United States Patent Office 3,232,879 Patented Feb. 1, 1966

3,232,879

DETERGENT BARS HAVING GOOD SUDSING AND LIME SOAP DISPERSANT CHARACTERISTICS

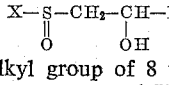
Henry Y. Lew, El Cerrito, Calif., assignor to Chevron Research Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Filed Mar. 8, 1962, Ser. No. 178,255
12 Claims. (Cl. 252—121)

This invention relates to detergent bars containing soap which do not react with the curd-forming components of hard water to form insoluble soaps. The bars may, in addition, contain a synthetic detergent. More particularly, the detergent bars of the present invention contain a lime soap dispersing agent which is either a methyl-β-hydroxyalkyl sulfioxide, an ethyl-β-hydroxyalkyl sulfoxide, or a β-hydroxyethyl-β-hydroxyalkyl sulfoxide. The sulfoxide of the present invention inhibits or prevents curd formation of the bar when used in hard water, and in some instances improves the foam characteristics as well.

It is well known that the use of ordinary toilet soaps in hard water gives rise to the formation and precipitation of insoluble fatty acids salts, commonly referred to as "lime soaps." These precipitated lime soaps tend to coagulate and form a sticky curd, which is especially noticeable in washstands, bathtubs, and the like, where it rises to the surface of the water and adheres around the tub or wash basin as a ring. In laundry applications the scum or curd affects the laundry tub in like manner but, in addition, adheres to the clothes. As a result, the clothes take on a gray, dingy appearance, develop spots upon ironing, and often a rancid odor. Similarly, when used for washing the hair, lime soaps are deposited thereon, giving the hair a coarse feeling and a dull appearance.

It has now been found that lime soap formation and precipitation can be substantially avoided by incorporating in the soap, e.g., a tallow soap, a minor but effective amount of a lime-soap dispersing agent which can be represented by the formula:



wherein R is an alkyl group of 8 to 16 carbon atoms, preferably 12 carbon atoms, and X, a member selected from the group of radicals having the formulae

—CH_3(methyl)

—C_2H_5(ethyl), or $HOCH_2CH_2$—(β-hydroxyethyl). It has further been found that a methyl-β-hydroxyalkyl sulfoxide, an ethyl-β-hydroxyalkyl sulfoxide, or a β-hydroxyethyl-β-hydroxyalkyl sulfoxide herein contemplated is effective to inhibit or prevent curd formation without, in the preferred embodiments, substantially impairing the foam properties of the soap. The lime soap dispersing agent of the present invention is effective in amounts ranging from about 5 to 90, preferably 10 to 25, percent by weight, based on soap and lime soap dispersing agent.

The soap which can be used in accordance with the present invention is not critical. Any of the water-soluble soaps in bar form normally used in industrial, laundering, and toilet applications are contemplated. As is known, these soaps can be prepared from a variety of fatty and oily materials, such as tallow, coconut oil, cottonseed oil, corn oil, soybean oil, olive oil, palm oil, lard, greases, fish oils, and the like. The cation portion of the soap is so selected as to impart sufficient hardness to the soap to form a bar. Thus, the cation can be sodium, potassium, or nitrogen-containing, such as the ammonium soaps or those derived from triethanolamine. In general, water-soluble sodium salts of fatty acids derived from tallow and coconut oil are preferred because of the ease with which they can be formed into a bar.

As indicated earlier, the invention also encompasses

ternary mixtures of soap, of the type hereinabove described, a methyl-β-hydroxyalkyl sulfoxide, an ethyl-β-hydroxyalkyl sulfoxide, or a β-hydroxyethyl-β-hydroxyalkyl sulfoxide and a synthetic detergent.

Indeed, it has been proposed in the past to use synthetic detergents, such as the organic alkyl sulfonates, alkyl sulfates, and alkyl benzene sulfonates, admixed with soap, to decrease its curd-forming tendency when used in hard water. Even here, however, the problem of lime soap formation and precipitation is not satisfactorily overcome.

