

1

3,444,086

DETERGENT COMPOSITIONS

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4 Claims

ABSTRACT OF THE DISCLOSURE

A built detergent composition is described containing a water soluble alkali metal polyphosphate and a water soluble alkali metal mono-higher alkylbenzene sulfonate, said alkylbenzene sulfonate characterized by the alkyl group having n-hexene-1-trimer type structure containing from about 70% to about 85% in the form of methylene groups, having branching on from about 5% to about 25% of its alpha-carbon atoms, and containing an average of from about 16 to about 20 carbon atoms as well as detergent compositions containing, in addition to the foregoing, a water soluble normally high foaming mono-higher alkyl aromatic sulfonate such as alkylbenzene, alkyltoluene and alkylxylene sulfonates and characterized by the alkyl group having branching on at least about 45% of the alpha-carbon atoms, containing at most about 45% of the carbon atoms in the form of methylene groups and averaging from about 10 to about 20 carbon atoms.

This is a continuation-in-part of application Ser. No. 332,854, filed Dec. 23, 1963, now abandoned.

The present invention relates to polyphosphate built detergent compositions. More particularly, the present invention relates to low foaming polyphosphate built detergent compositions that contain, as their major surface active agent, an alkylaryl sulfonate.

By far the majority of detergent compositions that are sold to the consuming public today contain alkylbenzene sulfonates. The alkylbenzene sulfonates that are presently utilized and sold commercially derive the alkyl portions of their molecules, to a very large extent from olefin polymers, which in turn are derived from propylene. Propylene tetramers, propylene pentamers, and fractions intermediate therebetween are examples of such conventional olefin polymers. The water-soluble alkylaryl sulfonates that are derived from such propylene-based polymer olefins have proved to be excellent detergent active ingredients. They have at least one important shortcoming, however, insofar as users of automatic laundry washing machines are concerned: they foam excessively. Since alkylbenzene sulfonates represent a relatively inexpensive class of surfactants, as compared to practically all other classes of good water-soluble surfactants, it can be appreciated that the production of a water-soluble alkylaryl sulfonate which is an excellent detergent, but which is either a non-foamer or is at most, a low foaming surfactant is a desirable and valuable goal for practically every producer of surfactants.

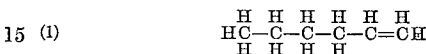
It is a primary object of the present invention to provide low-foaming detergent compositions which contain significant amounts of certain water-soluble alkylaryl sulfonates.

It is another primary object of this invention to provide

2

low-foaming detergent compositions which are not only excellent laundry or fabric detergents, but which are also excellent general purpose detergent compositions.

These objects, as well as others which will become apparent from the following discussion and claims, are obtained, surprisingly, by the use of water-soluble alkylbenzene sulfonates, the alkyl portions of which have structures like that resulting from the trimerization of n-hexene-1 in phosphate built detergent formulations. (The numerical designation after the word "hexene" indicates the position in the n-hexene molecule at which the double bond occurs.) For example, n-hexene-1 is represented by the Formula 1:



The fact that polyphosphate built detergent compositions that contain such water-soluble alkylaryl sulfonates as those derived from n-hexene-1 trimer are low foaming is surprising not only because the use of practically any of the water-soluble alkylaryl sulfonates suggested heretofore for use in similar "phosphate built" detergent formulations cause large quantities of foam or lather, but also because evaluation of the water-soluble alkylaryl sulfonates made from n-hexene-1 trimer alone (in the absence of alkali metal polyphosphate detergent builders) leads one to believe that these materials are not low foaming surfactants. For example, in the well-known Ross-Miles lather test, relatively "pure" sodium octadecylbenzene sulfonate, wherein octadecyl portion is derived from trimerized n-hexene-1, gave a 5 minute lather value of about 10 centimeters (indicating that the material is a fairly good foaming or lathering agent). However, surprisingly, when this same sample was "built" into a detergent formulation containing about 30 weight percent of sodium tripolyphosphate, the 5 minutes lather value for the phosphate built sample was less than 2 centimeters (it was a very low foaming detergent formulation). By comparison, conventional sodium pentadecylbenzene (wherein the "pentadecyl" portion is derived from propylene pentamer) shows practically identical, very high 5 minute "Ross-Miles" lather values, whether it was "polyphosphate built" or unbuild.

