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**Laughlin et al.**

[11] **3,929,678**
[45] **Dec. 30, 1975**

# [54] DETERGENT COMPOSITION HAVING ENHANCED PARTICULATE SOIL REMOVAL PERFORMANCE

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[21] Appl. No.: **493,953**

[52] **U.S. Cl.** ................ **252/526;** 252/545; 252/546; 260/501.12
[51] **Int. Cl.**$^2$ ...................... **C11D 3/066;** C11D 1/18
[58] **Field of Search** .... 252/526, 527, 545, DIG. 11; 260/501.12

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*Primary Examiner*—John D. Welsh
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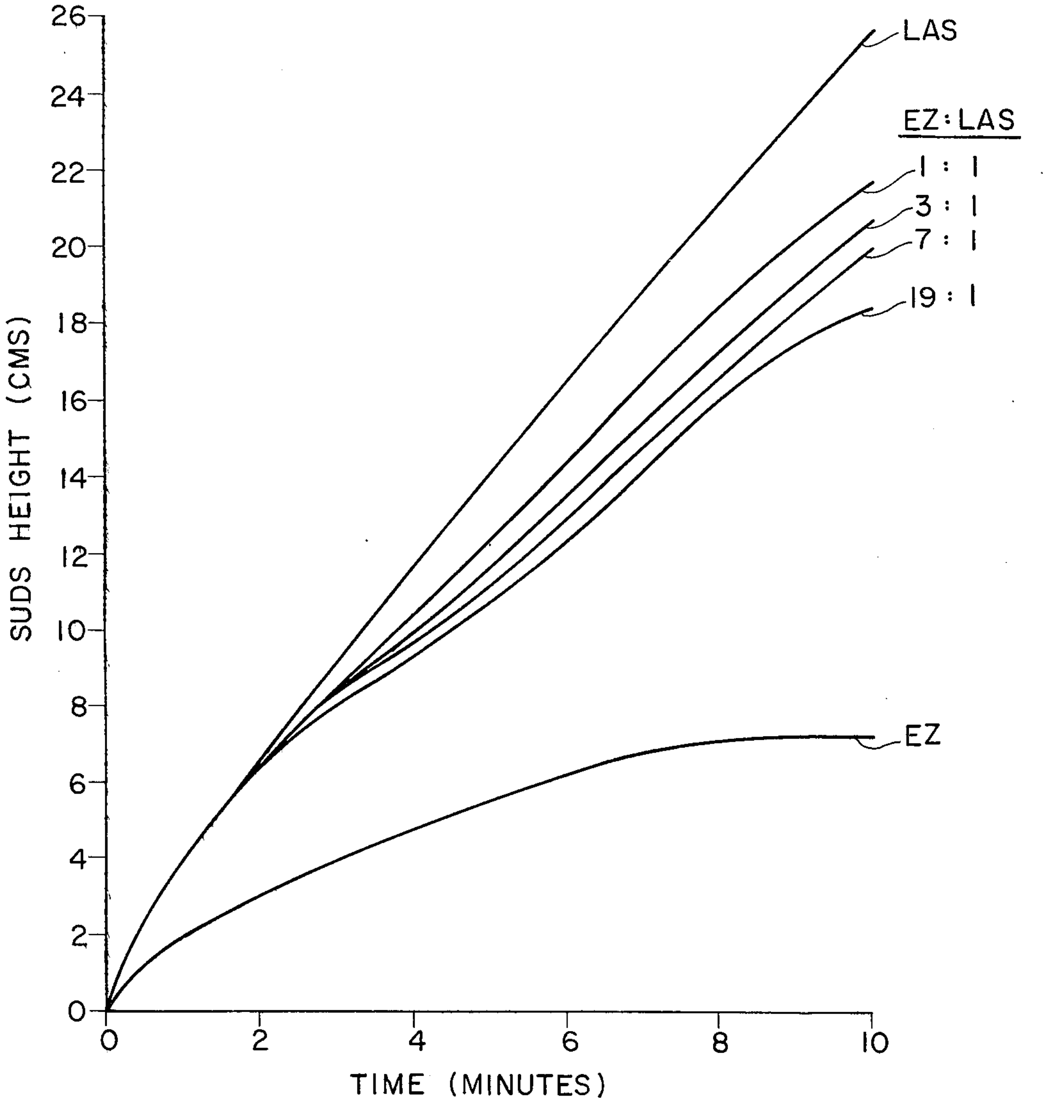
## [57] ABSTRACT

Detergent compositions are disclosed incorporating combinations of specified ethoxylated zwitterionic compounds with other types of surfactants and with detergent builders to give enhanced particulate soil removal.

**29 Claims, 1 Drawing Figure**

SUDSING EVALUATION OF COMBINATIONS OF $C_{16}$ ETHOXYLATED ZWITTERIONIC COMPOUND ($C_{16}$EZ) AND ANIONIC CO-SURFACTANT ($C_{11\text{-}8}$LAS)

TOTAL SURFACTANT CONCENTRATION : 200 ppm
TEMPERATURE : 100°F.
MINERAL HARDNESS : 5,5 grains/gal.
Ca : Mg = 3 : 1



# DETERGENT COMPOSITION HAVING ENHANCED PARTICULATE SOIL REMOVAL PERFORMANCE

## BACKGROUND OF THE INVENTION

This invention relates to detergent compositions having improved particulate soil removal capability. More particularly, this invention relates to detergent compositions incorporating certain ethoxylated compounds which provide unexpectedly good clay soil removal.

Zwitterionic surfactants, i.e., those surface active compounds that contain both positive and negative charge centers in the same molecule while being electrically neutral, are known. For example, U.S. Pat. Nos. 3,668,240 and 3,764,568 to Melvin A. Barbera, issued respectively on June 6, 1972, and Oct. 9, 1973, disclose zwitterionic surfactants having a 2, 3-butene moiety between the charge centers. U.S. Pat. No. 3,332,875 to Adriaan Kessler and Phillip Floyd Pflaumer also discloses mixtures of certain olefin sulphonates with zwitterionic detergents in which the charge centers are separated by a 2-hydroxy propane group. U.S. Pat. Nos. 3,452,066 and 2,781,390 to Hans S. Mannheimer, issued respectively on June 24, 1969, and Feb. 12, 1957, outline a range of zwitterionic surfactants which optionally may be substituted with a wide variety of oxygen-containing groups between the positive and negative charge centers. U.S. Pat. No. 3,769,311 to Leonard J. Armstrong and Eldon de Vere Dawald issued Oct. 30, 1973, discloses carboxylic compounds having ethylene oxide groups between the charge centers but fails to recognize the effect of the various structural parameters on the performance of the molecule in removing soil, especially particulate soil.

In contrast, the present invention concerns detergent compositions incorporating certain zwitterionic surfactants in a polyethenoxy group of a size that permits not only adsorption of the molecule from an aqueous system onto particulate and other soils, and the subsequent removal of the soil by emulsification or dispersion but also the continued maintenance of the removed soil in suspension in the aqueous solution.

Some of these compounds are effective in the absence of conventional detergent additives such as builders, surfactants etc. and form the subject of the commonly assigned co-filed Applications by Robert G. Laughlin, Eugene P. Gosselink, William A. Cilley, and Vincent P. Heuring Ser. No. 493,951, filed Aug. 1, 1974 and Robert G. Laughlin, Eugene P. Gosselink, and William A. Cilley Ser. No. 493,956, filed of even date, both Applications being entitled "Detergent Compounds." The disclosures of both said Applications are hereby incorporated herein by reference.

However, the present invention is directed to the discovery that a wider range of zwitterionic compounds, of the type disclosed in the above identified Applications, in combination with certain other surfactant and detergent builder materials can provide unexpectedly good particulate soil removal and also good oily soil removal from hard surfaces and textile materials. The ethoxylated zwitterionic compounds useful in the present invention possess an ability to remove particulate soil that is independent of water hardness over a very wide range or $Ca^{++}$ and $Mg^{++}$ levels. Furthermore, this performance is relatively insensitive to temperature changes in the range of 70°-140°F, the normal range for domestic cleaning functions.

The importance of such a development is readily apparent as it permits a high level of soil removal performance to be obtained with a range of detergent formulations. Furthermore, the nature and level of other components of the formulation can be controlled by the selection of an ethoxylated zwitterionic material having the appropriate level of performance.

Accordingly, it is an object of the present invention to provide detergent compositions incorporating ethoxylated zwitterionic compounds that have good particulate and oily soil removal performance.

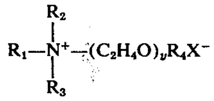
Another object of the present invention is the provision of detergent compositions having improved particulate and oily soil removal performance in both liquid and granular forms.

## SUMMARY OF THE INVENTION

In its broadest aspect the present invention embraces a detergent composition comprising:

A. 1 to 99% by weight of the composition of a water-soluble compound having a formula selected from the group consisting of:

i)



$$R_1-\overset{\displaystyle R_2}{\underset{\displaystyle R_3}{\overset{|}{\underset{|}{N^+}}}}-(C_2H_4O)_yR_4X^-$$

wherein

R$_1$ is selected from the group consisting of straight and branched chain $C_8$–$C_{30}$ alkyl and alkenyl moieties and alkaryl moieties in which the alkyl group has 10–24 carbon atoms;

R$_2$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, and $C_{1\text{-}4}$ alkyl and hydroxyalkyl moieties;

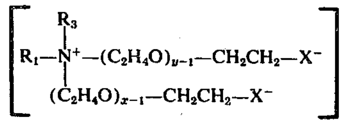
R$_3$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, $C_{1\text{-}4}$ alkyl and hydroxyalkyl moieties and $-(C_2H_4O)_xH$ wherein $x$ has a value of about 3 to about 50;

R$_4$ is selected from the group consisting of $C_{1\text{-}8}$ alkylene, $C_3$-$C_8$ alkenylene, 2-hydroxy $C_3$ alkylene and 2- and 3- hydroxy $C_4$ alkylene moieties and $C_1$–$C_4$ alkarylene moieties provided that where $R_3$ is $-(C_2H_4O)_xH$ then $R_4$ is $-CH_2-CH_2-$;

$X^-$ is an anion selected from the group consisting of sulfate and sulfonate radicals;

and $y$ has a value in the range of 2-100 provided that where $R_3$ is $-(C_2H_4O)_xH$ then $x + y \geqslant 10$.

ii)



$$\left[R_1-\overset{\displaystyle R_3}{\underset{\displaystyle (C_2H_4O)_{x-1}-CH_2CH_2-X^-}{\overset{|}{\underset{|}{N^+}}}}-(C_2H_4O)_{y-1}-CH_2CH_2-X^-\right]M^+$$

wherein

R$_1$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals;

R$_2$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals and $C_1$–$C_4$ alkyl and hydroxyalkyl radicals; $X^-$ is selected from the group consisting of sulfate and sulfonate;

$y$ and $x$ have values in the range of 2–100 provided that $y + x \geqslant 12$;

M is a cation selected from the group consisting of alkali metal, ammonium and alkanolammonium ions.

B. 99 to 1% by weight of the composition of an organic detergent, preferably selected from the group consisting of anionic, nonionic, ampholytic, and zwitterionic detergents.

In the context of the present invention, ethoxylated zwitterionic compounds having hydroxy substituents on the carbon atoms immediately adjacent the nitrogen atom and/or $X^-$ moiety are not preferred as they are unstable in water, especially at pH's other than neutrality, and are extremely difficult to prepare compared to other hydroxy substituted compounds.

Preferably, the ethoxylated zwitterionic compound is one of either:

ω-(N-$C_{16-18}$ alkyl,N-$C_{1-3}$ alkyl,N- polyethenoxy ammonio)-2-polyethenoxyethane-1-sulphonate wherein the total number of ethylene oxide groups lies in the range 15–25

or

ω-(N-$C_{12-18}$ alkyl,N,N-di$C_1$-$C_3$ alkylammonio)-2-polyethenoxy ethane-1-sulphonate wherein the number of ethylene oxide groups in the polyethenoxy chain is in the range 6–12.

## DESCRIPTION OF THE DRAWING

The FIGURE illustrates the sudsing characteristics of a series of blends of an ethoxylated zwitterionic compound ($C_{16}$ EZ) and an anionic cosurfactant ($C_{11.8}$ LAS). The FIGURE constitutes a plot of the suds height (in cms.) developed by the Recirculating Suds Generator (R.S.G.) as a function of time (in minutes) for $C_{16}$ EZ alone, for blends of $C_{16}$ EZ:$C_{11.8}$ LAS of 19:1, 7:1, 3:1 and 1:1 by weight and for $C_{11.8}$ LAS alone.

## PERFORMANCE TESTING

In this specification the assessment of particulate and oily soil removal performance both of detergent formulations of the invention and of comparative formulations is carried out using the following procedures.

### a. Particulate soil removal testing

This is carried out in either an automatic mini washing machine (AMW) having a capacity of 4,700 ml. and a cloth/liquor ratio of 1:30 or a Tergotometer having a capacity of 1,000 ml. and a cloth/liquor ratio of 1:140. In both instances the machines are fitted with horizonally rotating paddle agitators, the AMW having a speed of 100 RPM, while the Tergotometer uses a speed of 80 RPM.

The AMW washing procedure involves a 12-minute wash cycle at 105°F in 7 grains per U.S. gallon hard water (calculated as $CaCO_3$) using a 2:1 ratio of Ca:Mg salts. The first two minutes of the cycle are used for product dissolution following which the fabric load is added and washed for the remaining 10 minutes. A 5-minute rinse cycle then follows, 2 minutes of which is with agitation, the remaining 3 minutes being a spin to remove excess moisture. The fabrics are then tumble-dried prior to being graded.

A similar washing procedure is used for the Tergotometer with the exception that 5.5 grains/gallon water is employed having a 3:1 ratio of Ca:Mg salts (calculated as $CaCO_3$). The wash is followed by one rinse cycle of 3 minutes in 80°F water of the same hardness, level, and type as for the wash, after which the swatches are machine-dried before being graded.

The fabric load for particulate soil removal testing comprises a mixture of white cotton, polycotton (65% DACRON/35% cotton), and polyester (KODEL) swatches which are stained with a standardized illite clay soil. For the AMW, three 5 × 5 inch swatches of each fabric are used in each load, while in the Tergotometer, three 2½ × 2½ inch swatches of each fabric type are employed.

The results (expressed as relative clay removal index) for each formulation represent a percentage of the whiteness value achieved by a commercial synthetic detergent standard tested at the same time under identical conditions. This standard formulation hereinafter designated as A has the following composition by weight:

| | |
|---|---|
| Sodium $C_{12}$ alkylbenzene sulphonate | 7.55 |
| Sodium Tallow alkyl sulphate | 9.25 |
| Coconut alcohol + 6 mole EO | 0.60 |
| Diethanolamide | 1.60 |
| Sodium Tripolyphosphate | 50.00 |
| Sodium Silicate solids | 5.90 |
| Sodium sulphate | 14.20 |
| Moisture | 10.00 |
| Miscellaneous | 0.30 |
| | 100.00 |

## GRADING OF PERFORMANCE

Swatches are graded before and after washing on a Gardner Whiteness meter reading the L, *a*, and *b* coordinates. Whiteness (W) is calculated as:

$$W = \frac{7L^2 - 40Lb}{700}$$

Performance is determined by finding the difference in whiteness (ΔW) before and after washing as:

$$\Delta W = W_{after} - W_{before}$$

This is compared to the commercial Control Product A by calculating ΔW as a percentage of ΔW given by the Control Product in each batch.

The Relative Clay Removal Index =

$$\frac{\Delta W \text{ for Test Sample}}{\Delta W \text{ for Control Product A}} \times 100$$

### b. Grease and oil removal testing

Identical equipment and washing conditions are used to evaluate grease and oil removal performance. The fabric load comprises a mixture of green polycotton (65% DACRON/35% cotton) and polyester (KODEL) swatches, four 2½ × 2½ inch swatches of each type being used in the tergotometer. Two triglyceride stains, namely bacon grease and vegetable oil, and two hydrocarbon-based stains, namely dirty motor oil and simulated lipid soil are employed.

Following washing and drying, the swatches are graded visually on a scale whose absolute values are described below:

5. Complete removal
4. Discernible stain remaining
3. Moderate amount of soil remaining
2. Large amount of soil remaining

1. Very large amount of soil remaining
0. No change, original amount of stain remaining

As in the particulate soil removal performance test, the results are expressed as a percentage of the soil removal achieved by the standard A under the same conditions.

## SUDSING EVALUATION

In this Application, the evaluation of the sudsing characteristics of detergent compositions is carried out using a Recirculating Suds Generator.

This apparatus basically consists of a 1000 ml. graduated cylinder which holds the bulk of the test solution and a circulating pump which is connected to the base of the cylinder and which discharges to an exit jet located in the cylinder above the level of the test solution. The desired solution temperature is maintained by heating tapes secured around tubing connecting the pump to the exit jet.

