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SULFONATE DETERGENT COMPOSITIONS WITH IMPROVED FOAM CHARACTERISTICS

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The present invention relates to washing compositions containing anionic synthetic alkyl benzene sulfonate detergents capable of producing stable, good-quality, persistent suds in conventional dilute aqueous washing solutions under conditions of agitation and in the presence of soil.

Alkyl benzene sulfonate detergents, such as are produced in the art by sulfonating C_9–C_{18} monoalkyl benzenes which have been obtained either by condensing chlorinated paraffins with benzene in the presence of a Friedel-Crafts catalyst, or by alkylating benzene with long branched-chain olefins or olefin polymers having a branched-chain structure, as in polypropylene, likewise in the presence of a suitable catalyst, e.g., HF, are widely employed by laundries and in homes because of their excellent soil-removal characteristics.

However, the foam performance of these sulfonate determents during the washing of soiled clothes and fabrics is far from being as satisfactory as their ability to remove soil. As a matter of fact, although C_9–C_{18} branched-chain monoalkyl benzene sulfonates when present in dilute aqueous solutions in the bowl of a washing machine produce relatively large amounts of suds, these suds are extremely unstable, lacy in texture, and readily break down and disappear under agitation and in contact with soil. This inability to produce stable, satisfactory suds represents a drawback in the eyes of a large fraction of the consumer public who are not only accustomed to a high, creamy foam of conventional fatty acid soaps and expect the same kind of foam from synthetic detergents, but frequently consider the foam to be an index of the washing efficiency and a measure of the quantity of powdered soap or synthetic detergent required for efficient washing.

A large number of additives thought likely to improve the foam performance of branched-chain alkyl benzene sulfonate detergents has been proposed in the past without succeeding, in most cases, to secure satisfactory foam characteristics and, in particular, to secure a greater foam stability and a better foam quality, i.e., a texture approximating that of conventional soapsuds. Besides, many of these puroposed additives were relatively expensive and their inclusion in alkyl benzene sulfonate detergent formulations tended to increase unduly the ultimate sales price of these formulations.

Thus, the search for new, inexpensive and efficient foam-improving agents for alkyl benzene sulfonate detergents continued on unabated.

I have now discovered that by combining detergent branched-chain C_9–C_{18} monoalkyl benzene sulfonates with effective proportions of a normal primary C_{10}–C_{18} alkyl benzene sulfonate and an alcohol from the group consisting of C_{14}–C_{16} straight-chain saturated aliphatic alcohols and straight-chain C_{14}–C_{22} alkane 1,2-glycols, detergent formulations can be prepared which, upon being dissolved in water to form dilute solutions of 0.1 to 0.4% concentration, conventional in laundry practice, produce stable, good-quality, persistent suds.

As shown later in this specification, the two-component combination of a detergent branched-chain alkyl benzene sulfonate and a normal primary C_{10}–C_{18} alkyl benzene sulfonate is incapable of producing suds of good stability and quality. On the other hand, the addition of a C_{14}–C_{16} straight-chain saturated aliphatic alcohol or a straight-chain C_{14}–C_{22} alkane 1,2-glycol, to the dedetergent branched-chain alkyl benzene sulfonate, while stabilizing the foam of this latter, provides but an inadequate volume of the foam. In fact, the alcohol tends to act as a "defoamer" and to decrease the formation of foam. It is, therefore, entirely unexpected that the three-component combination of a detergent branched-chain alkyl benzene sulfonate, a normal primary C_{10}–C_{18} alkyl benzene sulfonate, and a C_{14}–C_{16} straight-chain saturated aliphatic alcohol, or a straight-chain C_{14}–C_{22} alkane 1,2-glycol, is capable of producing a stable, good-quality, and persistent foam.

In the aforementioned three-component combination, the normal primary C_{10}–C_{18} alkyl benzene sulfonate can be present in amounts ranging from about 5 to about 50% by weight, whereas, the alcohol or 1,2-glycol component can be present in amounts ranging from about 2 to about 15% by weight, the balance to make up 100% by weight being the detergent branched-chain alkyl benzene sulfonate. More aliphatic alcohol or glycol in proportions up to 25% by weight may be added, if it is desired, to increase the opacity, whiteness, and bulk density and volume of the foam.

