United States Patent

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Continuation-in-part of application Ser. No. 581,720, Sept. 26, 1966, now abandoned, which is a continuation-in-part of application Ser. No. 413,948, Nov. 25, 1964, now abandoned, which is a continuation-in-part of application Ser. No. 163,041, Dec. 29, 1961, now abandoned.
The portion of the term of the patent subsequent to Nov. 10, 1987, has been disclaimed.

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[54] **COOL WATER LAUNDERING PROCESS**
5 Claims, No Drawings

[52] **U.S. Cl.** **8/137,** 252/137, 252/151, 252/152, 252/355, 260/501
[51] **Int. Cl.** **D06f**
[50] **Field of Search** 252/137, 152, 151, 355; 8/137; 260/50

[56] **References Cited**

UNITED STATES PATENTS

2,129,264	9/1938	Downing et al.	252/152 UX
2,702,278	2/1955	Cuper et al.	252/152 UX
2,739,942	9/1961	Drew et al.	252/138 X
3,213,030	10/1955	Diehl	252/152

FOREIGN PATENTS

1,018,421	10/1952	Germany	252/161
1,051,439	2/1959	Germany	252/152
751,273	7/1956	Great Britain	252/137

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ABSTRACT: A process for laundering fabrics in 60° F.–90° F. Water containing .05–.5 percent of a detergent composition containing 4–35 percent of specific zwitterionic detergents and 8–90 percent of detergency builders which complex the calcium and magnesium ions in hard water.

COOL WATER LAUNDERING PROCESS

This application is a continuation-in-part of our copending application, Ser. No. 581,720, filed Sept. 26, 1966, entitled LAUNDERING PROCESS AND DETERGENT COMPOSITION THEREFOR, Now abandoned which was in turn a continuation-in-part of our copending application, Ser. No. 413,948, filed Nov. 25, 1964, entitled LAUNDERING PROCESS AND DETERGENT COMPOSITION THEREFOR, Now abandoned which was in turn, a continuation-in-part of our earlier field application, Ser. No. 163,041, filed Dec. 29, 1961. entitled LAUNDERING PROCESS AND DETERGENT COMPOSITION THEREFOR, now abandoned.

The present invention relates to the laundering of textile fabrics in cool aqueous media employing a composition containing a specific type of synthetic detergent compound. More particularly, it relates to a process of, and product for, laundering fabrics in cool water using products containing specific sulfo betaine (sultaine) detergent compounds as hereinafter more fully described.

At the present time the synthetic detergent washing compounds used in laundering clothes and other textile fabrics are utilized in home and commercial operations at water temperatures ranging from 110°–150° F., with the usual washing temperature being at a median of about 120° to 130° F. It is within this temperature range that the most effective washing action is achieved for the common laundry fabrics such as cottons, woolens, and synthetic fabrics, using the conventional detergent materials.

However, it is well known that some fabrics have a pronounced tendency to shrink, wrinkle, or draw up when washed in water at temperatures ranging from 110°–150° F. Such fabrics are the new wash-wear materials like Dacron, Creslan, resin treated cotton, cloth made from Kodel polyester fibers, and several other additional ones. It is also well known that sweaters, blankets, and other articles made from natural wool shrink considerably when washed at the normal temperatures. The shrinkage not only alters the size of the article but also changes the characteristic and feel of it, making it less soft and pleasant to the touch. Because of these facts, these fabrics are washed in lukewarm or cool water where shrinkage and drawing up is kept at a minimal level.

Below the normal washing temperature range of 110° to 150° F., the efficiency of the commonly used detergent compositions such as those containing sodium dodecyl benzene sulfonate, the dodecyl group being derived from tetrapropylene, (currently the most commonly used active ingredient), higher alkyl sulfates, sulfated and sulfonated amides and amines as the active detergent compound, is reduced considerably. In some instances, sudsing ability of such detergent compounds in cool waters also reduced, necessitating the addition of organic enhancing agents to the detergent composition to increase sudsing; whiteness maintenance is poor and in general, conventional detergent compounds simply have a marked lower level of detergency performance at lower temperatures. Therefore, it can readily be seen that when fabrics are washed in cool water to avoid shrinkage and other problems, the housewife will usually pour more detergent composition than normal into the washing solution in an attempt to achieve the same cleaning level as would be obtained at normal temperatures. This is both wasteful and uneconomical because there is little indication that the same cleaning level could be achieved in cool water by the addition of excess detergent composition as is obtained in washing clothes at the normal temperatures using normal amounts of detergent composition in the solution.

Additionally, in many of the economically less well developed areas of the world, particularly the South American and Asian countries, clothes washing and other laundry tasks are commonly performed at temperatures below 100° F. using comparatively crude methods. At these cool water temperatures, as previously mentioned, the most commonly used synthetic detergent compositions have only moderate detergency power, and as a result it tends to promote wastefulness

for the reason that excess detergent material is then used in an effort to achieve higher cleaning performance.

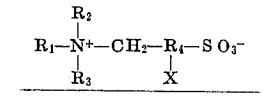
It can be appreciated too that considerable savings in fuel bills would be realized over a period of time if an effective way were to be found to wash clothes in cool water because it takes considerably less fuel to heat water to a temperature of about 80° F. than it does to heat it to the higher temperatures at which clothes are normally washed.

With the foregoing considerations in mind, it is an object of the present invention to provide a process nd a product for washing fabrics using a detergent composition that will clean as efficiently in cool water as conventional compositions do at normal washing temperatures. The term "cool water" as used herein is defined to mean water which is at a temperature ranging from about 40° F. to about 100° F.

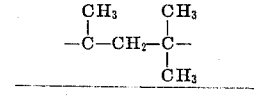
It is a further object of the present invention to provide a process and a product for washing fabrics which will minimize the amount of shrinking, drawing up, or wrinkling of fabrics that occurs under normal washing conditions.

Other objects and advantages of the invention will be apparent during the course of the ensuing description.

