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[54] **BUILT ANIONIC DETERGENT COMPOSITION HAVING INVERSE FOAM-TO-TEMPERATURE RELATIONSHIP AND PROCESS FOR PRODUCING SAME**

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[51] **Int. Cl.** **C11d 3/30,** C11d 7/32

[58] **Field of Search**......252/137, 152, 321, 358, 110, 252/117, 121, 527, 546, 525, 544

[56] **References Cited**

UNITED STATES PATENTS

2,906,712	9/1959	Edwards et al.	252/321
2,954,347	9/1960	St. John et al.	252/358

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[57] **ABSTRACT**

A detergent composition having an inverse foam to temperature relationship is disclosed, as well as a binary composition for accomplishing this relationship when added to a detergent system. The inverse foam to temperature relationship is provided by a synergistic mixture of a fatty acid having a saturated or unsaturated alkyl chain of from about 14 to 22 carbon atoms and a high molecular weight primary, secondary or tertiary amine containing between about eight and 30 carbon atoms in the alkyl chain.

16 Claims, No Drawings

BUILT ANIONIC DETERGENT COMPOSITION HAVING INVERSE FOAM-TO-TEMPERATURE RELATIONSHIP AND PROCESS FOR PRODUCING SAME

This application is a continuation-in-part of copending application, Ser. number 41,359, filed May 28, 1970 (Docket No. 2346).

This invention relates to detergent compositions. More particularly, this invention relates to detergent compositions which have an inverse foam-to-temperature relationship and to means for accomplishing this relationship.

The use of synthetic detergents for washing clothes has assumed worldwise importance, due to the efficiency and cheapness of such products. These detergents are compounded with various additives to provide compositions having improved and desirable characteristics. Among these characteristics is that of maintaining a proper level of foam for suds.

Foaming, or sudsing, of detergents is an extremely important factor to consider when formulating a detergent composition. It is known, for example, that a detergent which over-foams does not do an efficient job of cleaning in a washing machine. On the other hand, in hand washing there is a desire on the part of most consumers for a substantial amount of foam produced by a detergent. It is therefore necessary to provide a detergent composition which produces enough foam to reassure the consumer but yet not so much foam as to inhibit the detergent action of the composition. This need has been satisfactorily achieved in many ways.

There is, however, another situation which requires a totally different approach to foam control in a detergent system. There are geographical areas where hot water is not readily available for one reason or another. In such areas, as well as others washing machines are designed with internal water heating systems which begin their cycle with cold water and gradually heat the same to the desired operating temperature which is usually the "boil." Such washing machines are used extensively, for instance, in many European countries. It is well known, however, that a detergent system which provides an adequate level of foam when used with hot water will not foam at all in cold water. Conversely, a detergent system which is compounded so that a sufficient level of foam is produced in cold water will over-foam to the extent of overflowing the washing machine when used with hot water. Of course, a detergent system which over-foams can have a foam suppressor included therein. The problem then, naturally, is that such a system will produce no foam when used with cold water. In other words, most detergent systems have essentially a direct relationship between temperature and foam, wherein as the temperature increases the amount of foam increases.

The invention disclosed and claimed in the aforementioned co-pending application, Ser. number 41,359, filed May 28, 1970 (Docket No. 2346), provided the necessary inverse foam-to-temperature relationship through a synergistic binary system of a fatty acid and a polyethoxylated quaternary ammonium salt. It has been found, however, that when extremely high temperatures, i.e., about 200°F., are encountered, over-foaming occurs. The present invention solves this problem by utilizing a binary system of a fatty acid and

a high molecular weight primary, secondary or tertiary amine.

Accordingly, it is a primary object of the present invention to provide a detergent system free of the aforementioned and other such disadvantages.

It is still another object of the present invention to provide a detergent system which can be used in an environment wherein it will be subject to cold water as well as hot water and still provide satisfactory foam level.

It is yet another object of the present invention to provide a composition which will impart an inverse foam-to-temperature relationship to a detergent system.

Other objects and advantages of the present invention will become apparent from the following detailed description thereof.

According to the present invention, a composition is provided for regulating the foam profile of a detergent system, comprising a binary synergistic mixture of a fatty acid and a high molecular weight primary, secondary or tertiary amine.

In another aspect of the present invention, a detergent composition is provided having an inverse foam-to-temperature relationship which comprises an anionic detergent, inorganic builders, and a synergistic mixture of a fatty acid and a high molecular weight primary, secondary or tertiary amine.

The detergent composition could have other additives such as brighteners, germicides, soil suspending agents, antioxidants, bleaches, coloring materials, and perfume. It is quite unexpected to find that the mixture of a fatty acid and an amine provides the inverse foam-to-temperature relationship, since each of the ingredients, when used alone, do not exhibit any such properties.