The synthetic detergent component, like the soap, is also not critical. Broadly, it falls within the class of surface-active materials which are the water-soluble salts of organic sufonic acids and water-soluble salts of aliphatic sulfuric acid esters. In other words, synthetic detergents are contemplated which are water-soluble salts of organic sulfuric reaction products having in the molecular structure either a sulfonic acid or sulfuric acid ester radical.

As more specific examples of satisfactory synthetic detergent, there can be mentioned the water-soluble salts of alkyl benzene sulfonates, particularly those in which the alkyl group is a polypropylene radical or other carbon-containing chain, e.g., straight-chain radical, having an average of 8 to 15 carbon atoms in the radical; the water-soluble salts of alkyl sulfuric acid, having 8 to 18 carbon atoms in the alkyl group; the water soluble salts, such as the alkali metal salts of sulfuric acid esters of primary normal aliphatic alcohols containing 10 to 18 carbon atoms, such as lauryl and oleyl alcohol; primary and secondary alkyl sulfates having pronounced detergent power and obtained from primary or secondary alcohols and olefins. Other examples of the synthetic detergent component include the sulfuric acid esters which are the water-soluble salts of sulfuric acid esters of polyhydric alcohols incompletely esterified with high molecular weight soap-forming carboxylic acids, such as the water-soluble salts of sulfuric acid esters of higher molecular weight fatty acids monoglycerides, more specific examples being sodium glyceryl monolaurate sulfate and potassium glyceryl monopalmitate sulfate.

Also useful are the water-soluble salts of sulfuric acid esters of the hydroxy ethers resulting from the reaction of an aliphatic alcohol and ethylene glycol. These compounds have the general formula:

$$C_nH_{2n+1}—O—(CH_2CH_2—O)_xSO_3M$$

wherein n=8 to 20; x=1 to 4; and M is an alkali metal. A typical example is the sodium salt of lauryl ether of ethylene glycol monosulfuric acid.

Another type of useful detergents are the water-soluble salts of monosulfuric acid esters of the monoethers of lower molecular weight aliphatic alcohols and glycerine. These compounds have the general formula:

$$C_nH_{2n+1}—O—CH_2—CHOH—CH_2—O—SO_3M$$

wherein n=8 to 20 and M is an alkali metal. A typical example is the sodium salt of monolauryl ether of glycerine monosulfuric acid.

Still additional examples of sulfuric acid ester synthetic detergents are water-soluble salts of sulfated higher fatty acid alkanolamides, such as the sodium salt of sulfated coconut oil fatty acid ethanolamide, and the potassium salt of sulfated tallow oil fatty acid isopropanolamide.

The method of addition of the additive of the present invention is not critical. It thus can be added to the crutcher after the soap has been made by saponification of fats. Or the additive can be added to soap chips and detergent in the amalgamator, if desired, along with other soap additives conventionally used, such as coloring agents, perfume, fillers and the like.

The ternary mixtures of the invention will generally comprise, in weight percent, based on soap, synthetic detergent, and lime soap dispersant, 5 to 90, preferably 30 to 50, soap; 5 to 90, preferably 30 to 50, synthetic detergent; and 5 to 90, preferably 10 to 40, lime soap dispersant.

In evaluating a satisfactory lime soap dispersant, a good method and the one used in the examples hereinbelow appearing is as follows: A stock solution of the test dispersant is prepared by dissolving 1 part by weight of the dispersant in 99 parts of distilled water. Stock solutions of tallow soap[1] and of the various synthetic detergents are also prepared, again the concentration of the organic material in the solution being 1% by weight.

[1] Tallow soap had 5.5% water, and on acidification and extraction with petroleum ether gave 85.6% fatty acids. The fatty acid component had an acid number of 202 and an iodine number of 50, and contained 2% lauric acid, 4% myristic acid, 33% palmitic acid, 22% stearic acid, and 39% oleic acid.