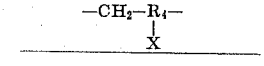
It has been found that these objects can be accomplished by a washing process comprising the step of washing fabrics in cool aqueous solution, the solution containing a detergent composition consisting essentially of a builder salt and a quaternary ammonium compound having the general formula



wherein R_1 represents an alkyl radical having from about 12 to about 18 carbon atoms, R_2 and R_3 are each selected from the group consisting of methyl, ethyl, propyl, butyl, and ethanol radicals, R_4 is an alkylene chain having from 1 to about 3 carbon atoms, and X is selected from the group consisting of hydrogen and hydroxyl radicals, wherein the sum of the R_1, R_2, and R_3 radicals total 14–20 carbon atoms. Branched chain alkylene groups, e.g.,



can be substituted for the



group in the above formula.

Compounds which conform to the above general formula are characterized by the presence of both positive and negative charges which are internally neutralized (i.e., zwitterionic). Where R_1 is 16 carbon atoms, R_2 and R_3 are methyl groups, and R_4 is an ethylene group, the chemical name is 3-(N,N-dimethyl-N-hexadecylammonio) propane-1-sulfonate. Where R_1 is 16 carbon atoms, R_2 and R_3 are methyl groups and R_4 is an ethylene chain with a hydroxy radical attached to the second carbon atom, the compound can be described as 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate. These compounds are commonly called sultaines or sulfo betaines and can be prepared in the manner disclosed in U.S. Pat. No. 2,129,264 and German Pat. No. 1,018,421.

The most preferred compounds of this invention are the ones which have been shown to have cleaning effectiveness at 80° F. which is equivalent to or greater than that exhibited by sodium tetrapropylenebenzenesulfonate at 140° F. These compounds are the sultaine detergents selected from the group consisting of

1. 3-(N,N-bibutyl-N-alkylammonio)propane-1-sulfonates wherein the alkyl group contains from about 12 to about 16 carbon atoms;

2. 3-(N,N-dibutyl-N-alkylammonio)propane-1-sulfonates wherein the alkyl group contains about 12 carbon atoms;

3. 3-(N,N-diemthyl-N-alkylammonio)-2-hydroxypropane-1-sulfonates wherein the alkyl group contains from about 12 to about 16 carbon atoms;

4. 3-(N,N-dimethyl-N-alkylammonio)-1,1,3-trimethylpropane-1-sulfonate wherein the alkyl group contains about 12 carbon atoms;

5. 2-(N,N-dimethyl-N-alkyl)ethane-1-sulfonate wherein the alkyl is coconut oil-derived; and

6. Mixtures thereof.

Within the above preferred compounds there are several compounds which are particularly outstanding. For example, compound 1 is most effective at cleaning fabrics in cool water when the alkyl group contains 16 carbon atoms. Also, when in compound 3, the alkyl group contains 12 carbon atoms or is a mixture of alkyl groups such as those derived from coconut oil (or an equivalent synthetic source) and containing 12, 14, and 16 carbon atoms, the sultaines are especially effective at cleaning fabrics in cool water. Compounds 2, 4 and 5, as disclosed above, are very effective, as hereinafter demonstrated.

The sum of the carbon chain lengths of the R_1, R_2, and R_3 component groups of the compounds have been found to be a critical factor in achieving good detergency performance. The carbons in the R_1, R_2, and R_3 groups must total 14–20 with the R_1 group being not less than 12 nor more than 18 carbon atoms because it has surprisingly been found that the sultaine compounds having such chain length combinations have a significantly greater cool water cleaning performance and whiteness maintenance than do those sultaine compounds not so limited and which fall outside the range of the invention.

Convenient sources of the R_1 component are coconut fatty alcohols. (These normally consist of a mixture of chain lengths, being approximately 0.7 percent C_8, 8.9 percent C_8, 6.8 percent C_{10}, 47.2 percent C_{12}, 18.6 percent C_{14}, 8.3 percent C_{16} and 9.5 percent C_{18}.) and tallow fatty alcohols. (These normally consist of a mixture of chain lengths, being approximately 66 percent C_{18}, 30 percent C_{16}, and 4 percent C_{14} and others.) R_1 can also be derived from other naturally occurring substances and can also be derived from petroleum fractions, e.g., by polymerizing alkylenes or cracking waxes to form the proper chain lengths, e.g., in the form of olefins. The method of deriving the alkyl chains is immaterial. The alkyl chains can be unsaturated.

Another convenient source of the R_1 component of the sultaine where R_1 is to average about 12 carbon atoms is that obtained from the middle cut of distilled coconut fatty alcohol which also consists of a mixture of various chain lengths, being approximately 2 percent C_{10}, 66 percent C_{12}, 23 percent C_{14}, and 9 percent C_{16}.

Specific sultaine compounds within the general formula set forth above useful in this invention are: 3-(N,N-diemthyl-N-hexadecylammonio)-2-hydroxypropane-13-(N,N-diemthyl-N-alkylammonio)-2-hydrosypropane-1-sulfonate; the alkyl group derived from tallow fatty alcohol; 3-(N,N-diethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate; 3-(N,N-diethyl-N-hexadecylammonio)propane-1-sulfonate; 3-(N,N-diethyl-N-tetradecylammonio)propane-1-sulfonate; 3-(N,N-diethyl-N-tetradecylammonio)-2-hydroxypropane-1-sulfonate; 3-N,N-dimethyl-N,N-tetradecylammonio)-2-hydroxypropane-1-sulfonate, the alkyl group being derived from the middle cut of coconut fatty alcohol; 3-(N,N-dimethyl-N-octadecylammonio)-2-hydroxypropane-1-sulfonate; 3-(N-2-hydroxyethyl-N-methyl-N-tetradecylammino)propane-1-sulfonate; 3-(N-2-hydroxyethyl-N-methyl-N-tetradecyl-ammonio)butane-butane-1-sulfonate; butane-1-sulfonate; 3-(N,N,-dimethyl-N-dodecylammonio)-propane-1-sulfonate; 4-(N-2-hydroxyethyl-N-methy)-N-tetra-decylammonio)-3-hydroxybutane-1-sulfonate; and 3-[N,Nbis(2-hydroxyethyl), N-tetradecylammonio]propane-1-sulfonate. Specific reference to the above compounds is given only for the purpose of illustration and it will be appreciated that many other similar variations may be used in this invention so long as the important R_1, R_2, R_3 and R_4 requirements described above are observed.