The useful fatty acids which may be employed in the present invention include those saturated linear acids containing between about eight and 30 carbon atoms in their alkyl chain. These include:

capric acid
lauric acid
myristic acid
palmitic acid
stearic acid
arachidic acid
behenic acid
lignoceric acid
cerotic acid
melissic acid
oleic acid
linoleic acid

as well as various natural and synthetic mixtures thereof.

The preferred fatty acids, however, are those having alkyl chains of from about 14 to 22 carbon atoms. One such preferred fatty acid is stearic acid. Another preferred acid composition is available commercially under the name "Hyfac 431." Hyfac 431 is a hydrogenated fish fatty acid having the following approximate composition:

8 percent myristic acid
29 percent palmitic acid
18 percent stearic acid
26 percent arachidic acid
17 percent behenic acid

2 percent oleic acid

Other commercially available mixtures of fatty acids are those which are available under the name "Hystrene." For instance, Hystrene 7022 comprises about 70 percent C_{20} to C_{22} fatty acids. Hystrene 9022 comprises about 90 percent C_{20} to C_{22} fatty acids, and Hystrene 9018 has about 90 percent stearic acid. Another such commercial product is "Neofat 18–58," which is a hydrogenated tallow acid. The fatty acid, used in combination with the amine should be present in the final detergent composition in an amount from about 1 to about 6 by weight of the total detergent composition.

The second component of the synergistic binary foam-suppressing system is a high molecular weight amine. By "high molecular weight" amine is meant a primary, secondary, or tertiary amine having a saturated or unsaturated alkyl chain of from about 14 to about 22 carbon atoms. Amines which were found particularly useful are products by Humko available under the name "Kemamine." Representative of these are:

Kemamine S-970	di-hydrogenated tallow amine
Kemamine S-190	di-arachidyl/behenyl amine
Kemamine P-190	arachidyl/behenyl amine

While primary, secondary and tertiary amines all work in the composition of the present invention, the preferred amines are the secondary and tertiary amines. Still more preferred are the secondary amines.

The useful detergents which may be used in conjunction with the foam profile regulating composition of the present invention include anionic detergents such as alkylbenzene-sulfonic acid and its salts, and compounds of the formula alkyl-phenyl-SO_3—M, wherein alkyl is an alkyl radical of a fatty acid and M is hydrogen or an alkali metal, which compounds comprise a well-known class of anionic detergents and include sodium dodecyl-benzene sulfonate, potassium dodecylbenzenesulfonate. Others are the alkali metal dialkyl sulfosuccinates, e.g., sodium dioctylsulfosuccinate, and sodium dihexylsulfosuccinate, sodium sulfoethylphthalate, sodium lauryl-p-anisidinesulfonate; sodium tetradecanesulfonate; sodium diisopropylnapthalenesulfonate; sodium octylphenoxyethoxyethylsulfonate, etc.; and the alkali metal alkyl sulfates, e.g., sodium lauryl sulfate.

Among the above noted alkylbenzene-sulfonic acid and salts thereof, the preferred compounds included those which are biodegradable and which are particularly characterized by a linear alkyl substituent of from C_8 to C_{22} and preferably from C_{10} to C_{15}. It is, of course, understood that the carbon chain length represents, in general, an average chain length since the method for producing such products usually employs alkylating reagents of mixed chain length. It is clear, however, that substantially pure olefins as well as alkylating compounds used in other techniques can and do give alkylated benzene sulfonates wherein the alkyl moiety is substantially (i.e., at least 99 percent) of one chain length; i.e., C_{12}, C_{13}, C_{14}, or C_{15}. The linear alkyl benzene sulfonates are further characterized by the position of the benzene ring in the linear alkyl chain, with any of the position isomers (i.e., alpha to omega) being operable and contemplated.

The linear alkyl benzene sulfonates are generally and conveniently prepared by sulfonating the corresponding alkyl benzene hydrocarbons which in turn may be prepared by alkylating benzene with a linear alkyl halide, a 1-alkene or a linear primary or secondary alcohol. Pure isomers (of the 1-phenyl isomer) are prepared by reduction of the acylated benzene (alkyl phenyl ketone) using a modification of the Wolff-Keshner reaction. The 2-phenyl isomer is obtained from n-undecyl phenyl ketone and methyl magnesium bromide to form the tertiary alcohol which is dehydrated to the alkene and then hydrogenated. The 5-phenyl isomer is obtained similarly from a n-heptyl phenyl ketone and n-butyl magnesium bromide. The other isomers are obtained in a similar manner from the appropriate n-alkyl phenyl ketone and n-alkyl magnesium bromide.

