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LOW FOAMING DETERGENT COMPOSITIONS

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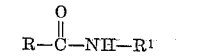
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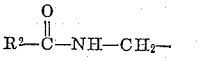
The present invention relates to improved detergent compositions of the anionic organic sulfate and sulfonate types, aqueous solutions of which are characterized by a very low degree of foam formation under conditions of vigorous and continued agitation.

Although the formation of abundant foam has been considered a desirable property of a washing agent as indicative of lasting detergent power, it is also recognized that copious suds formation is not necessarily an indication of detergent effectiveness. In fact, with certain household and commercial appliances and apparatus, production of copious suds is a handicap and not an advantage.

It has now been found that excessive foaming upon use of dilute aqueous solutions of anionic organic sulfate- and sulfonate-type detergents can be reduced substantially by adding to these detergents an effective amount of a foam-suppressing agent having the general formula:



in which R is a C_{15}–C_{21} saturated alkyl radical, or mixtures thereof, and R^1 is a hydrocarbyl radical of 1 to 22 carbon atoms, or



in which R^2 is an alkyl radical of 15 to 21 carbon atoms.

Some typical compounds that perform as very effective foam suppressors are N-methyl hexadecanamide, N-methyl octadecanamide, N-ethyl hexadecanamide, N-propyl heptadecanamide, N-octadecyloctadecanamide, N-phenyl hexadecanamide; the methylene-bis-amides, e.g., methylene-bis-octadecanamide, methylene - bis - hexadecanamide; the mixed methylene diamides, e.g., those prepared from hydrogenated tallow acid amides and formaldehyde.

The effective amount of this foam suppressor may range from about 2 to about 35% by weight, based on the active organic sulfate or sulfonate in the detergent formulation, the preferred range being from about 5% to 15% by weight.

The anionic detergent component of the invention falls within the class of surface active materials which are the water-soluble salts of organic sulfonic acids and water-soluble salts of aliphatic sulfuric acid esters. In other words, synthetic detergents are contemplated which normally tend to produce much foaming before treatment and are the salts of organic sulfuric reaction products having in the molecular structure either a sulfonic or sulfuric ester radical. Ordinarily, for the purposes of laundering and dishwashing, sodium and potassium salts are used. On the other hand, ammonium and magnesium salts are preferred in certain specialized applications.

As more specific examples of satisfactory synthetic detergents, there can be mentioned the water-soluble salts of alkyl benzene sulfonates, particularly those in which the alkyl group is a polypropylene radical or other carbon-containing chain, e.g., a straight-chain radical, having an average of 8 to 15 carbon atoms; the water-soluble salts of alkyl sulfuric acid, having 8 to 20 carbon atoms in the alkyl group; the water-soluble salts, such as the alkali metal salts of sulfuric acid esters of primary normal aliphatic alcohols containing 10 to 18 carbon atoms, such as lauryl and oleyl alcohol; secondary alkyl sulfates having pronounced detergent power and obtained from secondary alcohols or olefins. Other examples of the synthetic detergent components include the sulfuric acid esters which are the water-soluble salts of sulfuric acid esters of polyhydric alcohols incompletely esterified with high molecular weight soap-forming carboxylic acids, such as the water-soluble salts of sulfuric acid esters of higher molecular weight fatty acid monoglycerides, more specific examples being sodium glyceryl monolaurate sulfate and potassium glyceryl monopalmitate sulfate.

Specific types of anionic detergents whose dilute solutions foam less in the presence of the foam suppressor of the invention are certain alkyl aryl sulfonates, namely, the alkyl benzene sulfonates containing an average from 9 to about 15 carbon atoms in the alkyl chain, and, in particular, the polypropylene benzene sulfonates of the kind described by A. H. Lewis in his U.S. Patent No. 2,477,383. These detergents exhibit a particularly satisfactory foam behavior when formulated in accordance with the invention. Within the detergent range of molecular weights, the higher molecular weight compounds form a more persistent foam than do the lower molecular weight compounds.

Other similar benzene sulfonates, such as keryl benzene sulfonates and the essentially straight-chain alkyl benzene sulfonates obtained by the alkylation of benzene with monochlorinated normal paraffins or with straight-chain olefins, can likewise be employed for the preparation of satisfactory low foam formulations.

Specific types of organic sulfate detergents whose foam is suppressed by the foam-suppressing agent of this invention are both primary and secondary alcohol sulfates, in which the alkyl group contains from 10 to 20 carbon atoms. For practical reasons and for improved detergency, the alkyl group of these sulfates is usually a mixture of alkyl groups having from 10 to 20 carbons present. Typical secondary sulfates are readily prepared by the reaction of an olefin and concentrated sulfuric acid, as disclosed, for example, in U.S. Patent 2,587,990. Primary sulfates, on the other hand, are prepared by the reaction of a primary alcohol and concentrated sulfuric acid, for example, as described in U.S. Patent 2,452,943.