In this invention the active sultaine detergent compound is incorporated into the total detergent composition at an active to builder ratio ranging from about 5:1 to 1:25, desirably at levels ranging from about 4 percent to about 35 percent of the composition. Below a level of about 4 percent it has been found that the total amount of composition needed in the wash solution to utilize the detergent compounds described in the present invention to full advantage is inconveniently large. (A 4 percent usage level (liquid composition) is approximately equal to a concentration of detergent compound in solution of about 0.0088 percent, assuming conventional amounts of water and composition are being used.); preferably not more than about 35 percent of the sultaine is used in the detergent composition because the best results are achieved when the remaining 65 percent of the detergent composition comprises substantial amounts of builder salts together with whatever other valuable detergency aids (e.g., antiredeposition agents such as carboxymethylcellulose or anticorrosive agents such as sodium silicate) are desired.

An essential component of the composition utilized in this invention is a water-soluble inorganic alkaline builder salt or an organic alkaline sequestrant builder salt. Suitable inorganic builders include sodium and potassium tripolyphosphates and pyrophosphates. Examples of organic alkaline sequestrant builder salts are 1 alkali metal amino polycarboxylates [e.g., sodium and potassium ethylene diamine-tetraacetates, N-(2-hydroxyethyl)-ethylene diamine triacetates, nitrilotriacetates, and N-(2-hydroxyethyl)-nitrilo diacetates]; 2 alkali metal salts of phytic acid e.g., sodium and potassium phytates—see U.S. Pat. No. 2,739,942); 3 water soluble salts of methylene disphosphonic acid e.g., trisodium and tripotassium methylene diphosphonate and the other diphosphonate salts described in the copending application of Francis L. Diehl, Ser. No. 266,025, filed Mar. 18, 1963, now U.S. Pat. No. 3,213,030 4 water soluble salts of substituted methylene diphosphonic acids e.g., trisodium and tripotassium ethylidene, isopropylidene, benzylmethylidene, and halomethylidene diphosphonates and the other substituted methylene diphosphonates disclosed in the copending application of Clarence H. Roy, Ser. No. 266,055, filed Mar. 18, 1963 now U.S. Pat. No. 3,422,021 ; and 5 mixtures thereof.

Any of the above builders can be used in the form of their ammonium, triethanolammonium,diethanolammonium, monoethanolammonium, sodium, and potassium salts, and mixtures thereof.

These alkaline compounds serve to complex the calcium and magnesium ions present in hard water and they also serve to increase the level of detergency obtainable with synthetic detergent compounds. Other compounds such as sodium or potassium orthophosphate, sodium, silicate, sodium carbonate and sodium borate can be added to increase detergency although they do not complex the calcium and magnesium ions present in hard water.

The above designated builders are employed at a ratio of builder to detergent compound of from about 1:5 to about 25:1, desirably at levels from about 8 percent to about 90 percent by weight of the total composition. The balance of the composition, in addition to the detergent compound as mentioned previously, can consist of water, sodium sulfate, and other additives valuable as detergency aids, as, for example, anti-redeposition agents, anticorrosion agents, perfume and the like.

It is believed that the sultaine detergent compounds of this invention, when used alone in a composition without the presence of builders and other electroyltes, are not good cool water detergents because they do not possess the essential solubility characteristics for such use. The builders are added, not only to improve detergency as is ordinarily the case with most synthetic detergent compounds but also to act as an electrolyte in reducing the Krafft point of the sultaine compounds of this invention to such an extent that they are soluble in cool water and are capable of acting as outstanding detergent compounds. If a nonbuilt composition is desired, then sufficient inorganic or organic electrolytes must be added to insure solu-

bility of the sultaines in aqueous solution. Suitable electrolytes may be, for example, NaCl, KCl, Na_2SO_4, and NAI.

The discovery that the sultaine-type compounds described in this invention show exceptional cool water detergency was unpredictable in view of the fact that there is no published theory or background information on the mechanics of cool water detergency. Moreover, those conventional compounds such as dodecyl benzene sulfonate which are good hot water (130° F.–140° F.) detergent compounds show a minimum of activity in cool water. From the published literature one would be led to assume that these compounds of the invention would be, comparatively speaking, as poor as any other conventional detergent compounds when used in cool water; however, as has been discovered, the sultaines described in the present invention are far more effective in cool water than many of the commonly used commercially available detergent compounds are in hot water. It can therefore be seen that the structure of a given detergent compound effective in hot water has little or no relation to the effectiveness of such compounds in cool water.

It has also surprisingly been found that the compounds used in this invention exhibit good detergent properties when used in wash water at very low concentrations. For example, it was found that the cleaning ability of the preferred 3-(N,N-dimethyl-N-hexadecylammonio) propane-1 -sulfonate in the presence of 0.06 percent sodium tripolyphosphate builder in solution decreases only slightly as the concentration of the detergent compound in solution is substantially decreased from 0.03 percent to 0.01 percent. Other common detergent compounds lose their effectiveness at such low concentrations. The concentration of a detergent compound in solution usually employed is conventional household washing situations ranges from about 0.45 percent for granules to 0.026 percent for liquids.

It has also been found that the maximum detergency of the compositions of this invention is achieved when the pH of the washing solution, at cool water temperatures, is within a range of about 8 to about 12 with the preferred pH being 10.5 to 11.5. Using normal amounts of water for washing, a pH of 11 of the solution can be obtained by incorporating into the compositions of this invention a normal amount of silicate, i.e., up to 8 percent by weight. The silicate acts as a buffer and also as a corrosion inhibitor. The washing step in the laundering method of this invention can be practiced in a number of different, but conventional, ways so long as the essential detergent composition is used. Preferably the step of washing is followed by rinsing and drying the fabrics. For example, the washing solution to be used in the washing step can be prepared by adding the detergent composition of this invention to a tub or automatic washer or any other container which contacts cool water at a temperature ranging from about 40° F. to about 100° F. The detergent product concentration in solution can range from about 0.05 percent to 0.50 percent by total weight, and should be added in sufficient amount to provide a sultaine detergent compound concentration of at least 0.005 percent.

