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DETERGENT COMPOSITIONS

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The present invention relates to anionic synthetic detergent compositions. More particularly, it relates to improved anionic alkyl sulfate detergent compositions capable of producing dense, stable foam when aqueous solutions of these compositions are employed in conventional concentrations for household or commercial laundering.

Small scale users of synthetic anionic detergents insist that the detergent products be capable of producing substantial lather or foam and that this foam remain stable during the washing process. The average housewife persists in the belief that satisfactory detergency and formation of copious foam go hand in hand and seeks detergent products which would produce rich, dense lathers or foams constituted by little bubbles and on contact with the hand would give the feeling of a cream-like consistency of soap suds. This persistent prejudice is responsible for the slow customer acceptance of synthetic anionic detergents for laundering purposes, particularly in the home, since many efficient detergents have but little foaming power, and also since the foam produced by them is rather poor in texture and lacy, and does not possess sufficient stability.

In U. S. Patents Nos. 2,166,314 and 2,166,315, Martin proposed to add higher saturated C₈-C₁₈ aliphatic alcohols to compositions containing sulfated alcohol detergents for the purpose of improving the sudsing properties of these compositions. However, such an addition, while improving the sudsing ability, brings about certain disadvantages, namely: (1) a relatively large portion of the aliphatic alcohols added to the neutralized slurry of alkyl sulfate detergent is lost in the subsequent drying of the slurry; (2) a fatty odor characteristic of these alcohols is imparted to the product.

I have now found that desirable foaming characteristics and satisfactory foam stability can be imparted to detergent compositions which contain as their surface-active ingredient an anionic water-soluble salt of a straight-chain C₁₂-C₂₂ alkyl sulfuric acid, by adding to these compositions a minor amount of a salt of a primary C₁₂-C₁₈ straight-chain alkyl amine and an organic acid from the group consisting of higher C₁₂-C₁₈ saturated fatty acids, C₉-C₁₈ monoalkyl benzene sulfonic acids and C₁₂-C₁₈ straight-chain monoalkyl sulfuric acids. In general, from about 0.5 to about 10% by weight of this salt, based on the solid constituents of the detergent composition, suffices to secure a satisfactory, stable foam.

When aqueous solutions of the detergent com-

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positions containing as their surface-active ingredient said water-soluble salt of a C₁₂-C₂₂ straight-chain alkyl sulfuric acid and the aforementioned alkyl ammonium salt additive are employed to wash fabrics, in concentrations conventional in the laundering practice (0.1 to 0.4%), they produce a rich, creamy foam of densely agglomerated small bubbles readily recognizable by squeezing through the fingers. This foam retains its stability for relatively long periods of time, and the detergency of the wash solutions containing these detergent compositions not only is unaffected by the presence of the alkyl ammonium salt additive which promotes and stabilizes the foam, but frequently is enhanced thereby.

As stated hereinbefore, the detergent compositions of my invention capable of producing satisfactory, stable foam contain as their surface-active ingredient water-soluble salts of an alkyl sulfuric acid in which the hydrophobic alkyl radical is constituted by a straight carbon to carbon chain of 12 to 22 carbon atoms.

The term "a salt of an alkyl sulfuric acid," as employed in this specification, includes alkyl sulfates, and alpha- and beta-hydroxyalkyl sulfates. In all of these alkyl sulfates, the hydrophilic group occupies the terminal position on the carbon chain.

The term "a water-soluble salt" as used in this specification is intended to include all water-soluble detergent salts of C₁₂-C₂₂ alkyl sulfuric acids, namely, inorganic alkali metal salts, alkaline earth metal salts, e. g., calcium and magnesium; ammonium salts; alkyl and alkylol ammonium salts, e. g., triethanol ammonium salts.

Generally speaking, the N-n-alkyl ammonium salts which promote foam formation and stabilize the foam of alkyl sulfate detergents in accordance with the invention, can be formed by reacting the organic base, i. e., primary normal C₁₂-C₁₈ alkyl amine, with an acid from the group consisting of higher saturated C₁₂-C₁₈ fatty acids, C₉-C₁₈ monoalkyl benzene sulfonic acids, and C₁₂-C₁₈ straight-chain monoalkyl sulfuric acids.

The ammonium salts of saturated C₁₂-C₁₈ fatty acids, C₉-C₁₈ monoalkyl benzene sulfonic acids and C₁₂-C₁₈ straight-chain monoalkyl sulfuric acids can also be obtained by reacting a salt of the primary amine, e. g., a hydrochloride, a formate, or an acetate, with a water-soluble inorganic salt of a fatty acid, an alkyl benzene sulfonic acid, or an alkyl sulfuric acid. In so doing a suitable solvent, e. g., ethanol, will be employed to separate the phase containing ammonium salt,

dissolved in ethanol or other appropriate organic solvent, from the phase containing the water-soluble salt such as NaCl, NaOOCCH₃, and the like.