In addition to the benzene sulfonates, one may also employ the lower alkyl (C_1 to C_4) analogs of benzene such as toluene, xylene, the trimethyl benzenes, ethyl benzene, isopropyl benzene, and the like. The sulfonates are generally employed in the water soluble salt form which includes as the cation the alkali metals, ammonium, and lower amine and alkanolamine.

Examples of suitable linear alkyl benzene sulfonates are:

- sodium n-decyl benzene sulfonate
- sodium n-dodecyl benzene sulfonate
- sodium n-tetradecyl benzene sulfonate
- sodium n-pentadecyl benzene sulfonate
- sodium n-hexadecyl benzene sulfonate

and the lower corresponding lower alkyl substituted homologues of benzene, as well as the salts of the cations previously referred to. Mixtures of these sulfonates may, of course, also be used with mixtures which may include compounds wherein the linear alkyl chain is smaller or larger than indicated herein, provided that the average chain length in the mixture conforms to the specific requirements of C_{10} to C_{22}.

Other anionic detergents are the olefin sulfonates including long chain alkene sulfonates, long chain hydroxyalkane sulfonates or mixtures of alkensulfonates and hydroxyalkanesulfonates. These olefin sulfonate detergents may be prepared, in known manner, by the reaction of SO_3 with long chain olefins (of eight – 25, preferably 12 – 21, carbon atoms) of the formula $RCH{=}CHR_1$, where R is alkyl and R_1 is alkyl or hydrogen, to produce a mixture of sultones and alkenesulfonic acids, which mixture is then treated to convert the sultones to sulfonates.

The linear paraffin sulfonates are also a well-known group of compounds and include water soluble salts (alkali metal, amine, alkanolamine, and ammonium) of:

- 1-decane sulfonic acid
- 1-dedecane sulfonic acid
- 1-tridecane sulfonic acid
- 1 tetradecane sulfonic acid
- 1-pentadecane sulfonic acid
- 1-hexadecane sulfonic acid

as well as the other position isomers of the sulfonic acid group.

In addition to the paraffin sulfonates illustrated above, others with the general range of C_{10} to C_{22} alkyls may be used, with the most preferable range being from C_{12} to C_{20}.

The linear alkyl sulfates which are contemplated in this invention comprise the range of C_{10} to C_{20}. Specific examples include sodium n-decyl sulfate; sodium n-dodecyl sulfate; sodium n-octadecyl sulfate; and the exthoxylated (1 to 100 moles ethylene oxide) derivatives; and, of course, the other water soluble salt-forming cations mentioned above.

The composition of the present invention may also include in addition to the foam profile regulating compounds and conventional anionic detergent compositions builders, brighteners, hydrotropes, germicides, soil suspending agents, anti-redeposition agents, antioxidants, bleaches, coloring materials (dyes and pigments), perfumes, water soluble alcohols, non-detergent alkali metal benzene sulfonates, fabric softening compounds, enzymes, etc.

The builder is, generally, a water soluble, inorganic salt which may be a neutral salt, e.g., sodium sulfate or an alkaline builder salt such as phosphates, silicates, bicarbonates, carbonates, and borates. The preferred builders are those characterized as condensed phosphates such as polyphosphates and pyrophosphates. Specific examples of alkaline salts are: tetrasodium pyrophosphates, pentasodium tripolyphosphate (either Phase I or Phase II), sodium hexametaphosphate, and the corresponding potassium salts of these compounds, sodium and potassium silicates, e.g., sodium metasilicate and alkaline silicates (Na_2O; $2SiO_2$ and Na_2O; $3SiO_2$), sodium carbonate, potassium carbonate and sodium and potassium bicarbonate. Other salts may also be used where the compounds are water soluble. These include the general class of alkali metal, alkaline earth metal, amine, alkanolamine, and ammonium salts. Other builders which are salts of organic acids may also be used, and in particular the water soluble (alkali metal, ammonium, substituted ammonium and amine) salts of aminopolycarboxylic acids such as:

ethylene diamine tetra-acetic acid
nitrilo triacetic acid
diethylene triamine penta-acetic acid
N-(2-hydroxyethyl)-ethylene diamine triacetic acid
2hydroxyethyl-iminodiacetic acid
1,2-diaminocyclohexane diacetic acid, and the like.

In addition to the above ingredients, one may as previously delineated, employ hydrotropes in connection with the compositions of the instant invention. The useful hydrotropes include such compounds as sodium xylene sulfonate, potassium xylene sulfonate, sodium and potassium toluene sulfonates, in the position isomers thereof, and ethyl benzene sulfonate.