In operation, approximately 200 ml. of test solution is placed in the cylinder and continuously circulated at a selected temperature within the range of 70°–125°F. The force of the downward-directed solution from the exit jet onto the bulk of the test solution in the graduated cylinder generates a level of suds in the cylinder which is measured at one-minute intervals.

## DETAILED DESCRIPTION OF THE INVENTION

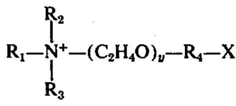
The compositions of the present invention contain two essential components, namely the ethoxylated zwitterionic compound and a surfactant compound. The zwitterionic and surfactant may be present in a ratio of from 99:1 to 1:99 by weight, preferably 10:1 to 1:10 by weight, and most preferably 4:1 to 1:10 by weight depending on the nature of the zwitterionic compound and the type of product to be formulated. For example, a product intended for prewash treatment of laundry to remove specific stains by direct application to the fabric will be formulated to contain a lower level of zwitterionic compound and different optional ingredients than a product designed as a main wash detergent.

For use as a main wash detergent, the level of ethoxylated zwitterionic compound in the product will lie in the range 5–35% by weight, preferably 10–25%, and most preferably 15–20%, the level of the surfactant compound being 0.5–15%, preferably 1–10%, and most preferably 1–5% by weight. Such a main wash detergent can be formulated as a conventional granule or as a liquid, paste, flake, ribbon, noodle, pellet, or tablet. As will be shown hereinafter, this formulation flexibility is due, at least in part, to the ability of the zwitterionic surfactants of the present invention to achieve satisfactory particulate soil removal performance equivalent to that of commercial heavy duty laundry detergents when used in blends with other surfactants.

## ETHOXYLATED ZWITTERIONIC COMPOUNDS

Ethoxylated zwitterionic compounds useful in the present invention may have one or other of the following formulae:

(i)



$$R_1-\overset{\overset{R_2}{|}}{\underset{\underset{R_3}{|}}{N^+}}-(C_2H_4O)_y-R_4-X^-$$

a. Mono-long chain derivatives

In this derivative, $R_1$ is a hydrocarbon moiety that can be a straight or branched chain $C_8$–$C_{30}$ alkyl or alkenyl group or an alkaryl group in which the alkyl portion has 10–24 carbon atoms; $R_2$ and $R_3$ are $C_1$–$C_4$ alkyl or hydroxyalkyl groups; $R_4$ is a $C_1$–$C_8$ alkylene, $C_3$–$C_8$ alkenylene or 2-hydroxy propylene or 2- or 3-hydroxy butylene group or a $C_1$–$C_4$ alkarylene group; $X^-$ is a sulfonate or sulfate radical; and $y$ has a value in the range 2–100.

In this embodiment, preferred groups for $R_1$ are $C_{12}$–$C_{18}$ alkyl, particularly $C_{14}$–$C_{16}$ alkyl, while preferred groups for $R_2$ and $R_3$ are $C_{1-3}$ alkyl and $C_{2-3}$ hydroxyalkyl, the most preferred groups being methyl- and hydroxyethyl- radicals. The preferred range of values for $y$ is 6–50, more preferably 6–25, and most preferably 9–12.

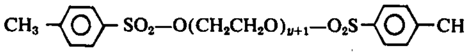
The synthesis of the above compounds can be achieved using readily available commercial starting materials. One such synthetic route is as follows. Sodium hydride is slowly and stoichiometrically reacted (2:1 molar ratio) with polyethylene glycol in a solution of tetrahydrofuran under an atmosphere of an inert gas, e.g., argon. The reaction is carried out over a period of 4–10 hours in an ice bath to cool the reaction, which is exothermic. The polyethylene glycol used is the commercially available material comprising a mixture of compounds having chain lengths from about 4 to about 100. The resultant product is the sodium salt represented by

(I) $Na^+O^-(CH_2CH_2O)_yCH_2CH_2O^-Na^+$

wherein $y$ can be, for example, 3, 21, 32, 67, or 99.

A stoichometric amount of tosyl chloride dissolved in tetrahydrofuran is then added slowly to reaction product (I), cooled in an ice bath, and the resultant mixture is stirred for 12 to 20 hours to form

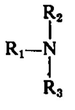
(II)



i.e., the polyethylene glycol ditosylate. Pyridine or other suitable base is added to the mixture, and the solution is then poured into ice water and acidified with HCl to a pH of about 2–3. The aqueous solution is then extracted with chloroform, rinsed with water and the chloroform extract is dried over sodium sulfate to give purified polyethylene glycol ditosylate (II).

The ditosylate (II) is then reacted with a tertiary amine of the structure

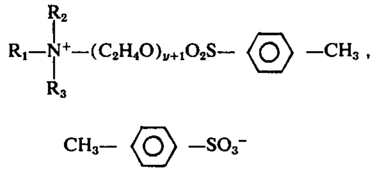
(III)



$$R_1-\overset{\overset{R_2}{|}}{\underset{\underset{R_3}{|}}{N}}$$

wherein $R_1$, $R_2$ and $R_3$ are as defined above. The reaction of (III) with (II) is conveniently carried out neat, or with a suitable solvent as N,N-dimethyl formamide or $CH_3CN$ at temperatures of 80° to about 100°C to produce a mixture of

(IV)



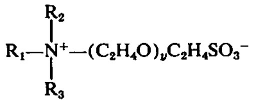
$$R_1-\overset{R_2}{\underset{R_3}{N^+}}-(C_2H_4O)_{y+1}O_2S-C_6H_4-CH_3,\quad CH_3-C_6H_4-SO_3^-$$

and

(V) dicationic ammonium byproducts

The mixture of (IV) and (V) is then dissolved in methanol and refluxed from 20–40 hours with an aqueous solution of sodium sulfite. The unreacted (V) and other ionic materials are removed by contacting the above solution with a mixed bed ion exchange resin, followed by filtration of the solution and evaporation of the solvent to give, as the predominant zwitterionic product,

(VI)



$$R_1-\overset{R_2}{\underset{R_3}{N^+}}-(C_2H_4O)_yC_2H_4SO_3^-$$

Compound (VI) can optionally be further purified using the mixed bed resin and tested for purity by thin layer chromatography.

It will be appreciated that zwitterionic compounds of the general formula (VI) can be prepared using any of a variety of tertiary amines (III). Moreover, zwitterionic compounds having any desired, specific degree of ethoxylation (y) can be prepared by fractionating the polyethylene glycol used in the reaction and using the desired fraction in the synthesis scheme. Alternatively, relatively narrowly defined distillation "cuts" of polyoxyethylene glycol having any desired average degree of ethoxylation, and containing individual compounds having differing degrees of ethoxylation within the desired range, can be used in the reaction. It will be further understood that sodium salt (I) can be reacted with a variety of epoxy compounds (e.g., butylene epoxide) or halohydrins (e.g., 6-chlorohexanol or 8-bromooctanol) to provide zwitterionics having various $R_4$ groups within the scope of this invention.

A specific preparation of a mono-long chain ethoxylated zwitterionic compound useful in the present invention was as follows:

### Preparation of 26-dimethyloctadecylammonio-3,6,9,12,15,18,21,24 octaoxahexacosane-1-sulfonate

#### Preparation of Nonaethyleneglycol (A)

Under nitrogen, 46 grams (2 moles) of sodium pellets were added cautiously to 2,664 ml (20 moles) of previously dried and distilled triethyleneglycol. The temperature was kept below 100°C. After all the sodium had reacted, the temperature was adjusted to 100°C and 187 grams (1 mole) of 1,2-bis-(2-chloroethoxy) ethane was added in a slow stream. The mixture was heated overnight at 100°C (still under nitrogen) and then filtered hot to remove most of the sodium chloride. Excess triethyleneglycol was stripped under vacuum and the mixture was again filtered while hot. The material was purified by molecular distillation and has a b.p. of 170°–175°C at 0.001 mm.

#### Preparation of Nonaethyleneglycol ditosylate (B)

The nonaethyleneglycol (A), 300 grams, (0.72 moles) was dissolved in 800 ml (10.3 moles) of dry pyridine and cooled to 0°C. Tosyl chloride (i.e., p-toluene-sulfonyl chloride, 420 grams, 2.2 moles) was added, with stirring, in small portions. After the addition was complete, the temperature increased to 10°C and the clear reaction mixture became cloudy. The mixture was stirred at 0°–10°C for an additional 3 hrs., then poured into an equal volume of ice water and acidified to pH 2–3 with 6N HCl. The aqueous solution was then extracted 3 times with $CHCl_3$. The $CHCl_3$ was washed with water, sodium bicarbonate solution, and again with water, then dried over anhydrous sodium sulfate. Evaporation of the $CHCl_3$ gave 520 grams of a slightly yellow oil. Thin layer chromatography indicated an impurity which remained at the origin. The oil was dissolved in warm benzene (40°C) and extracted with warm water to remove the polar impurity. The benzene was dried filtered and concentrated to yield 423 grams of a yellowish oil (B).

#### Preparation of dimethyloctadecyl-26-tosyloxy-3,6,9,12,15,18,21,24 octaoxahexacosylammonium tosylate (C)

The ditosylate (B) 86.7 grams (0.12 mole) and 35.8 grams of distilled dimethyloctadecylamine were heated at reflux for 5 hrs. in 400 ml of acetonitrile. The solvent was then removed to give 120 grams of a mixture consisting of the monoquaternary tosylate (C), diquaternary ammonium byproduct (D) and some unreacted ditosylate (B).

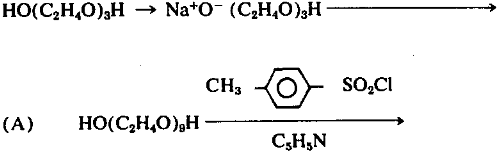
#### Preparation of 26-dimethyloctadecylammonio-3,6,9.12,15,18,21,24 octaoxahexacosane-1-sulfonate

The mixture of monoquat (C) and diquaternary ammonium byproduct (D) prepared above was dissolved in 1 liter of methanol. Sodium sulfite (100 grams, 0.79 mole) was added and the reaction mixture was refluxed with stirring for 5 hours. Additional methanol was added and the insoluble salts were filtered. The solvents were removed to yield a solid product.

#### Purification

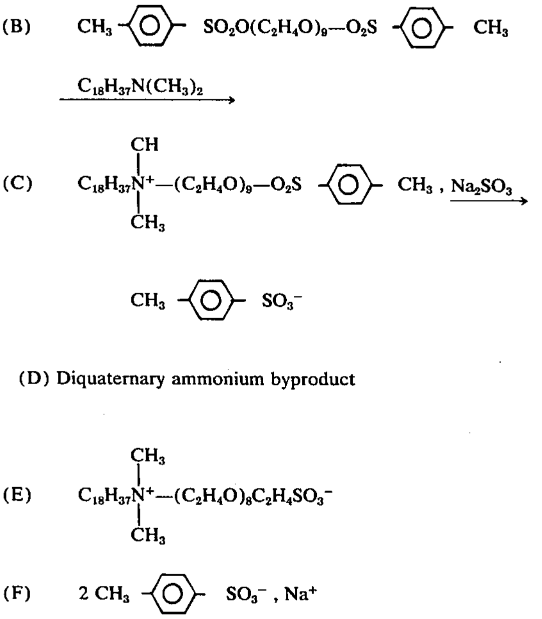
The above solid reaction product was dissolved in 1 liter of methanol and stirred with 386 grams of a mixed bed (Rexyn 300 H–OH, commercially available from the Fisher Scientific Co.) resin for 5 hours. The solution was then passed through a column of fresh resin (350 grams of Rexyn 30C) at a rate of 2 liters per 7 hours. The methanol solution was then concentrated to yield 31.8 grams of a light yellow oil which was recrystallized from acetone to give a white crystalline, hygroscopic product. This product was identified as the title compound (E in the following schematic).

The following sequence sets forth the above procedure in abbreviated form to clarify the structures of compounds prepared thereby. In the sequence, the dimethyloctadecylamine can be replaced by dimethylhexadecylamine, dimethylnonadecylamine, dimethyleicosylamine, and dimethyldocosylamine, respectively, and the corresponding compounds wherein $R_1$ is $C_{16}$, $C_{19}$, $C_{20}$, and $C_{22}$ are secured, respectively.



$$HO(C_2H_4O)_3H \xrightarrow{Na} Na^+O^-\ (C_2H_4O)_3H \xrightarrow{(ClCH_2CH_2O)_2C_2H_4}$$

-continued

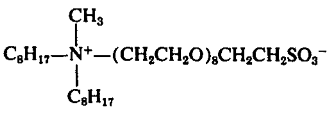


## b. Di-long chain derivatives

In this derivative, both $R_1$ and $R_2$ are hydrocarbon moieties that can be straight or branched chain $C_6$–$C_{21}$ alkyl or alkenyl groups; $R_3$, $R_4$, and $X^-$ are as in (i) (a.) above and $y$ has an average value in the range 6–100. Preferably $R_1$ and $R_2$ are identical and comprise alkyl groups each having 10 to 16 carbon atoms, most preferably alkyl groups each having 10 to 24 carbon atoms. Preferred values for y lie in the range 9 to 50, most preferably in the range 12 to 25.

A specific preparation of a di-long chain alkyl ethoxylated zwitterionic compound useful in the present invention was as follows:

Methylation of di-n-octylamine was accomplished by slowly mixing 50 grams of the secondary amine with, first, formic acid (30.03 grams), and then formaldehyde, at 0°C. The reaction mixture was kept at 80°C for 24 hours, then adjusted to pH 8–9 with 10% NaOH solution. The resulting tertiary amine was extracted with $CHCl_3$ and dried over $Na_2SO_4$. The tertiary amine (25.6 grams, 0.10 mole) was then refluxed with 72 grams (0.10 mole) of nonaethylene glycol ditosylate (compound B, prepared as in the previous procedure) in acetonitrile for 6 hours. The solvent was evaporated and the resulting mixture of mono- and diquaternary compounds was dissolved in methanol and refluxed with 100 grams of sodium sulfite (predissolved in water) for 16 hours. Excess sulfite and other salts were filtered and the filtrate was stirred for 16 hours with 500 grams of a mixed bed resin (Rexyn 300). A second treatment with fresh resin was necessary to remove all impurities. The solvents were evaporated to complete dryness and the product, 22 grams of a light yellow viscous oil, was identified as



$$C_8H_{17}-\overset{\displaystyle CH_3}{\underset{\displaystyle C_8H_{17}}{N^+}}-(CH_2CH_2O)_8CH_2CH_2SO_3^-$$

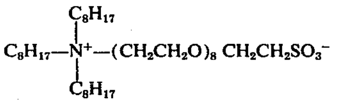
or 26-dioctylmethylammonio-3,6,9,12,15,18,21,24-octaoxahexacosane-1-sulfonate.

## c. Tri-long chain derivatives

In this derivative, $R_1$, $R_2$, $R_3$ are all hydrocarbon moieties that can be straight or branched chain $C_6$–$C_{16}$ alkyl or alkenyl groups; $R_4$ and $x$ are as in (i) (a.) and (b.) above and y has a value in the range 6–100. Preferably $R_1$, $R_2$, and $R_3$ are each identical and each comprise an alkyl group having 8–16 carbon atoms in the chain. Most preferably each chain contains 8–12 carbon atoms. $y$ has a preferred value in the range 9–50, most preferably in the range 12–50.

A specific preparation of a tri-long chain alkyl ethoxylated zwitterionic compound was as follows:

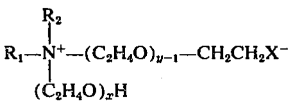
Tri-n-octylamine was distilled to insure purity and 42 grams of the purified product (0.12 mole) was reacted with 87 grams (0.12 mole) of the ditosylate of nonaethylene glycol (compound B in the mono-long chain preparation) in dry N,N-dimethylformamide at 100°C for 2 hours. The dimethylformamide was removed and the mixture of mono- and diquaternary material was dissolved in methanol. This mixture was refluxed for 16 hours with 100 grams of $NA_2SO_3$ predissolved in water. The insoluble salts were filtered and the filtrate was stirred with 500 grams mixed bed resin (Rexyn 300 H—OH) for 24 hours. An additional treatment with 500 grams fresh resin was used to further purify the product. Thin layer chromatography still indicated an impurity, which was subsequently removed by dissolving the product in $H_2O$, acidifying to pH 4, and extracting with $CHCl_3$. The $CHCl_3$ extract was rinsed with sodium bicarbonate, dried and evaporated to give a light yellow viscous oil, identified as



$$C_8H_{17}-\overset{\displaystyle C_8H_{17}}{\underset{\displaystyle C_8H_{17}}{N^+}}-(CH_2CH_2O)_8\,CH_2CH_2SO_3^-$$

or trioctylammonio-3,6,9,12,15,18,21,24-octaoxahexacosane-1-sulfonate.

ii)



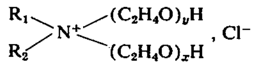
$$R_1-\overset{\displaystyle R_2}{\underset{\displaystyle (C_2H_4O)_xH}{N^+}}-(C_2H_4O)_{y-1}-CH_2CH_2X^-$$

(I)

In this structure, $R_1$ can be a linear or branched $C_8$–$C_{30}$ alkyl or alkenyl group, preferably a $C_{16\text{-}18}$ alkyl or alkenyl group; $R_2$ can also be a $C_8$ -$C_{30}$ alkyl or alkenyl group or can be a $C_1$-$C_4$ alkyl or hydroxyalkyl group, preferably a methyl group; and $X^-$ can be a sulfonate or sulfate radical.