Since the stock solutions are made up to the same concentration, the relative amount of each solution determines the relative percents of tallow soap or tallow soap plus synthetic detergents and dispersant for each test. For example, a 10% dispersant test is carried out as follows: Place 1 ml. of the dispersant solution and 9 ml. of the tallow soap containing solution in the bottom of a 100 ml. stoppered graduate cylinder and swirl it gently. When well mixed, dilute with 90 ml. of 334 p.p.m. hard water (2 parts calcium to 1 part magnesium, calculated as carbonates) at 110° F. The final hardness is 300 p.p.m. The graduate is then shaken vigorously for 15 seconds, and then allowed to stand for 5 minutes. At the end of this time, the milliliters of curd and the milliliters of foam are measured and recorded.

The following tabulated examples illustrate the practice of the invention.

TABLE I

Lime soap dispersants—binary systems (β-hydroxyalkyl sulfoxides and soap)

Ex.	Compound	Concentration	Soap	Concentration	Ml. Curd	Ml. Foam
1	None		Tallow	100%	10	5
	This is the base case, i.e., soap without any dispersant.					
2	$CH_3-\overset{\overset{O}{\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{10}H_{21}$	15%	Tallow	85%	0	15
	In contrast to Example 1, all curd is eliminated, and three times as much foam is formed.					
3	$CH_3-\overset{\overset{O}{\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{12}H_{25}$	15%	Tallow	85%	0	8
	The example shows the effect of increasing chain length 2 carbon atoms over Example 2. The curd is still eliminated; the foam volume is still greater than the control (Example 1).					
4	$CH_3-\overset{\overset{O}{\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{14}H_{29}$	15%	Tallow	85%	0	0
	No curd formation occurs, though the chain length is increased by two more carbon atoms over Example 3.					
5	$CH_3-\overset{\overset{O}{\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_8H_{17}$	15%	Tallow	85%	0	10
	This example shows the effect of decreasing chain length 2 carbon atoms (see Example 2). The curd is still eliminated and the foam is two times the control value (Example 1).					
6	$CH_3(CH_2)_2-\overset{\overset{O}{\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_6H_{13}$	15%	Tallow	85%	10	10
	This example using n-propyl-β-hydroxyoctyl sulfoxide is unsatisfactory.					
7	$CH_3-\overset{\overset{O}{\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{14}H_{29}$	10%	Tallow	90%	1	3
	This shows the effect of decreasing the additive concentration as compared with Example 4. A small amount of curd forms, and there is some foam.					
8	$HOCH_2CH_2-\overset{\overset{O}{\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{10}H_{21}$	10%	Tallow	90%	0	10
	This example shows the effectiveness of β-hydroxyethyl-β-hydroxyalkyl sulfoxides. All curd is eliminated and good foam is obtained.					
9	$HOCH_2CH_2-\overset{\overset{O}{\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{10}H_{21}$	75%	Tallow	25%	0	25
	This example shows effect of increasing the additive concentration 7½ times as compared with Example 8. Now the foam is increased and no curd is formed.					

TABLE I—Continued

Lime soap dispersants—binary systems (β-hydroxyalkyl sulfoxides and soap)

Ex.	Compound	Concentration	Soap	Concentration	Ml. Curd	Ml. Foam
10	$HOCH_2CH(O)S-CH_2-CH(OH)-C_{10}H_{21}$	5%	4:1 Tallow: Coconut.	95%	2	10
	Reducing the additive concentration below the preferred range (see Example 8) gives some curd, but the foam is satisfactory.					
11	$C_{12}H_{25}$-(benzene)-SO_3Na	20%	Tallow	80%	10	20
	A commercial polypropylene benzene sulfonate, a typical detergent, was used in this example. It does not eliminate curd, although foam property is improved.					
12	$CH_3CH_2S(O)CH_2CH(OH)-C_{10}H_{21}$	15%	Tallow	85%	1	15
	Ethyl-β-hydroxyalkyl sulfoxides are also effective as shown in this example.					

