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2,944,028

SULFONATE DETERGENT COMPOSITIONS

Richard D. Stayner, Berkeley, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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2 Claims. (Cl. 252—161)

This invention relates to improved washing formulations which contain a branched-chain polypropylene benzene sulfonate as their active detergent component, and which are capable of producing a large volume of stable suds maintaining a satisfactory high level in the continuously agitated aqueous solutions thereof in the presence of soil.

C_9 - C_{18} polypropylene benzene sulfonates, which may be also designated as sulfonated monophenyl-substituted acyclic C_9 - C_{18} polypropylenes are known in the art to be effective detergents and, when suitably formulated, are used in a variety of industrial and household cleaning applications, particularly in the washing of soiled clothes, fabrics and dishes. A number of washing formulations, based on these polypropylene benzene sulfonate detergents and containing different additives for the purpose of modifying one or another particular property of these detergents, have been described in the art. In U.S. Patent 2,712,530, Baumgartner proposed to add to these detergent sulfonates from 5 to 50% by weight of a secondary alkylaryl sulfonate of the general structural formula



in which R' was a straight-chain C_1 - C_5 alkyl group, R'' was a straight-chain C_8 - C_{14} alkyl group, the sum of R' and R'' equalled 9 to 15 carbons and M was an alkali metal. The addition of this secondary alkyl benzene sulfonate was said to improve the detergent property of the polypropylene benzene sulfonate at concentrations below about 0.25%.

British Patent No. 702,013 disclosed the addition to C_9 - C_{18} polypropylene benzene sulfonate detergents of at least 20% by weight of sulfonated 2-phenyl alkanes containing a straight alkyl chain of 10 to 16 carbon atoms in their alkane portion for the purpose of reducing the caking tendency of the formulations containing the aforementioned detergent polypropylene benzene sulfonates as their main active component.

In his U.S. Patent 2,477,383, Lewis described detergent branched-chain polypropylene benzene sulfonates (sulfonated mono-phenyl substituted acyclic polypropylenes), pointing out that commercial polypropylene benzene sulfonates characterized by an average content of about 12 carbon atoms in the polypropylene chain were particularly effective as detergent ingredients in formulations employed for a great many household and industrial applications. It has been noted in the actual practice that dilute soft water solutions of these commercial C_{12} (dodecyl) polypropylene benzene sulfonate detergents, when employed in the tub of agitator-type washing machines at low-use concentrations (of the order of 0.15%) and at temperatures above 100° F., and usually from about 120 to about 140° F., generally fail to produce an adequate volume of persistent suds, lasting the entire period of agitation and, particularly, in contact with soil (soiled clothes, etc.). Although the volume of suds initially produced on starting the washing cycle is relatively large, these suds are

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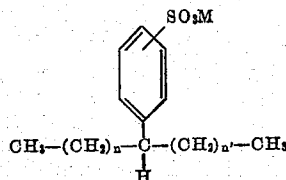
weak and lacy and rapidly collapse and disappear during the agitation of the contents of the tub containing the washing solution and the soiled articles. This constitutes a serious drawback since a considerable proportion of the consumer public still believe that a large volume of suds is concomitant with the washing efficiency and gives an indication of the amount of the detergent necessary for effective washing.

This deficiency with respect to the ability of producing persistent suds is noted only in using solutions of polypropylene benzene sulfonates derived from propylene tetramer fractions, such as commercial dodecyl benzene sulfonate. It is clearly in contrast with the foam performance of polypropylene benzene sulfonates derived from propylene pentamer fractions characterized by an average content of about 15 carbon atoms, the solutions of which produce adequate and persistent suds, and which therefore need not be improved as regards their foam performance.

A number of additives and of combinations of additives have been proposed in the past for the purpose of improving the foam performance of commercial C_{12} polypropylene benzene sulfonates. However, in most cases, these additives fail to secure in warm soft water solutions of the polypropylene benzene sulfonate detergents a satisfactory foam which would persist under continued agitation in the presence of soil. The term "soft water," as employed in this description designates water of a Ca-Mg hardness from about 50 to less than about 100 p.p.m., calculated as parts per million of $CaCO_3$ and $MgCO_3$, in a weight ratio of about 2:1. Furthermore, most of the proposed additives were comparatively expensive and their employment resulted in an undue increase of the sales price of the final detergent formulations.