The sultaine detergent compound concentration can be as high as about 0.175 percent based upon the use of a 0.5 percent concentration of a detergent composition containing 35 percent of said sultaine detergent compound. The detergency builder is present in the washing solution in an amount from about 0.004 percent to about 0.45 percent, these figures corresponding respectively to 0.05 percent of a detergent composition containing 8 percent detergency builder and 0.5 percent of a detergent composition containing 90 percent detergent builder. The fabrics can be added to the container or washer before or after the washing solution is added. As is usual in a washing step, the fabrics are then agitated in the detergent solution for varying periods of time, but sufficient to obtain the desired amount of cleaning. With an automatic agitator type washer, it has been found that good cleaning can be achieved using a washing cycle which ranges from 8 to 15 minutes.

After the desired level of cleaning is achieved in the washing step, the washing liquor is then drained off or the fabrics are separated from the liquor and thereafter the fabrics are rinsed in substantially pure water. The fabrics can be rinsed as many times as desirable in order to insure that all of the washing liquor an other undissolved material is separated from them. Using an automatic washer, it has been found that six spray rinses and one deep rinse is usually sufficient for this purpose. Between and after rinsing steps, the bulk of the rinse water is usually drawn from, or spun out of the fabrics. After rinsing the fabrics can be dried by conventional means, using a machine dryer or simply hanging them on a line. Although rinsing and drying are usual and desirable steps, the important advantage of the invention is achieved in the washing step.

In the following described examples there will be mentioned three different methods of testing the effectiveness of the detergent compositions used. These tests will be described herein, and are termed, respectively, the Cloth Swatch Test, the White Shirt Detergency Test, and the Regular Wash and Wear Test.

CLOTH SWATCH TEST

In a cloth swatch test the detergency effectiveness of the sultaine compounds of this invention were determined by washing naturally soiled cloth (desized print cloth) for 10 minutes in an aqueous solution of a detergent composition containing the sultaine compound to be tested and a builder (0.03 percent detergent compound concentration and 0.06 percent builder concentration in the wash solution at a pH of 10, water at 7 grains per gallon hardness at 80° F. or 140° F.). No fluorescers, bleaches, or antiredeposition agents were used. After washing, rinsing and drying the percent of lipid soil removed from the swatch during the washing process was calculated. The percentage of soil removed by the sultaine test composition was then compared with the percentage of lipid soil removed by washing with a known standard (sodium tetrapropylene benzene sulfonate) and in that way the relative effectiveness of the compound was determined. A Tergotometer was used for the washing operation. (Tergotometer testing is described in "Detergency Evaluation and Testing", by J. C. Harris, Interscience Publishers, Inc. (1954) page 60.)

WHITE SHIRT DETERGENCY TEST

In addition to the Cloth Swatch Test described above, the detergency of the sultaine compounds utilized in compositions of this invention was evaluated by washing naturally soiled white dress shirts. Shirts are worn by male subjects under ordinary conditions for two normal working days. The degree to which the detergent composition containing a detergent compound to be tested cleans the collars and cuffs of the soiled shirts, relative to the cleaning degree of a similar composition containing a standard detergent compound is considered a measure of the detergency effectiveness of the test compound.

The washing solution used in the test contains 0.03 percent organic surface active agent and 0.06 percent sodium tripolyphosphate. (No fluorescers, bleaches, or antiredeposition agents were used.) The pH of the washing solution is 10 and water of 7 grains per gallon hardness is used. A conventional agitator type washer is used. The detergent compound in the standard detergent composition was sodium tetrapropylene benzene sulfonate, the most commonly used organic detergent compound in heavy duty laundry detergent compositions. The test detergent composition contains the detergent compound to be tested, i.e., compared with the standard composition.

WASH-WEAR TEST

The standard Wash-wear test mentioned in the examples is conducted as follows:

White dress shirts, cotton T-shirts and other fabrics are distributed among various male individuals and each shirt and T-shirt is worn for one normal working day under uniform condi-

tions. The soiled shirts and fabrics are then washed in an automatic agitatingntype washer, for a period of 10 minutes, with detergent solutions at 80° F. temperature. After washing the clothes are rinsed (six spray rinses and one deep rinse) and then dried. The water has a hardness of 7 grains per gallon and the detergent composition concentration in solution is 0.15 percent. (No fluorescers or bleaches are used.) Direct comparisons are made by a panel of 3 skilled graders between pairs of shirts and fabrics worn and soiled by the same individual. The shirts and fabrics are graded on the degree of cleanness and whiteness maintenance obtained, paying particular attention to the collars and cuffs. The relative cleaning effectiveness of each detergent composition is graded on a raw score under simulated U.V.-free light and simulated north daylight, averaged, and then translated onto a 1–10 scale wherein on the scale 1 is filthy, 5 is acceptable, and 10 is clean, with the remaining numbers representing intermediate values of these conditions.

Having described the various methods of testing the cleaning effectiveness of the sultaine compounds used in this invention, the following described examples will serve to illustrate their detergent power.

EXAMPLE I.

The following test was conducted to illustrate the cleaning efficacy of a detergent composition containing the preferred sultaine compound of the invention at cool water temperatures as compared to compositions containing other commonly used commercially available synthetic detergent compounds. The cleaning grade of these detergent compounds described hereafter was established by conducting a standardized Wash-wear test as previously described. In this example the detergency effectiveness of the sultaine compounds of this invention in cool water (80° F.) is determined by a comparison test in which the sultaine compounds and several well known and commonly used hot water detergent compounds are substituted for the active compound in a commercial detergent formulation which has excellent detergent power (in hot water) and the results are graded on a comparative basis for efficacy in cleaning. The standardized commercial detergent composition is:

17 percent detergent compound
50 percent sodium tripolyphosphate
6 percent silicates (1:2.45 ratio of $Na_2O:SiO_2$)
0.4 percent sodium carboxymethylcellulose
23 percent Na_2SO_4
3.6 percent water and miscellaneous

Detergent Compound (active ingredient	Cleaning Grade 1.0 difference is statistically significant
A. 3-(N,N-dimethyl-N-hexadecyl ammonio propane-1-sulbonate	10.0
B. Condensation product of tetra propylene benzene and 11 moles of ethylene oxide	6.95
*C. Sodium tallow alkyl sulfate	5.47
D. Sodium tetrapropylene benzene sulfonate	3.87
E. Potassium coconut oil soap	0.33

*The alkyl chain length distribution of tallow alkyl sulfate is approximately 66 percent C_{18}, 30 percent C_{16} and 4 percent other.