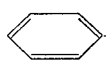
TABLE II

Lime soap dispersants—ternary system (β-hydroxyalkyl sulfoxide, soap, and a detergent)

Ex.	Additive	Concentration	Detergent	Concentration	Soap	Concentration	Ml. Curd	Ml. Foam
1	None		None		Tallow	100%	10	5
2	None		Polypropylene benzene Sulfonate	20%	Tallow	80%	10	20
	This example shows that the presence of the synthetic detergent has no effect on curd but increases foam volume.							
3	$CH_3-S(O)-CH_2-CH(OH)-C_{10}H_{21}$	10%	Polypropylene benzene Sulfonate	20%	Tallow	70%	0	12
	In contrast to Examples 1 and 2, the presence of a lime soap dispersant improves the curd property of the composition.							
4	$CH_3-S(O)-CH_2-CH(OH)-C_{14}H_{29}$	10%	Polypropylene benzene Sulfonate	20%	Tallow	70%	0	12
	This example shows that increasing the chain length four carbon atoms does not adversely affect foam and curd properties.							
5	$HOCH_2CH_2-S(O)-CH_2-CH(OH)-C_{10}H_{21}$	7%	Polypropylene benzene Sulfonate	20%	Tallow	73%	0	22
	Replacement of the methyl group (Example 3) with a β-hydroxyethyl group still gives good results. Even at a lower concentration of additive there is no curd, and the foam is equivalent to the best.							
6	$HOCH_2CH_2-S(O)-CH_2-CH(OH)-C_{10}H_{21}$	10%	Sodium Lauryl Sulfate	10%	Tallow	80%	0	20
	The additive of Example 5 is effective with another type of detergent, i.e., a primary sulfate.							
7	$HOCH_2CH_2-S(O)-CH_2-CH(OH)-C_{10}H_{21}$	10%	Sodium Paraffin Sulfonate	10%	4:1 Tallow: Coconut.	80%	0	5
	The paraffin group of the sulfonate is a mixture of C_{10} to C_{20} straight chain compounds. No curd appears here.							
8	$HOCH_2CH_2-S(O)-CH_2-CH(OH)-C_{10}H_{21}$	5%	Mixed Secondary Alcohol Sulfates	10%	Tallow	85%	1	10
	These mixed alcohol sulfates contain alkyl groups ranging from C_{10} to C_{20} in carbon content. Compared with Examples 1 and 5, shows that even at very low concentrations this additive reduces curd by a factor of 10 and doubles the foam.							

TABLE II—Continued

Lime soap dispersants—ternary system (β-hydroxyalkyl sulfoxide, soap, and a detergent)

Ex.	Additive	Concentration	Detergent	Concentration	Soap	Concentration	Ml. Curd	Ml. Foam
9	$HOCH_2CH_2-\overset{\overset{O}{\|\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{10}H_{21}$	10%	Ammonium Nonylphenol Tetraethylene Glycol Sulfate.	10%	Tallow	80%	0	2
	Compared with Example 5, it is shown that the additive still eliminates all curd with this type of detergent.							
10	$HOCH_2CH_2-\overset{\overset{O}{\|\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{10}H_{21}$	10%	1:1 Sodium Lauryl Sulfate:Polypropylene Benzene Sulfonate.	20%	Tallow	70%	0	25
	This example shows the additive to function very well with a mixture of detergents.							
11	$HOCH_2CH_2-\overset{\overset{O}{\|\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{10}H_{21}$	65%	Polypropylene Benzene Sulfonate.	5%	4:1 Tallow: Coconut.	30%	0	25
	Even at very high concentrations of additive, the foam properties are excellent, and no curd is formed, as shown in this example.							
12	$HOCH_2CH_2-\overset{\overset{O}{\|\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_{10}H_{21}$	10%	Polypropylene Benzene Sulfonate.	70%	Tallow	20%	0	25
	High concentrations of detergent has no adverse effects on either foam or curd.							
13		10%	Polypropylene Benzene Sulfonate.	20%	Tallow	70%	5	12
	Compared with Examples 3 and 5, it is shown that a phenyl group in place of a methyl or β-hydroxyethyl group destroys the lime soap dispersant properties.							
14	$CH_3(CH_2)_2-\overset{\overset{O}{\|\|}}{S}-CH_2-\overset{\overset{OH}{\|}}{CH}-C_6H_{13}$	10%	Polypropylene Benzene Sulfonate.	10%	Tallow	80%	8	12
	Compared with Examples 3 and 5, it is shown that a propyl group in place of a methyl, an ethyl, or β-hydroxydodecyl group destroys the lime soap dispersant properties.							
15	$CH_3CH_2-\overset{\overset{O}{\|\|}}{S}-CH_2\overset{\overset{OH}{\|}}{CH}-C_{10}H_{21}$	10%	Polypropylene Benzene Sulfonate.	10%	Tallow	80%	Trace	12
	An ethyl group in place of the methyl group does not substantially impair foam and curd-dispersing properties.							