It is therefore the object of the present invention to provide a new and inexpensive foam-improving agent for commercial C_{12} polypropylene benzene sulfonates, capable of assuring persistence of the suds formed by dilute washing solutions of these detergent sulfonates under agitation and in the presence of soil.

I found that the persistence of the suds produced by dilute solutions of commercial C_{12} polypropylene benzene sulfonates can be markedly and unexpectedly enhanced by combining these detergent sulfonates with effective proportions of an improving agent from the group of straight-chain alkyl benzene sulfonates characterized by the general formula



in which n is an integer from 5 to 7, n' is an integer from 5 to 8, and M is selected from the group consisting of alkali metal and ammonium cations. As examples of these straight-chain alkylbenzene sulfonates, there may be mentioned: 7-phenyl tetradecane sulfonate, 8-phenyl hexadecane sulfonate, 9-phenyl octadecane sulfonate and the like. When a sulfonate having a structure corresponding to this formula is added to a commercial C_{12} polypropylene benzene sulfonate detergent, dilute aqueous solutions of the resulting combination in conventional low-use concentrations from about 0.1 up to about 0.2% form large volumes of suds, and these suds persist above the surface of the solution in the tube of a washing machine, notwithstanding the continued agitation of the contents of the tub and notwithstanding the presence therein of soiled clothes or fabrics.

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The effective amounts of the foam-improving sulfonate added to the detergent C₁₂ polypropylene benzene sulfonate may vary from about 5 to about 50% by weight, and preferably from about 10 to about 35% by weight, based on the total weight of sulfonates in the detergent composition.

This improvement in the foam persistence of commercial C₁₂ polypropylene benzene sulfonate detergents is entirely unexpected and specific to the group of alkylbenzene sulfonate additives described hereinbefore. The length of the alkyl chain and the point of attachment to the aromatic (benzene) ring in the molecule of the sulfonate additive are critical to the production of an adequate and persistent layer of suds above the liquid surface in the tub. This specificity is surprising because neither the sulfonate detergency improvers of the aforementioned Baumgartner patent, such as 6-phenyl dodecane sulfonate, nor the sulfonated 2-phenyl alkane caking preventives of British Patent 702,013, for instance, 2-phenyl dodecane and tetradecane sulfonates, are capable of providing the desired persistent suds above the liquid level in the tub of an agitator-type washing machine.

The presence of the foam-improving additive of the invention does not detract in any way from the excellent soil-removing ability (detergency) of the C₁₂ polypropylene benzene sulfonates.

The polypropylene benzene sulfonate detergents which have an average of twelve carbon atoms in the polypropylene chains and the foam persistence of which is enhanced by their combination with the aforementioned sulfonate additive, are generally employed in the form of water-soluble alkali metal and ammonium salts, sodium salts being preferred. Heavy-duty formulations based on these C₁₂ polypropylene benzene sulfonates usually contain from about 20 to about 35% of the sulfonates by weight of the total solids in the formulation.

Formulations containing these detergent commercial C₁₂ polypropylene benzene sulfonates in combination with from 5 to 50% by weight of the sulfonate additive for achieving foam persistence may contain conventional water-soluble inorganic salt detergent builders, such as salts of strong inorganic acids, exemplified by sodium sulfate, sodium chloride and potassium chloride, ammonium sulfate and/or alkaline salts of weak inorganic acids, exemplified by various polyphosphates, for instance, tetrasodium pyrophosphate, sodium tripolyphosphate, sodium hexametaphosphate, and salts, such as sodium carbonate, sodium silicate and borax. From 60 to 90 parts by weight of these inorganic salt detergent builders, preferably as sodium salts, may be present in each 100 parts by weight of a detergent formulation containing the two aforementioned sulfonates (detergent and additive) in accordance with the invention. Where heavy-duty formulations are prepared, from about 10 to about 90% by weight of the inorganic salt builders may consist of inorganic polyphosphates, such as Na₄P₂O₇ and Na₅P₃O₁₀, and the like. Fatty acid alkylolamides such as lauric isopropanolamide and lauric ethanolamide known in the art to enhance the tolerance of the foam with respect to soil, may also be included in the detergent formulations of this invention in conventional small quantities. Other conventional additives, such as carboxymethylcellulose and oxidized cellulose (celluronic acid) organic builders or extenders, anti-caking agents, optical bleaches, corrosion inhibitors, perfume, dyes and skin emollients, such as alkyl glycines, may be employed in the sulfonate detergent formulations of the present invention, the total weight of these various additives seldom exceeding 5% by weight of the entire amount of solids in a formulation, and, in all events, being such that the presence of these additives does not interfere with the improved persistence of the suds produced by the agitated dilute solutions of the detergent formulations.

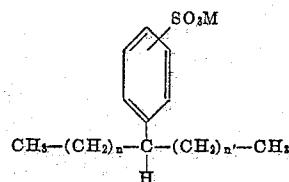
The preparation of the detergent formulations of this invention may be effected by blending the detergent C₁₂

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polypropylene benzene sulfonates with the sulfonate additive for the improvement of foam persistence into an aqueous slurry, or solution, adding the desired builders and other additives to the slurry, and reducing this slurry by drying, if necessary, to the desired form (liquid concentrate, paste or solid particle).

Another way of preparing the detergent formulations of the present invention consists in blending the C₁₂ polypropylene benzenes with from about 5 to about 50% by weight thereof, of suitable mono-phenyl substituted straight-chain alkanes and then sulfonating the resulting hydrocarbon blend with the aid of an appropriate sulfonating agent, such as fuming sulfuric acid, neutralizing the sulfonation product mixture, introducing into the resulting neutralized slurry the desired builders and other additives and, finally, reducing the slurry to the desired form, such as liquid concentrate, paste or solid particle.

The improvement in the foam persistence was repeatedly observed by preparing dilute aqueous solutions of different detergent formulations containing in their organic active portion a blend of C₁₂ polypropylene benzene sulfonates and of from 5 to 50% by weight of straight-chain alkylbenzene sulfonates of the previously given formula



and testing these solutions in an agitator-type automatic washing machine under the conditions approximating those of actual household laundering practice. The results of the tests were compared with the results of numerous test runs which employed detergent formulations containing blends of the C₁₂ polypropylene benzene sulfonate detergents with straight-chain alkylbenzene sulfonates other than those defined by the aforementioned formula, and also with the results of test runs in which no sulfonate additive was blended with the polypropylene benzene sulfonate detergent component. The solutions for the tests were prepared by using water of 50 p.p.m. hardness, the hardness being figured as parts per million of CaCO₃ and MgCO₃ hardness in a weight ratio of 2:1.

The tub of the machine was filled with water, and a specified quantity of soil thoroughly distributed therein, followed by such a quantity of the detergent formulation as to give a 0.15% concentration in the water. Thereafter, a charge of clean cotton towels was placed in the tub assuring an even distribution below the surface of the solution which had a temperature of about 120° F. The agitation was commenced and the level of the suds was observed after 2, 5, 10, 15 and 20 minutes. After observing the foam at the 15 minute interval, a conventional amount of 5% solution of hypochlorite bleach was added to the wash solution, and the run resumed for 5 minutes more to complete the 20 minute cycle.

Persistence of the suds was rated as follows: When suds lasted through a complete washing cycle of 20 minutes, or even longer, and presented a substantially unbroken blanket of foam of ½" or more above the surface of the liquid in the tub, their persistence was rated to be "Good." When suds lasted through the whole washing cycle but rose to less than ½" above the liquid surface and did not cover the entire surface of the washing solution, the persistence was rated to be "Fair." Finally, when practically no suds were formed or, if formed, the suds disappeared before the completion of the washing cycle, the persistence was rated to be "Poor."