It should be emphasized at this point that the term "n-hexene-1 trimer" as used herein in conjunction with such terms as "mono higher alkyl benzene," "benzene," and the like is intended to be indicative solely of the type of structure of the "higher alkyl" portion of the particular "mono higher alkyl benzene" compound being discussed. Thus, the use of the term "n-hexene-1 trimer" herein does not necessarily mean that the compound under discussion was derived by trimerizing n-hexene-1, although the compound could well have been manufactured in this way. The essential property of the "n-hexene-1 trimer" materials encompassed by this invention is their chemical structure. Thus, any material which has the structure like those compounds which can be manufactured by trimerizing n-hexene-1 (under conditions which do not result in excessive rearrangement of the molecules during and after their trimerization, such as those conditions under which Friedel-Crafts trimerizations are conventionally accomplished) can be utilized in the practice of the present invention. A more definitive discussion of the actual chemical structure of the "n-hexene-1 trimer" compound contemplated to be within the scope of the present invention will be presented hereinbelow.

It will also be readily appreciated by those in the art

that the "n-hexene-1 trimer" mono higher alkyl benzene materials referred to specifically herein are not necessarily "pure" materials, but are rather generally mixtures of materials having similar molecular weights, the average molecular weight of such mixtures being the one desired and discussed specifically herein.

In accordance with the present invention, it has been found that detergent compositions containing water-soluble polyphosphates and water-soluble alkali metal "n-hexene-1 trimer" mono higher alkyl benzene sulfonates in a weight ratio, respectively, of at least about 1:1 and preferably from about 1:1 to about 10:1 demonstrate the surprisingly low foaming characteristic described above. Usually amounts of the water-soluble polyphosphates of at least about 15% by weight of the detergent composition are sufficient and preferably from about 15% to about 85% by weight of the detergent composition. Usually amounts of the alkali metal n-hexene-1 trimer benzene sulfonate of at least about 3% by weight of the detergent composition are sufficient and preferably from about 3% to about 50% by weight of the detergent composition.

The water-soluble polyphosphates which are preferred for use in the practice of the present invention are those that are generally conventionally employed in "built" heavy duty detergents, and include the alkali metal tri-polyphosphates, pyrophosphates, water-soluble tri- and tetra-metaphosphates, as well as the longer open chain alkali metal polyphosphates containing as many as 50 or more phosphorus units per molecule such as alkali metal hexametaphosphates. Of the water-soluble alkali metal polyphosphates, the sodium and potassium polyphosphates are particularly preferred for use in the practice of the present invention. While for most purposes, such as for use as a hard surface cleaning composition, the compositions of the present invention will contain the alkali metal (preferably sodium or potassium) n-hexene-1 trimer benzene sulfonates as the sole or only organic detergent active material in the overall detergent composition, it is nevertheless distinctly advantageous for some purpose to have in the detergent compositions of the present invention an ordinarily high foaming alkyl benzene sulfonate. The weight ratio of the alkali metal n-hexene-1 trimer benzene sulfonate to the ordinarily high foaming alkyl benzene sulfonate should be at least about 5:1 and preferably from about 5:1 to about 20:1. Typical examples of such high foaming alkali metal alkyl benzene sulfonates (which yield "five-minutes" lather values in the well-known Ross-Miles lather test at 50°C. at the 0.1 weight percent level in distilled water and in the presence of an equal amount of sodium tripolyphosphate of at least about 10) include the well-known alkali metal alkyl benzene sulfonates wherein the alkyl portion is a propylene tetramer, a propylene pentamer, intermediate fractions or mixtures thereof. Such materials are well known in the art, and have generally very highly branched alkyl groups. One particular area of utility for which such binary combinations of the very low foaming anionic surfactants of the present invention and the minor amounts of high foaming surfactants can be utilized to advantage is that wherein the small amount of foam which is present in aqueous solutions of these compositions is required to be unusually stable in the presence of dissolved greases, for example, wherein the compositions are to be used as hand dishwashing detergents. In the presence of large amounts of dissolved greases, the small amount of high foaming surfactant in the composition described above surprisingly does not add significantly to the total amount or volume of lather formed initially, but rather contributes significantly to the stability of the lather that is formed. The data in the following Table I illustrates the surprising advantage of using a detergent composition containing a combination of an alkali metal n-hexene-1 trimer benzene sulfonate with a minor amount of some of the well-known "high foaming" detergent active materials.