Also contemplated are the water-soluble salts of sulfuric acid esters of the hydroxy ethers resulting from the reaction of an aliphatic alcohol and ethylene oxide. These compounds have the general formula:

$$C_nH_{2n+1}—O—(CH_2CH_2—O)_xSO_3M$$

wherein n=8 to 20, x=1 to 6, preferably 3 to 6, and M is an alkali metal. A typical example is the sodium salt of lauryl ether of ethylene glycol monosulfuric acid.

Other types of detergents which can be treated in accordance with the invention are the water-soluble salts of monosulfuric acid esters of the monoethers of high

molecular weight aliphatic alcohols and glycerine. These compounds have the general formula:

$$C_nH_{2n+1}—O—CH_2—CHOH—CH_2—O—SO_3M$$

wherein n=8 to 20 and M is an alkali metal. A typical example is the sodium salt of monolauryl ether of glycerine monosulfuric acid.

Still additional examples of sulfuric acid ester synthetic detergents are water-soluble salts of sulfated higher fatty acid alkanolamides, such as the sodium salt of sulfated coconut oil fatty acid ethanolamide, and the potassium salt of sulfated lauric isopropanolamide.

In addition to the above detergent active materials, the present compositions may also contain auxiliary detergent agents, such as soap in amounts of, for example, 1% to 200% based on detergent active and foam suppressor. The fatty acid soap auxiliary detergent component may be any one of the several higher molecular weight saturated fatty acids, for example, sodium or potassium, salts of fatty acids containing 14 to 22 carbon atoms.

The blending of the amide foam suppressor with the organic sulfate or sulfonate detergent presents no difficulties. It is preferred to add the foam suppressor, as a powder or in the molten state, calculated to give an amount in the general range of proportions specified hereinbefore, to the slurry or solution of the synthetic detergent, and then to dry the mixture to a concentrated liquid or solid particulate state. For instance, in the case of alkyl benzene sulfonate detergents, such as are prepared by sulfonating alkyl benzene stocks and neutralizing the sulfonic acid product to form a slurry of sulfonate, the foam suppressor is added to the slurry, which is then reduced by conventional drying to the desired form. Similarly, the optional auxiliary detergent component can be added at any time, i.e., before or after the addition of the foam suppressor or along with it.

The presence of conventional amounts of inorganic salt

detergent builders, such as various water-soluble inorganic polyphosphates, sulfates, silicates, borates and carbonates, does not interfere with the action of the foam suppressor. These builders, the total amount of which may range from about 45 to as high as 95% by weight based on them and detergent component, have no adverse effect on the foam suppressing action of the foam suppressors of the invention and contribute their different specific effect toward a more satisfactory washing treatment of soiled clothing, dishes, etc. The same is true of the presence of small amounts, usually less than 5% by weight, based on final composition, of well known minor additives, such as carboxymethyl cellulose, optical bleach and perfume.

In the examples that follow, detergent compositions containing the foam suppressor were prepared by mixing the synthetic detergent and foam suppressor in the indicated amounts. Unless otherwise indicated, the compositions contained in addition tetrasodium pyrophosphate (45%), commercial grade "N" sodium silicate (8%), sodium carboxymethyl cellulose (1%), water (4%), the balance, where required to bring the total weight to 100%, being sodium sulfate.

In a representative test series, soft wtaer (50 p.p.m.[1]) solutions of 0.25% concentrations of test formulations were prepared, and aliquots of 1000 ml. were tested at temperatures of 120±10° F. This test consisted of mechanically stirring the test solution a 2000 ml. beaker for one minute, and then measuring the foam height in mm. at 0, 1 and 10 minutes after the stirring was stopped. Foam heights of 7 mm. and below at 10 minutes are considered satisfactory. The results of this test are presented in the following table.

[1] The hardness of water as employed herein is defined in parts per million of calcium and magnesium, calculated as calcium carbonate and magnesium carbonate, in a weight ratio of 2 : 1.