It can be seen that the cool water cleaning efficiency of the sultaine compound contained in a standard composition is markedly and surprisingly superior to the other commonly used hot water detergent compounds, when used under the same test conditions.

Another Wash-Wear Test was conducted using five well known detergent compositions available commercially. The tests showed the detergent composition utilizing sodium tetrapropylene benzene sulfonate as the active detergent compound to be superior to the other commercial compositions overall cleaning effectiveness at 100° F. yet as indicated in ample 1 above, the sultaine detergent composition is marke superior to a composition containing sodium tetrapropyle benzene sulfonate at 80° F.

A White Shirt Detergency Test, previously described, w conducted using several commercially available deterg compounds in a formulation (containing the detergent co pound to be tested and a builder) in comparison with the tergent compounds utilized in this invention. The washi solution contained 0.03 percent detergent compound a 0.06 percent sodium tripolyphosphate. (No fluoresce bleaches or antiredeposition agents were used.) The washi solution had a pH of 10 and the water was 7 grains per gall hardness. The detergent compounds used in this test were (N,N-dimethyl, N-hexadecylammonio)propane-1-sulfonate (N,N-dimethyl,N-hexadecylammonio)2-hydroxypropane-1-sulfonate, (two of the preferred compounds of this inventio dimethyldodecylamine oxide, sodium tetrapropylene benze sulfonate, and sodium tallow alkyl sulfate. Under the test cc ditions, the detergency effectiveness of 3-(N,N,-diemthyl-hexadeylammonio) propane-1-sulfonate and 3-(N, diemthyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate in wash water of 80° F. was quite superior to the det gency effectiveness of dimethyldodecylamine oxide at 80° and tetrapropylene benzene sulfonate at 140° F., and w greatly superior to the detergency effectiveness of sodium t low alkyl sulfate and sodium tetrapropylene benzene sulfon at 80° F. If the pH of the washing solution at 80° F. 11(equivalent to the hydroxyl ion concentration in solution pH =10 at 140° F.), the margin of superiority of the sultai compounds is increased.

Similar comparative results are obtained if, in the Wh Shirt Detergency Test, an organic alkaline sequestrant builc salt, sodium ethylene diamine tetraacetate or potassiu nitriloacetate, is used instead of the sodium tripolyphosphat

EXAMPLE II. Here a Cloth Swatch Test, previously described, was conducted under the following conditions: water at a temperature of 80° F. or 140° F. and 7 grains pe gallon hardness, 0.03 percent detergent compound and 0.0 percent sodium tripolyphosphate builder concentration in tl washing solution (NO fluorescers, bleaches, or antiredeposition agents were used.) The detergent washing solution had a pH of 10.

Detergent agent	Lipid removal, [1] percent	Temp at °
A. 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate	66.2	
B. Sodium tallow alkyl sulfate	66.0	
C. Sodium tetrapropylene benzene sulfonate	64.0	
D. 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate	62.9	
E. Sodium tallow alkyl sulfate	56.9	
F. Condensation product of tallow alcohol and 17 moles ethylene oxide	56.3	
G. 3-(N,N-dimethyl-N-octadecylammonio)-propane-1-sulfonate	54.3	
H. Sodium tetrapropylene benzene sulfonate	50.7	

[1] Based on cloth swatches.

It can be seen that the sultaine compounds of the present i vention, A & D exhibit superior lipid soil removing properti in cool water as compared to the commonly used hot wat commercial detergent compounds, and in cool water a about equal to commercial detergent compounds used in 14 F. The octadecyl homolog, while not as effective as t preferred hexadecyl compounds, is superior to sodiu tetrapropylene benzene sulfonate in cool water.

Substantially the same performance advantages are c served by the housewife when doing the home laundry water ranging from 40° to 100° F., using conventio

procedures. Woolens and synthetic fibers washed in the same manner are cleaned as efficiently when washed according to the process of this invention and using the compositions of this invention as they would be if they were washed in conventional detergent compositions at hot water temperatures, yet a minimum of shrinkage and wrinkling takes place and the feel of the wool is preserved to a greater extent.

While the compositions of this invention are outstandingly effective in water at a temperature ranging from 40° F. to 100° F., the temperature range in which the most outstanding results are seen is about 60° F. to 90° F. Below about 60° F. it has been found that the granular detergent compositions of this invention are slow to dissolve, consequently, it is preferred to use the liquid compositions at the lower temperatures.

The following compositions will illustrate the manner in which the product invention can be practiced. Included are both liquid and granular formulations. It will be understood, however, that the examples are not to be construed as limiting the scope of conditions claimed hereinafter. These compositions are useful in automatic washers and conventional type washers as well as hand washing operations.

Solid:
- 7% — 3-(N,N-dimethyl-N-hexadecylammonio) propane-1-sulfonate.
- 50% — Sodium tripolyphosphate.
- 5% — Sodium xylene sulfonate.
- 7% — Sodium silicate ($Na_2O:SiO_2$=1:2.5).
- .16% — Fluorescent dye.
- .2% — Perfume.
- .02% — Benzotriazole.
- 20.62% — Sodium sulfate.
- 10% — Water and minor amounts of miscellaneous.