TABLE I.—PLATE WASHING DATA¹

Sample	Material tested ²	Plates washed
5	A----- Control, 35% sodium hexene-1-trimer benzene sulfonate.	9
	B----- 31.5% sodium hexene-1-trimer benzene sulfonate+3.5% sodium decylbenzene (from propylene) sulfonate.	16
	C----- 31.5% sodium hexene-1-trimer benzene sulfonate+3.5% sodium tridecylbenzene (from propylene) sulfonate.	28
10	D----- 31.5% potassium hexene-1-trimer benzene sulfonate+3.5% potassium dodecylbenzene (from propylene) sulfonate.	25
	E----- 35% sodium tridecylbenzene (from propylene) sulfonate.	25

¹ Procedural details of this test described after Example II, below. Detergent compositions tested at 0.75 weight percent in 100 p.p.m. hard water at 50° C.

² Remainder (other than surfactants) is sodium tripolyphosphate.

While the aromatic portion of the surprisingly low foaming alkylaryl sulfonate in the mixtures illustrated in Table I is apparently restricted to benzene, it is apparent from Table I that no such limitation or restriction exists with respect to the alkyl portion of "ordinarily high foaming" water soluble alkylaryl sulfonate(s) in such mixtures. As a matter of fact, in order to lend the unexpected foam stabilizing benefit to compositions containing the water soluble "n-hexene-1 trimer" sulfonates, apparently the only criterion that the "high foaming" water soluble alkylaryl sulfonate must meet is that its aqueous solutions (in the absence of other surfactants) be high foaming solutions. For example, if at a concentration of 0.1 weight percent in distilled water (which also contains 0.1 weight percent of sodium tripolyphosphate dissolved therein) the "5-minute" Ross-Miles lather value of the resulting solution at about 50° C. is at least about 10 cm., then the material can be utilized in conjunction with the water soluble "n-hexene-1 trimer" benzene sulfonates to produce the improved lather stability described above. Thus, the "high foaming" fraction or portion of the very desirable mixtures which are particularly useful as "hand" dishwashing detergents can be any of the mono higher alkyl (wherein the alkyl portion contains an average of from about 10 to about 20 carbon atoms and preferably contains an average of from about 12 to about 16 carbon atoms) benzene, toluene or xylene sulfonate, or even a mixture of these sulfonates. Alkali metal and ammonium are the preferred cations in these materials, and of these preferred cations, sodium and potassium are still further preferred.

The alkali metal n-hexene-1 benzene sulfonate components of the compositions of the present invention can be manufactured by first alkylating benzene with an olefin derived by trimerizing hexene-1 under pressure and in the presence of a Friedel-Crafts type catalyst; and subsequently sulfonating and neutralizing the resulting n-hexene-1 trimer benzene intermediate compound with an alkali metal source such as a sodium, potassium or lithium salt or hydroxide, for example. They can also be made, for example, by alkylating benzene with an olefin derived by reacting together various mixtures of olefins under pressure and in the presence of an appropriate catalyst (such as a Friedel-Crafts type catalyst) including mixtures of linear terminal C₅, C₆ and C₇ olefins, C₄, C₆ and C₈ olefins, C₅ and C₇ olefins, and similar mixtures to prepare mono alkyl benzene compounds wherein the alkyl group contains an average of from about 16 to about 20 carbon atoms and wherein the alkyl group is similar in structure to the alkyl group of alkyl benzene derived by trimerizing hexene-1. Generally the fraction of polyolefin reaction products (resulting from reacting together such mixtures) that is very similar in structure to that of hexene-1-trimer olefin is that fraction boiling between about 85° C. and about 105° C. under a pressure of about 1 mm. pressure.

As it was mentioned hereinbefore, the alkali metal mono higher alkyl (n-hexene-1 trimer) benzene sulfonates

that are useful in the compositions of the present invention have structures like those derived by trimerizing n-hexene-1. These materials can be identified by well-known analytical techniques, for example, by employing recognized nuclear magnetic resonance (n.m.r.) techniques in which, by means of a Varian Model A-60 spectrometer with spinning 5 mm. bore glass sample tubes at ambient temperatures (about 30° C.), and using tetramethylsilane as a standard, recording peak positions in cycles per second and p.p.m. of the magnetic field. In this manner, the minimum number of methylene ($-\text{CH}_2-$) groups in a given alkyl benzene hydrocarbon or its corresponding sulfonate sample can be distinguished with fairly high accuracy. Thus, the n-hexene-1 trimer benzene hydrocarbons and their corresponding sulfonates that are contemplated within the scope of the present invention have been found to contain from about 70% to about 85% of its carbon atoms in the form of methylene groups. In addition, the percent fraction of molecules in these materials (the mono n-hexene-1 trimer benzenes) that have branching on the alpha-carbon atoms is from about 5% to about 25%, according to the n.m.r. analysis. These figures are to be compared with similar data for dodecyl benzene, for example, derived from conventional tetrapropylene or conventional hexapropylene, which have at most about 45% of its carbon atoms in the form of methylene groups and more than 65% of its molecules being branched on the alpha-carbon atom.