To illustrate: A primary straight-chain C₁₂-C₁₈ fatty amine, e. g., lauryl amine, may be melted together with an equimolar amount of a higher C₁₂-C₁₈ saturated fatty acid, such as myristic acid. In this case the product will be N-n-dodecyl ammonium myristate. The same ammonium salt may be obtained by dissolving the aforementioned reactants in ethanol or other appropriate inert solvent, and substantially evaporating the solvent medium.

In order to obtain the foam stabilizing salt of a C₁₂ primary fatty amine and a C₁₂ monoalkyl benzene sulfonic acid, the amine is reacted with the sulfonic acid and yields the desired ammonium salt. One may also obtain this salt by reacting a hydrochloride of the amine, e. g., octadecyl amine hydrochloride, with sodium monoalkyl benzene sulfonate in ethanol as a solvent medium. Sodium chloride is precipitated, and, upon filtering and evaporating the alcohol, the desired octadecyl ammonium sulfonate additive is recovered. Salts of C₁₂-C₁₈ fatty amines and alkyl sulfuric acids may be prepared in a similar manner. For instance, a salt of the primary amine, e. g., N-n-tetradecyl ammonium acetate, can be reacted with an alcohol sulfate, e. g., sodium dodecyl sulfate, and, upon separation of phases with the aid of a suitable solvent, will yield the desired foam-promoting and foam-stabilizing additive, namely, N-n-tetradecyl ammonium alkyl sulfate.

In addition to the surface-active alkyl sulfates and the foam promoting alkyl ammonium salt additives, the detergent compositions of the invention may contain builders conventionally employed in conjunction with anionic detergents such as inorganic sulfates, phosphates and silicates, extenders such as sodium carboxymethyl cellulose, optical bleaches, perfumes, etc. These additives are employed in amounts readily determinable by those skilled in the art to suit the requirements of each particular formulation. Ordinarily, aqueous solutions (in 0.1 to 0.4% concentration) of detergent compositions which contain in each 100 parts by weight from 10 to 50 parts of the surface-active ingredient, the balance being the aforementioned inorganic builders and other conventional additives, will produce good, stable foam upon adding thereto from 0.5 to 10% by weight of the foam-promoting ammonium salt.

In heavy-duty, all-purpose detergent compositions generally containing from 15 to 30 parts of the surface-active ingredient in each 100 parts of solid constituents, from about 0.5 to 5% by weight, and preferably from 1.0 to 2.5% by weight, of the foam-promoting ammonium salt provides the desired effect.

I have furthermore found that salts of C₁₂-C₂₂ straight-chain alkyl sulfuric acids which constitute the principal surface-active ingredient of my improved detergent compositions may be replaced in part by compatible water-soluble salts of C₉-C₁₈ monoalkyl benzene sulfonic acids, and preferably C₁₂-C₁₅ monoalkyl benzene sulfonic acids. So long as at least 25% of the combined weight of surface-active ingredients in such modified composition is constituted by the water-soluble C₁₂-C₂₂ alkyl sulfate, the foam characteristics will be improved by the introduction of from about 0.5 to about 10% by weight of the ammonium salt additive in accordance with the invention. This

represents an important finding, since the fatty alcohols reported in the art as suitable agents for improving the foaming characteristics of alkyl sulfate detergents are ineffective in detergent compositions containing alkyl benzene sulfonate as the only surface-active ingredient. Furthermore, salts of fatty amines and organic acids, disclosed in the present specification as effective additives for improving the foaming characteristics of alkyl sulfates are likewise inefficient in detergent compositions where an alkyl benzene sulfonate is the sole surface-active constituent.

A number of tests was carried out with the various formulations prepared in accordance with my invention and their results were compared with the results obtained employing other known compositions of the trade. Stock solutions for these tests were prepared, using a small amount of isopropanol, and heating if necessary, to dissolve a sample of the detergent formulation in order to obtain a 5% solution in distilled water. In a representative test series the composition contained 24% by weight of total surface-active ingredients, including the foam-promoting ammonium salt; 55% of sodium tripolyphosphate; and 21% of sodium sulfate. By dissolving 20 g. of such a 5% solution in 500 ml. of warm water (110° to 115° F.) in a 2 liter beaker, a 0.2% solution was obtained for actual use in the tests.