The number of ethylene oxide groups in each chain can be from 1 to 100 but their sum should be greater than 10. Normally there will be approximately the same number in each chain, the sum of the groups in both chains preferably having a value in the range 12–50 and most preferably in the range 12–25.

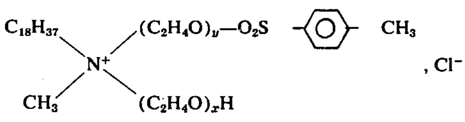
The preparation of zwitterionic compounds of this type is accomplished using commercially available starting materials. A typical starting material is marketed under the tradename Ethoquad, by the Armak Company of the Armour Company. Ethoquad is a mixture of quaternary ammonium compounds whose predominant component is a di-ethoxylate of the structure



wherein $y$ and $x$ are each non-zero integers whose average sum is, for example, 5, 10, 15, 50, depending on the "cut" selected, and $R_1$ and $R_2$ are $C_{12}$–$C_{18}$ alkyl and $C_1$–$C_3$ alkyl, respectively.

In general terms, the compounds herein are prepared by dissolving Ethoquad in pyridine or other suitable base and cooling the mixture to a temperature of about 0°C. Tosyl chloride is slowly added to the Ethoquad mixture at a 1:1 stoichiometric ratio while the reaction mixture is kept at about 0°C–5°C in an ice bath. The mixture is then stirred for about 24 hours at 0°C–5°C. At the end of that time the reaction mixture is poured into water and acidified to a pH of 2–3 with HCl.

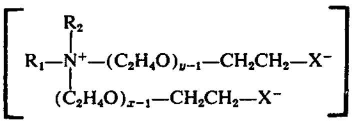
The foregoing acidified reaction mixture is then extracted with chloroform and the extract is rinsed first with sodium bicarbonate solution, then with water; the extract is then dried over anhydrous sodium sulfate. After evaporation of the chloroform extract, an oily residue is obtained. This is the mono-tosylate ester of the structure



wherein $y$ and $x$ are as above.

The foregoing tosylate ester is then dissolved in methanol and refluxed for about 24 hours with about a 10 molar excess of sodium sulfite predissolved in $H_2O$. The reaction mixture is cooled and excess sodium sulfite and sodium tosylate are removed by filtration. The filtrate is stirred with a mixed bed (anion-cation) resin to purify the product. A second resin treatment can optionally be used to remove substantially all traces of all cationic and anionic impurities. The purified monosulfonate corresponding to (I) above is recovered by evaporating the solvent. The product can optionally be recrystallized from acetone.

iii)



$$\left[R_1-\overset{R_2}{\underset{(C_2H_4O)_{x-1}-CH_2CH_2-X^-}{N^+}}-(C_2H_4O)_{y-1}-CH_2CH_2-X^-\right]M^+$$

(II)

where $R_1$, $R_2$, and $X^-$ are as in (ii) and $y$ and $x$ each have a value in the range of 1–100 provided that the sum of $y + x \geqslant 10$. Preferred values for the sum of $y + x$ will lie in the range 12–50 and most preferably in the range 15–25. The cation $M^+$ can be alkali metal, ammonium, and alkanolammonium, e.g. ethanolammonium or methanolammonium but is most preferably sodium.

The disulfonate (II) is prepared in the same manner as the mono-sulfonate (I), but using excess tosyl chloride (about 3:1 mole ratio, or greater) in the first step and a larger excess of sodium sulfite (20:1 mole ratio) in the second step. If a cation, M, other than sodium is desired in the final product, the corresponding sulfite can be used in the second step. Alternatively, the sodium form of compound (II) can be ion-exchanged in standard fashion to any desired cation, M. The resin purification treatment is unnecessary when preparing the disulfonate.

The sulfates of the type (I) and (II) are easily prepared by reacting one of two moles of chlorosulfonic acid with the Ethoquads, respectively. The same consideration with regard to selection of cation M holds true for the sulfates as for the sulfonates.

It will be appreciated that a variety of diethoxylated amino starting materials can be employed in the foregoing reaction scheme. For example, Ethoquad derivatives having variations in groups $R_1$ and $R_2$ are commercially available, e.g., compounds wherein $R_1$ is an average $C_{12}$ cut. Moreover, precursor compounds having varying sums of $y$ and $x$ (within the recited range) can be selected according to the desires of the user. Compounds wherein $y$ and $x$ are of approximately equal length, the sum of $y$ and $x$ being from about 12 to about 25, most preferably fom 15 to about 25, are especially useful herein.

It will be further appreciated that a variety of other starting materials can be employed to prepare various di-ethoxylated precursors of the present zwitterionic compounds. For example, the Ethomeens (a tradename of a clas of compounds marketed by the Armak Company, a division of the Armour Company) can be quaternized to produce variations of the commercial Ethoquads. Thus, Ethomeens of the general formula $R—N(C_2H_4O)_xH(C_2H_4O)_yH$, when R is alkyl, can be reacted with excess alkyl iodide or hydroxy-substituted alkyl iodide ($CH_3I$, $C_2H_5I$, etc.) to produce a quaternary ammonium compound which can be sulfated or sulfonated on one or both ethylene oxide groups in the manner disclosed above.

It should be appreciated that mixtures of any of these zwitterionic compounds in any proportions may be used in the compositions of the present invention. Such mixtures may be produced intentionally by blending individual species or may arise as a result of the choice of feedstocks or as a result of the processing steps involved.

The ethoxylated zwitterionic compounds useful in the present invention desirably display appreciable solubility in aqueous media. A solubility in water at 25°C of at least 50 ppm, preferably more than 75 ppm appears to be necessary for satisfactory particulate soil removal performance, but the preferred materials have solubilities in water of 10–30% by weight.

The second essential component of a composition in accordance with the present invention is an organic detergent. This can be present at a level of from 1–99% by weight of the composition, the actual level being dependent on the end use of the composition and its desired physical form.

A wide range of organic detergents can be mixed i.e. can be considered compatible with the ethoxylated zwitterionic compounds to form compositions useful in the present invention. In the context of this invention "compatible" is defined as causing no appeciable decrease in the ability of the ethoxylated zwitterionic compound to remove and suspend particulate soil.

Classes of compatible detergents that can serve as cosurfactants include the nonionic, zwitterionic, and ampholytic surfactants which can be used in a broad range of proportions to the ethoxylated zwitterionic compound. In contrast, most anionic detergents do not enhance the particulate soil removal performance of the ethoxylated zwitterionic compounds to the same extent, especially on synthetic fibers, although delayed solubility of the anionic surfactant improves the performance of the combination. Amongst the cationic surfactants, only those having a polyoxyalkylene function are compatible with the ethoxylated zwitterionic compounds useful in the present invention.

## NONIONIC SYNTHETIC DETERGENTS

Most commonly, nonionic surfactants are compounds produced by the condensation of an alkylene oxide (hydrophilic in nature) with an organic hydrophobic compound which is usually aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene moiety which is condensed with any particular hydrophobic compound can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Another variety of nonionic surfactant is the semi-polar nonionic typified by the amine oxides, phosphine oxides, and sulfoxides.

Examples of suitable nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerized propylene, diisobutylene, octene, or nonene. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol, dodecyl phenol condensed with about 12 moles of ethylene oxide per mole of phenol, dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol, di-isooctylphenol condensed with about 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-610 marketed by the GAF Corporation; and Triton X-45, X-114, X-100 and X-102, all marketed by the Rohm and Haas Company.

2. The condensation products of aliphatic alcohols with ethylene oxide. The alkyl chain of the aliphatic alcohol may either be straight or branched and generally contains from about 8 to about 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of about 6 moles of ethylene oxide with 1 mole of tridecanol, myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of myristyl alcohol, the condensation product of ethylene oxide with coconut fatty alcohol wherein the coconut alcohol is a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms and wherein the condensate contains about 6 moles of ethylene oxide per mole of alcohol, and the condensation product of about 9 moles of ethylene oxide with the above-described coconut alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol 15-S-9 marketed by the Union Carbide Corporation, Neodol 23-6.5 marketed by the Shell Chemical Company and Kyro EOB marketed by The Procter & Gamble Company. Preferred nonionic surfactants which, when blended with the ethoxylated zwitterionic compounds, enhance their particulate soil removal performance, are the primary alcohol ethoxylates which are the subject of the commonly assigned copending Application Ser. No. 453,464 of Jerome H. Collins entitled "Detergent Compositions." This Application discloses a grease and oil-removing composition that consists essentially of at least one ethoxylate material consisting essentially of a mixture of compounds having at least two levels of ethylene oxide addition and having the formula

$$R_1\,R_2 - O(CH_2CH_2O)_n\,H$$

wherein $R_1$ is a linear alkyl residue and $R_2$ has the formula

$$—CHR_3CH_2—$$

$R_3$ being selected from the group consisting of hydrogen and mixtures thereof with not more than 40% by weight of lower alkyl, wherein $R_1$ and $R_2$ together form an alkyl residue having a mean chain length in the range of 8–15 carbon atoms, at least 65% by weight of said residue having a chain length within ± 1 carbon atoms of the mean, wherein $3.5 < n_{av} < 6.5$ provided that the total amount by weight of components in which $n = O$ shall be not greater than 5% and the total amount by weight of components in which $n = 2–7$ inclusive shall be not less than 63% based on the total weight of the, or each, said ethoxylate material and the HLB of the or each said ethoxylate material shall lie in the range 9.5–11.5, said composition being otherwise free of nonionic surfactants having an HLB outside of this range.

Preferred embodiments of this invention utilize blends of primary alcohols in which at least 90% and most preferably 95% by weight of the alcohol has a chain length within ± 1 carbon atom of the mean, wherein the amount of unethoxylated alcohol is less than 1% by weight and wherein the amount of ethoxylated alcohols having 2–7 ethylene oxide groups is at least 70% by weight. Preferably ethoxylates having a mean chain length of $C_{12}$ and below contain at least 55% by weight of material having 2–6 ethoxylate groups while for ethoxylates having a chain length of $C_{12}$–$C_{13}$ at least 55% by weight of the material has 3–7 ethoxylate groups. Ethoxylates having a chain length in the $C_{14-15}$ range preferably have at least 55% by weight of $E_3$–$E_8$ material. In the preferred embodiments of the invention the HLB of the ethoxylates are in the range 10.0–11.1.

3. The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds has a molecular weight of from about 1500 to 1800 and of course exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water-solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product. Examples of compounds of this type include certain of the commercially available Pluronic surfactants marketed by the Wyandotte Chemicals Corporation.

4. The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. The hydrophobic base of these products consists of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of from about 2500 to about

3000. This base is condensed with ethylene oxide to the extent that the condensation product contains from about 40 to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic compounds marketed by the Wyandotte Chemicals Corporation.

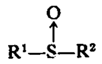
5. Surfactants having the formula $R^1R^2R^3N \rightarrow O$ (amine oxide surfactants) wherein $R^1$ is an alkyl group containing from about 10 to about 18 carbon atoms, from 0 to about 2 hydroxy groups and from 0 to about 5 ether linkages, there being at least one moiety of $R^1$ which is an alkyl group containing from about 10 to about 18 carbon atoms and no ether linkages, and each $R^2$ and $R^3$ is selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms;

Specific examples of amine oxide surfactants include: dimethyldodecylamine oxide, dimethyltetradecylamine oxide, ethylmethyltetradecylamine oxide, cetyldimethylamine oxide, dimethylstearylamine oxide, cetylethylpropylamine oxide, diethyldodecylamine oxide, diethyltetradecylamine oxide, dipropyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, bis-(2-hydroxyethyl)-3-dodecoxy-2-hydroxypropylamine oxide, (2-hydroxypropyl)methyltetradecylamine oxide, dimethyloleylamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, and the corresponding decyl, hexadecyl and octadecyl homologs of the above compounds.

6. Surfactants having the formula $R^1R^2R^3P \rightarrow O$ (phosphine oxide surfactants) wherein $R^1$ is an alkyl group containing from about 10 to about 28 carbon atoms, from 0 to about 2 hydroxy groups and from 0 to about 5 ether linkages, there being at least one moiety of $R'$ which is an alkyl group containing from about 10 to about 18 carbon atoms and no ether linkages, and each $R^2$ and $R^3$ is selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms.

Specific examples of the phosphine oxide detergents include: dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, cetyldimethylphosphine oxide, dimethylstearylphosphine oxide, cetylethylpropylphosphine oxide, diethyldodecylphosphine oxide, diethyltetradecylphosphine oxide, dipropyldodecylphosphine oxide, dipropyldodecylphosphine oxide, bis-(hydroxymethyl)dodecylphosphine oxide, bis-(2-hydroxyethyl)-dodecylphosphine oxide, (2-hydroxypropyl)methyltetradecylphosphine oxide, dimethyloleylphosphine oxide, and dimethyl-(2-hydroxydodecyl)phosphine oxide and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds.

7. Surfactants having the formula:



$$R^1-\overset{\overset{O}{\uparrow}}{S}-R^2$$

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

Table 1 illustrates the clay soil removal performance of mixtures of ethoxylated zwitterionic compounds and various nonionic surfactants. Experimental Run 1 shows that the $C_{16}$ ethoxylated zwitterionic material alone at a level of 250 ppm in water closely approaches the cleaning performance of the fully formulated control product A on polyester and polycotton fabrics and achieves a major proportion of the control product performance on cotton. Experimental Run 2 shows that an appreciable proportion of this performance is retained at half the level of the ethoxylated zwitterionic compound. The addition of 125 ppm of several different nonionic cosurfactants in Runs 3, 5, 7, and 9 to the $C_{16}$ ethoxylated zwitterionic material enables the performance at 250 ppm to be approached and even exceeded, the extent of the recovery being dependent on the cosurfactant type. It can also be seen that the addition of sodium tripolyphosphate to these systems, while providing an additional benefit in one or two instances, does not give an overall advantage. While the reason for this is not fully understood, it is believed that the lack of benefit is a function of the ability of the better ethoxylated zwitterionic compounds, of which the $C_{16}$ compound is an example, to remove soil in the presence of free mineral hardness ion.

Experimental Runs 11–20 inclusive record similar data for the $C_{14}$ ethoxylated compound which, as Runs 11 and 12 demonstrate, is not as effective a material on its own as the $C_{16}$ ethoxylated compound. However, Runs 13, 15, 17, and 19 again show that the performance of the $C_{14}$ ethoxylated compound at 125 ppm can be improved by the addition of various nonionic surfactants, the improvement being seen over all fabric types and in almost every instance providing performance that exceeds that for the $C_{14}$ material at 250 ppm. Addition of sodium tripolyphosphate at 250 ppm leads to a further performance improvement which is not inconsistent with the theory that the benefit that can be derived from detergent builders in compositions of the present invention is related to the particulate soil removal performance of the ethoxylated zwitterionic materials.

Table V is a presentation of the grease and oil removal performance achieved by detergent compositions of the present invention. Runs 4 and 5 show respectively combinations of 125 p.p.m. $C_{16}$ ethoxylated zwitterionic compound of Table 1 with 125 ppm of Neodol 45 E7 and with 125 ppm of $C_{11}$–$_{15}$ secondary alcohol ethoxylate (Tergitol 15-S-9 marketed by Union Carbide Corporation). Runs 11 and 12 give the same data for the $C_{14}$ ethoxylated zwitterionic of Table 1. For both $C_{14}$ and $C_{16}$ ethoxylated zwitterionic compounds advantages can be seen on polyester fabric for the combinations relative to the performance of the ethoxylated zwitterionic compound alone at 250 ppm.

Thus for compositions of nonionic surfactants with ethoxylated zwitterionic materials useful in the present invention, it can be seen that for ethoxylated zwitterionics having good particulate soil removal performance, nonionic surfactants can be used to reduce the level of ethoxylated zwitterionic necessary to achieve a given level of performance. For ethoxylated zwitterionics not having such good particulate soil removal performance, the level of performance can be raised by the addition of nonionic surfactants and builders.