It should be noted that all of the "high-foaming" water soluble mono higher alkylaryl sulfonates that can advantageously be utilized in the "foam stabilized" mixtures described heretofore are fairly highly branched in the mono higher alkyl portion of their molecules, contain at most about 65% of their carbon atoms in the form of methylene groups, according to n.m.r. analysis, as described above. As a general rule, the high foaming sulfonates are also highly branched on their alpha-carbon atoms. For example, usually at least about 45% of the alpha-carbon atoms contain more than one alkyl carbon attached thereto, and thus can be termed "branched."

Often the polyphosphate builders can be employed advantageously in conjunction with other detergent builders (supplementary builders) in the detergent compositions of the present invention which include the amino polycarboxylic acids and salts such as the sodium, potassium and ammonium salts of nitrilotriacetic acid (trisodium, -potassium, or -ammonium nitrilotriacetate), the sodium, potassium and ammonium salts of amino tri (methylene phosphonic acid) as well as the free acid (penta- sodium, -potassium or -ammonium tri-methylene phosphonate) and the diphosphonic acids and salts (methylene diphosphonic acid and 1-hydroxy, ethylidene diphosphonic acid) as disclosed and described in Canadian Patent 718,385 issued Sept. 21, 1965 which is incorporated herein by reference. Generally speaking, a weight ratio of a polyphosphate builder and a foregoing described builder or builder mixtures of from about 1:1 to 10:1, respectively, have been found suitable.

The detergent compositions of the present invention can be prepared in any of the several commercially desirable composition forms such as, bar, granular, flake, liquid and tablet form.

The detergent compositions of the present invention are generally effective when used in aqueous systems in conventional amounts which are generally about 0.2% concentration or below.

The invention is not to be limited to any particular method of preparing the detergent compositions. The polyphosphate builder may be mechanically mixed in, crutched in the n-hexene-1 trimer benzene sulfonate in the form of a slurry, and then dried, or dissolved in a solution of the n-hexene-1 trimer benzene sulfonate. In addition, the polyphosphate builder may be admixed with the n-hexene-1 trimer benzene sulfonate in any of the forms in which the benzene sulfonate is manufactured

in, as well as being added simultaneously or separately to an aqueous solution.

While a detergent composition in accordance with this invention need contain only a n-hexene-1 trimer benzene sulfonate of the type described and a polyphosphate builder, it will be appreciated that the incorporation in the composition of additional ingredients commonly used with cleansing agents, such as alkali metal carbonates, sulfates and silicates, perfumes, antiredeposition agents (e.g., carboxymethylcellulose), brightening agents (e.g., fluorescent dyes) and the like, are contemplated as being within the invention.

EXAMPLE I

A detergent slurry containing the following ingredients (parts by weight) is prepared by blending together in the following order:

Ingredient:	Parts
Water -----	4000
Sodium monooctadecyl (n-hexene-1 trimer) benzene sulfonate -----	1500
Sodium tripolyphosphate hexahydrate ($-\text{200 mesh}$) -----	4000
Sodium sulfate ($-\text{200 mesh}$) -----	300
Sodium carboxymethylcellulose -----	100
Optical brightener -----	20
Perfume -----	20

After being well blended, the slurry is then dried in a conventional spray tower via a conventional technique, yielding a product which, in the well-known Ross-Miles Lather test at 50° C. (and at a concentration of the total detergent product of 0.50 weight percent in distilled water), yields a "5-minute" lather value of only 1.5 cm. This is surprising in view of the fact that a 0.075 weight percent solution of the same surfactant, alone, yields a "5-minute" 50° C. Ross-Miles Lather value of about 11.5 cm. Tested at the level of 0.25 weight percent in 25 p.p.m. hardness water at 125° F. in an upright conventional automatic washing machine having reciprocating action (with an 8 pound load of soiled clothes), the use of the material of Example I, above resulted in the level of lather on the surface of the water in the machine after about 10 minutes being only 4¾ inches. This lather value is extremely low, as compared with a value (from an otherwise identical test) of 8¼ inches for an otherwise identical detergent formulation containing sodium n-octadecane-1-sulfonate as the active ingredient, and with a figure of approximately 12 inches or more (the foam ran over the top of the machine) for a similar formulation containing conventional sodium tridecylbenzene sulfonate (made from propylene) as the active ingredient.