The tests were carried out in accordance with the following technique: The test solution was agitated vigorously for 1 minute (with the aid of a mechanically driven propeller stirrer) and then allowed to stand for an additional 1 minute, whereupon the foam height in millimeters was measured. Heights of more than 30 mm. were rated as high; heights between 20 to 30 mm. were rated as medium; and those of less than 20 mm. were rated as low. Fifteen minutes after the agitation was terminated, the foam height was measured again, and the stability and quality of the foam were ascertained.

The foam stability was rated by blowing on a small volume of foam gently with air. In the case of unstable foam, this procedure resulted in a rapid decay (collapse) of foam bubbles. The quality of the foam, i. e., the size of the foam bubbles and the feel, or body, of the foam, was rated by comparing them with the foams produced by two formulations: detergent composition A which contains 10% by weight of sodium C₁₂-C₁₄ alkyl sulfate, 50% by weight of sodium tripolyphosphate, 10% by weight of sodium C₁₂-C₁₅ alkyl benzene sulfonate, 2% by weight of lauryl alcohol, the balance to make 100% being Na₂SO₄ builder; and detergent composition B which contains 24% by weight of sodium C₁₂-C₁₅ alkyl benzene sulfonate; 55% by weight of sodium tripolyphosphate and 21% by weight of Na₂SO₄ builder. Composition A produces excellent creamy, small size foam bubbles and a heavy stable dense-bodied suds and its foam stability and quality are, therefore, rated to be Good. Composition B produces lacy, rapidly collapsing foam, and its foam quality and stability are rated Poor. The designation Fair is employed in the specification to rate those foams approaching the stability and quality of the foam formed by composition A.

The experimental data obtained by the aforementioned evaluation technique clearly show that the addition of salts of primary fatty amines and organic acids described hereinbefore to the anionic detergent compositions containing straight-chain C₁₂-C₂₂ alkyl sulfates provides an improved

foam and stabilizes this foam, rendering these detergent compositions attractive for the user.

The following Table I contains the results of a few representative tests selected from the extensive experimental data to illustrate the advantages attained by the detergent compositions of the present invention. In this table, the amounts of the foam-promoting additive are given in percent of the total weight of surface-active and inert ingredients of the detergent composition which contained (except where otherwise indicated): 20% of surface-active materials, 55% of sodium tripolyphosphate and 25% of sodium sulfate builder. The surface-active portion of the composition in all tests (except where otherwise indicated) contained 10% of sodium C₁₂-C₁₅ monoalkyl benzene sulfonate, from 1 to 2% of the foam-promoting ammonium salt, the balance being sodium C₁₄-C₁₈ straight-chain alkyl sulfates produced by sulfonation of a blend of C₁₄-C₁₈ alcohols, derived in turn by catalytic hydrogenation from the higher fatty acids (or esters thereof) present in tallow.

The foam heights are designated by H—high, M—medium, L—low; foam stability and foam quality are designated by G—good, F—fair and P—poor. The sodium alkyl benzene sulfonate was prepared in accordance with the description of U. S. Patent No. 2,477,383 to A. H. Lewis, by sulfonation of C₁₂-C₁₅ polypropylene benzene. The concentration of test solutions was 0.2%, employing tap water of 50 p. p. m. hardness ($\frac{2}{3}$ CaCO₃; $\frac{1}{3}$ MgCO₃).

TABLE I

Foam evaluation data

[Concentration of Solution: 0.2% in Tap Water]

Test No.	Name of Additive	Amount of Additive in percent	Comparative Foam Heights		Foam Stability	Foam Quality
			After 1 min.	After 15 min.		
1	N-n-dodecyl ammonium laurate.....	2	H	H	G	G
2	Same.....	1	H	H	G	G
3	N-n-dodecyl ammonium myristate.....	2	H	H	G	G
4	Same.....	1	H	H	G	G
5	N-n-dodecyl ammonium palmitate.....	1	H	H	G	G
6	Salt of primary n-dodecyl amine and C ₁₄ -C ₁₈ tallow fatty acids.....	2	H	H	G	G
7	Same.....	1	H	H	F	G
8	Salt of primary C ₁₂ -C ₁₅ alkyl amine ¹ and C ₁₄ -C ₁₈ tallow fatty acids.....	2	H	H	G	G
9	N-n-dodecyl ammonium C ₁₂ -C ₁₅ alkyl benzene sulfonate.....	2	H	H	G	G
10	Salt of primary C ₁₂ -C ₁₅ alkyl amine ¹ and C ₁₂ -C ₁₅ alkyl benzene sulfonic acids.....	2	H	H	G	G
11	N-n-octadecyl ammonium laurate.....	2	H	M	F	F
12	Salt of primary alkyl amine and fatty acids, both derived from tallow.....	2	M	M	F	F
13	Same.....	1	M	M	F	F
14	N-n-tetradecyl ammonium salt ² of a mixture of C ₁₂ -C ₁₅ alkyl benzene sulfonic and C ₁₄ -C ₁₈ alkyl sulfuric acids.....	2	H	H	F	F
15	N-n-dodecyl amine.....	2	L	L	P	P
16	Tert.dodecyl anilinium laurate.....	2	H	L	P	P
17	N-n-dodecyl ammonium ³ myristate.....	4	M	M	G	G

¹ Primary amine derived from a mixture of coconut fatty acids.