Table

Ex. No:	Foam suppressant	Percent (wt.)	Surface active material	Percent (wt.)	Foam height after 10 min. (mm.)
1			ABS (348) [1]	17	46
2	N-methyl hexadecanamide	1	ABS (348) [1]	17	4
3	do	0.5	ABS (348) [1]	17	6
4	do	0.2	ABS (348) [1]	17	14
5	do	3	ABS (348) [1]	17	1
6	do	5	ABS (348) [1]	17	1
7	do		ABS (348) [1]	8	32
8	do	0.5	ABS (348) [1]	8	3
9	do	3	ABS (368) [2]	17	2
10			ABS (368) [2]	17	42
11			ABS (348) [1 3]	17	37
12	N-methyl hexadecanamide	3	ABS (348) [1 3]	17	Trace
13			ABS (348) [1 4]	17	35
14	N-methyl hexadecanamide	3	ABS (348) [1 4]	17	Trace
15			ABS (381) [5]	17	28
16	N-methyl hexadecanamide	3	ABS (381) [5]	17	6
17	N-hexadecylhexadecanamide	3	ABS (348) [1]	17	3
18			ABS (339) [6]	17	36
19	N-methyl hexadecanamide	3	ABS (339) [6]	17	0
20	Methylene-bis-octadecanamide	3	ABS (348) [1]	17	6
21	N-phenyl-octadecanamide	3	ABS (348) [1]	17	6
22	N-methyl hexadecanamide	3	ABS (348) [1]	10	6
			Sodium lauryl sulfate	5	
23			Sec. C_{16}-C_{20} alkyl sulfate	17	27
24	N-methyl hexadecanamide	3	do	17	3
25			C_{12} n-alkyl Na sulfonate	15	23
26	N-methyl hexadecanamide	3	do	15	0
27	Methylene-bis-octadecanamide	3	Sec. C_{16}-C_{20} alkyl sulfate	15	6
28	Oleylamide	3	ABS (348) [1]	17	32
29	N-methyl tetradecanamide	3	ABS (348) [1]	17	8
30	N, N-dimethyl octadecanamide	3	ABS (348) [1]	17	31
31	N-octadecanoylmorpholide	3	ABS (348) [1]	17	30
32	N-methyl hexadecanoylethanolamide	3	ABS (348) [1]	17	32
33	N-methyl coconut fatty acid amides	3	ABS (348) [1]	17	30
34			Hydrogenated [7] tallow soap	3	25
			ABS (348) [1]	17	
35	N-methyl hexadecanamide	2	Hydrogenated [7] tallow soap	3	0
			ABS (348) [1]	15	

[1] Sodium polypropylene benzene sulfonate having an average molecular weight of 348.

[2] Sodium polypropylene benzene sulfonate having an average molecular weight of 368.

[3] Formulation also contains about 2% sodium sulfate and the balance is water.

[4] Formulation contains no sodium sulfate or builder. Balance of formulation is water.

[5] Sodium alkyl benzene sulfonate having an average molecular weight of 381 and prepared from a mixture of straight-chain olefins of 11 through 19 carbon atoms.

[6] Sodium alkyl benzene sulfonate having an average molecular weight of 339 and prepared from a mixture of straight-chain olefins of 10 to 13 carbon atoms.

[7] Sodium salts of a mixture of saturated fatty acids composed of about 22% C_{16} fatty acids and 78% of C_{18} fatty acids.

The effect of varying the amounts of foam-suppressing agent is shown by Examples 1 to 6. When no foam-suppressing additive is present, the foam height has an undesirably high value (Example 1). Acceptable foam height modifications by varying the amount of additive from 3% to 30% of the surface active material are shown in Examples 2, 3, 5 and 6. Lowering the foam suppressant to 1% did not give a satisfactory result as shown in Example 4.

It appears that when the concentration of detergent active or surface active component is low, then the foam-suppressing agent is more effective, and less of the foam suppressant is required for the same foam level. This is shown by a comparison of Example 7 with Example 1 and Example 8 with Example 3.

Different surface active components are affected by the foam-suppressing agent of the present invention. Polypropylene-based detergents of varying molecular weight, as indicated by Examples 9 and 10, as well as straight-chain alkyl benzene sulfonates as shown by Examples 15 and 16, and 18 and 19, can be used. Alkyl sulfates can also have their foam properties modified as shown by Examples 23, 24 and 27. Mixtures of alkyl benzene sulfonate and sulfates are affected as shown by Example 22, and paraffin sulfonates by Examples 25 and 26.

As specified, the alkyl group of the acyl radical of the foam-suppressing agent is required to be saturated. When using oleylamide, containing an unsaturated acyl radical, substantially no foam supression is noted as shown in Example 28.

The modifying effect of the foam-suppressing agent of the invention occurs with the surface active component alone in the absence of inorganic salt detergent builders, as shown in Examples 11–14.

Similarly, foam-suppressing effect is achieved in combinations with soap, as illustrated by Examples 34 and 35.