Liquid:
- 12% — 3-(N,N-dimethyl-N-alkylammonio[1])-2-hydroxypropane-1-sulfonate.
- 20% — Tetrapotassium pyrophosphate.
- 3.8% — Sodium silicate ($Na_2O:SiO_2$=1:1.6)
- 8.5% — Potassium toluene sulfonate.
- .3% — Sodium carboxymethyl hydroxy ethyl cellulose.
- .12% — Fluorescent dye.
- .15% — Perfume.
- .02% — Benzotriazole.
- 55.11% — Water.

Liquid:
- 22% — 3-(N,N-dimethyl-N-tetradecylammonio)-2-hydroxypropane-1-sulfonate.
- 19% — Tetrapotassium pyrophosphate.)
- 3.8% — Sodium silicate ($Na_2O:SiO_2$=1:16).
- 8.5% — Potassium toluene sulfonate.
- .3% — Sodium carboxy methyl hydroxy ethyl cellulose.
- .2% — Perfume.
- .02% — Benzotriazole.
- 46.18% — Water and minor amounts of miscellaneous.

Liquid:
- 12% — 3-(N,N-dimethyl-N-alkylammonio[2])-2-hydroxypropane-1-sulfonate.
- 19% — Tetrapotassium pyrophosphonate.
- 3.8% — Sodium silicate ($Na_2O:SiO_2$=1:1.6).
- 8.5% — Potassium toluene sulfonate.
- .3% — Sodium carboxy methyl cellulose.
- .2% — Perfume.
- 56.20% — Water.

Solid:
- 17% — 3-(N,N-dimethyl-N-alkylammonio[2])-2-hydroxypropane-1-sulfonate.
- 50% — Sodium tripolyphosphate.
- 6% — Sodium silicate ($Na_2O:SiO_2$=1:2.5).
- 2% — Sodium toluene sulfonate.
- .3% — Sodium carboxy methyl cellulose.
- 13% — Sodium sulfate.
- .16% — Fluorescent dye.
- 8% — Water.
- Balance — Miscellaneous.

Liquid:
- 10% — 3-(N,N-dimethyl-N-alkylammonio [2])-2-hydroxypropane-1-sulfonate.
- 60% — Sodium pyrophosphate.
- 6% — Sodium silicate ($Na_2O:SiO_2$=1:2.5).
- 2% — Sodium toluene sulfonate.
- .3% — Sodium carboxy methyl cellulose.
- 11.3% — Water.
- Balance — Miscellaneous (fluorescers, perfume, anti-tarnish agents, sodium sulfate, etc.).

Solid:
- 35% — 3-(N,N-dimethyl-N-alkylammonio [3])-2-hydroxypropane-1-sulfonate.
- 35% — Sodium tripolyphosphate.
- 6% — Sodium silicate ($Na_2O:SiO_2$=1:2.5).
- 2% — Sodium toluene sulfonate.
- .3% — Sodium carboxy methyl cellulose.
- 10% — Sodium sulfate.
- 11% — Water.
- Balance — Miscellaneous.

Solid:
- 17% — 3-(N,N-dimethyl-N-alkylammonio [3]) propane-1-sulfonate.
- 45% — Sodium tripolyphosphate.
- 6% — Sodium silicate ($Na_2O:SiO_2$=1:2.5).
- .3% — Sodium carboxy methyl cellulose.
- 28% — Sodium sulfate.
- 3.5% — Water.
- Balance — Miscellaneous.

Liquid:
- 12% — 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate.
- 19% — Sodium nitrilo triacetate.
- 3.8% — Sodium silicate ($Na_2O:SiO_2$=1:1.6).
- .3% — Sodium carboxy methyl cellulose.
- 63% — Water.
- Balance — Miscellaneous.

[1] Alkyl referring to the R_1 group derived from the middle cut of coconut fatty alcohol (2% C_{10}, 66% C_{12}, 23% C_{14}, 9% C_{16}).
[2] Alkyl referring to the R_1 group obtained from tallow fatty alcohol (66% C_{18}, 30% C_{16}, 4% C_{14} and others)
[3] Alkyl referring to the R_1 group derived from the middle cut of coconut fatty alcohol (2% C_{10}, 66% C_{12}, 23% C_{14}, 9% C_{16}).

It will be appreciated that the sultaine compounds used in the present invention can be incorporated into liquid or granular detergent compositions with suitable adjustments being made in the other components.

EXAMPLE III

Here a Cloth Swatch Test, previously described, was conducted under the following conditions: water at a temperature of 80° F. or 140° F. and 7 grains per gallon hardness, 0.03 percent detergent compounds and 0.06 percent sodium tripolyphosphate builder concentration in the washing solution. (No fluorescers, bleaches, or antiredeposition agents were used.) The detergent washing solution had a pH of 10. The coconut alkyl groups hereinafter mentioned are the middle cut coconut alkyl groups described hereinbefore on page 20, lines 22–24.

Detergent agent	Lipid removal,[1] percent	Temperature, ° F.
A. 3-(N,N-dimethyl-N-dodecylammonio)-propane-1-sulfonate	[2] 62.0	80
B. 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate	[3] 65.2	80
C. 3-(N,N-dimethyl-N-octadecylammonio)-propane-1-sulfonate	[2] 55.8	80
D. 3-(N,N-dimethyl-N-dodecylammonio)-2-hydroxypropane-1-sulfonate	64.2	80
E. 3-(N,N-dimethyl-coconutalkylammonio)-2-hydroxypropane-1-sulfonate	[2] 66.5	80
F. 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate	[2] 65.7	80
G. 3-(N,N-dimethyl-N-octadecylammonio)-2-hydroxypropane-1-sulfonate	[3] 52.8	80
H. 3-(N,N-dimethyl-N-dodecylammonio)-1,1,3-trimethylpropane-1-sulfonate	[2] 67.1	80
I. 3-(N,N-dibutyl-N-dodecylammonio)-propane-1-sulfonate	[2] 68.2	80
J. 2-(N,N-dimethyl-N-coconut alkyl)-ethane-1-sulfonate	[2] 74.2	80
K. Sodium tetrapropylenebenzene-sulfonate	64.0	140

[1] Based on cloth swatches.
[2] Average of two tests.
[3] Average of three tests.