Any suitable effective detergent water-soluble salt of a branched-chain C_9–C_{18} monoalkyl benzene sulfonic acid, e.g., an alkali metal, an alkaline earth metal, an ammonium, an alkyl ammonium, and an alkylol ammonium sulfonate may be employed. Water-soluble C_9–C_{18} monoalkyl benzene sulfonates such as are described in U.S. Patent 2,477,383 to Lewis and keryl benzene sulfonates described in U.S. Patent 2,218,472 to Kyrides are usually preferred. Particularly satisfactory, owing to their excellent soil-removing ability, are branched-chain C_{12}–C_{15} monoalkyl benzene sulfonates, such as polypropylene benzene sulfonates. Employment of such sulfonate detergent materials made up of predominantly C_{15} polypropylene benzene sulfonates is found to be particularly effective, resulting in an enhanced volume of stable, good-quality foam.

The term "a normal primary C_{10}–C_{18} alkyl benzene sulfonate," as employed throughout this description refers to water-soluble salts of normal 1-phenyl C_{10}–C_{18} alkane sulfonic acids having the general formula: $RASO_3M$, wherein M is a cation from the group consisting of alkali metal, alkaline earth metal, ammonium, alkyl ammonium, and alkylol ammonium cations, R is a straight-chain saturated C_{10}–C_{18} aliphatic radical, and A is a phenylene linkage.

The effective foam-stabilizing alcohols of the detergent composition of the present invention are straight-chain saturated C_{14}–C_{16} alcohols and straight-chain C_{14}–C_{22} alkane 1,2-glycols (C_{14}–C_{16} alkanols and C_{14}–C_{22} alkane 1,2-diols).

If desired, a fatty acid alkylolamide such as lauric ethanolamide, lauric isopropanolamide or lauric glyceryl-amide may be added to the three-component combination of this invention in amounts which may range from about 2 to about 25% by weight thereof.

The improved foam characteristics of alkyl benzene sulfonate detergent compositions formulated in accordance with the invention are not affected adversely by the presence of conventional water-soluble inorganic salt builders, i.e., neutral salts of strong inorganic acids, such as sodium chloride, potassium chloride, sodium sulfate, and the like, and alkaline salts of weak inorganic acids, such as sodium carbonate, tetrasodium pyrophosphate,

sodium tripolyphosphate, sodium silicate, borax, and the like. From 60 to 90 parts by weight of these inorganic salt builders, preferably as sodium salts, may be present in each 100 parts by weight of a detergent formulation containing the three-component combination of the present invention.

If so desired, other conventionally employed additives such as anti-caking agents, optical bleaches, corrosion inhibitors, e.g., sodium silicate, perfume and dyes, may be added in small amounts to the formulation. Carboxymethyl cellulose or celluronic acid salts also may be employed in small amounts to prevent redeposition of the soil. Likewise, N-alkyl glycines and diglycines may be added to prevent occurrence of skin rashes and erythemas. All of these additives are introduced in comparatively small amounts, rarely exceeding 5% by weight based on the total amounts of solids in the formulation, and in all events in such amounts as not to interfere with the improvement of foam performance in accordance with the invention.

Ordinarily, the blending of these several components of the improved detergent composition of the present invention is carried out in a straightforward manner by mixing the components to form a solution or slurry, drying this slurry to the solid particle-form; or, if so desired, evaporating it to form a paste; or, yet, diluting it to produce a liquid concentrate.