² Formed by reacting N-n-tetradecyl ammonium acetate with a mixture of sodium C₁₂-C₁₅ alkyl benzene sulfonates and sodium C₁₄-C₁₈ alkyl sulfates.

³ Added to a detergent composition containing: 8% by weight of sodium stearyl sulfate, 12% by weight of sodium C₁₂-C₁₅ alkyl benzene sulfonate, 55% by weight of sodium tripolyphosphate, 21% by weight of sodium sulfate.

In addition to pointing out the superior foam characteristics of the detergent composition prepared in accordance with the invention, the evaluation tests have shown that a primary straight-chain C₁₂-C₁₈ alkyl amine must be employed to furnish the ammonium salts capable of promoting foam formation, and foam stability and of improving foam quality. Amines other than the primary straight-chain amines were found in-

effective for this purpose, as may be seen on the example of tertiary dodecyl anilinium salt of Test #16.

Furthermore, the tests have shown that the primary straight-chain fatty amine must be first reacted with the appropriate organic acid from the particular group of operative fatty, alkyl benzene sulfonic and alkyl sulfuric acids, and only then the resulting salt should be introduced into the mixture of surface-active and inert ingredients. In contradistinction to a practice proposed for cationic detergents, the introduction of N-n-alkyl amine, as shown in Test #15 of the table, brings no improvement of foam properties.

Simultaneously with the aforescribed foam tests, a number of foam samples, produced by detergent compositions containing the ammonium salt additive in accordance with the invention, were tested by letting the suds slide down a vertical glass surface. All of the samples slid down rapidly, indicating a high degree of desirable wetness.

As mentioned hereinbefore, the presence of the foam-promoting ammonium salts of my invention does not affect adversely the detergency characteristics of the anionic alkyl sulfate detergent compositions containing these salts. Frequently their presence appears, in fact, to be beneficial with respect to detergency. A series of tests were carried out by employing a conventional automatic agitator-type washing machine. The solutions employed were those of detergent compositions, prepared in accordance with the

invention and containing 9% by weight of sodium salts of C₁₄-C₁₈ alkyl sulfuric acids derived from tallow; 10% by weight of sodium salts of C₁₂-C₁₅ alkyl benzene sulfonic acids, produced in accordance with the technique described in U. S. Patent No. 2,477,383 to A. H. Lewis; 1% by weight of the foam-promoting ammonium salt additive of the invention; 55% by weight of sodium tripolyphosphate builder; and 25% by weight of sodium sul-

fate builder. Comparison tests were made with a solution of the previously mentioned detergent composition A. The following concentrations were used: 0.1%, 0.15% and 0.2% in hard water (300 p. p. m.=200 p. p. m. CaCO₃+100 p. p. m. MgCO₃) and 0.15% in soft water (50 p. p. m.; CaCO₃:MgCO₃=2:1). The machine in each test received a load of 6 pounds of clean cotton towels, having pinned thereto a strip or swatch of cotton, uniformly soiled with a paste of oil, tallow and carbon black. The temperature of the wash solutions was about 140° F., and each test consisted of one washing of 20 minutes' duration followed by two 5-minute rinses. On completion of each test the swatches were removed, and the degree of whiteness obtained was measured in a photoelectric apparatus, free of human equation. The detergency was rated with reference to an arbitrarily chosen detergency standard, namely, the whiteness level secured with the 0.4 concentration of a well-known fatty acid soap in hard water (300 p. p. m.), and taken to be equal to 100.