TABLE I

CLAY SOIL REMOVAL OF ETHOXYLATED ZWITTERIONIC COMPOUNDS IN COMBINATION WITH NONIONIC SURFACTANTS

Conditions: 10 Minute Tergotometer Wash in 7 grain/gal. Mineral Hardness (2:1 Ca:Mg) at 105°F

| NO. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILDER TYPE | LEVEL PPM IN SOLUTION | RELATIVE CLAY REMOVAL INDEX | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | COTTON | POLY-COTTON | POLY-ESTER |
| 1 | N—$C_{16}H_{33}$ N,N—bisCH$_3$ $(C_2H_4O)_8CH_2CH_2SO_3$ | 250 | — | — | — | — | 75 | 96 | 95 |
| 2 | " | 125 | — | — | — | — | 62 | 88 | 77 |
| 3 | " | 125 | Neodol 45-7* | 125 | — | — | 91 | 91 | 86 |
| 4 | " | 125 | " | 125 | STP | 250 | 80 | 100 | 71 |
| 5 | " | 125 | Stripped $C_{10}E_3$** | 125 | — | — | 87 | 91 | 74 |
| 6 | " | 125 | " | 125 | STP | 250 | 96 | 116 | 98 |
| 7 | " | 125 | $CnE_6$*** | 125 | — | — | 85 | 89 | 86 |
| 8 | " | 125 | " | 125 | STP | 250 | 80 | 100 | 71 |
| 9 | " | 125 | Ethomeen 18/60**** | 125 | — | — | 78 | 96 | 80 |
| 10 | " | 125 | " | 125 | STP | 250 | 90 | 113 | 88 |
| 11 | N—$C_{14}H_{29}$ N,N—bisCH$_3$ $(C_2H_4O)_8CH_2CH_2SO_3$ | 250 | — | — | — | — | 53 | 69 | 46 |
| 12 | " | 125 | — | — | — | — | 41 | 52 | 24 |
| 13 | " | 125 | Neodol 45-7* | 125 | — | — | 68 | 81 | 51 |
| 14 | " | 125 | " | 125 | STP | 250 | 78 | 98 | 94 |
| 15 | " | 125 | Stripped $C_{10}E_3$** | 125 | — | — | 57 | 92 | 52 |
| 16 | " | 125 | " | 125 | STP | 250 | 78 | 98 | 94 |
| 17 | " | 125 | $CnE_6$*** | 125 | — | — | 74 | 84 | 49 |
| 18 | " | 125 | " | 125 | STP | 250 | 80 | 93 | 59 |
| 19 | " | 125 | Ethomeen 18/60**** | 125 | — | — | 73 | 89 | 43 |
| 20 | " | 125 | " | 125 | STP | 250 | 68 | 86 | 55 |
| 21 | Formulation A | 1400 | — | — | — | — | 100 | 100 | 100 |

*Neodol 45-7 is a linear primary $C_{14-15}$ alcohol containing 15% 2-methyl branching condensed with an average of seven moles of ethylene oxide per mole of alcohol, marketed by Shell Chemical Company.

**Stripped $C_{10}E_3$ is a linear primary $C_{10}$ alcohol condensed with approximately 3 moles of ethylene oxide per mole of alcohol and then stripped to remove at least 95% of the unethoxylated alcohol and a proportion of the monoethoxylate, so as to leave a condensate having a mean of 4 moles ethylene oxide per mole of alcohol.

***Middle cut coconut alcohol condensed with an average of 6 moles of ethylene oxide per mole of alcohol.

****Ethomeen 18/60 is a tertiary $C_{18}$ amine having 2 ethoxy side chains directly attached to the nitrogen atom and containing a total of 50 ethylene oxide groups.

TABLE V

GREASE AND OIL REMOVAL OF ETHOXYLATED ZWITTERIONICS IN COMBINATION WITH OTHER SURFACTANTS

Conditions: 10 Minute Tergotometer Wash at 100°F in 5.5 grains/gal. Mineral Hardness (Ca:Mg = 3:1)

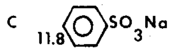
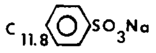
| NO. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILDER TYPE | LEVEL PPM IN SOLUTION | RELATIVE SOIL REMOVAL INDEX POLYCOTTON | | RELATIVE SOIL REMOVAL INDEX POLYESTER | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | TG | HG | TG | HC |
| 1 | N—$C_{16}H_{33}$ N,N—bisCH$_3$ $(CH_2CH_2O)_8CH_2CH_2SO_3$ | 250 | — | — | — | — | 91 | 132 | 75 | 102 |
| 2 | " | 125 |  | 125 | — | — | 88 | 157 | 91 | 110 |
| 3 | " | 125 | $C_{16}$–$C_{18}$ alkyl $(EO)_6OSO_3Na$ | 125 | — | — | 59 | 100 | 35 | 21 |
| 4 | " | 125 | $C_{14}$–$C_{15}$ primary alcohol condensed with 7 moles ethylene oxide | 125 | — | — | 62 | 83 | 91 | 126 |
| 5 | " | 125 | $C_{11}$–$C_{15}$ secondary alcohol condensed with 9 moles ethylene oxide | 125 | — | — | 100 | 136 | 86 | 109 |
| 6 | " | 125 | 3(N—$C_{16}H_{33}$N-,N—dimethyl ammonio)propane-1-sulphonate | 125 | — | — | 80 | 58 | 111 | 126 |
| 7 | " | 125 | 3(N—$C_{14.8}$ alkyl N,N-dimethyl ammonio)2-hydroxypropane-1-sulphonate | 125 | — | — | 78 | 163 | 75 | 127 |
| 8 | N—$C_{14}H_{29}$ N,N—bisCH$_3$ $(CH_2CH_2O)_8CH_2CH_2SO_3$ | 250 | — | — | — | — | 100 | 75 | 80 | 99 |
| 9 | " | 125 |  | 125 | — | — | 88 | 107 | 118 | 135 |
| 10 | " | 125 | $C_{16}$–$C_{18}$ alkyl $(EO)_6OSO_3Na$ | 125 | — | — | 55 | 120 | 43 | 36 |
| 11 | " | 125 | $C_{14}$–$C_{15}$ primary alcohol condensed with 7 moles ethylene oxide | 125 | — | — | 50 | 58 | 89 | 129 |
| 12 | " | 125 | $C_{11}$–$C_{15}$ secondary alcohol condensed with 3 moles ethylene oxide | 125 | — | — | 57 | 36 | 79 | 116 |
| 13 | " | 125 | 3(N—$C_{16}H_{33}$N- | 125 | — | — | 120 | 42 | 124 | 131 |

TABLE V-continued

GREASE AND OIL REMOVAL OF ETHOXYLATED ZWITTERIONICS IN COMBINATION WITH OTHER SURFACTANTS

Conditions: 10 Minute Tergotometer Wash at 100°F in 5.5 grains/gal. Mineral Hardness (Ca:Mg = 3:1)

| NO. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILDER TYPE | LEVEL PPM IN SOLUTION | RELATIVE SOIL REMOVAL INDEX POLYCOTTON TG | HG | POLYESTER TG | HC |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | ,N—dimethyl ammonio)propane-1-sulphonate | | | | | | | |
| 14 | " | 125 | 3(N—$C_{14.8}$ alkyl N,N-dimethyl ammonio)-2-hydroxypropane-1-sulphonate | 125 | — | — | 47 | 88 | 112 | 133 |

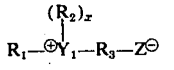
## AMPHOLYTIC SYNTHETIC DETERGENTS

Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfato. Examples of compounds falling within this definition are sodium 3-(dodecylamino)propionate, sodium 3-(dodecylamino)-propane-1-sulfonate, sodium 2-(dodecylamino)ethyl sulfate, sodium 2-(dimethylamino)octadecanoate, disodium 3-(N-carboxymethyldodecylamino)propane-1-sulfonate, disodium octadecyl-iminodiacetate, sodium 1-carboxymethyl-2-undecylimidazole, and sodium N,N-bis(2-hydroxyethyl)-2-sulfato-3-dodecoxy-propylamine. Sodium 3-(dodecylamino)propane-1-sulfonate is preferred.

## ZWITTERIONIC SYNTHETIC DETERGENTS

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

1. Compounds corresponding to the general formula



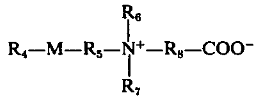
$$R_1-\overset{(R_2)_x}{\overset{|}{\oplus Y_1}}-R_3-Z^{\ominus}$$

wherein $R_1$ is alkyl, alkenyl or a hydroxyalkyl containing from about 8 to about 18 carbon atoms and containing if desired up to about 10 ethylene oxide moieties and/or a glyceryl moiety; $Y_1$ is nitrogen, phosphorus or sulfur, $R_2$ is $C_1$–$C_3$ alkyl or a $C_2$–$C_3$ $\beta$- or $\gamma$-monohydroxy alkyl containing 1 to 3 carbon atoms; $x$ is 1 when $Y_1$ is S, 2 when $Y_1$ is N or P; $R_3$ is $C_1$–$C_4$ alkylene or 2-hydroxy-, 3-propylene or 2- or 3-hydroxy butylene containing from 1 to about 5 carbon atoms; and Z is a carboxy, sulfonate, sulfate, phosphate or phosphonate group. Examples of this class of zwitterionic surfactants include 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate; 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; N,N-dimethyl-N-dodecylammonio acetate; 3-(N,N-dimethyl-N-dodecylammonio)propionate; 2-(N,N-dimethyl-N-octadecylammonio)ethyl sulfate; 3-(P,P-dimethyl-P-dodecylphosphonio)propane-1-sulfonate; 2-(S-methyl-S-tert-hexadecylsulfonio)ethane-1-sulfonate; 3-(S-methyl-S-dodecylsulfonio)propionate; 4-(S-methyl-S-tetradecylsulfonio)butyrate; 3-(N,N-dimethyl-N-4-dodecenylammonio)propane-1-sulfonate; 3-(N,N-dimethyl-N-2-diethoxyhexadecylammonio)propyl hydrogen phosphate; and 3-(N,N-dimethyl-N-4-glyceryldodecylammonio)propionate.

Preferred compounds of this class from a commercial standpoint are 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate, the alkyl group being derived from tallow fatty alcohol; 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-suffonate; 3-(N,N-dimethyl-N-tetradecylammonio)-propane-1-sulfonate; 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonate, the alkyl group being derived from the middle cut of coconut fatty alcohol; 3-(N,N-dimethyldodecylammonio)-2-hydroxypropane-1-sulfonate; 4-(N,N-dimethyl-tetradecylammonio)butane-1-sulfonate; 4-(N,N-dimethyl-N-hexadecylammonio)butane-1-sulfonate; 4-(N,N-dimethylhexadecylammonio)butyrate; 6-(N,N-dimethyl-N-octadecylammonio)hexanoate; 3-(N,N-dimethyl-N-eicosylammonio)-3-methylpropane-1-sulfonate; and 6-(N,N-dimethyl-N-hexadecylammonio)hexanoate.

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

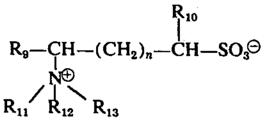
2. Compounds having the general formula:



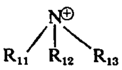
$$R_4-M-R_5-\overset{R_6}{\underset{R_7}{N^+}}-R_8-COO^-$$

wherein $R_4$ is an alkyl, cycloalkyl, aryl, aralkyl or alkaryl group containing from 10 to 20 carbon atoms; M is a bivalent radical selected from the group consisting of aminocarbonyl, carbonylamino, carbonyloxy, oxycarbonyloxy, aminocarbonylamino, the corresponding thio groupings and substituted amino derivatives; $R_5$ and $R_8$ are alkylene groups containing from 1 to 12 carbon atoms; $R_6$ is alkyl or hydroxyalkyl containing from 1 to 10 carbon atoms; $R_7$ is selected from the group consisting of $R_6$ groups $R_4—M—R_5^-$, and $—R_8—COOMe$ wherein $R_4$, $R_5$, $R_6$ and $R_8$ are as defined above and Me is a monovalent salt-forming cation. Compounds of the type include N,N-bis(oleylamidopropyl)-N-methyl-N-carboxymethylammonium betaine; N,N-bis(stearamidopropyl)-N-methyl-N-carboxymethylammonium betaine; N-(stearamidopropyl)-N-dimethyl-N-carboxymethylammonium betaine; N,N-bis-(oleylamidopropyl)-N-(2-hydroxyethyl)-N-carboxymethylammonium betaine; and N-N-bis-(stearamidopropyl)-N-(2-hydroxyethyl)-N-carboxymethylammonium betaine. Zwitterionic surfactants of this type are prepared in accordance with methods described in U.S. Pat. No. 3,265,719 and DAS 1,018,421.

3. Compounds having the general formula:

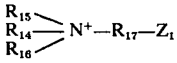


wherein $R_9$ is an alkyl group, $R_{10}$ is a hydrogen atom or an alkyl group, the total number of carbon atoms in $R_9$ and $R_{10}$ being from 8 to 16 and



represents a quaternary ammonio group in which each group $R_{11}$, $R_{12}$, and $R_{13}$ is an alkyl or hydroxyalkyl group or the groups $R_{11}$, $R_{12}$, and $R_{13}$ are conjoined in a heterocyclic ring
and $n$ is 1 or 2. Examples of suitable zwitterionic surfactants of this type include the γ and δ hexadecyl pyridino sulphobetaines, the γ and δ hexadecyl γ-picolino sulphobetaines, the γ and δ tetradecyl pyridino sulphobetaines and the hexadecyl trimethylammonio sulphobetaines. Preparation of such zwitterionic surfactants is described in British patent specification No. 1,277,200.

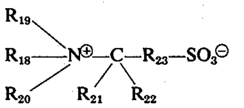
4. Compounds having the general formula



wherein $R_{14}$ is an alkarylmethylene group containing from about 8 to 24 carbon atoms in the alkyl chain; $R_{15}$ is selected from the group consisting of $R_{14}$ groups and alkyl and hydroxyalkyl groups containg from 1 to 7 carbon atoms; $R_{16}$ is alkyl or hydroxyalkyl containing from 1 to 7 carbon atoms; $R_{17}$ is alkylene or hydroxyalkylene containing from 1 to 7 carbon atoms and $Z_1$ is selected from the group consisting of sulfonate, carboxy and sulfate. Examples of zwitterionic surfactants of this type include 3-(N-4-n-dodecylbenzyl-N,N-dimethylammonio)propane-1-sulfonate; 4-(N-4-n-dodecylbenzyl-N,N-dimethylammonio)butane-1-sulfonate; 3-(N-4-n-hexadecylbenzyl-N,N-dimethylammmonio)-propane-1-sulfonate; 3-(N-4-n-dodecylbenzyl-N,N-dimethylammonio)propionate; 4-(N-4-n-hexadecylbenzyl-N,N-dimethylammonio)butyrate; 3-(N-4-n-tetradecylbenzyl-N,N-dimethylammonio)propane-1-sulfate; 3-(N-4-n-dodecylbenzyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate; 3-[N,N-di(4-n-dodecylbenzyl)-N-methylammonio]propane-1-sulfonate; 4-[N,N-di(4-n-hexadecylbenzyl)-N-methylammonio]butyrate; and 3-[N,N-di(4-n-tetradecylbenzyl)-N-methylammonio]-2-hydroxypropane-1-sulfonate.

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

5. Compounds having the general formula:



wherein $R_{18}$ is an alkylphenyl, cycloalkylphenyl or alkenylphenyl group containing from 8 to 20 carbon atoms, in the alkyl, cycloalkyl or alkenyl moiety; $R_{19}$ and $R_{20}$ are each aliphatic groups containing from 1 to 5 carbon atoms; $R_{21}$ and $R_{22}$ are each hydrogen atoms, hydroxyl groups or aliphatic groups containing from 1 to 3 carbon atoms and $R_{23}$ is an alkylene group containing from 2 to 4 carbon atoms.

Examples of zwitterionic surfactants of this type include 3-(N-dodecylphenyl- N,N-dimethylammonio)-propane-1-sulfonate; 4-(N-hexadecylphenyl-N,N-dimethylammonio)butane-1-sulfonate; and 3-(N-dodecylphenyl-N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate. Compounds of this type are described more fully in British Pat. Nos. 970,883 and 1,046,252, incorporated herein by reference.

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

Clay soil removal performance results for combinations of the ethoxylated zwitterionic compounds of the present invention with other zwitterionic surfactants are shown in Table II. Experimental Runs 1 and 2 reproduce the Table 1 results at 250 ppm and 125 ppm for the $C_{14}$ ethoxylated zwitterionic compound on its own while Runs 3 and 10 provide the same data for the $C_{16}$ material.

The data shows that for both $C_{14}$ and $C_{16}$ ethoxylated zwitterionics, combination with other zwitterionic cosurfactants results in an improvement in performance which is further enhanced by the addition of a builder (sodium tripolyphosphate).

Performance results for the $C_{16}$ APS cosurfactant at 125 ppm together with a three-component builder combination are shown in Run 19, while Runs 23 and 24 respectively show the performance of 250 ppm of a single chain length $C_{16}$ APS and a $C_{16}$ average chain length APS both built with a sodium carbonate-sodium silicate system.

It will be seen that the $C_{16}$ ethoxylated zwitterionic material on its own at 250 ppm is as good as the $C_{16}$ APS material at 125 ppm with 1000 ppm of builder and better than $C_{16}$ APS at 250 ppm with 400 ppm of builder, on both cotton and polyester fabrics.

Grease and oil removal data for combinations of the $C_{14}$ and $C_{16}$ ethoxylated zwitterionic compounds with zwitterionic cosurfactants are shown in Table V, Runs 6 and 7 ($C_{16}$) and 13 and 14 ($C_{14}$). Advantages are again apparent for the combinations in removing both triglyceride and hydrocarbon stains from polyester fabrics although the results for polycotton are more variable.

TABLE II

CLAY SOIL REMOVAL OF ETHOXYLATED ZWITTERIONIC COMPOUNDS IN COMBINATION WITH ZWITTERIONIC SURFACTANTS

Conditions: 10 Minute Tergotometer Wash in 7 grains/gal. Mineral Hardness (2:1 Ca:Mg) at 105°F

Cosurfactants were 3-(N-alkyl N,N-dimethyl ammonio)propane-1-sulphonate(APS) and 3-(N-alkyl N,N-dimethyl ammonio)-2-hydroxy propane-1-sulphonate(HAPS)

| NO. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILDER TYPE | LEVEL PPM IN SOLUTION | RELATIVE CLAY REMOVAL INDEX | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | COTTON | POLY-COTTON | POLY-ESTER |
| 1 | N—$C_{14}H_{29}$ N,N—bisCH$_3$ ($C_2H_4O$)$_8$CH$_2$CH$_2$SO$_3$ | 250 | — | — | — | — | 53 | 69 | 46 |
| 2 | 〃 | 125 | — | — | — | — | 41 | 52 | 24 |
| 3 | 〃 | 125 | $C_{14}$ APS | 125 | — | — | 79 | 84 | 80 |
| 4 | 〃 | 125 | 〃 | 125 | STP | 250 | 94 | 102 | 101 |
| 5 | 〃 | 125 | $C_{16}$ APS | 125 | — | — | 77 | 91 | 89 |
| 6 | 〃 | 125 | 〃 | 125 | STP | 250 | 96 | 105 | 103 |
| 7 | 〃 | 125 | $C_{14.8}$ HAPS | 125 | — | — | 81 | 90 | 77 |
| 8 | 〃 | 125 | 〃 | 125 | STP | 250 | 112 | 101 | 107 |
| 9 | N—$C_{16}H_{33}$ N,N—bisCH$_3$ ($C_2H_4O$)$_8$CH$_2$CH$_2$SO$_3$ | 250 | — | — | — | — | 75 | 96 | 95 |
| 10 | 〃 | 125 | — | — | — | — | 62 | 88 | 77 |
| 11 | – | 125 | $C_{14}$ APS | 125 | — | — | 84 | 84 | 90 |
| 12 | 〃 | 125 | 〃 | 125 | STP | 250 | 114 | 100 | 105 |
| 13 | 〃 | 125 | $C_{16}$ APS | 125 | — | — | 92 | 88 | 94 |
| 14 | 〃 | 125 | 〃 | 125 | STP | 250 | 110 | 99 | 104 |
| 15 | 〃 | 125 | $C_{14.8}$ HAPS | 125 | — | — | 86 | 90 | 80 |
| 16 | 〃 | 125 | 〃 | 125 | STP | 250 | 106 | 97 | 103 |
| 17 | N—$C_{18}H_{37}$ N,N—bisCH$_3$ ($C_2H_4O$)$_8$CH$_2$CH$_2$SO$_3$ | 125 | $C_{16}$ APS | 125 | Alumino-silicate*<br>$Na_2CO_3$<br>$Na_2SiO_3$** | 600<br>200<br>200 | 108 | — | 104 |
| 18 | 〃 | 63 | 〃 | 63 | 〃<br>〃<br>〃 | 600<br>200<br>200 | 94 | — | 106 |
| 19 | 〃 | 0 | 〃 | 125 | 〃<br>〃<br>〃 | 600<br>200<br>200 | 76 | — | 96 |
| 20 | 〃 | 125 | 〃 | 125 | $Na_2CO_3$<br>$Na_2SiO_3$** | 200<br>200 | 86 | — | 106 |
| 21 | 〃 | 25 | 〃 | 225 | 〃<br>〃 | 200<br>200 | 81 | — | 94 |
| 22 | 〃 | 13 | 〃 | 237 | 〃<br>〃 | 200<br>200 | 81 | — | 90 |
| 23 | 〃 | 0 | 〃 | 250/pure | 〃<br>〃 | 200<br>200 | 65 | 87 | 51 |
| 24 | 〃 | 0 | 〃 | 250/avge | 〃<br>200 | 200 | 70 | — | 84 |

*The Aluminosilicate builder used had the formula $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$

**$SiO_2$ : $Na_2O$ ratio = 3.2:1

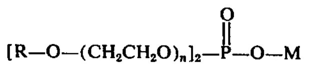
## ANIONIC DETERGENTS

This class of detergents includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkylolamminium salts of higher fatty acids containing from about eight to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Suitable fatty acids can be obtained from natural sources such as, for instance, from plant or animal esters (e.g., palm oil, coconut oil, babassu oil, soybean oil, caster oil, tallow, whale and fish oils, grease, lard, and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Napthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Anionic synthetic detergents include water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 22 carbon atoms and a moiety selected from the group consisting of sulfonic acid and sulfuric acid ester moieties. (Included in the term alkyl is the alkyl portion of higher acyl moieties.) Examples of this group of synthetic detergents are the sodium and potassium 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 and potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 20 carbon atoms in straight-chain or branched-chain configuration, e.g. those of the type described in U.S. Pat. Nos. 2,220,099 and 2,477,383 (especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 11.8 carbon atoms and commonly abbreviated as $C_{11.8}LAS$); sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates.

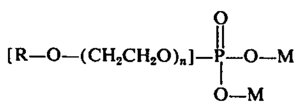
Anionic phosphate surfactants are also useful in the present invention. These are surface active materials having substantial detergent capability in which the anionic solubilizing group connecting hydrophobic moieties is an oxy acid of phosphorus. The more common solubilizing groups, of course, are $—SO_4H$ and $—SO_3H$. Alkyl phosphate esters such as $(R—O)_2PO_2H$ and $ROPO_3H_2$ in which R represents an alkyl chain containing from about 8 to about 20 carbon atoms are useful herein.

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



$$[R—O—(CH_2CH_2O)_n]_2—\overset{\overset{\displaystyle O}{\|}}{P}—O—M$$

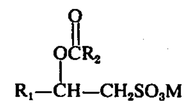
or



$$[R—O—(CH_2CH_2O)_n]—\underset{\underset{\displaystyle O—M}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}—O—M$$

in which R represents an alkyl group containing from about 8 to 20 carbon atoms, or an alkylphenyl group in which the alkyl group contains from about 8 to 20 carbon atoms, and M represents a soluble cation such as hydrogen, sodium, potassium, ammonium or substituted ammonium; and in which n is an integer from 1 to about 40.

Another class of suitable anionic organic detergents particularly useful in this invention includes salts of 2-acyloxyalkane-1-sulfonic acids exemplified by 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. These salts have the formula



$$R_1—\overset{\overset{\displaystyle O\overset{\overset{\displaystyle O}{\|}}{C}R_2}{|}}{C}H—CH_2SO_3M$$

where $R_1$ is alkyl of about 9 to about 23 carbon atoms (forming with the two carbon atoms an alkane group); $R_2$ is alkyl of 1 to about 8 carbon atoms; and M is a water-soluble cation.

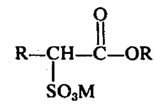
The water-soluble cation, M, in the hereinbefore described structural formula can be, for example, an alkali metal cation (e.g., sodium, potassium, lithium), ammonium or substituted-ammonium cation. Specific examples of substituted ammonium cations include methyl-, dimethyl-, and trimethyl- ammonium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

Specific examples of beta-acyloxy-alkane-1-sulfonates, or alternatively 2-acyloxy-alkane-1-sulfonates, useful herein include the sodium salt of 2-acetoxy-tridecane-1-sulfonic acid; the potassium salt of 2-propionyloxy-tetradecane-1-sulfonic acid; the lithium salt of 2-butanoyloxy-tetradecane-1-sulfonic acid; the sodium salt of 2-pentanoyloxy-pentadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-hexadecane-1-sulfonic acid; the potassium salt of 2-octanoyloxy-tetradecane-1-sulfonic acid; the sodium salt of 2-acetoxy-heptadecane-1-sulfonic acid; the lithium salt of 2-acetoxy-octadecane-1-sulfonic acid; the potassium salt of 2-acetoxy-nonadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-uncosane-1-sulfonic acid; the sodium salt of 2-propionyloxy-docosane-1-sulfonic acid; the isomers thereof.

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

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

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



$$R—\underset{\underset{\displaystyle SO_3M}{|}}{C}H—\overset{\overset{\displaystyle O}{\|}}{C}—OR'$$

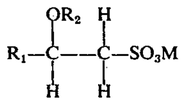
wherein R is $C_8$ to $C_{20}$ alkyl, M is a water-soluble cation as hereinbefore disclosed, preferably sodium ion, and R' is either short chain length alkyl, e.g., methyl, ethyl, propyl, and butyl or medium chain length alkyl, e.g., hexyl, heptyl, octyl, and nonyl. In the latter case, i.e. the medium chain length esters, the total number of carbon atoms should ideally be in the range 18–20 for optimum performance. These compounds are prepared by the esterification of α-sulfonated carboxylic acids, which are commercially available, using standard techniques. Specific examples of the alkylated α-sulfocarboxylates preferred for use herein include:

a. Short chain length esters
ammonium methyl-α-sulfopalmitate,
triethanolammonium ethyl-α-sulfostearate,
sodium methyl-α-sulfopalmitate,
sodium ethyl-α-sulfopalmitate,
sodium butyl-α-sulfostearate,
potassium methyl-α-sulfolaurate,
lithium methyl-α-sulfolaurate,
as well as mixtures thereof.

b. Medium chain length esters
sodium hexyl-α-sulphomyristate

potassium octyl-α-sulpholaurate
ammonium methyl-hexyl-α-sulpholaurate
and mixtures thereof.

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



$$R_1-\overset{\displaystyle OR_2}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-SO_3M$$

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

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

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

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula

$$R_1 - SO_3 - M$$

wherein $R_1$ is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from 8 to 24, preferably 12 to 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, meso-, and n-paraffins, having 8 to 24 carbon atoms, preferably 12 to 18 carbon atoms and a sulfonating agent e.g. $SO_3$, $H_2SO_4$, oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated $C_{12-18}$ n-paraffins.

Other synthetic anionic detergents useful herein are alkyl ether sulfates. These materials have the formula $RO(C_2H_4O)_xSO_3M$ wherein R is alkyl or alkenyl of about 10 to about 20 carbon atoms, $x$ is 1 to 30, and M is a water-soluble cation as defined hereinbefore. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having about 10 to about 20 carbon atoms. Preferably, R has 14 to 18 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols are reacted with 1 to 30, and especially 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 6 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates of the present invention are sodium coconut alkyl triethylene glycol ether sulfate; lithium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alky hexaoxyethylene sulfate. Highly preferred alkyl ether sulphates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to 16 carbon atoms and an average degree of ethoxylation of from about 1 to 4 moles of ethylene oxide. Such a mixture also comprises from about 0 to 20% by weight $C_{12-13}$ compounds; from 60 to 100% by weight of $C_{14-15-16}$ compounds; from about 0 to 20% by weight of $C_{17-18-19}$ compounds; from about 3 to 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to 90% by weight of compounds having a degree of ethoxylation of from 1 to 4; from about 10 to 25% by weight of compounds having a degree of ethoxylation of from 4 to 8; and from about 0.1 to 15% by weight of compounds having a degree of ethoxylation greater than 8.

Additional examples of anionic synthetic detergents which come within the terms of the present invention are the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic detergents of this variety are set forth in U.S. Pat. Nos. 2,486,921; 2,486,922; and 2,396,278.

Additional examples of anionic synthetic detergents, which come within the terms of the present invention, are the compounds which contain two anionic functional groups. These are referred to as di-anionic detergents. Suitable dianionic detergents are the disulfonates, disulfates, or mixtures thereof which may be represented by the following formulae:

$$R(SO_3)_2M_2,\ R(SO_4)_2M_2,\ R(SO_3)\ (SO_4)M_2$$

where R is an acyclic aliphatic hydrocarbyl group having 15 to 20 carbon atoms and M is a water-solubilizing cation, for example, the $C_{15}$ to $C_{20}$ disodium 1,2-alkyldisulfates, $C_{15}$ to $C_{20}$ dipotassium-1,2-alkyldisulfonates or disulfates, disodium 1,9-hexadecyl disulfates, $C_{15}$ to $C_{20}$ disodium-1,2-alkyldisulfonates, disodium 1,9-stearyldisulfates and 6,10-octadecyldisulfates.

The aliphatic portion of the disulfates or disulfonates is generally substantially linear, thereby imparting desirable biodegradable properties to the detergent compound.

The water-solubilizing cations include the customary cations known in the detergent art, i.e., the alkali metals, and the ammonium cations, as well as other metals in group IIA, IIB, IIIA, IVA and IVB of the Periodic Table except for boron. The preferred water-solubilizing cations are sodium or potassium. These dianionic detergents are more fully described in British Pat. No. 1,151,392 which is hereby incorporated by reference.

Still other anionic synthetic detergents include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfo-succinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic detergents utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid $SO_2$, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous $SO_2$, etc., when used in the gaseous form.

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

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific $\alpha$-olefin sulfonate mixture of the above type is described more fully in the U.S. Pat. No. 3,332,880 of Phillip F. Pflaumer and Adrian Kessler, issued July 25, 1967, titled "Detergent Composition", the disclosure of which is incorporated herein by reference.

In Table II A–D clay soil removal results are given for combinations of ethoxylated zwitterionic compounds and anionic surfactants. Experimental Runs 1, 2, 33, and 34 represent comparative results for the $C_{16}$ and $C_{14}$ ethoxylated zwitterionic compounds respectively at levels of 250 and 125 ppm. Experimental Runs 3–14 inclusive also give comparative results for various anionic surfactants and, with the exception of the alkyl ether sulphate, these materials all show very poor clay soil removal when used alone in water.

Runs 35–40 inclusive demonstrate the effect of various anionic cosurfactants on the performance of the $C_{14}$ ethoxylated zwitterionic compound, both with and without builder at a level of 125 ppm each (i.e. a 1:1 ratio) of the $C_{14}$ compound and cosurfactant. It can be seen that for ethoxylated zwitterionic compounds having mediocre particulate soil removal performance addition of anionic cosurfactants provides a benefit but that incorporation of builder gives little further improvement.

Runs 15–32 and 41–88 demonstrate the effect of various anionic cosurfactants on the performance of the $C_{16}$ ethoxylated zwitterionic compound in the presence and absence of builder. Runs 15–32 show that, at 125 ppm each of $C_{16}$ compound and anionic cosurfactant in the absence of builder, particulate soil removal performance of the ethoxylated zwitterionic compound is depressed. It is restored, in varying degrees, by either delaying the solution of the anionic cosurfactant (Runs 16, 19, 22, 25, 28, and 31) which produces a marked effect on the performance on polyester fabrics, or by adding builder to the system, which shows a benefit for the more hydrophilic cotton-containing fabrics.

Runs 41–58 duplicate Runs 15–32 except that the level of $C_{16}$ ethoxylated zwitterionic compound is at 250 ppm in solution, i.e. a ratio of $C_{16}$ compound to anionic cosurfactant of 2:1. It can be seen that the depressive effect of the anionic surfactant is less evident, particularly for the composition containing sodium stearate. Furthermore, the effect of either delaying cosurfactant solution, or of adding builder, is to appreciably improve performance and in certain specific instances, to equal the performance attained by 250 ppm $C_{16}$ ethoxylated zwitterionic compound on its own.

Runs 59–88 provide further evidence of the extent to which anionic surfactants inhibit the particulate soil removal performance of the ethoxylated zwitterionic compounds of the present invention. A reduction in performance is still apparent at a ratio of ethoxylated zwitterionic to anionic cosurfactant of 4:1, the exception again being sodium stearate, but is much less noticeable at a ratio of 9:1, the addition of builder providing a benefit in each instance. At an ethoxylated zwitterionic compound level of 300 ppm in solution and with 25 ppm cosurfactant (12:1 ratio) substantially no diminution in particulate soil removal performance is seen.

As noted above, the results show the sequential dissolution of first the ethoxylated zwitterionic and then the anionic cosurfactant serves to minimize the adverse effect of the latter on the clay removal performance of the former. Such sequential dissolution can be achieved by any one of a number of known methods, e.g., by coating, granulation, or agglomeration of the anionic with other conventional detergent components such as $C_{12-20}$ fatty acids, $c_{12-18}$ fatty acid amides and alkanol amides, high molecular weight (i.e. MWt>1000) polyethylene glycols, hydratable inorganic builder salts such as alkali metal polyphosphates, and porous siliceous materials such as those sold under the Trade Name "Zeosyl" by J. M. Huber Corporation. Conveniently, the diluent component is incorporated at a level of 5 to 50%, preferably 10 to 25%, by weight of the mixture of anionic surfactant plus diluent so as to effect a delay of at least 60 seconds in the complete dissolution or dispersion of the mixture in an aqueous medium at 100°F.

Similarly, microencapsulation using, e.g., hydrolysed gelatin, agar, or polyvinyl alcohol wall materials can be employed where low levels of anionic material are desired. Techniques for microencapsulating materials, including detergent components, are well known in the art. A typical disclosure of such techniques is given in Kirk-Othmer Encyclopedia of Chemical Technology, 2nd edition, 13, pp. 436–456, published in 1967 by John Wiley & Sons, Inc. This disclosure is incorporated herein by reference.

## TABLE IIIA

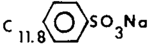
CLAY SOIL REMOVAL OF ETHOXYLATED ZWITTERIONIC COMPOUNDS IN COMBINATION WITH ANIONIC SURFACTANTS

Conditions: 10 Minute Tergotometer Wash at 105°F in 5.5 grains/gal. Mineral Hardness (Ca:Mg = 3:1)

| | | | | | | | RELATIVE CLAY REMOVAL INDEX | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILDER TYPE | LEVEL PPM IN SOLUTION | COTTON | POLY-COTTON | POLY-ESTER |
| 1 | N—$C_{16}H_{33}$ N,N—bis$CH_3$ $(C_2H_4O)_8CH_2CH_2SO_3$ | 250 | — | — | — | — | 90 | 92 | 95 |
| 2 | ″ | 125 | — | — | — | — | 69 | 88 | 93 |

TABLE IIIA-continued

CLAY SOIL REMOVAL OF ETHOXYLATED ZWITTERIONIC COMPOUNDS IN COMBINATION WITH ANIONIC SURFACTANTS
Conditions: 10 Minute Tergotometer Wash at 105°F in 5.5 grains/gal. Mineral Hardness (Ca:Mg = 3:1)

| No. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILD-ER TYPE | LEVEL PPM IN SOLUTION | RELATIVE CLAY REMOVAL INDEX COTTON | POLY-COTTON | POLY-ESTER |
|---|---|---|---|---|---|---|---|---|---|
| 3 | — | — |  | 125 | — | — | 23 | 64 | 20 |
| 4 | — | — | " | 250 | — | — | 41 | 69 | 21 |
| 5 | — | — | $C_{16-18}$ alkyl $OSO_3Na$ | 125 | — | — | 32 | 32 | 27 |
| 6 | — | — | " | 250 | — | — | 36 | 33 | 31 |
| 7 | — | — | $C_{16}$–$C_{18}$ alkyl $(EO)_6OSO_3Na$ | 125 | — | — | 71 | 71 | 45 |
| 8 | — | — | " | 250 | — | — | 84 | 79 | 51 |
| 9 | — | — | Na stearate | 125 | — | — | 30 | 40 | 30 |
| 10 | — | — | " | 250 | — | — | 30 | 43 | 34 |
| 11 | — | — | $C_{14}$–$C_{16}$ alkane $SO_3Na$ | 125 | — | — | 60 | 63 | 46 |
| 12 | — | — | " | 250 | — | — | 64 | 63 | 46 |
| 13 | — | — | Na Hexyl α-sulpho Laurate | 125 | — | — | 35 | 55 | 34 |
| 14 | — | — | " | 250 | — | — | 35 | 60 | 32 |
| 15 | N—$C_{16}H_{33}$ N,N—bis$CH_3$ $(C_2H_4O)_8CH_2CH_2SO_3$ | 125 |  | 125 | — | — | 39 | 81 | 34 |
| 16 | " | 125 | " | 125* | — | — | 64 | 71 | 78 |
| 17 | " | 125 | " | 125 | STP | 250 | 52 | 79 | 35 |
| 18 | " | 125 | $C_{16}$–$C_{18}$ alkyl $OSO_3Na$ | 125 | — | — | 38 | 60 | 30 |
| 19 | " | 125 | " | 125* | — | — | 61 | 67 | 77 |
| 20 | " | 125 | " | 125 | STP | 250 | 48 | 74 | 36 |
| 21 | " | 125 | $C_{16}$–$C_{18}$ alkyl $(EO)_6OSO_3Na$ | 125 | — | — | 38 | 65 | 31 |
| 22 | " | 125 | " | 125* | — | — | 66 | 65 | 72 |
| 23 | " | 125 | " | 125 | STP | 250 | 52 | 78 | 37 |
| 24 | " | 125 | Na stearate | 125 | — | — | 43 | 85 | 72 |
| 25 | " | 125 | " | 125* | — | — | 77 | 78 | 93 |
| 26 | " | 125 | " | 125 | STP | 250 | 61 | 96 | 89 |
| 27 | " | 125 | C $_{14}$–$C_{16}$ alkane $SO_3Na$ | 125 | — | — | 53 | 68 | 37 |
| 28 | " | 125 | " | 125* | — | — | 69 | 83 | 78 |
| 29 | " | 125 | " | 125 | STP | 250 | 55 | 69 | 37 |
| 30 | " | 125 | Na Hexyl α-sulpho Laurate | 125 | — | — | 53 | 68 | 34 |
| 31 | " | 125 | " | 125* | — | — | 55 | 78 | 78 |
| 32 | " | 125 | " | 125 | STP | 250 | 55 | 73 | 40 |

*Introduced 2 minutes after ethoxylated zwitterionic compound contacted with fabrics.

TABLE IIIB

CLAY SOIL REMOVAL OF ETHOXYLATED ZWITTERIONIC COMPOUNDS IN COMBINATION WITH ANIONIC SURFACTANTS
Conditions: 10 Minute Tergotometer Wash in 7 grains/gal. Mineral Hardness (2:1 Ca:Mg) at 105°F

| NO. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILD-ER TYPE | LEVEL PPM IN SOLUTION | RELATIVE CLAY REMOVAL INDEX COTTON | POLY-COTTON | POLY-ESTER |
|---|---|---|---|---|---|---|---|---|---|
| 33 | N—$C_{14}$ $H_{29}$ N,N—bis$CH_3$ $(C_2H_4O)_8CH_2CH_2SO_3$ | 250 | — | — | — | — | 53 | 69 | 46 |
| 34 | " | 125 | — | — | — | — | 41 | 52 | 24 |
| 35 | " | 125 |  | 125 | — | — | 69 | 89 | 38 |
| 36 | " | 125 | " | 125 | STP | 250 | 68 | 73 | 37 |
| 37 | " | 125 | $C_{16-18}$ alkyl $(EO)_6OSO_3Na$ | 125 | — | — | 65 | 70 | 34 |
| 38 | " | 125 | " | 125 | STP | 250 | 77 | 75 | 40 |
| 39 | " | 125 | Na stearate | 125 | — | — | 44 | 57 | 31 |
| 40 | " | 125 | " | 125 | STP | 250 | 72 | 62 | 24 |

TABLE IIIC

CLAY SOIL REMOVAL OF ETHOXYLATED ZWITTERIONIC COMPOUNDS IN COMBINATION WITH ANIONIC SURFACTANTS
Conditions: 10 Minute Tergotometer Wash at 105°F in 5.5 grains/gal. Mineral Hardness (Ca:Mg = 3:1)

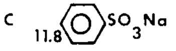
| NO. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILD-ER TYPE | LEVEL PPM IN SOLUTION | RELATIVE CLAY REMOVAL INDEX COTTON | POLY-COTTON | POLY-ESTER |
|---|---|---|---|---|---|---|---|---|---|
| 41 | N—$C_{16}H_{33}$ N,N—bis$CH_3$ $(C_2H_4O)_8CH_2CH_2SO_3$ | 250 |  | 125 | — | — | 68 | 53 | 37 |

TABLE IIIC – Continued

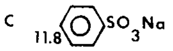
CLAY SOIL REMOVAL OF ETHOXYLATED ZWITTERIONIC COMPOUNDS IN COMBINATION WITH ANIONIC SURFACTANTS
Conditions: 10 Minute Tergotometer Wash at 105°F in 5.5 grains/gal. Mineral Hardness (Ca:Mg = 3:1)

| No. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILDER TYPE | LEVEL PPM IN SOLUTION | RELATIVE CLAY REMOVAL INDEX | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | COTTON | POLY-COTTON | POLY-ESTER |
| 42 | '' | 250 | '' | 125* | — | — | 89 | 82 | 100 |
| 43 | '' | 250 | '' | 125 | STP | 250 | 63 | 68 | 47 |
| 44 | '' | 250 | $C_{16}$–$C_{18}$ alkyl $OSO_3Na$ | 125 | — | — | 60 | 67 | 31 |
| 45 | '' | 250 | '' | 125* | — | — | 75 | 82 | 91 |
| 46 | '' | 250 | '' | 125 | STP | 250 | 77 | 74 | 42 |
| 47 | '' | 250 | $C_{16}$–$C_{18}$ alkyl $(EO)_6OSO_3Na$ | 125 | — | — | 30 | 68 | 42 |
| 48 | '' | 250 | '' | 125* | — | — | 113 | 83 | 62 |
| 49 | '' | 250 | '' | 125 | STP | 250 | 46 | 79 | 61 |
| 50 | '' | 250 | Na stearate | 125 | — | — | 84 | 92 | 95 |
| 51 | '' | 250 | '' | 125* | — | — | 95 | 92 | 96 |
| 52 | '' | 250 | '' | 125 | STP | 250 | 105 | 103 | 99 |
| 53 | '' | 250 | $C_{14}$–$C_{16}$ alkane $SO_3Na$ | 125 | — | — | 62 | 69 | 34 |
| 54 | '' | 250 | '' | 125 | — | — | 95 | 92 | 96 |
| 55 | '' | 250 | ''125 | STP | 250 | 55 | 31 | 87 | |
| 56 | '' | 250 | Na Hexyl α-sulpho Laurate | 125 | — | — | 67 | 73 | 36 |
| 57 | '' | 250 | '' | 125* | — | — | 75 | 89 | 89 |
| 58 | '' | 250 | '' | 125 | STP | 63 | 78 | 35 | |

*Introduced 2 minutes after ethoxylated zwitterionic compound contacted with fabrics.

TABLE IIID

CLAY SOIL REMOVAL OF ETHOXYLATED ZWITTERIONIC COMPOUNDS IN COMBINATIN WITH ANIONIC SURFACTANTS
Conditions: 10 Minute Tergotometer Wash at 105°F in 5.5 grains/gal. Mineral Hardness (Ca:Mg = 3:1)

| NO. | ETHOXYLATED SWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILDER TYPE | LEVEL PPM IN SOLUTION | RELATIVE CLAY REMOVAL INDEX | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | COTTON | POLY-COTTON | POLY-ESTER |
| 59 | N—$C_{16}H_{33}$ N,N—bis$CH_3$ $(CH_2CH_2O)_8CH_2CH_2SO_3$ | 200 |  | 50 | — | — | 44 | 79 | 36 |
| 60 | '' | 200 | '' | 50 | STP | 250 | 71 | 60 | 62 |
| 61 | '' | 225 | '' | 25 | — | — | 52 | 82 | 59 |
| 62 | '' | 225 | '' | 25 | STP | 250 | 93 | 97 | 96 |
| 63 | '' | 300 | '' | 25 | — | — | 91 | 90 | 96 |
| 64 | '' | 200 | $C_{16}$–$C_{18}$ alkyl $OSO_3Na$ | 50 | — | — | 54 | 68 | 32 |
| 65 | '' | 200 | '' | 50 | STP | 250 | 59 | 71 | 34 |
| 66 | '' | 225 | '' | 25 | — | — | 70 | 81 | 64 |
| 67 | '' | 225 | '' | 25 | STP | 250 | 86 | 94 | 92 |
| 68 | '' | 300 | '' | 25 | — | — | 88 | 88 | 96 |
| 69 | '' | 200 | $C_{16}$–$C_{18}$ alkyl $(EO)_6OSO_3Na$ | 50 | — | — | 59 | 72 | 39 |
| 70 | '' | 200 | '' | 50 | STP | 250 | 63 | 67 | 42 |
| 71 | '' | 225 | '' | 25 | — | — | 71 | 83 | 73 |
| 72 | '' | 225 | '' | 25 | STP | 250 | 82 | 88 | 96 |
| 73 | '' | 300 | '' | 25 | — | — | 88 | g3 | 95 |
| 74 | N—$C_{16}H_{33}$ N,N—bis$CH_3$ $(CH_2CH_2O)_8CH_2CH_2SO_3$ | 200 | Na stearate | 50 | — | — | 89 | 87 | 91 |
| 75 | '' | 200 | '' | 50 | STP | 250 | 92 | 99 | 99 |
| 76 | '' | 225 | '' | 25 | — | — | 94 | 89 | 93 |
| 77 | '' | 225 | '' | 25 | STP | 250 | 101 | 100 | 101 |
| 78 | '' | 300 | '' | 25 | — | — | 88 | 90 | 96 |
| 79 | '' | 200 | $C_{14}$–$C_{16}$ alkane $SO_3Na$ | 50 | — | — | 70 | 72 | 36 |
| 80 | '' | 200 | '' | 50 | STP | 250 | 71 | 63 | 42 |
| 81 | '' | 225 | '' | 25 | — | — | 75 | 76 | 45 |
| 82 | '' | 225 | '' | 25 | STP | 250 | 84 | 78 | 73 |
| 83 | '' | 300 | '' | 25 | — | — | 93 | 83 | 96 |
| 84 | '' | 200 | Na Hexyl α-sulpho Laurate | 50 | — | — | 50 | 71 | 42 |
| 85 | '' | 200 | '' | 50 | STP | 250 | 50 | 79 | 41 |
| 86 | '' | 225 | '' | 25 | — | — | 61 | 82 | 74 |
| 87 | '' | 225 | '' | 25 | STP | 250 | 70 | 94 | 79 |
| 88 | '' | 300 | '' | 25 | — | — | 70 | 90 | 91 |

Grease and oil removal data are shown in Table V for combinations of $C_{11.8}$ LAS and $C_{16-18}$ alkyl $E_6S$ respectively with both $C_{16}$ and $C_{14}$ ethoxylated zwitterionic compounds, and it can be seen that $C_{11.8}$ LAS provides performance advantages relative to the control product. In contrast, the ethoxylated sulphate surfactant serves to inhibit grease and oil removal.

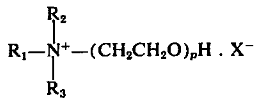
The effect of anionic cosurfactants on the sudsing characteristics of the ethoxylated zwitterionic compounds of the present invention is illustrated in the Figure in which the suds heights developed by the Recirculating Suds Generator (RSG) are plotted for different blends of $C_{16}$ ethoxylated zwitterionic compound and sodium $C_{11.8}$ linear alkyl benzene sulphonate over a 10-minute time interval. It can be seen that an appreciable fraction of the sudsing performance achieved by 100% $C_{11.8}$ LAS is given by blends in which the level of $C_{11.8}$ LAS is as low as 5%, the sudsing performance increasing with increasing $C_{11.8}$ LAS level.

Thus anionic surfactants can be incorporated in detergent compositions in accordance with the present invention although they should not exceed 50% by weight of the ethoxylated zwitterionic-cosurfactant mixture if the desirable particulate soil removal properties of the ethoxylated zwitterionic compound are to be retained. Alkali metal salts of aliphatic carboxylic acids can be incorporated at these levels without special formulation precautions but most anionic cosurfactant levels in excess of 20% of the mixture, more preferably in excess of 10% of the mixture, require incorporation in a manner that will delay the cosurfactant solubility.

## CATIONIC DETERGENTS

Only those cationic detergents having a hydrophilic grouping with the molecule have been found to be compatible with the ethoxylated zwitterionic compounds useful in the present invention.

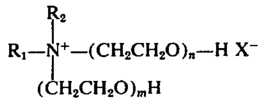
Thus compounds of the class



$$R_1-\overset{\overset{R_2}{|}}{\underset{\underset{R_3}{|}}{N^+}}-(CH_2CH_2O)_pH\ .\ X^-$$

can be employed where $R_1$ is a $C_{12}$–$C_{18}$ linear or branched alkyl or alkenyl group $R_2$ and $R_3$ are $C_1$–$C_4$ alkyl or hydroxy alkyl groups, p has a value in the range 3–50, and $X^-$ is a compatible anion such as chloride, bromide, iodide, sulphate, methosulphate acetate or phosphate.

Similarly, compounds having the structure



$$R_1-\overset{\overset{R_2}{|}}{\underset{\underset{(CH_2CH_2O)_mH}{|}}{N^+}}-(CH_2CH_2O)_n-H\ X^-$$

where $R_1$, $R_2$, and X are as previously defined and wherein the sum of $m+n$ has a value in the range 3–50 can also be combined satisfactorily with the ethoxylated zwitterionics useful in the present invention. Compounds of the above type are available under the trade name "Ethoquad" from the Armour Chemical Company.

The effect of cationic cosurfactants on the clay soil removal performance of ethoxylated zwitterionic compounds of the present invention is shown in Table IV. It can clearly be seen that the $C_{16}$ trimethyl quaternary has an adverse effect on clay soil removal which is mitigated by the addition of a builder whereas the $C_{18}$ ethoxylated quaternary cosurfactant enhances performance. This effect can be seen for both the $C_{14}$ and $C_{16}$ ethoxylated zwitterionic compounds and characterizes a general tendency for quaternary cosurfactants having hydrophilic structural components to have beneficial effects on the particulate soil removal performance of the ethoxylated zwitterionic compounds while for quaternary cosurfactants not having hydrophilic structural components, the reverse effect is seen.

TABLE IV

CLAY SOIL REMOVAL OF ETHOXYLATED ZWITTERIONIC COMPOUNDS IN COMBINATION WITH CATIONIC SURFACTANTS

Conditions: 10 Minute Tergotometer Wash in 7 grains/gal. Mineral Hardness (2:1 Ca:Mg) at 105°F

| NO. | ETHOXYLATED ZWITTERIONIC COMPOUND | LEVEL PPM IN SOLUTION | COSURFACTANT | LEVEL PPM IN SOLUTION | BUILDER TYPE | LEVEL PPM IN SOLUTION | RELATIVE CLAY REMOVAL INDEX COTTON | POLY-COTTON | POLY-ESTER |
|---|---|---|---|---|---|---|---|---|---|
| 1 | N—$C_{16}H_{33}$ N,N—bis$CH_3$ $(CH_2CH_2O)_8CH_2CH_2SO_3$ | 250 | — | — | — | — | 75 | 96 | 95 |
| 2 | " | 125 | — | — | — | — | 68 | 88 | 77 |
| 3 | " | 125 | $[C_{16}H_{33}(CH_3)_3]$ $N^+$ $Br^-$ | 125 | — | — | 26 | 63 | 28 |
| 4 | " | 125 | " | 125 | STP | 250 | 90 | 84 | 61 |
| 5 | " | 125 | $C_{18}$ alkyl di-polyethenoxy Ammonium Bromide* | 125 | — | — | 88 | 93 | 96 |
| 6 | " | 125 | " | 125 | STP | 250 | 98 | 108 | 104 |
| 7 | N—$C_{14}H_{29}$ N,N—bis$CH_3$ $(CH_2CH_2O)_8CH_2CH_2SO_3$ | 250 | — | — | — | — | 53 | 69 | 46 |
| 8 | " | 125 | — | — | — | — | 41 | 52 | 24 |
| 9 | " | 125 | $[C_{16}H_{33}(CH_3)_3]$ $N^+$ $Br^-$ | 125 | — | — | 15 | 46 | 13 |
| 10 | " | 125 | " | 125 | STP | 250 | 46 | 60 | 26 |
| 11 | " | 125 | $C_{18}$ alkyl di-polyethenonxy Ammonium Bromide* | 125 | — | — | 71 | 82 | 61 |
| 12 | " | 125 | " | 125 | STP | 250 | 71 | 89 | 70 |

*Total No. of ethylene oxide groups per mole = 50.

## OPTIONAL COMPONENTS

In addition to the ethoxylated zwitterionic compound and the organic surfactant, the detergent compositions may also contain other ingredients conventionally employed in such products. The principal optional component is an inorganic or organic detergent builder to assist in mineral hardness control which may be used at levels between 1 and 99% by weight of the detergent composition, preferably between 10 and 75% and most preferably between 25 and 60%.

Suitable inorganic builders include the alkali metal polyphosphates (including the pyrophosphates and glassy high polymeric phosphates) phosphonates, carbonates, sesquicarbonates, bicarbonates, borates, silicates, sulphates, and aluminosilicates.

Aluminosilicate builder salts found to be useful in the present invention have the general formula:

$Na_z[(AlO_2)_z\,(SiO_2)_y] \times H_2O$

wherein $z$ and $y$ are integers of at least 6, the molar ratio of $z$ to $y$ is in the range from 1.0 to about 0.5 and $x$ is an integer from about 15 to about 15 to about 264. Such aluminosilicates also should have a particle size diameter in the range 0.1 to 100 microns, a calcium ion exchange capacity of at least about 200 milligram equivalent/gram and a calcium ion exchange rate of at least about 2 grains/U.S. gallon/minute/gram. Detergent compositions incorporating aluminosilicate builder salts of this type are disclosed in the commonly assigned copending application Ser. No. 450,266 of Corkill, Madison, and Burns filed Mar. 11, 1974, which disclosure is incorporated herein by reference.

Suitable organic builders include alkali metal salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, citric acid, oxydisuccinic acid, carboxy methoxysuccinic acid, polymaleic acid, benzene hexa- and pentacarboxylic acid, 1,3,5-trihydroxy benzene 2,4,6-trisulphonic acid and copolymers of maleic anhydride with ethylene or methyl vinyl ether. Examples of these and similar organic builders are set forth in U.S. Pat. No. 3,308,067 issued Mar. 7, 1967, to Francis L. Diehl, the disclosures of which are hereby incorporated by reference. The commonly assigned cofiled Application, Ser. No. 493,952, of Robert G. Laughlin and Robert L. Stewart, now U.S. Pat. No. 3,925,262, entitled Detergent Compositions discloses combinations of the above mentioned detergent builder salts with ethoxylated zwitterionic compounds, and this disclosure is incorporated herein by reference.

Another optional ingredient that may be incorporated is an enzyme for removal of protein-based or carbohydrate-based stains. Enzymes for removing protein-based stains are proteolytic in nature such as those sold under the trade names "Alcalase" and "Esterase" by Novo Industries A/S. Denmark or under the trade names "Maxatase" and "AZ Protease" by Gist-Brocades N.V. The Netherlands. These materials are normally incorporated at levels of up to 1% by weight, preferably 0.25 to 0.75% by weight, and are preferably coated or prilled with inert additives to minimize dust formation and improve storage stability. A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is disclosed in U.S. Pat. No. 3,553,139 issued on Jan. 5, 1971, to McCarty, Roald, DeOude, Blomeyer, and Cracco which disclosure is hereby incorporated by reference.

A further ingredient that may be incorporated to improve product performance is a bleaching agent of the halogen of oxygen-containing type. Examples of the hypohalite bleach type include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5–10% by weight of the finished product, preferably 1–5% by weight.

Examples of oxygen-containing bleaches include sodium perborate, sodium percarbonate, and potassium non-opersulphate that are incorporated at levels of 5–30%, preferably 10–25% by weight of the final product. The inclusion of organic bleach activators such as phthalic anhydride, tetra acetyl ethylene diamine, tetra acetyl methylene diamine or tetra acetyl glycouril lead to the in situ production during the washing process of the corresponding organic peroxy acids which have enhanced low temperature bleaching performance. Activators of this type are normally used with sodium perborate, at usage levels of 5–15% by weight of the final product.

Materials to boost or modify the sudsing pattern of the compositions of the present invention may also be included. Examples of suds boosters include coconut and tallow mono- and di-alkanolamides, particularly ethanolamides and $C_{12\text{-}15}$ alkyl di-lower alkyl amine oxides. Typical suds depressors include long chain fatty acids such as those disclosed in U.S. Pat. No. 2,954,347 issued Sept. 27, 1960, to Wayne St. John and combinations of certain nonionics therewith as disclosed in U.S. Pat. No. 2,954,348 issued Sept. 27, 1960, to Eugene Schwoeppe, both disclosures being incorporated herein by reference.

Other optional ingredients in granular products include hydrotropes and anticaking additives such as salts of lower alkyaryl sulphonic acids, salts of $\alpha$-sulphosuccinic acid, and $\alpha$-sulphobenzoic acid, and urea, normally utilized at levels of 0.5 to 5% by weight of the final product, preferably at levels of 1–3% by weight. $C_{12}$–$C_{18}$ alkyl acid phosphates and their condensation products with ethylene oxide may also be incorporated at similar levels for control of crutcher mix viscosity. Antiredeposition agents such as carboxymethyl cellulose, hydroxyethyl cellulose, and their derivatives may also be incorporated.

Anti-tarnish and anti-corrosion agents, perfume and colour may also be included, the last ingredient being conveniently added either as a general colour or in the form of a speckle applied to a separate granule fraction of the entire formulation or to a granulate of one or more of the ingredients.

The pH of detergent formulations in accordance with the present invention can lie anywhere within the range **5–12** but is preferably chosen to fall within the range 8.0 –10.5 as this provides a slight particulate soil removal benefit on synthetic fabrics. However, the use of specific optional components such as enzymes may require the selection of a product pH that will permit optimum functioning of the component concerned.

Granular formulations embodying the compositions of the present invention may be formed by any of the conventional techniques i.e., by slurrying the individual components in water and then atomizing and spray-drying the resultant mixture, or by pan or drum granulation of the components.

Liquid formulations embodying the compositions of the present invention may contain builders or may be unbuilt. If the compositions are unbuilt, they will conventionally contain approximately 30–50% total surfactant, from 1–10% of an organic base such as mono, di, or tri-alkanolamine, a solubilization system such as alkali metal halide and a lower primary alcohol such as ethanol or isopropanol and approximately 30–40% water. Such compositions will normally be homogeneous single phase liquids of low viscosity (approximately 100–150 centipoises at 75°F).

Built liquid detergent compositions may also be single phase liquids provided that the builder can be solubilized in the mixture at its level of use. Such liquids conventionally contain 10–25% total surfactant, 10–20% builder which may be organic or inorganic, 5–10% of a hydrotrope system and 50–60% of water.

Liquids of this type also have low viscosity (100–150 c.p.s. at 75°F). Built liquid detergents incorporating components that form heterogeneous mixtures or levels of builder that cannot be completely dissolved can also embody the compositions of the present invention. Such liquids conventionally employ viscosity modifiers to produce systems having plastic shear characteristics to maintain stable dispersions and to prevent phase separation or solid settlement.

The following examples serve to illustrate the present invention:

## EXAMPLE I

A granular detergent composition was made up having the following composition:

| | |
|---|---|
| Ω-(N-octadecyl-N,N-dimethylammonio)-2-octaethenoxy-ethane-1-sulphonate | 9.3% |
| 3-(N-myristyl N,N-dimethylammonio)prpane-1-sulphonate | 9.3% |
| $Na_{12}(SiO_2:AlO_2)_{12}$ $15H_2O$ | 51.8% |
| $Na_2CO_3$ | 14.8% |
| Sodium Silicate ($SiO_2$:$Na_2O$=3.2:1) | 14.8% |
| | 100.0% |

The composition was dissolved in water having a mineral hardness of 7 grains/U.S. gallon (Ca:Mg = 2:1) to give a 0.12% solution and was then used in a Tergotometer to give a 10 minute wash at 105°F to a mixture of cotton, polycotton, and polyester cloth swatches, employing the Test Procedure previously described. A similar wash using Control Product A at a level of 1400 ppm in solution was also carried out, and the particulate soil removal given by the composition expressed as a percentage of the performance of the control product was:

| Cotton | Polycotton | Polyester |
|---|---|---|
| 110 | 102 | 108 |

## EXAMPLE II

Liquid laundry detergents were made up having the following compositions:

| | P | Q | R | S | T |
|---|---|---|---|---|---|
| $C_{14-14}$ alcohol with 7 moles ethylene oxide | 33.0 | 33.0 | 33.0 | 33.0 | 33.0 |
| $C_{11.8}$ linear alkyl benzene sulphonate | 23.0 | 23.0 | — | — | — |
| Triethanolamine | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| KCL | 2.5 | 2.5 | — | — | — |
| Ethanol | 5.0 | 15.0 | 15.0 | 15.0 | 15.0 |
| N-octadecyl N,N-dimethyl ammonio-2-octaethenoxy-ethane-1-sulphonate | — | — | — | 2.0 | 5.0 |
| Water | to 100 ⟶ | | to 100 ⟶ | ⟶ | |

Each composition was used to pretreat a 5 inch square knitted polyester swatch presoiled with a clay solution prior to the latter being washed. In each pretreatment, three drops of the composition were applied to a 1 inch square cut out from the swatch, and this cut out and the remainder of the swatch were then given a 10 minute wash at 105°F in a Tergotometer using water having 7 grains/gallon hardness (Ca/Mg = 2:1). The wash, rinse, and dry cycles were as hereinbefore described in the standard procedure.

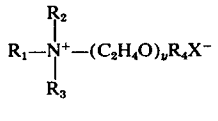
The swatches and cut outs were then graded visually for particulate soil removal. Compositions P and Q showed no pretreatment benefit on the respective cut outs and little if any clay soil removal from the swatches. Composition R achieved discernible clay removal from the swatch and a visible benefit for pretreatment. Compositions S and T also showed some clay removal from the swatches but the areas of the cut outs which had been pretreated were restored to their original condition before clay soiling.

What is claimed is:

**1.** A detergent composition comprising

A. 1 to 99% by weight of the composition of a compound having a formula selected from the group consisting of

i)



$$R_1-\overset{\overset{R_2}{|}}{\underset{\underset{R_3}{|}}{N^+}}-(C_2H_4O)_yR_4X^-$$

wherein

R$_1$ is selected from the group consisting of straight and branched chain $C_8$–$C_{30}$ alkyl and alkenyl moieties and alkaryl moieties in which the alkyl group has 10–24 carbon atoms;

R$_2$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, and $C_{1-4}$ alkyl and hydroxyalkyl moieties;

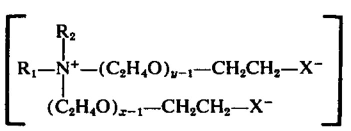
R$_3$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, $C_{1-4}$ alkyl and hydroxyalkyl moieties and $-(C_2H_4O)_xH$ wherein x has a value of about 3 to about 50;

R$_4$ is selected from the group consisting of $C_1$–$C_8$ alkylene, $C_3$–$C_8$ alkenylene, 2-hydroxy propylene, 2- and 3-hydroxy butylene moieties and $C_1$–$C_4$ alkarylene moieties provided that where $R_3$ is $-(C_2H_4O)_xH$ then $R_4$ is $-CH_2-CH_2-$;

$X^-$ is an anion selected from the group consisting of sulfate and sulfonate radicals; and

*y* has a value in the range of 2–100 provided that where $R_3$ is $-(C_2H_4O)_xH$ then $x + y \geqslant 10$; and

ii)



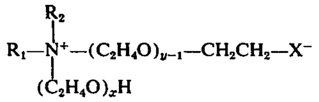
$$\left[\begin{array}{l} \quad R_2 \\ \quad | \\ R_1-N^+-(C_2H_4O)_{y-1}-CH_2CH_2-X^- \\ \quad | \\ \quad (C_2H_4O)_{x-1}-CH_2CH_2-X^- \end{array}\right] M^+$$

wherein R$_1$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals; R$_2$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals and $C_1$–$C_4$ alkyl and hydroxyalkyl radicals; $X^-$ is selected from the group consisting of sulfate and sulfonate; *y* and *x* have values in the range of 2–100 provided that $y+x \geqslant 12$; M is a cation selected from the group consisting of alkali metal, ammonium and alkanolammonium ions; and

B. 99 to 1% by weight of the composition of an organic detergent.

**2.** A detergent composition according to claim **1** wherein the detergent is selected from the group consisting of nonionic, ampholytic, and zwitterionic surfactants and mixtures thereof.

**3.** A detergent composition according to claim **1** wherein the zwitterionic compound has the formula:



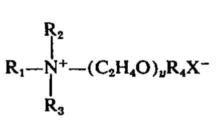
$$R_1-\underset{\underset{\displaystyle (C_2H_4O)_xH}{|}}{\overset{\overset{\displaystyle R_2}{|}}{N^+}}-(C_2H_4O)_{y-1}-CH_2CH_2-X^-$$

wherein $R_1$ is selected from the group consisting of straight and branched chain $C_{16}$–$C_{22}$ alkyl and alkenyl moieties, $R_2$ is a $C_1$–$C_3$ alkyl group and $x+y$ has a value in the range of 14–50.

**4.** A detergent composition according to claim **3** wherein $R_1$ is selected from the group consisting of straight and branched chain $C_{16}$–$c_{18}$ alkyl and alkenyl moieties and $x + y$ has a value in the range of 15–25.

**5.** A detergent composition comprising

A. 1 – 99% by weight of the composition of a compound having the formula



$$R_1-\underset{\underset{\displaystyle R_3}{|}}{\overset{\overset{\displaystyle R_2}{|}}{N^+}}-(C_2H_4O)_yR_4X^-$$

wherein

$R_1$, $R_2$, and $R_3$ are each selected from the group consisting of branched and straight chain $C_6$-$C_{16}$ alkyl and alkenyl radicals;

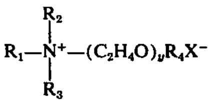
$R_4$ is selected from the group consisting of $C_{1-4}$ alkylene and 2-hydroxy propylene and 2- and 3-hydroxy butylene moieties and alkarylene moieties in which the alkyl group contains from 1–4 carbon atoms; X is an anion selected from the group consisting of sulfate and sulfonate radicals; and $y$ has an average value in the range of 6 to 100; and

B. 99 – 1% by weight of the composition of an organic detergent selected from the group consisting of nonionic, ampholytic, and zwitterionic surfactants and mixtures thereof.

**6.** A detergent composition according to claim **3** wherein $y$ has a value of at least 9.

**7.** A detergent composition comprising

A. 1 – 99% by weight of the composition of a compound having the formula



$$R_1-\underset{\underset{\displaystyle R_3}{|}}{\overset{\overset{\displaystyle R_2}{|}}{N^+}}-(C_2H_4O)_yR_4X^-$$

wherein

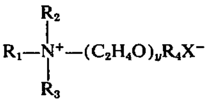
$R_1$ and $R_2$ are each selected from the group consisting of branched and straight chain $C_6$–$C_{21}$ alkyl and alkenyl radicals;

$R_3$ is selected from the group consisting of $C_1$–$C_4$ alkyl and hydroxyalkyl moieties;

$R_4$ is selected from the group consisting of $C_1$–$C_4$ alkylene and 2-hydroxy propylene and 2- and 3-hydroxy butylene moieties, and alkarylene moieties in which the alkyl group contains 1–4 carbon atoms; $X^-$ is an anion selected from the group consisting of sulfate and sulfonate radicals and $y$ has an average value in the range of 6 to 100; and

B. 99–1% by weight of the composition of an organic detergent selected from the group consisting of nonionic, ampholytic, and zwitterionic detergents and mixtures thereof.

**8.** A detergent composition according to claim **1** wherein the compound has the formula:



$$R_1-\underset{\underset{\displaystyle R_3}{|}}{\overset{\overset{\displaystyle R_2}{|}}{N^+}}-(C_2H_4O)_yR_4X^-$$

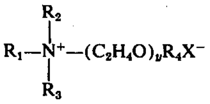
wherein $R_1$ is selected from the group consisting of branched and straight chain $C_8$–$C_{30}$ alkyl and alkenyl radicals; $R_2$ and $R_3$ are each selected from the group consisting of $C_1$–$C_4$ alkyl and hydroxyalkyl moieties; $R_4$ is selected from the group consisting of $C_1$–$C_4$ alkylene and 2-hydroxy propylene and 2- and 3-hydroxy butylene radicals and alkyarylene moieties in which the alkylene group has 1 to 4 carbon atoms; and $y$ has a value of from about 6 to about 20.

**9.** A detergent composition according to claim **8** wherein $R_1$ is a $C_{12}$–$C_{18}$ alkyl moiety; $R_2$ and $R_3$ are independently selected from $C_1$–$C_3$ alkyl and hydroxyalkyl moieties; and y has a value from about 6 to 12.

**10.** A detergent composition comprising

A. 50 to 99% by weight of the composition of a compound having a formoula selected from the group consisting of

i)



$$R_1-\underset{\underset{\displaystyle R_3}{|}}{\overset{\overset{\displaystyle R_2}{|}}{N^+}}-(C_2H_4O)_yR_4X^-$$

wherein

$R_1$ is selected from the group consisting of straight and branched chain $C_8$–$C_{30}$ alkyl and alkenyl moieties and alkaryl moieties in which the alkyl group has 10–24 carbon atoms;

$R_2$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, and $C_{1-4}$ alkyl and hydroxyalkyl moieties;

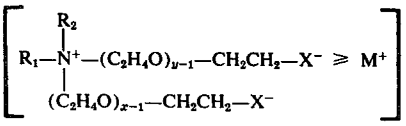
$R_3$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, $C_{1-4}$ alkyl and hydroxyalkyl moieties and $-(C_2H_4O)_xH$ wherein $x$ has a value of about 3 to about 50;

$R_4$ is selected from the group consisting of $C_1$–$C_8$ alkylene, $C_3$–$C_8$ alkenylene, 2-hydroxy propylene and 2- and 3-hydroxy butylene moieties and $C_1$–$C_4$ alkarylene moieties provided that where $R_3$ is $-(C_2H_4O)_xH$ then $R_4$ is $-CH_2-CH_2-$;

$X^-$ is an anion selected from the group consisting of sulfate and sulfonate radicals; and

$y$ has a value in the range of 2–100 provided that where $R_3$ is $-(C_2H_4O)_xH$ then $x+y \geq 10$; and

ii)



$$\left[R_1-\underset{\underset{\displaystyle (C_2H_4O)_{x-1}-CH_2CH_2-X^-}{|}}{\overset{\overset{\displaystyle R_2}{|}}{N^+}}-(C_2H_4O)_{y-1}-CH_2CH_2-X^- \geq M^+\right]$$

wherein

$R_1$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals;

$R_2$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals and $C_1$–$C_4$ alkyl and hydroxyalkyl radicals;

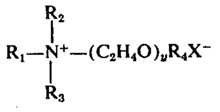
$X^-$ is selected from the group consisting of sulfate and sulfonate;

$y$ and $x$ have values in the range of 2 to 100 provided that $y + x \geqslant 12$;

M is a cation selected from the group consisting of alkali metal, ammonium and alkanolammonium ions; and

B. 50 to 1% by weight of the composition of an anionic detergent.

**11.** A detergent composition according to claim **10** wherein the compounds has the formula



$$R_1-\underset{R_3}{\overset{R_2}{N^+}}-(C_2H_4O)_yR_4X^-$$

wherein $R_1$ is selected from the group consisting of branched and straight chain $C_8$–$C_{30}$ alkyl and alkenyl radicals; $R_2$ and $R_3$ are each selected from the group consisting of $C_1$–$C_4$ alkyl and hydroxyalkyl moieties; $R_4$ is selected from the group consisting of $C_1$–$C_4$ alkylene and 2-hydroxy propylene and 2- and 3- hydroxy butylene radicals and alkarylene moieties in which the alkylene group has 1 to 8 carbon atoms; and y has a value from about 6 to about 20.

**12.** A detergent composition according to claim **11** wherein $R_1$ is a $C_{12}$–$C_{18}$ alkyl moiety; $R_2$ and $R_3$ are independently selected from the group consisting of $C_1$–$C_3$ alkyl and hydroxyalkyl moieties; $R_4$ is selected from $C_1$–$C_3$ alkylene and hydroxyalkylene moieties; and y has a value from about 6 to about 12.

**13.** A detergent composition according to claim **12** wherein the anionic detergent is selected from the group consisting of alkali and alkaline earth metal, ammonium and alkanol ammonium linear and branched $C_{10}$–$C_{14}$ alkyl benzene sufonates, $C_{10}$–$C_{20}$ alpha-sulfo carboxylic acid salts and esters in which the alkyl group has 1–8 carbon atoms, $C_{10}$–$C_{20}$ alkane sulfonates, $C_{14}$–$C_{18}$ olefin sulfonates, $C_{10}$–$C_{18}$ alkyl sulfates and condensation products thereof with 1–20 moles of ethylene oxide, and mixtures thereof.

**14.** A detergent composition according to claim **13** wherein the anionic surfactant is incorporated in an intimate mixture with 5 to 50% by weight of the mixture of a material requiring more than 60 seconds for substantially complete dissolution or dispersion in an aqueous medium at 100°F.

**15.** A detergent composition according to claim **14** wherein the material is an organic material selected from the group consisting of polyethylene glycols of MWt greater than 1000, $C_{12}$–$C_{18}$ fatty acid amides, $C_{12}$–$C_{18}$ fatty acid alkanolamides, $C_{12}$–$C_{20}$ fatty acids and mixtures thereof.

**16.** A detergent composition according to claim **14** wherein the material is an inorganic hydratable salt.

**17.** A detergent composition according to claim **16** wherein the hydratable salt is an alkali metal polyphosphate.

**18.** A detergent composition according to claim **14** wherein the anionic surfactant is incorporated by coating with a material requiring more than 60 seconds for substantially complete dissolution or dispersion in an aqueous medium at 100°F.

**19.** A detergent composition according to claim **18** wherein the material is selected from the group consisting of polyethylene glycols of MWt >1000.

**20.** A detergent composition according to claim **9** incorporating a nonionic detergent selected from the group consisting of ethylene oxide condensates of $C_8$–$C_{20}$ branched and linear aliphatic primary and secondary alcohols, alkyl phenols wherein the alkyl group contains 6–12 carbon atoms, $C_{10}$–$C_{22}$ aliphatic carboxylic acid esters in which the alkyl group has 1–8 carbon atoms, ethylene oxide-propylene oxide condensates.

**21.** A detergent composition according to claim **20** wherein the nonionic detergent is a primary alcohol ethoxylate of the formula

$$R_1 - R_2 - O(CH_2CH_2O)_nH$$

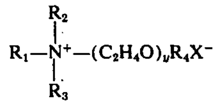
wherein $R_1$ is a linear alkyl residue and $R_2$ has the formula $CHR_3CH_2$—; $R_3$ being selected from the group consisting of hydrogen and mixtures thereof with not more than 40% by weight of $C_{1\text{-}4}$ alkyl groups, wherein $R_1$ and $R_2$ together form an alkyl residue having a mean chain length in the range of 8–15 carbon atoms at least 65% by weight of said residue having a chain length within ±1 carbon atoms of the mean, wherein the average value of n lies between 3.5 and 6.5 provided that the total amount by weight of components in which $n = 0$ shall be not greater than 5% and the total amount by weight of components in which $n = 2$–$7$ inclusive shall be not less than 63%, based on the total weight of the ethoxylate and wherein the HLB of the ethoxylate lies in the range of 9.5–11.5.

**22.** A detergent composition according to claim **9** wherein the nonionic surfactant is a $C_{10\text{-}15}$ alkyl, di-lower alkyl, or hydroxy lower alkyl amine oxide.

**23.** A detergent composition according to claim **9** wherein the zwitterionic surfactant is selected from the group consisting of 3-(N-$C_{10\text{-}16}$ alkyl N,N-dimethylammonio)propane-1-sulfonate, 3-(N-$C_{10\text{-}16}$ alkyl N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate, 3-(N-$C_{10\text{-}15}$ alkyl benzyl, N,N-dimethylammonio)-2-hydroxypropane-1-sulfonate.

**24.** A detergent composition comprising a mixture of (A) 5–95% by weight of the mixture of a detergent builder and (B) 95–5% by weight of the mixture of a combination consisting essentially of 5 to 95% by weight of the combination of a water soluble compound having a formula selected from the group consisting of

i)



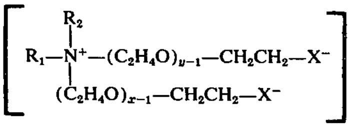
$$R_1-\underset{R_3}{\overset{R_2}{N^+}}-(C_2H_4O)_yR_4X^-$$

wherein

$R_1$ is selected from the group consisting of straight and branched chain $C_8$–$C_{30}$ alkyl and alkenyl moieties and alkaryl moieties in which the alkyl group has 10–24 carbon atoms;

- $R_2$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, and $C_{1\text{-}4}$ alkyl and hydroxyalkyl moieties;
- $R_3$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, $C_{1\text{-}4}$ alkyl and hydroxyalkyl moieties and $—(C_2H_4O)_xH$ wherein $x$ has a value of about 3 to about 50;
- $R_4$ is selected from the group consisting of $C_1$–$C_8$ alkylene, $C_3$–$C_8$ alkenylene, 2-hydroxy propylene and 2- and 3- hydroxy butylene moieties and $C_1$–$C_4$ alkarylene moieties provided that where $R_3$ is $—(C_2H_4O)_xH$ then $R_4$ is $—CH_2—CH_2—$;
- $X^-$ is an anion selected from the group consisting of sulfate and sulfonate radicals; and
- $y$ has a value in the range of 2–100 provided that where $R_3$ is $—(C_3H_4O)_xH$ then $x + y \geqslant 10$; and

ii)



$$\left[\begin{array}{l} \quad R_2 \\ \quad | \\ R_1—N^+—(C_2H_4O)_{y-1}—CH_2CH_2—X^- \\ \quad | \\ \quad (C_2H_4O)_{x-1}—CH_2CH_2—X^- \end{array}\right] M^+$$

wherein

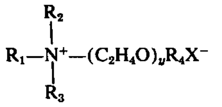
- $R_1$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals;
- $R_2$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals and $C_1$–$C_4$ alkyl and hydroxyalkyl radicals;
- $x^-$ is selected from the group consisting of sulfate and sulfonate;
- $y$ and $x$ have values in the range of 2 to 100 provided that $y + x \geqslant 12$;
- M is a cation selected from the group consisting of alkali metal, ammonium and alkanolammonium ions and 95–5% by weight of the combination of an organic detergent selected from the group consisting of nonionic, zwitterionic, and ampholytic detergents.

**25.** A detergent composition according to claim **24** wherein the detergent builder is an inorganic builder, selected from the group consisting of ammonium and alkali metal polyphosphates, phosphonates, carbonates, bicarbonates, silicates, alumino silicates, and sulfates.

**26.** A detergent composition according to claim **21** wherein the detergent builder is an organic builder selected from the group consisting of alkali metal nitrilotriacetates, citrates, oxydisuccinates, carboxylmethoxysuccinates, polymaleates, and copolymers of maleic anhydride with methyl vinyl ether or ethylene.

**27.** A detergent composition comprising a mixture of (A) 5–95% by weight of the mixture of a detergent builder and (B) 95–5% by weight of the mixture of a combination consisting essentially of 50 to 95% by weight of the combination of a water soluble compound having a formula selected from the group consisting of

i)

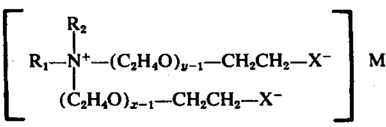


$$\begin{array}{l} \quad\; R_2 \\ \quad\; | \\ R_1—N^+—(C_2H_4O)_yR_4X^- \\ \quad\; | \\ \quad\; R_3 \end{array}$$

wherein

- $R_1$ is selected from the group consisting of straight and branched chain $C_8$–$C_{30}$ alkyl and alkenyl moieties and alkaryl moieties in which the alkyl group has 10–24 carbon atoms;
- $R_2$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, and $C_{1\text{-}4}$ alkyl and hydroxyalkyl moieties;
- $R_3$ is selected from the group consisting of straight and branched chain $C_8$–$C_{21}$ alkyl and alkenyl moieties, alkaryl moieties in which the alkyl group has 6–16 carbon atoms, $C_{1\text{-}4}$ alkyl and hydroxyalkyl moieties and $—(C_2H_4O)_xH$ wherein $x$ has a value of about 3 to about 50;
- $R_4$ is selected from the group consisting of $C_1$–$C_8$ alkylene, $C_3$–$C_8$ alkenylene, 2-hydroxy propylene and 2- and 3-hydroxy butylene moieties and $C_1$–$C_4$ alkarylene moieties provided that where $R_3$ is $—(C_2H_4O)_xH$ then $R_4$ is $—CH_2—CH_2—$;
- $X^-$ is an anionic selected from the group consisting of sulfate and sulfonate radicals; and
- $y$ has a value in the range of 2–100 provided that where $R_3$ is $—(C_2H_4O)_xH$ then $x + y \geqslant 10$; and

ii)



$$\left[\begin{array}{l} \quad R_2 \\ \quad | \\ R_1—N^+—(C_2H_4O)_{y-1}—CH_2CH_2—X^- \\ \quad | \\ \quad (C_2H_4O)_{x-1}—CH_2CH_2—X^- \end{array}\right] M^+$$

wherein

- $R_1$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals;
- $R_2$ is selected from the group consisting of linear and branched $C_8$–$C_{30}$ alkyl and alkenyl radicals and $C_1$–$C_4$ alkyl and hydroxyalkyl radicals;
- $X^-$ is selected from the group consisting of sulfate and sulfonate;
- $y$ and $x$ have values in the range of 2 to 100 provided that $y + x \geqslant 12$;
- M is a cation selected from the group consisting of alkali metal, ammonium, and alkanolammonium ions and 5–50% by weight of the combination of an anionic detergent.

**28.** A detergent composition according to claim **27** wherein the detergent builder is an inorganic builder selected from the group consisting of ammonium and alkali metal polyphosphates, phosphonates, carbonates, bicarbonates, silicates, alumino silicates and sulfates.

**29.** A detergent composition according to claim **28** wherein the detergent builder is an organic builder selected from the group consisting of alkali metal nitrilotriacetates, citrates, oxydisuccinates, carboxylmethyloxysuccinates, and copolymers of maleic anhydride with methyl vinyl ether or ethylene.

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