Foam evaluation bench tests were carried out at the laboratory on aqueous wash solutions of the detergent formulations prepared in accordance with the present invention. In these tests, each 100 parts by weight of a solid, dried, particulate detergent composition contained from 20 to 24 parts by weight of the active three-component combination of the invention. Sodium C_{12}–C_{15} polypropylene benzene sulfonate was employed as a typical monoalkyl benzene sulfonate detergent component. A number of representative sodium salts of normal 1-phenyl C_{10}–C_{18} alkane sulfonic acids (sodium n-alkyl benzene sulfonates) were combined therewith together with effective proportions of a normal aliphatic C_{14}–C_{16} alcohol or a normal C_{14}–C_{22} alkane 1,2-glycol. Detergent builders were present in the following amounts: 30 parts by weight of sodium tripolyphosphate, 20 parts by weight of tetrasodium pyrophosphate, 5 parts by weight of commercial liquid "N" sodium silicate, and the remainder to make up 100 parts by weight was sodium sulfate.

The particles of the detergent formulation were dissolved in soft water obtained from the laboratory tap and having a hardness of 50 p.p.m., calculated as calcium carbonate and magnesium carbonate in a weight ratio of 2:1. The temperature of the 0.15% solution was 120° F., and in each test run 500 ml. thereof was placed in a two-liter beaker. The solutions were tested at the bench by agitating the contents of the beakers with the aid of propeller-type stirrers for one minute, whereupon foam height in millimeters was measured and the foam quality and foam stability were observed. Fifteen minutes after agitation the foam height, quality and stability were again observed. The stability was rated by observing the rate of foam decay under mechanical stress as by blowing on a small volume of foam gently with air. A foam that withstands being blown upon without collapse of surface bubbles has Good stability. A foam having poor stability rapidly collapses when blown upon. Intermediate stabilities are rated as Fair. A foam characterized by Good quality is made up of uniformly small-sized, dense-bodied bubbles of high bulk viscosity. This foam is white and opaque. Foam of Poor quality displays large-sized bubbles, has a low bulk viscosity, and tends to be lacy. It is, furthermore, grayish in color and relatively transparent. Foams intermediate in quality between Poor and Good are rated to be Fair.

The data from these representative test runs are tabulated in the following table.

Test Run No.	n-Alkyl Benzene Sulfonate (as Na salt)—Name	Parts by Weight	Branched-Chain Alkyl Benzene Sulfonate Detergent in Parts by Weight	Saturated Aliphatic Alcohol Component—Name	Parts by Weight	Foam Height in mm.		Foam Stability	Foam Quality
						After 1 Min.	After 15 Min.		
1	None		20	None		87	68	Poor	Poor.
2	None		20	n-Hexadecanol	2	78	12	do	Fair.
3	None		20	n-Hexadecane 1,2-glycol.	4	83	52	do	Poor.
4	n-Hexadecyl benzene sulfonate.	20		None		Less than 10		do	Do.
5	do	20		n-Hexadecanol	2	Less than 10		Good	Fair.
6	do	10	10	None		62	0	Poor	Poor.
7	n-Tetradecyl benzene sulfonate.	10	10	n-Hexadecanol	3	56	42	Good	Good.
8	n-Hexadecyl benzene sulfonate.	10	10	do	0.4	50	36	do	Do.
9	sec. n-Octadecyl benzene sulfonate.	10	10	do	2	68	57	Poor	Poor.
10	n-Hexadecyl benzene sulfonate.	10	10	do	2	50	36	Good	Good.
11	do	1	19	do	1	82	70	Fair	Fair.
12	do	5	15	do	4	33	30	Good	Good.
13	Mixture of n-C_{14}–C_{18} alkyl benzene sulfonates [1]	5	15	n-Tetradecanol	2	68	57	do	Do.
14	do	5	15	n-Octadecane 1,2-glycol.	2	71	60	do	Do.
15	n-Hexadecyl benzene sulfonate.	10	10	n-Dodecanol	2	68	42	Poor	Fair.
16	do	10	10	n-Octadecanol	2	52	30	do	Do.

[1] The alkyl portion derived from tallow by hydrogenation and hydrolysis.

In the table, run No. 1 shows that branched alkyl benzene sulfonate detergent produces foam which, although possessing considerable volume, utterly lacks stability and quality, and, consequently, will not persist under agitation in the presence of soil.