The results of the aforementioned test runs are tabulated in the following Table II:

TABLE II

Test No.	Name of Additive	Concentration of Washing Solution			
		In Hard Water (300 p. p. m.)			In Soft Water (50 p. p. m.)
		0.1	0.15	0.2	0.15
1.....	N,n-dodecyl ammonium C ₁₂ -C ₁₅ alkyl benzene sulfonate.	30	78	86	97
2.....	N,n-dodecyl ammonium laurate.	19	62	72	102
3.....	N,n-dodecyl ammonium palmitate.	29	74	-----	-----
4.....	Control Composition "A" with Lauryl Alcohol as Additive.	24	69	94	-----
5.....	Control Composition "A" without Additive.	-----	77	95	106

The actual preparation of the detergent compositions of my invention presents no difficulties. The only condition precedent for the preparation of these compositions is that the foam-promoting ammonium salt be prepared first and then only blended with the mixture of surface-active and inert ingredients, since, as it was shown, direct addition of primary amine to the detergent composition is ineffective. Blending with the detergent slurry and drying of the blended product are carried out in the conventional manner. The blended slurry may be worked up by spray-drying or drum-drying to give a particulate, flake or chip product, or it may be processed into a paste, or yet may be diluted and sold as a liquid concentrate.

It is to be understood that the foregoing description and examples are merely illustrative of the invention, and that all modifications consistent with the spirit and scope thereof are included within the terms of the following claims.

I claim:

1. A detergent composition comprising as its surface-active ingredient a water-soluble salt of an alkyl sulfuric acid, having in its molecular structure a straight-chain alkyl radical containing from 12 to 22 carbon atoms, and a minor amount of a salt of a primary C₁₂-C₁₈ straight-chain alkyl amine and an organic acid from the group consisting

of C₁₂-C₁₈ saturated fatty acids, C₉-C₁₈ monoalkyl benzene sulfonic acids and C₁₂-C₁₈ monoalkyl sulfuric acids, said amount being sufficient to impart stability to the foam of dilute aqueous solutions of said detergent composition of concentrations in the range from 0.1 to 0.4%.

2. A detergent composition, each 100 parts by weight whereof contains from 10 to 50 parts of surface-active ingredients constituted by a water-soluble salt of a straight-chain C₁₂-C₂₂ alkyl sulfuric acid, and from about 0.5 to about 10%, based on the weight of solid ingredients in said detergent composition, of a salt of a primary C₁₂-C₁₈ straight-chain alkyl amine and an organic acid from the group consisting of C₁₂-C₁₈ saturated fatty acids, C₉-C₁₈ monoalkyl benzene sulfonic acids and C₁₂-C₁₈ monoalkyl sulfuric acids.

3. A detergent composition, each 100 parts by weight whereof contains from 15 to 30 parts of surface-active ingredients present as a mixture of water-soluble salts of a C₁₂-C₂₂ straight-chain alkyl sulfuric acid and of a C₉-C₁₈ monoalkyl benzene sulfonic acid, at least 25% of the total weight of these surface-active ingredients being constituted by salts of said alkyl sulfuric acid, said detergent composition further comprising from about 0.5 to about 5% by weight, based on the total weight of solid ingredients therein, of a salt of a primary C₁₂-C₁₈ straight-chain alkyl amine and an organic acid from the group consisting of C₁₂-C₁₈ saturated fatty acids, C₉-C₁₈ monoalkyl benzene sulfonic acids and C₁₂-C₁₈ monoalkyl sulfuric acids.

4. A detergent composition, each 100 parts by weight whereof contains from 15 to 30 parts of surface-active ingredients present as a mixture of water-soluble salts of a C₁₂-C₂₂ straight-chain alkyl sulfuric acid and of a C₉-C₁₈ monoalkyl benzene sulfonic acid, at least 25% of the total weight of these surface-active ingredients being constituted by salts of said alkyl sulfuric acid, said detergent composition further comprising from about 1.0 to about 2.5% by weight, based on the total weight of solid ingredients therein, of a salt of a primary C₁₂-C₁₈ straight-chain alkyl amine and an organic acid from the group consisting of C₁₂-C₁₈ saturated fatty acids, C₉-C₁₈ monoalkyl benzene sulfonic acids and C₁₂-C₁₈ monoalkyl sulfuric acids.

5. A detergent composition containing in each 100 parts thereof from 15 to 30 parts by weight of surface-active water-soluble salts of a C₁₂-C₂₂ straight-chain alkyl sulfuric acid and of a C₁₂-C₁₈ monoalkyl benzene sulfonic acid, at least 25% of the total weight of said surface-active ingredients being constituted by salts of said alkyl sulfuric acid, said detergent composition further containing from 85 to 70 parts by weight of inorganic alkali metal builders, and from 1.0 to 2.5%, based on the total weight of the solid constituents in said detergent composition, of a salt of a primary C₁₂-C₁₈ straight-chain alkyl amine and an organic acid from the group consisting of C₁₂-C₁₈ saturated fatty acids, C₉-C₁₈ monoalkyl benzene sulfonic acids and C₁₂-C₁₈ monoalkyl sulfuric acids.

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