It has now been found, quite unexpectedly, that when the synergistic mixture of a fatty acid and an amine, as disclosed above, is added to a conventional detergent system, or is used in combination with the above detergents and other conventional detergent additives, an inverse foam-to-temperature relationship is exhibited by the resulting system.

In the composition for regulating the foam profile of a detergent according to the present invention, there is employed from about 20 to 90 percent fatty acid and from about 10 to about 80 percent amine. Preferably, there employed from about 35 to 60 percent fatty acid and from about 20 to about 40 percent amine. In terms of the total detergent system, there is employed from about 1 to 6 percent fatty acid and from about 1 to about 6 percent amine; and preferably from about 2 to 5 percent fatty acid and from about 1 to about 3 percent amine. All of said percentages are by weight, based on the total amount of the composition being used. In the case of the detergent systems, the percentages are based on an anionic detergent concentration of about 8 to 18 percent by weight. When less anionic detergent is present in the system, a correspondingly lesser amount of each of the fatty acid and the amine can be used. In built detergents the amount of builder or mixture of builder salts may range from 10 to 85 percent by weight.

The present invention will now be illustrated by the following, more detailed examples thereof. It is noted, however, that the present invention is not deemed as being limited thereto.

The following examples demonstrate the foam profiles of various detergent systems under the conditions of use to be encountered in Europe. The detergent compositions were tested in a Miele automatic washing machine, which is of German manufacture. The machine is a front-loading, tumbler type washing machine equipped with a heater that raises the water temperature from room temperature to the boil. The machine operates on 200 volts, 50 cycle alternating current. In each instance, the machine was set on the white clothes setting, and a five-pound load of clean clothing was used. The water capacity if 11 liters. A detergent concentration of 0.5 percent was used in each cycle. This detergent concentration was provided by using 56 grams of detergent.

The machine operates on two cycles, a pre-wash cycle and a wash cycle. In the pre-wash cycle, the temperature of the water climbs from 70° to 120°F., and the total cycle is 12 to 14 minutes. The drum rotates for about 10 seconds, rests for 4 seconds, reverses direction, and the operation is repeated. At the end of the cycle, the machine stops, drains, and remains "motionless" unto the wash cycle starts.

The wash cycle is divided into two stages, the heating stage and the washing stage. In the heating stage, cold water washes a second charge of detergent into the drum. During this 30-minute stage, the temperature climbs from about 90°F. to over 190°F. The drum rotates for 4 to 5 seconds, rests for 10 seconds, reverses direction, and repeats the operation. At the end of the heating period, the machine changes its drum action and goes into the washing stage. The washing stage lasts 18 minutes. During this time, the drum action is the same as that described for the pre-wash cycle. The temperature fluctuates between 190° and 200°F. during the whole washing stage.

EXAMPLE 1

Detergent compositions were made having the following makeup:

TABLE I

Ingredients	(1)	(2)	(3)	(4)
Sodium dodecyl benzene sulfonate	8.00	8.00	8.00	8.00
Fatty acid*	3.00	—	3.00	2.00
Amine**	—	2.00	1.00	1.00
Sodium tripolyphosphate	35.00	35.00	35.00	35.00
Sodium silicate	7.00	7.00	7.00	7.00

Sodium Carboxymethyl-cellulose	0.50	0.50	0.50	0.50
Polyvinyl alcohol	0.20	0.20	0.20	0.20
Sodium sulfate	7.50	8.50	6.50	7.50
Sodium perborate tetrahydrate	30.00	30.00	30.00	30.00
Balance***	0.30	0.30	0.30	0.30

* 70 percent saturated C_{18}, 28 percent saturated C_{16} and about 2 percent saturated C_{14}

** bis-hydrogenated tallow amine

*** optical brighteners and antioxidant

Products 1 to 4 were evaluated using the Miehle washing machine. Formulations 1 and 2, after the prewash in which no detergent was used, foamed rapidly and overflowed. Formulations 3 and 4 showed high, but no overfoam during the initial washing (15 –35 minutes) and low, controlled foam thereafter.

EXAMPLE 2

Formulation 3 of Example 1 is repeated except that the fatty acid has the following composition:

saturated	C_{18}—14%
	C_{16}—26%
	C_{14}—7%
	C_{12} & less—12%
unsaturated	C_{18}—41%

Excellent results are obtained.

EXAMPLE 3

Example 2 is repeated employing the fatty acid mixture as a sodium soap in the following concentrations:

3–A	1.0%
3–B	1.5%
3–C	2.5%
3–D	4.0%
3–E	5.0%
3–F	6.0%

Again the results are excellent.