Runs Nos. 2 and 3 show that addition of C_{14}–C_{16} saturated aliphatic alcohols, or C_{14}–C_{22} alkane 1,2-glycols, is incapable of providing stability for the foam of branched alkyl benzene sulfonated detergents.

Run No. 4 indicates that normal primary C_{10}–C_{18} alkyl benzene sulfonates are incapable of forming a substantial volume of suds which, furthermore, utterly lack quality and stability.

Run No. 5 shows that the addition of a C_{14}–C_{16} saturated aliphatic alcohol fails to impart a satisfactory foam performance to a solution of a normal primary C_{10}–C_{18} alkyl benzene sulfonate; the volume of foam is so low that the improvement in stability is inadequate to insure foam persistence under agitation.

Run No. 6 illustrates the fact that two-component

mixtures of branched-chain alkyl benzene sulfonate detergents with normal primary C_{10}–C_{18} alkyl benzene sulfonates in the absence of an alcohol, or a 1,2-glycol, is incapable of producing stabilized suds which would persist throughout the complete washing cycle in the bowl of a washing machine.

In contrast to the aforementioned runs, test runs Nos. 7, 8, 10, 11, 12, 13 and 14 clearly demonstrate the ability of the active three-component combination of the present invention to create adequate suds of fair to good stability and quality, which persist throughout the washing operation.

Run No. 9 points out the criticality of the bonding of normal alkane groups to the phenylene linkage in the normal primary C_{10}–C_{18} alkyl benzene sulfonates through the terminal carbon. Secondary normal octadecyl benzene sulfonate failed to provide a stable foam, when employed in the three-component combination of the invention.

The detergent formulations prepared in accordance with the invention are highly effective in laundering operations in automatic and non-automatic agitator-type washing machines, their dilute solutions maintaining a persistent level of good quality suds in the machine throughout the complete washing cycle of at least 20 minutes and providing a satisfactory detergency, i.e., effectively removing the soil from dirty laundry when employed in concentrations of 0.1 to 0.4, comomn to laundry practice.

The improvement in the foam performance of detergent compositions containing active branched-chain alkyl benzene sulfonates, when formulated in accordance with the invention, is entirely unexpected, particularly in view of the fact that neither n-dodecanol, mentioned in the prior art as a foam stabilizer, nor the lower molecular weight saturated aliphatic alcohols, such as decanol, octanol, etc., nor the higher molecular weight saturated aliphatic alcohols containing 18 and more carbon atoms,

e.g., octadecanol, etc., are found capable of improving the foam stability of these sulfonate detergent formulations, In fact, these alcohols tend to act as defoamers.

I claim:

1. A detergent composition consisting essentially, by weight, of 10 to 40% of active organic detergent material and 60 to 90% of water-soluble inorganic salt detergent builders, said organic detergent material consisting essentially, by weight, of about 5 to 50% normal primary C_{10}–C_{18} monoalkylbenzene sulfonate, 35 to 90% branched-chain C_9–C_{18} monoalkyl benzene sulfonate detergent, and 2 to 15% of a normal alcohol selected form the group consisting of C_{14}–C_{16} saturated primary monohydric alcohols and C_{14}–C_{22} 1,2-glycols.

2. A detergent composition according to claim 1 wherein the alcohol is a saturated primary normal C_{14}–C_{16} monohydric alcohol.

3. A detergent composition according to claim 1 wherein the normal primary alkyl benzene sulfonate and the branched-chain alkylbenzene sulfonate are sodium sulfonates.

4. A detergent composition according to claim 2 wherein the branched-chain alkylbenzene sulfonate is a C_{12}–C_{15} branched-chain alkylbenzene sulfonate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,166,314	Martin	July 18, 1939
2,477,383	Lewis	July 26, 1949
2,519,062	Miskel	Aug. 15, 1950
2,679,482	Ross	May 25, 1954
2,712,530	Baumgartner	July 5, 1955
2,746,932	Vitale	May 22, 1956
2,768,095	Tadema et al.	Oct. 23, 1956
2,770,600	Ricciardi	Nov. 13, 1956
2,796,429	Kreps et al.	June 18, 1957