It can be seen from this data that detergent agents A, B, D, E, F, H, I and J are superior in cool water detergency effectiveness to C and G. They are also markedly superior in cool water to K in hot water, K being the longtime standard organic detergent compound. The variation in effectiveness within the preferred compounds can be seen in the above results.

When, in detergent agents B and D in tetradecyl group is substituted for the hexadecyl and dodecyl groups, respectively substantially equivalent results are obtained in that the detergent agents are effective cleaning agents at 80° F.

When, in the above example, mixtures of any and all of detergent agents A, B, D, E, F, H, I and J, are substituted for any or all of detergent agents A, B, D, E, F, H, I or J, substantially equivalent results are obtained in that effective cool water cleaning is obtained.

EXAMPLE IV

Here a Cloth Swatch Test, previously described, was conducted under the following conditions: water at a temperature of 80° F. or 140° F. and 7 grains per gallon hardness, 0.03 percent detergent compound and 0.06 percent sodium

tripolyphosphate builder concentration in the washing solution. (No fluorescers, bleaches or antiredeposition agents were used.) The detergent washing solution had a pH of 10. Seven cycles of soiling and cleaning were used.

LIPID REMOVAL BASED ON CLOTH SWATCHES

Detergent Agent	Percent Removal	Temperature
A. Sodium coconutalkyl beta ammonio propionate (Deriphat 151)	21.4	80° F
B. 3-(N,N-dimethyl-N-hexadecyl ammonio)propane-1-sulfonate	33.7	80° F
C. 3-(N,N-dimethyl-N-conconutalkyl ammonio)-2-hydroxypropane-1-sulfonate	44.0	80° F
D. Sodium tetrapropylene benzene Sulfonate	28.5	140° F

As can be seen from the above table, detergent agent C is clearly superior to any of the other detergent agents but that detergent agent B is clearly superior to both detergent agents A and D. It will be noted that detergent agent A at 80° F. cannot approach the performance of detergent agent D at 140° F. The performance of detergent agent D at 140° F. is a standard criteria for adequate cleaning.

With reference to example III, it will be noted that the detergent agents of this invention are all better in performance at 80° F. than the performance of detergent agent D at 140° F.

When examples III and IV pyrophosphates; ethylene diaminetetraacetates; N-(2-hydroxyethyl)-ethylenediamine triacetates; nitrilo triacetates; N-(2-hydroxyethyl)-nitrilodiacetates; phytates; methylenediphosphonates; ethylidene diphosphonates; isopropylidene diphosphonates; benzylmethylidene diphosphonates; chloromethylidene diphosphonates; and mixtures thereof in the form of their sodium, potassium, triethanolammonium, diethanolammonium, and monoethanolammonium salts and mixtures thereof are substituted, either wholly or in part, e.g., a 50 percent substitution, for the sodium tripolyphosphate builder substantially equivalent results are obtained in that for each builder substitution the detergent agents used in the process of this invention are effective cleaning agents at temperatures of about 80° F. and the above detergency building agents provide their building function with such agents. The surprising cool water superiority of these combinations of such agents and builders is found on a relative basis throughout the cool water range of 60° F.–90° F.

Materials which are considered normal and desirable additives in liquid or granule detergent compositions can also be added to the compositions of this invention without substantially modifying the basic characteristics of the sultaine detergent surfactants. For example, a tarnish inhibitor such as benzotriazole or ethylene thio-urea may be added in amounts up to about 1percent. Fluorescers, perfume, color, antiredeposition agents, germicides, thickening agents, opacifiers, blending or viscosity control agents, suds boosters and depressants, and other detergent compounds, while not essential in the composition of this invention, can also be added.

All parts, percentages, and ratios herein are by weight unless otherwise specified.

Since certain changes can be made in the process and composition without departing from the scope of the invention, it is intended that the description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of washing wash-wear fabrics in a washing solution having a temperature of from about 60° F. to about 90° F. and consisting essentially of

A. from about 0.005 percent to about 0.175 percent of a zwitterionic quaternary ammonium compound selected from the group consisting of

1. 3-(N,N-dimethyl-N-alkylammonio) propane-1-sulfonates wherein the alkyl group contains from about 12 to about 16 carbon atoms;
2. 3-(N,N-dibutyl-N-alkylammonio) propane-1sulfonates wherein the alkyl group contains about 12 carbon atoms;
3. 3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonates wherein the alkyl group contains from about 12 to about 16 carbon atoms;
4. 3-(N,N-diemthyl-N-alkylammonio)1,1,3-trimethylpropane-1-sulfonate wherein the alkyl group contains about 12 carbon atoms;
5. 2-(N,N,-dimethyl-N-coconutalkylammonio)-ethane-1-sulfonates; ethane-1-sulfonates; and
6. mixtures thereof;

B. from about 0.004 percent to about 0.45 percent of a detergency builder selected from the group consisting of

1. pyrophosphates;
2. ethylenediaminetetraacetates;
3. N-(2-hydroxyethyl)-ethylenediamine-triacetates;
4. nitrilotriacetates,
5. N-(2-hydroxyethyl)-nitrilodiacetates;
6. phytates;
7. tripolyphosphates; and
8. mixtures thereof in the form of their sodium, potassium, triethanolammonium, diethanolammonium, and monoethanol-ammonium salts and mixtures thereof; and

C. water, wherein the ratio of A to B by parts, ranges from about 5:1 to about 1:25 , all percentages herein being by weight.