I claim:

1. A detergent bar having good sudsing and lime soap dispersant characteristics, and suitable for use in hard water consisting essentially of water-soluble solid soap normally having poor lime soap dispersant characteristics, and a lime soap dispersant having the formula

$$X-\overset{\overset{O}{\|}}{S}-CH_2\overset{\overset{OH}{|}}{CH}-R$$

wherein X is a member selected from the group consisting of the methyl, ethyl and β-hydroxyethyl radicals, and R, an alkyl radical of 8 to 16 carbon atoms; said lime soap dispersant being present in an amount of 5 to 90 percent by weight, based on it and soap.

2. A detergent bar according to claim 1, wherein the lime soap dispersant is present in an amount of 10 to 25 percent.

3. A detergent bar according to claim 1, wherein R is an alkyl radical of 8 to 12 carbon atoms.

4. A detergent bar according to claim 1, wherein the lime soap dispersant is a methyl-β-hydroxyalkyl sulfoxide having 10 to 16 carbon atoms in the alkyl group.

5. A detergent bar according to claim 1, wherein the lime soap dispersant is an ethyl-β-hydroxyalkyl sulfoxide.

6. A detergent bar according to claim 1, wherein the lime soap dispersant is a β-hydroxyethyl-β-hydroxyalkyl sulfoxide.

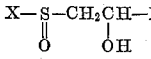
7. A detergent bar having good sudsing and lime soap dispersant characteristics, and suitable for use in hard water, consisting essentially of a mixture of a water-soluble solid soap and a water-soluble synthetic detergent salt of an organic sulfuric reaction product having in its molecular structure a member selected from the group consisting of sulfonic acid and sulfuric acid ester radicals, said mixture having poor lime-soap dispersing characteristics and a lime soap dispersant to impart lime soap dispersing properties to the mixture, said lime soap dispersant having the formula

$$X-\overset{\overset{O}{\|}}{S}-CH_2-\overset{\overset{OH}{|}}{CH}-R$$

wherein X is a member selected from the group consisting of the methyl, ethyl, and β-hydroxyethyl radicals; and R, an alkyl radical of 8 to 16 carbon atoms; the aforesaid ingredients being present in amounts by weight percent based on soap, lime soap dispersant, and synthetic detergent ranging from 5 to 90 soap; 5 to 90 synthetic detergent; and 5 to 90 lime soap dispersant.

8. A detergent bar according to claim 6, wherein the ingredients are present in amounts of 30 to 50 percent soap, 30 to 50 percent synthetic detergent, and 10 to 40 percent lime soap dispersant.

9. A detergent bar according to claim 6 wherein the lime soap dispersant has the formula



wherein X is a member of the group consisting of ethyl, methyl, and hydroxyethyl radicals, and R is an alkyl radical of 8 to 14 carbon atoms.

10. A detergent bar according to claim 8, wherein the lime soap dispersant is a methyl-β-hydroxyalkyl sulfoxide.

11. A detergent bar according to claim 8, wherein the lime soap dispersant is a hydroxyethyl-β-hydroxyalkyl sulfoxide.

12. A detergent bar according to claim 8, wherein the lime soap dispersant is an ethyl-β-hydroxyalkyl sulfoxide.

References Cited by the Examiner

UNITED STATES PATENTS

2,390,295	12/1945	Flett	252—121
2,407,647	9/1946	Bodman	252—121
2,515,120	7/1950	Harman	260—607
2,654,667	10/1953	Goodhue et al.	252—161
2,658,038	11/1953	Proell	252—161
2,749,315	6/1956	Faier	252—117
2,787,595	4/1957	Webb	252—138
3,043,824	7/1962	Oswald et al.	260—607

JULIUS GREENWALD, *Primary Examiner.*

ALBERT T. MEYERS, *Examiner.*