The use of foam-suppressing agents falling outside the definition herein given gives poor results, as shown in Examples 28–33.

As indicated, compositions exhibiting a foam height of 7 mm. and lower are considered satisfactory. This is determined by comparing the various formulations in a tumbler-type washing machine under simulated household-use conditions, as follows: To a tumbler-type washing machine is charged 26 liters of water (50 p.p.m. hardness) at 120° F., containing 0.25%, by weight, of the test formulation. Then six pounds of shop towels, ten polyethylene sheets, several small soiled cotton swatches (for detergency measurements) and 1 gram of lard oil are added. The machine is started and the foam height, as viewed through the door window, is measured periodically over a 10-minute wash cycle. Formulations exhibiting a foam height greater than 7 mm. will give in the washing machine a foam height greater than one-half of the height of the window.

The improved detergent formulations of this invention are suitable for use in dilute aqueous solutions in a variety of washing appliances, such as rotary drum or tumbler-type washers, top-loading agitator washers, bottle washers, etc. When so employed, little or no foam is formed, without any adverse effect on the detergency characteristics, in operating at temperatures from about 65 to 140° F., as commonly used in washing practice. This suppression of suds in accordance with the invention permits employing a larger concentration of the active detergents in the preparation of washing solutions, as compared with the concentrations heretofore considered permissible maxima for tumbler-washer operations. A greater washing efficiency can therefore be achieved. Furthermore, the tendency to froth upon rinsing is substantially obviated.

The effectiveness of the low foaming detergent formulations of the present invention can be used in tumbler-type washers, as well as in any other washing equipment

which utilizes strongly foaming organic detergent materials from the group of sulfates and sulfonates. In fact, these formulations can be employed to reduce foaming in a number of solutions and emulsions, which, upon agitation, produce unduly high suds, causing spillage, pumping difficulties and interfering with a satisfactory filling of containers.

I claim:

1. A detergent composition characterized by a low degree of foaming in agitated dilute aqueous solutions thereof consisting essentially of a normally high foaming detergent component selected from the group consisting of water-soluble salts of organic sulfonic acids and water-soluble salts of sulfuric acid alkyl esters, and to suppress foaming of said detergent component about to 35%, by weight, of said detergent component of a foam-suppressing agent of the formula:



wherein R is a saturated alkyl radical of 15 to 21 carbon atoms, and R^1 is selected from the group consisting of a hydrocarbyl radical of 1 to 22 carbon atoms, and N-methyleneamide radicals, the alkyl group in the last mentioned amide radical having 15 to 21 carbon atoms.

2. A composition according to claim **1** wherein the foam-suppression agent is one in which R^1 is a phenyl radical.

3. A composition according to claim **1** wherein the foam-suppressing agent is one in which R^1 is a N-methyleneamide radical.

4. A composition according to claim **1** wherein the foam-suppressing agent is present in an amount of 5 to 15 weight percent, based on the detergent component.

5. A composition according to claim **4** wherein the detergent component is an alkylaryl sulfonate having 9 to 20 carbon atoms in the alkyl group.

6. A composition according to claim **4** wherein the detergent component is alkyl sulfate having 10 to 20 cabon atoms.

7. A detergent composition characterized by a low degree of foaming in agitated dilute solutions thereof consisting of (1) a normally high foaming detergent component selected from the group consisting of water-soluble salts of organic sulfonic acids and water-soluble salts of sulfuric acid alkyl esters, (2) to suppress foaming of said detergent about 2 to 35%, by weight, based on said detergent of a foam-suppressing agent having the formula:

wherein R is a saturated alkyl radical of 15 to 21 carbon atoms, and R^1 is selected from the group consisting of a hydrocarbyl radical of 1 to 22 carbon atoms, and N-methyleneamide radicals, the alkyl group in the last-mentioned amide radical having 15 to 21 carbon atoms, and (3) inorganic detergent salt builders in an amount of 45 to 95%, by weight, based on said inorganic detergent builders and detergent component.

8. A composition according to claim **7** wherein the foam-suppressing agent is one in which R^1 is the phenyl radical.

9. A composition according to claim **7** wherein the foam-suppressing agent is one in which R^1 is a N-methyleneamide radical.

10. A composition according to claim **7** wherein the detergent component is an alkylaryl sulfonate having 9 to 20 carbon atoms in the alkyl group.

11. A composition according to claim **7** wherein the detergent component is alkyl sulfate having 10 to 20 carbon atoms.

12. A composition according to claim 7 wherein the foam-suppressing agent is present in an amount of 5 to 15 weight percent based on detergent component.

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