2. The process of claim 1 wherein Compound (A) is 3-(N,N-dimethyl-N-hexadecylamminio)propane-1-sulfonate.

3. The process of claim 1 wherein Compound (A) is 3(N,N-dimethyl-N-dodecylammonio)-2-hydroxypropane-1-sulfonate.

4. The process of claim wherein Compound (A) is 3-(N,N-dimethyl-N-coconutalkylammonio)-1-sulfonate.

5. The process of claim 1 wherein Compound (B) consists essentially of tripolyphosphates.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,115 Dated November 9, 1971

Inventor(s) Francis L. Diehl and Norman R. Smith

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

Column 1, line 52, "waters" should read --water is--.
Column 2, line 10, "nd" should read --and--.
Column 2, line 73, "3-(N,N-bibutyl-N-alkylammonio)propane-1-sulfonates" should read --3-(N,N-dimethyl-N-alkylammonio)-propane-1-sulfonates--.
Column 3, line 3, "3-(N,N-diemthyl-N-alkylammonio)-2-hydroxypropane-1-sulfonates" should read --3-(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulfonates--.
Column 3, line 52, "3-(N,N-diemthyl-N-" should read --3-(N,N-dimethyl-N---.
Column 3, line 53, after "hydroxypropane-1" should read ---sulfonate;--.
Column 3, line 53, "3-(N,N-diemthyl-N-" should read --3-(N,N-dimethyl-N---.
Column 3, line 54, "hydrosypropane" should read --hydroxypropane--.
Column 3, line 60, "3-N,N-dimethyl-N,N-tetradecylammonio)" should read --3-(N,N-dimethyl-N-alkylammonio)--.
Column 3, line 64, "tetradecylammino" should read --tetradecylammonio--.
Column 3, line 66, "monio)butane-butane-1-sulfonate; butane-1-sulfonate;" should read --monio)butane-1-sulfonate;--.
Column 3, line 68, "(N-2-hydroxyethyl-N-methy)" should read --(N-2-hydroxyethyl-N-methyl)--.
Column 4, line 26, "1" should read --(1)--.
Column 4, line 29, the second "2" should read --(2)--.
Column 4, line 30, "e.g.," should read --(e.g.,--.
Column 4, line 31, the second "3" should read --(3)--.

Column 4, line 35, "4" should read --(4)--.
Column 4, line 37, "e.g.," should read --(e.g.,--.
Column 4, line 42, "3,422,021; and 5 mixtures thereof" should read --3,422,021); and (5) mixtures thereof.

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,115 Dated November 9, 1971

Inventor(s) Francis L. Diehl and Norman R. Smith

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

Column 4, line 51, "sodium, silicate" should read --sodium silicate--.

Column 5, line 33, "is" should read --in--.
Column 5, line 34, "0.45" should read --.045--.
Column 6, line 6, "an" should read --and--.
Column 7, line 2, "agitatingntype" should read --agitating-type--.
Column 7, line 55, "sulbonate" should read --sulfonate--.
Column 8, end of line 1, should read --in--.
Column 8, end of line 2, should read --Ex---.
Column 8, end of line 3, should read --markedly--.
Column 8, end of line 4, should read --tetrapropylene--.
Column 8, end of line 6, should read --was--.
Column 8, end of line 7, should read --detergent--.
Column 8, end of line 8, should read --com---.
Column 8, end of line 9, should read --de---.
Column 8, end of line 10, should read --washing--.
Column 8, end of line 11, should read --and--.
Column 8, end of line 12, should read --fluorescers,--.
Column 8, end of line 13, should read --washing--.
Column 8, end of line 14 or 15, should read --gallon--.
Column 8, end of line 16, should read --3---.
Column 8, end of line 17, should read --, 3---.
Column 8, end of line 19, should read --invention),--.
Column 8, end of line 20, should read --benzene--.
Column 8, end of line 21, should read --con---.
Column 8, end of line 22, should read --N---.
Column 8, end of line 23, should read --N---.
Column 8, end of line 25, should read --deter---.
Column 8, end of line 26, should read --80°F.--.
Column 8, end of line 27, should read --was--.

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,115 Dated November 9, 1971

Inventor(s) Francis L. Diehl and Norman R. Smith

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

Column 8, end of line 28, should read --tal---.
Column 8, end of line 29, should read --sulfonate--.
Column 8, end of line 30, should read --is--.
Column 8, end of line 31, should read --at--.
Column 8, end of line 32, should read --sultaine--.
Column 8, end of line 34, should read --White--.
Column 8, end of line 35, should read --builder--.
Column 8, end of line 36, should read --potassium--.
Column 8, end of line 37, should read --tripolyphosphate.--.
Column 8, end of line 42, should read --0.06--.
Column 8, end of line 43, should read --the--.
Column 8, end of line 50, should read --Temperature, °F.--.
Column 8, end of line 53, should read --80--.
Column 8, end of lines 54 & 55, should read --140--.
Column 8, end of lines 56-60, should read --80--.
Column 8, end of line 65, should read --in---.
Column 8, end of line 66, should read --properties--.
Column 8, end of line 67, should read --water--.
Column 8, end of line 68, should read --are--.
Column 8, end of line 69, should read --140°--.
Column 8, end of line 70, should read --the--.
Column 8, end of line 71, should read --sodium--.
Column 8, end of line 73, should read --ob---.
Column 8, end of line 74, should read --in--.
Column 8, end of line 75, should read --conventional--.
Column 9, line 53, "pyrophosphate.)" should read --pyrophosphate.--.
Column 10 line 59, the second "in" should read --a--.
Column 11, line 10, "214" should read --21.4--.
Column 11, line 12, "337" should read --33.7--.
Column 11, line 14, "440" should read --44.0--.
Column 11, line 16, "285" should read --28.5--.

PO-1050
(5/69)

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Patent No. 3,619,115 Dated November 9, 1971

Inventor(s) Francis L. Diehl and Norman R. Smith

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

Page 4

Column 12, line 24, "3-(N,N-diemthyl-N-alkylammonio)1,1,3-trimethyl- should read --3-(N,N-dimethyl-N-alkylammonio)-1,1,3-trimethyl---.

Column 12, line 25, "propane-1-sulfonate" should read --propane-1-sulfonates--.

Column 12, line 28, the second "ethane-1-sulfonates;" should be deleted.

Column 12, line 47, "(N,N-dimethyl-N-hexadecylamminio)" should read --(N,N-dimethyl-N-hexadecylammonio)--.

Column 12, line 53, after "claim" and before "wherein" should read --1--.

Column 12, line 54, "dimethyl-N-coconutalkylammonio)-1-sulfonate" should read --dimethyl-N-coconutalkylammonio)-2-hydroxypropane-1-sulfonate--.

Signed and sealed this 18th day of July 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents