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SOAP COMPOSITION CONTAINING LIME SOAP DISPERSANT

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This invention relates to improved soap compositions. More particularly, the invention relates to soap compositions containing certain novel additives which eliminate or materially reduce the formation of lime soap curds in hard water. The novel additives which are incorporated in the improved soap compositions of the invention are the sequential condensation products of propylene and ethylene oxides with a nitrogen atom containing compound having two or more reactive hydrogen atoms.

This application is a continuation-in-part of my copending application Serial No. 349,558, filed April 17, 1953, now abandoned.

The fatty acid soaps have been known for centuries and are widely employed as general purpose detergents. These soaps are easily manufactured, are low in cost and are unexcelled on a performance basis in soft water areas. However, the fatty acid soaps have one very serious shortcoming in that they react with calcium and magnesium ions to form water-insoluble salts. These water-insoluble salts are known generically as lime soaps and cause the familiar bathtub ring and the floating scum that is noticed in dishwashing or clothes washing operations. The seriousness of this problem is evidenced by the fact that the fatty acid soaps have lost nearly one-half of the total market for heavy-duty laundry detergents to the newer synthetics, particularly the alkylarylsulfonates.

In accordance with my invention, the problem associated with the formation of lime soaps can be eliminated or substantially reduced by incorporating certain novel additives in a fatty acid soap composition. Henceforth, these novel additives will be referred to as lime soap dispersants. The action of these lime soap dispersants is not definitely known, but it is not believed that they actually prevent the formation of water-insoluble lime soaps. It is more probable that the lime soap dispersants become chemically or physically associated with the lime soap as it is formed, and subsequently prevent the agglomeration of the soap in curds. Consequently, the soap stays dispersed throughout the aqueous medium in extremely small size particles, and does not deposit on the walls of bathtubs and the like, or form surface scum.

The lime soap dispersants which are incorporated in the improved soap compositions of this invention are certain mixtures of polymeric surface active compounds which are disclosed and claimed in the copending application of Lester G. Lundsted, Serial No. 349,283, filed April 16, 1953, now abandoned. The lime soap dispersants are generally prepared by condensing ethylene oxide with a hydrophobic polyoxypropylene polymer. The polyoxypropylene polymer, in turn, is prepared by condensing propylene oxide with a nitrogen atom-containing compound having two or more reactive hydrogen atoms (henceforth referred to simply as the nitrogen base compound). Examples of suitable nitrogen base compounds include ammonia and the primary amines, such as methylamine, butylamine, amylamine, aniline, and the like. An analogous series of compounds includes hydrazine and its derivatives, such as ethylhydrazine, phenylhydrazine, N,N-dimethylhydrazine, N,N-dibutylhydrazine, and the like. Also, such classes of compounds as amides, imines, and guanidines can be used. The aliphatic primary polyamines are especially preferred, such as ethylenediamine and triethylene tetraamine.

However, a limitation on the nitrogen base compound employed in preparing the lime soap dispersant used in the soap composition of this invention is that the nitrogen base compound must not itself provide the hydrophobic characteristic for the polyoxypropylene polymer produced in making the lime soap dispersant. The hydrophobic character of the polyoxypropylene polymer is provided by the oxypropylene chains and the requirement that the molecular weight of the polymer be at least 900. To prevent the hydrophobic character for the polyoxypropylene polymer from being supplied by the nitrogen base compound, only those nitrogen base compounds of the type described are employed which are not sufficiently hydrophobic as to permit formation of a detergent upon being condensed with ethylene oxide. The hydrophobic characteristic of any nitrogen base compound can be expressed by its "detergency factor," determined as set forth below, and only those nitrogen base compounds having a detergency factor of less than 100 are employed in preparing the lime soap dispersant employed in the soap composition of this invention.

The test for detergency factor is carried out by adding varying quantities of ethylene oxide to the nitrogen base compound so as to prepare oxyethylene adducts containing 20±5%, 30±5%, 40±5%, 50±5% and 60±5% oxyethylene content. Distilled water solutions of 0.25% concentration are prepared with each of the adducts. The carbon soil removal value of each adduct is determined at 140° F. following the procedure described by Vaughn and Suter, The Journal of the American Oil Chemists' Society, vol. XXVII, No. 7, pp. 249–257. As a control, the carbon soil removal value of an 0.25% distilled water solution of a standard sodium alkylarylsulfonate detergent is determined concurrently at 140° F. and on the same batch of soiled cloth. The standard detergent is sodium kerylbenzenesulfonate which is prepared by effecting a Friedel-Crafts condensation of a chlorinated petroleum hydrocarbon distillate (derived from a hydrocarbon distillate having 9–16 carbon atoms and boiling in the range of 150–300° C.) with benzene and thereafter sulfonating the kerylbenzene compound to form the kerylbenzene sulfonic acid, which is subsequently neutralized with caustic soda to form the water-soluble sodium kerylbenzenesulfonate. After the neutralization of the sulfonic acid, sufficient sodium sulfate is added so that the final product contains 40% sodium kerylbenzenesulfonate and 60% sodium sulfate.

The carbon soil removal values of the oxyethylene adducts are reported on a comparative basis with the standard sodium alkylarylsulfonate detergent being assigned an arbitrary value of 100. The highest carbon soil removal value obtained with the five oxyethylene adducts is then taken as the detergency factor of the reactive hydrogen compound.

The term "reactive hydrogen atom" is well known and clearly understood by those skilled in the art. However, to remove any possible ambiguity in this regard, the term reactive hydrogen atom, as used herein and in the appended claims, includes any hydrogen atom fulfilling the following two conditions:

(1) It is sufficiently labile to open the epoxide ring of 1,2 propylene oxide, and

(2) It reacts with methyl magnesium oxide to liberate methane in the classical Zerewitinoff reaction (see Niederl and Niederl, Micro Methods of Quantitative Organic

Analysis, p. 263, John Wiley & Sons, New York city, 1946).

Although the lime soap dispersants derived from any of such nitrogen base compounds are operable in the invention, the products derived from ethylenediamine are especially outstanding and constitute a preferred embodiment of the present invention.

Alternatively, the hydrophobic polyoxypropylene polymer can be prepared by reacting a polyoxypropylene glycol with the nitrogen base compound with removal of water. Also, instead of condensing ethylene oxide with the hydrophobic polyoxypropylene polymer, the lime soap dispersants can be prepared by etherifying the polyoxypropylene polymer with polyoxyethylene glycol. Furthermore, any alkylene oxide having an oxygen/carbon atom ratio of at least 0.5, such as butadiene dioxide, glycidol, and the like, can be used in lieu of ethylene oxide.

It is not necessary to use pure propylene oxide when preparing the polyoxypropylene polymer. Thus, the propylene oxide can contain small amounts of ethylene oxide, such as up to about 10 weight percent, although larger amounts of ethylene oxide alter the hydrophobic character of the polyoxypropylene polymer. Where small amounts of ethylene oxide, such as about 2 weight percent, are present in the propylene oxide, it is desirable to prepare higher molecular weight polyoxypropylene polymers for comparable results.

The lime soap dispersants must fulfill certain structural requirements if they are to be operable in the present invention. The hydrophobic polyoxypropylene polymer, with which ethylene oxide is condensed, is a mixture of isomers and must have an average molecular weight of at least 900 and preferably should be 2000 or more. Since the determined molecular weight of the polyoxypropylene polymer will vary somewhat with the analytical procedure used, it will be understood that this molecular weight requirement is based upon a hydroxyl number analytical procedure such as described by Ogg et al., Industrial and Engineering Chemistry, Analytical Edition, vol. 17, p. 395 (1945). In calculating the molecular weight it is assumed that one hydroxyl group is formed for each hydrogen atom present in the nitrogen base compound. The quantity of ethylene oxide condensed with the polyoxypropylene polymer must be such that the oxyethylene content constitutes 20–90%, by weight, of the final resultant product, as determined by the weight of ethylene oxide added to the reaction. A preferred group of compounds are those in which the oxyethylene content constitutes 50–75%, by weight, of the product. The structure of the individual compounds which constitute the lime soap dispersants is represented by the following formula:

$$\text{Polyoxypropylene polymer }[(C_2H_4O)_nH]_x$$

where:

The polyoxypropylene polymer is the condensation product of a nitrogen atom-containing compound having 2 or more reactive hydrogen atoms and propylene oxide,

n is an integer, and

x is an integer not larger than the number of reactive hydrogen atoms present in the nitrogen atom-containing compound from which the polyoxypropylene polymer is derived.

In the over-all mixture the polyoxypropylene polymer must have an average molecular weight of at least 900, as determined by hydroxyl number, and the oxyethylene content must constitute 20–90%, by weight, of the mixture, as determined by the weight of ethylene oxide added to the reaction.

The only important limitation on the molecular weight of the polyoxypropylene polymer is that it be above 900. Any polyoxypropylene polymer as described herein and having a molecular weight of over 900 can be condensed with ethylene oxide and the lime soap dispersant resulting therefrom can be used. The polymeric surface active agents, which are employed as lime soap dispersants in accordance with this invention, are available commerically now wherein the molecular weight of the hydrophobic polyoxypropylene polymer is about 25,000 and this molecular weight can be up to 50,000, or higher. The only limitations on the upper limit of the molecular weight of the polyoxypropylene polymer are economic in character.

As has been indicated, the soaps with which the lime soap dispersant is combined to provide the improved soap compositions of this invention, are the fatty acid soaps. Specifically, the fatty acid soaps used are the alkali metal or ammonium fatty acid soaps. Thus, sodium, potassium, or ammonium soaps of tallow and coconut oil, which are mixtures of palmitic, oleic and stearic acids, as well as rosin acids, are examples of the fatty acid soaps with which this invention is concerned.

The proportion of lime soap dispersant that is included in the improved soap compositions of the invention can be varied within wide limits, but seldom exceeds 25 weight percent of the soap present in the composition. A 25 weight percent concentration of the lime soap dispersant will prevent the formation of hard water curds in even the hardest water, and higher concentrations are seldom employed since the lime soap dispersant is more expensive than soap. It should be noted, however, that the lime soap dispersants, per se, are excellent detergents and operable compositions are obtained even when the lime soap dispersant constitutes the major component of the system.

The minimum amount of the lime soap dispersant to be used in the soap composition of the invention is determined by many factors, among the most important of which are the following:

(1) The hardness of the water in which the improved soap composition is to be used.

(2) The molecular weight of the hydrophobic polyoxypropylene polymer and the oxyethylene content of the lime soap dispersant.

(3) The concentration at which the improved soap composition is to be employed.

For general uses in waters of varying hardness, the lime soap dispersant should be from 5–25 weight percent of the soap present in the composition. In any event, the proper proportion of lime soap dispersant to be employed under any given set of conditions can be readily determined through routine experimentation by one skilled in the art, and the selection of the exact proportion of lime soap dispersant does not constitute a critical feature of the present invention.

The following examples are set forth to more clearly illustrate the principle and practice of the invention to those skilled in the art.

EXAMPLE 1

Part A

Into a 3-neck, round-bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, and propylene oxide feed inlet, there were placed 94.1 grams (1.57 mols) of ethylenediamine and 15.6 grams water. The flask was purged with nitrogen to remove air and heated to 90° C. with stirring. Propylene oxide was then introduced into the ethylenediamine as fast as it would react until 367 grams (6.33 mols) of propylene oxide had reacted. The water content of the product was then reduced to ca. 0.01% by vacuum stripping. The product was a viscous, amber-colored liquid having a calculated molecular weight of 292.

Part B

The product of Part A, in the amount of 250.7 grams (0.88 mol), together with 7 grams of NaOH was charged into the apparatus described in Part A. A total of 615 grams (10.6 mols) of propylene oxide was added to the reaction mixture at 120° C. over a period of 21 hours. The resulting polyoxypropylene polymer was a viscous, yellow liquid and had a molecular weight of 885, as determined by hydroxyl number.

In an analogus manner, additional propylene oxide was added in increments to the above described polyoxypropylene polmer to prepare additional polyoxypropylene polymers having molecular weights of 1109, 1380, 1705, 2220 and 3240, respectively, all of the molecular weights being determined by hydroxyl number.

Part C

Fifty grams (0.04 mol) of the polyoxypropylene polymer having a molecular weight of 1109, as described in Part B, was charged into the apparatus described in Part A. The NaOH in the polyoxypropylene polymer was not neutralized and served as the catalyst in the present step. Fifty three grams (1.2 mol) of ethylene oxide was condensed with the polyoxypropylene polymer at a temperature 130° C. over a period of 7 hours. The resulting product was a dark, amber-colored liquid and contained slightly over 50 weight percent oxyethylene content.

The molecular weights of the polyoxypropylene polymers prepared in Parts A and B were determined by hydroxyl number as set forth by Ogg et al., cited above.

EXAMPLES 2–29

Several additional lime soap dispersants were prepared by comdensing varying quantities of ethylene oxide with several polyoxypropylene polymers following the procedure illustrated in Example 1, Part C. The polyoxypropylene polymers were prepared by condensing propylene oxide with triethylene tetraamine, triisopropanolamine or n-butylamine following the general procedures illustrated in Example 1, Parts A and B. The composition of the lime soap dispersants is set forth in Table I:

TABLE I

Example No.	Nitrogen Base Compound	Molecular Weight Polyoxypropylene Polymer	Oxyethylene Content, Weight Percent of Compound
2	Ethylenediamine	1,860	37.5
3	do	1,860	62.5
4	do	1,860	90.0
5	do	2,270	37.5
6	do	2,270	62.5
7	do	2,270	90.0
8	do	2,980	37.5
9	do	2,980	62.5
10	do	2,980	75.0
11	do	2,980	90.0
12	do	3,180	25.0
13	do	3,180	37.5
14	do	3,180	75.0
15	do	3,180	90.0
16	do	3,420	50.0
17	do	3,420	75.0
18	Triethylene tetraamine	2,435	25.0
19	do	2,435	50.0
20	do	2,435	75.0
21	do	3,965	25.0
22	do	3,965	50.0
23	do	3,965	75.0
24	Triisopropanolamine	1,716	25.0
25	do	1,716	50.0
26	do	1,716	75.0
27	n-Butylamine	1,893	25.0
28	do	1,893	50.0
29	do	1,893	75.0

EXAMPLE 30

The compounds shown by Examples 18–23, inc., were combined with an alkali metal fatty acid soap to determine their ability to prevent the formation of lime soap curds in hard water.

Dilute solutions (0.3%) of a formulated medium titer alkali metal fatty acid soap were prepared in 180 p.p.m. hard water (as $CaCO_3$ and containing a 2/1 mol ratio of Ca to Mg.). The formulated soap was a proprietary

product comprising 60% medium titer soap, approximately 30% builders (phosphates, silicates and soda ash) and 10% moisture. The soap ingredient was a sodium soap, 38° C. titer, having an acid number of 227 and being derived from a mixture of approximately 10 parts tallow and 1 part coconut oil. A small proportion (0.02%) of the lime soap dispersant was added to the above prepared soap solutions. This quantity of lime soap dispersant constituted 10 weight percent of the actual soap present in the proprietary formulation. One part of each of the soap solutions containing a lime soap dispersant was then diluted with nine parts of 180 p.p.m. hard water. The resulting solutions were maintained at 120° F. for twenty minutes and were stirred with a mechanical stirrer at 80 r.p.m. After this period of time, the solutions were examined visually for the presence of lime soap curds.

All of the solutions containing the lime soap dispersant were essentially free of insoluble soap curds, or at most contained only a slight trace of fluocculated material. Moreover, the solutions were opalescent, thus indicating that the lime soap was highly dispersed throughout the solution as a colloid. In contrast to these results, a control solution prepared as stated above but containing no lime soap dispersant contained copious quantities of lime soap curds.

Similar results were obtained when the proportion of lime soap dispersant was varied from 4 to 25 weight percent of the soap present in the proprietary formulation.

Thus, it can be seen that the new soap compositions of this invention do effectively minimize the disadvantages associated with the formation of lime soaps in hard water. Broadly speaking, my invention resides in the composition of an alkali metal or ammonium fatty acid soap and the lime soap dispersant described herein.

What is claimed is:

1\. An improved soap composition comprising a fatty acid soap selected from the group consisting of sodium, potassium and ammonium fatty acid soaps and, as a lime soap dispersant, a mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical which is the residue of a nitrogen atom-containing reactive hydrogen compound having at least two reactive hydrogen atoms, said compound being selected from the group consisting of ammonia, lower alkyl primary amines having up to about 5 carbon atoms, lower alkanolamines having up to about 4 carbon atoms in the alkanol radical, aniline, hydrazine, N,N'-di(lower alkyl)-hydrazines having up to about 4 carbon atoms in the lower alkyl radicals, phenylhydrazine and aliphatic primary polyamines having up to about 6 carbon atoms, the structure of the lime soap dispersant compounds being such that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at sites of reactive hydrogen atoms thereby constituting a polyoxypropylene polymer, the oxyethylene groups being attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture being from 900 to about 50,000, as determined by hydroxyl number, and the oxyethylene groups present in the mixture constituting 20–90%, by weight, of the mixture, and the proportion of said lime soap dispersant in the composition being sufficient to materially reduce the formation of lime soap curds in hard water.

2\. An improved soap composition comprising a fatty acid soap selected from the group consisting of sodium, potassium and ammonium fatty acid soaps and, as a lime soap dispersant, from about 4 to about 25 weight percent, based upon the fatty acid soap, of a mixture of conjugated polyoxypropylene - polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical which is the residue of a lower alkyl primary amine having up to about 5 carbon atoms, the structure of the compounds being such that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at sites of reactive hydrogen atoms thereby constituting a polyoxypropylene polymer, the oxyethylene groups being attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture being from 900 to about 50,000, as determined by hydroxyl number, and the oxyethylene groups present in the mixture constituting 20–90%, by weight, of the mixture.

3. An improved soap composition comprising a fatty acid soap selected from the group consisting of sodium, potassium and ammonium fatty acid soaps and, as a lime soap dispersant, a mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical which is the residue of ethylenediamine, the structure of the compounds being such that all of the oxypropylene groups are present in the polyoxypropylene chains that are attached to the organic radical at sites of reactive hydrogen atoms thereby constituting a polyoxypropylene polymer, the oxyethylene groups being attached to the polyoxy-propylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture being from 900 to about 50,000, as determined by hydroxyl number, and the oxyethylene groups present in the mixture constituting 20–90%, by weight, of the mixture, the proportion of said lime soap dispersant in the composition being sufficient to materially reduce formation of lime soap curds in hard water.

4. An improved soap composition comprising a fatty acid soap selected from the group consisting of sodium, potassium and ammonium fatty acid soaps and, as a lime soap dispersant, from about 4 to about 25 weight percent, based upon the fatty acid soap, of a mixure of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical which is the residue of ethylenediamine, the structure of the compounds being such that all of the oxypropylene groups are present in the polyoxypropylene chains that are attached to the organic radical at sites of reactive hydrogen atoms thereby constituting a polyoxypropylene polymer, the oxyethylene groups being attached to the polyoxypropylene polymer in the polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture being from 900 to about 50,000, as determined by hydroxyl number, and the oxyethylene groups present in the mixture constituting 20–90%, by weight, of the mixture.

5. An improved soap composition comprising a water-soluble alkali metal fatty acid soap and, as a lime soap dispersant, a mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical which is the residue of a nitrogen atom-containing reactive hydrogen compound having at least two reactive hydrogen atoms, said compound being selected from the group consisting of ammonia, lower alkyl primary amines having up to about 5 carbon atoms, lower alkanolamines having up to about 4 carbon atoms in the alkanol radical, aniline, hydrazine, N,N'-di(lower alkyl)-hydrazines having up to about 4 carbon atoms in the lower alkyl radicals, phenylhydrazine and aliphatic primary polyamines having up to about 6 carbon atoms, the structure of the lime soap dispersant compounds being such that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at sites of reactive hydrogen atoms thereby constituting a polyoxypropylene polymer, the oxyethylene groups being attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture being from 900 to about 50,000, as determined by hydroxyl number, and the oxyethylene groups present in the mixture constituting 20–90%, by weight, of the mixture, and the proportion of said lime soap dispersant in the composition being sufficient to materially reduce the formation of lime soap curds in hard water.

6. An improved soap composition comprising a water-soluble alkali metal fatty acid soap and, as a lime soap dispersant, from about 4 to about 25 weight percent, based upon the fatty acid soap, if a mixture of conjugated polyoxypropylene-polyoxyethylene compounds containing in their structure oxypropylene groups, oxyethylene groups and an organic radical which is the residue of a lower alkyl primary amine having up to about 5 carbon atoms, the structure of the compounds being such that all of the oxypropylene groups are present in polyoxypropylene chains that are attached to the organic radical at sites of reactive hydrogen atoms thereby constituting a polyoxypropylene polymer, the oxyethylene groups being attached to the polyoxypropylene polymer in polyoxyethylene chains, the average molecular weight of the polyoxypropylene polymers in the mixture being from 900 to about 50,000, as determined by hydroxyl number, and the oxyethylene groups present in the mixture constituting 20–90%, by weight, of the mixture.

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