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 C8-C14 monooxylkyl benzene 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 propylene, 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 detergents 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 C9-C13 branched-chain monooxylkyl 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 proposed 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 unabated.

I have now discovered that by combining detergent branched-chain C8-C14 monooxylkyl benzene sulfonates with effective proportions of a normal primary C9-C13 alkyl benzene sulfonate and an alcohol from the group consisting of C10-C14 straight-chain saturated aliphatic alcohols and straight-chain C10-C14 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 C9-C13 alkyl benzene sulfonate is incapable of producing good foam stability and quality. On the other hand, the addition of a C14-C18 straight-chain saturated aliphatic alcohol or a straight-chain C16-C22 alkane 1,2-glycol, to the detergent 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 C10-C13 alkyl benzene sulfonate, and a C14-C18 straight-chain saturated aliphatic alcohol, or a straight-chain C16-C22 alkane 1,2-glycol, is capable of producing a stable, good-quality, and persistent foam.

In the aforementioned three-component combination, the normal primary C10-C13 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 C9-C13 monooxylkyl benzene sulfonic acid, e.g., an alkali metal, an alkaline earth metal, an ammonium, an alkyl ammonium, and an alkylammonium sulfonate may be employed. Water-soluble C9-C14 monooxylkyl benzene sulfonates such as 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 C12-C13 monooxylkyl benzene sulfonates, such as polypropylene benzene sulfonates. Employment of such sulfonate detergent materials made up of predominantly C15 polypropylene benzene sulfonates is found to be particularly effective, resulting in an enhanced volume of stable, good-quality foam.

The term “normal primary C9-C13 alkyl benzene sulfonate,” as employed throughout this description refers to water-soluble salts of normal 1-phenyl C9-C13 alkane sulfonic acids having the general formula: RSO3M, wherein M is a cation from the group consisting of alkali metal, alkaline earth metal, ammonium, alkyl ammonium, and alkylammonium cations, R is a straight-chain saturated C9-C13 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 C10-C14 alcohols and straight-chain C10-C14 alkane 1,2-glycols (C14-C16 alkanoals and C16-C22 alkane 1,2-diols).

If desired, a fatty acid alkylolamide such as lauric ethanolamide, lauric isopropanolamide or lauric glycerylamine 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 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,
2,956,025

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 cellulosic 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 slurry 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 present invention. Sodium C<sub>12</sub>-C<sub>14</sub> polypropylene benzene sulfonate was employed as a typical monolauryl benzene sulfonate detergent component. A number of representative sodium salts of normal 1-phenyl C<sub>12</sub>-C<sub>14</sub> alkane sulfonic acids (sodium n-alkyl benzene sulfonates) were combined therewith to gather with effective proportions of a normal aliphatic C<sub>12</sub>-C<sub>14</sub> alcohol or a normal C<sub>12</sub>-C<sub>14</sub> alkane 1,2-glycols. Detergent builders were present in the following amounts: 30 parts by weight of sodium tripolyphosphate, 20 parts by weight of tetradecox myristate, 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 beaker with the aid of propeller-type stirrers for one minute, and then agitating the foam height in millimeters was measured and the ratio of foam 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.

<table>
<thead>
<tr>
<th>Test Run No.</th>
<th>n-Alkyl Benzene Sulfonate (as Na salt)</th>
<th>Parts by Weight</th>
<th>Branched-Chain Alkyl Ether Sulfonate Detergent in Parts by Weight</th>
<th>Saturated Aliphatic Alcohol Component</th>
<th>Parts by Weight</th>
<th>Foam Height in min.</th>
<th>Foam Stability</th>
<th>Foam Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>20</td>
<td>None</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>20</td>
<td>n-Branched-decadecanol</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>3</td>
<td>None</td>
<td>20</td>
<td>1,2-glycol</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>4</td>
<td>n-Hexadecyl benzene sulfonate</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>5</td>
<td>...</td>
<td>20</td>
<td>...</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>6</td>
<td>n-Undecyl benzene sulfonate</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>7</td>
<td>n-Hexadecyl benzene sulfonate</td>
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<td>20</td>
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<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>8</td>
<td>n-Hexadecyl benzene sulfonate</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>9</td>
<td>oct. Octadecyl benzene sulfonate</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>10</td>
<td>n-Hexadecyl benzene sulfonate</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
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<td>11</td>
<td>...</td>
<td>20</td>
<td>...</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>12</td>
<td>n-Decyl benzene sulfonate</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>13</td>
<td>Mixtures of n-C&lt;sub&gt;12&lt;/sub&gt;-C&lt;sub&gt;14&lt;/sub&gt; alkyl benzene sulfonate</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>14</td>
<td>...</td>
<td>20</td>
<td>...</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>15</td>
<td>n-Hexadecyl benzene sulfonate</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td>16</td>
<td>...</td>
<td>20</td>
<td>...</td>
<td>20</td>
<td>20</td>
<td>87</td>
<td>Poor</td>
<td>Poor</td>
</tr>
</tbody>
</table>

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 present invention.

Run Nos. 2 and 3 show that addition of C<sub>14</sub>-C<sub>18</sub> saturated aliphatic alcohols, or C<sub>14</sub>-C<sub>18</sub> alkane 1,2-glycols, is incapable of providing stability for the foam of branched alkyl benzene sulfonate detergents.

Run No. 4 indicates that normal primary C<sub>14</sub>-C<sub>18</sub> 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<sub>14</sub>-C<sub>18</sub> saturated aliphatic alcohol fails to impart a satisfactory foam performance to a solution of a normal primary C<sub>14</sub>-C<sub>18</sub> 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_{12} 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_{12} 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, comma 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.

1 claim:

5 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_{12} monoalkylbenzene sulfonate, 35 to 90% branched-chain C_{10}-C_{12} monoalkyl benzene sulfonate detergent, and 2 to 15% of a normal alcohol selected from the group consisting of C_{14}-C_{18} saturated primary monohydric alcohols and C_{14}-C_{18} 1,2-glycols.

2. A detergent composition according to claim 1 wherein the alcohol is a saturated primary normal C_{14}-C_{18} 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_{18} branched-chain alkylbenzene sulfonate.

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