein (A) is a sodium dodecyl benzene sulfonate.

19. A composition as defined in claim 11 wherein the ratio of (A) to (B) ranges from 15:1 to 1:2.

## References Cited

## UNITED STATES PATENTS

2,435,071	1/1948	Evans et al.	260—329
2,451,299	12/1948	Morris et al.	106—176 X
3,325,404	6/1967	Cohen et al.	252—8.75

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