EXAMPLE 4

Examples 1 through 3 are repeated except that the amine content is varied as follows:

4–A	1.5%
4–B	2.0%
4–C	3.0%
4–D	4.0%
4–E	5.0%
4–F	6.0%

In all instances an excellent foam control is obtained.

EXAMPLE 5

Example 1, formulation 3, is again repeated replacing the fatty acid mixture by the following:

5–A	stearic acid
5–B	sodium stearate
5–C	palmitic acid
5–D	myristic acid
5–E	oleic acid
5–F	eicosanoic acid
5–G	sodium docosanoate

The results are comparable to formulation 3 of Example 1.

EXAMPLE 6

Example 1, formulation 3, is once more repeated except that the amine is varied as follows:

6–A	1½% mixture of 1 part bis-hydrogenated tallow amine and 1/2 part bis-arachidyl behenyl amine
6–B	2% mixture of 1 part bis-stearyl-amine and 1 part bis-arachidyl-amine
6–C	2.5% bis-stearylamine
6–D	3% mixture of 2 part tri-stearylamine and 1 part di-myristyl amine
6–E	3% bis-arachidyl behenyl amine.

Excellent results are obtained in each case.

In the description and claims, reference to fatty acids or the like includes the corresponding water-soluble soaps thereof, preferably the alkali metal soaps such as sodium and potassium. In general, the fatty acids per se and soaps thereof may be used interchangeably depending upon economics, method of manufacture of the composition with other ingredients and its use in washing. For example, fatty acids may exist in the product when post-added to a detergent powder; or partly or wholly in the form of soap when added to a slurry or solution during manufacture of detergent products in the presence of alkaline materials or in alkaline washing solutions.

Thus, it can be seen that the objects set forth at the outset have been successfully achieved. The present invention has been described with reference to certain embodiments thereof which are to be considered exemplary, the invention being limited only by the claims.

What is claimed is:

1. A detergent composition having an inverse foam-to-temperature relationship consisting essentially of (1) from about 1 to 6 percent by weight of saturated linear fatty acid containing between about eight and 30 carbon atoms in the alkyl chain, (2) from about 1 to 6 percent by weight of primary, secondary or tertiary fatty amine having a saturated or unsaturated alkyl chain of from about 14 to 22 carbon atoms, and (3) from about 8 to 18 percent by weight of a built anionic detergent.

2. A composition according to claim **1**, wherein said anionic detergent is a linear alkyl benzene sulfonate having about eight to 22 carbon atoms in the alkyl group.

3. A composition according to claim **2**, wherein said alkyl group has about 10 to 15 carbon atoms.

4. A composition according to claim **1**, wherein said detergent is linear alkyl benzene sulfonate, and said builder salts are selected from the group consisting of alkali metal and ammonium polyphosphates, silicates, borates, sulfates, and combinations thereof.

5. A composition according to claim **1**, wherein said fatty acid contains from about 14 to 22 carbon atoms.

6. A composition according to claim **5**, wherein said fatty acid is hydrogenated fish fatty acid.

7. A composition according to claim **5**, wherein said fatty acid is a mixture of C_{20} to C_{22} fatty acids.

8. A composition according to claim **1**, wherein said fatty acid is present in from about 2 to 5 percent by weight of said composition.

9. A composition according to claim **1**, wherein said amine is a tertiary amine.

10. A composition according to claim **9**, wherein said amine is methyl bis-hydrogenated tallow amine.

11. A composition according to claim **1**, wherein said amine is a secondary amine.

12. A composition according to claim **11**, wherein said amine is arachidyl-behenyl amine.

13. A composition according to claim **11**, wherein said amine is bis-hydrogenated tallow amine.

14. A composition according to claim **9**, wherein said amine is di-arachidyl-behenyl amine.

15. A composition according to claim **1**, wherein the built anionic detergent is 8–18 percent C_8 to C_{22} alkyl benzene sulfonate and 10—85 percent builder.

16. In a process for producing a controlled foam profile built anionic detergent, the improvement which comprises adding to said built anionic detergent a foam profile composition in amounts sufficient to yield a detergent composition containing from about 8 to 18 percent by weight of detergent, from about 1 to 6 percent by weight of fatty acid and from about 1 to 6 percent by weight of fatty amine said foam profile composition consisting essentially of (1) from about 20 to 90 percent by weight of saturated, linear fatty acid containing between about eight and 30 carbon atoms in the alkyl chain and (2) from about 10 to 80 percent by weight of primary, secondary or tertiary fatty amine having a saturated or unsaturated alkyl chain of from about 14 to 22 carbon atoms.

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