EXAMPLE II

A detergent slurry is prepared as in Example I, above, except that 200 parts of sodium dodecylbenzene sulfonate (prepared from propylene tetramer) are also blended into the slurry before it is spray-dried. The resulting product contains approximately 65 weight percent of sodium tripolyphosphate hexahydrate and about 27 weight percent of total organic surfactant, about 12 weight percent of which is the ordinarily very high foaming sodium "propylene tetramer" benzene sulfonate.

In a standard "hand" dishwashing test described in detail in the Proceedings of the 43rd Annual Meeting of the Chemical Specialties Manufacturers' Association, December 1956 (Procedure No. 3, Page 191), wherein nine-inch dinner plates that have been presoiled with one teaspoonful each of a synthetic "soil" mixture consisting of 75 parts of shortening blended with 25 parts of flour are washed by hand, using a washcloth to remove the synthetic soil, a composition such as that of Example II, above, is found to effectively clean a total of 15 plates, whereas a composition without the very high foaming surfactant such as that made in accordance with Example I, above, is found to clean only about 5 dishes.

The total initial volume of lather on the dish-water in each of these tests is, however, surprisingly, practically the same.

What is claimed is:

1. A built detergent composition consisting essentially of sodium tripolyphosphate in an amount of from about 15% to about 85% by weight of said composition, and from about 3% to about 50% by weight of said composition of sodium octadecylbenzene sulfonate, the octadecyl portion of which has the structure of a n-hexene-1 trimer; the weight ratio of said sodium tripolyphosphate to said sodium octadecylbenzene sulfonate being at least about 1:1.

2. A built detergent composition consisting essentially of a water soluble alkali metal polyphosphate in an amount of at least about 15% by weight of said composition, a water soluble alkali metal mono higher alkylbenzene sulfonate in an amount of at least about 3% by weight of said composition, said alkylbenzene sulfonate characterized by the alkyl group having n-hexene-1-trimer type structure, containing from about 70% to about 85% of its carbon atoms in the form of methylene groups, having branching on from about 5% to about 25% of its alpha-carbon atoms, and containing an average of from about 16 to about 20 carbon atoms; the weight ratio of said alkali metal polyphosphate to said alkylbenzene sulfonate being at least about 1:1, respectively, and a water soluble normally high foaming mono higher alkyl aromatic sulfonate selected from the group consisting of alkylbenzene, alkyltoluene, and alkylxylene sulfonates and characterized by the alkyl group having branching on at least about 45% of the alpha-carbon atoms, containing at most about 45% of the carbon atoms in the form of methylene groups and averaging from about 10 to about 20 carbon atoms; the weight ratio of said mono higher alkylbenzene sulfonate to said high foaming mono higher alkyl aromatic sulfonate in said composition being at least about 5:1, respectively.

3. A composition according to claim 2, wherein said polyphosphate is sodium tripolyphosphate, said mono

higher alkyl benzene sulfonate is sodium n-hexene-1-trimer benzene sulfonate and said high foaming mono higher alkyl aromatic sulfonate is sodium tetrapropylene benzene sulfonate; the weight ratio of said n-hexene-1-trimer benzene sulfonate to said tetrapropylene benzene sulfonate in said composition being from about 5:1 to about 20:1, respectively.

4. A built detergent composition consisting essentially of sodium tripolyphosphate in an amount of from about 15% to about 85% by weight of said composition, from about 3% to about 50% by weight of said composition of sodium octadecylbenzene sulfonate, the octadecyl portion of which has the structure of a n-hexene-1-trimer; the weight ratio of said sodium tripolyphosphate to said sodium octadecylbenzene sulfonate being at least about 1:1, and a water soluble normally high foaming mono higher alkyl aromatic sulfonate selected from the group consisting of alkylbenzene, alkyltoluene, and alkylxylene sulfonates and characterized by the alkyl group having branching on at least about 45% of the alpha-carbon atoms, containing at most about 45% of the carbon atoms in the form of methylene groups and averaging from about 10 to about 20 carbon atoms; the weight ratio of said mono higher alkylbenzene sulfonate to said high foaming mono higher alkyl aromatic sulfonate in said composition being from about 5:1 to about 20:1, respectively.

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