In an illustrative test series, a representative formulation contained 20 parts of sodium polypropylene benzene sulfonate having an average of 12 carbon atoms in the polypropylene chain, 30 parts of sodium tripolyphosphate,

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20 parts of tetrasodium pyrophosphate, 5 parts of sodium silicate (commercial "N" grade), the balance to make 100 parts by weight being sodium sulfate. This formulation was blended as a slurry with different straight-chain alkylbenzene sulfonate additives, replacing in each instance 3 parts by weight of the polypropylene benzene sulfonate detergent by the sulfonate additive, and used in the tests as described hereinbefore.

Representative data from this test series are tabulated on the following page.

Suds persistence evaluation data

Test Run No.	Commercial C ₁₂ Polypropylene Benzene Sulfonate Detergent in Parts By Weight	Sulfonate Additive	Parts By Weight of Additive	Suds Persistence Rating
1	20	None		Poor.
2	33	do		Do.
3	17	1-phenyl tetradecane sulfonate	3	Do.
4	30	1-phenyl octadecane sulfonate	3	Do.
5	17	2-phenyl hexadecane sulfonate	3	Fair.
6	17	6-phenyl dodecane sulfonate	3	Poor.
7	17	11-phenyl docosane sulfonate	3	Do.
8	20	9-phenyl octadecane sulfonate	1	Fair.
9	17	do	3	Good.
10	17	8-phenyl hexadecane sulfonate	3	Do.
11	17	7-phenyl tetradecane sulfonate	3	Do.
12	20	7-phenyl tetradecane sulfonate	10	Do.
13	C ₁₅ (pentamer) polypropylene benzene sulfonate 20.	None		Do.

The data shown in the table clearly indicate the remarkable improvement in the foam persistence of dilute aqueous solutions of the formulations containing C₁₂ polypropylene benzene sulfonate detergents, under the conditions of agitation and in the presence of soil, due to the introduction of straight-chain alkylbenzene sulfonate additives in accordance with the invention (runs 8, 9, 10, 11 and 12). The table furthermore shows that straight-chain alkylbenzene sulfonates other than those of the subject invention are ineffective for the purpose of providing good foam persistence (runs 3, 4, 5, 6 and 7), when present in the solutions of washing formulations which contain C₁₂ polypropylene benzene sulfonate detergents. Run 13 is given to emphasize the deficiency of the "tetramer" polypropylene derived detergents (runs 1 and 2) in regard to the foam persistence as contrasted with the "pentamer" polypropylene derived detergents.

Throughout the aforegiven description of my invention the term "commercial C₁₂ polypropylene benzene sulfonate detergent" refers to those polypropylene benzene sulfonate detergent materials which have been obtained from a tetramer fraction of polypropylene characterized by an average content of about 12 carbon atoms.

It is to be understood that the aforegiven description

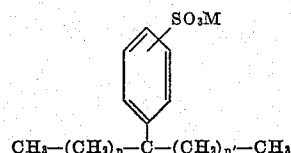
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and data are merely illustrative of the present invention, and that it may be modified without substantial departure from the spirit and scope thereof, provided that the modifications fall within the scope of the following claims:

I claim:

1. A detergent composition consisting essentially of a water-soluble polypropylene benzene sulfonate detergent having an average carbon content in the polypropylene chain of about 12 carbon atoms, and, in an amount suf-

ficient to enhance the sudsing properties of said polypropylene benzene sulfonate, of a straight-chain alkylbenzene sulfonate having the formula



wherein n is an integer from 5 to 7, n' is an integer from 5 to 8, and M is a radical selected from the group consisting of alkali metals and ammonium.

2. A built detergent composition consisting essentially of 10 to 40 parts, by weight, of the composition of claim 1 and 60 to 90 parts, by weight, of inorganic salt detergent builders.

References Cited in the file of this patent

UNITED STATES PATENTS

2,477,383	Lewis	July 26, 1949
2,712,530	Baumgartner	July 5, 1955
2,796,429	Kreps et al.	June 18, 1957

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