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[54] **SYNTHETIC DETERGENT BARS CONTAINING CALCIUM OLEFIN SULFONATES**

[76] Inventors: **Gar Lok Woo,** 4 Janet Way, Apt. 105, Tiburon, Calif. 94920; **Ralph House,** 3891 Linden Ln., Richmond, Calif. 94803

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[58] **Field of Search** 252/138, 161, 555

[56] **References Cited**

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Primary Examiner—Leon D. Rosdol

Assistant Examiner—P. E. Willis

[57] **ABSTRACT**

Nonsoap synthetic detergent bars consisting essentially of olefin sulfonates in which the hydrocarbon portions contain from 8 to 20 carbon atoms and have an average molecular weight of from 165 to 200, the sulfonates being salts of water-soluble salt-forming cations, at least 80 mol percent of the salts being calcium olefin sulfonates.

5 Claims, No Drawings

SYNTHETIC DETERGENT BARS CONTAINING CALCIUM OLEFIN SULFONATES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention is concerned with synthetic nonsoap detergent bars, and more particularly with bars or cakes for toilet or bath use prepared from mixtures of the calcium salts of olefin sulfonates.

Although synthetic detergents have largely replaced soaps for most household laundering and dishwashing uses, they have found little acceptance in the household toilet bar area. Although the detergent literature is replete with examples of synthetic detergent bars and synthetic detergent-soap combination bars, the toilet bar market continues to be dominated by soap bars. The combination bars have had appreciable acceptance, but they exhibit the high pH characteristic of soap bars. At the present time it appears that less than 1% of the bar market is satisfied by all-synthetic detergent bars.

Two factors seem to account for the small impact of all-synthetic detergent bars on the bar market, physical property deficiencies and high cost.

The essential physical properties required in a synthetic detergent bar use are relatively low solubility and a generally amorphous rather than crystalline character. High solubility results in high wear rate, short life in use and sloughing when the bar is laid aside wet or allowed to stand on a wet surface. High crystallinity makes it extremely difficult to press the detergent into a bar which has good physical strength and is resistant to cracking or crumbling. The alkyl benzene sulfonates are representative of the synthetic detergents which have failed in bar use because of too high solubility and while many suggestions have been made as to additives which would control the high solubility deficiency, no bar based on a highly soluble detergent has succeeded commercially. The alkyl sulfates are representative of synthetic detergents which have failed in bar use because of too crystalline a character. Various additives have been proposed for use with the alkyl sulfates in forming bars but no satisfactory combination appears to have been found. It is common experience that an additive which does tend to modify the undesirable properties of a synthetic detergent introduces new problems which arise out of the character of the additive itself—for example, the development of rancidity on storage.

Olefin sulfonates have been employed in detergent bars either in combination with soap or with other synthetic materials such as fatty acid sulfonates, fatty alcohol sulfonates, primary paraffin sulfonates, etc. Netherlands patent application No. 67/03874 discloses synthetic detergent bars prepared from sodium, potassium, ammonium, and magnesium salts of C_{12}–C_{24} alpha olefin sulfonates.

SUMMARY OF THE INVENTION

Nonsoap synthetic detergent bars are provided consisting essentially of olefin sulfonates, the hydrocarbon portions of which have from 8 to 20 carbon atoms and a molecular weight in the range of about 165 to 200, the sulfonates being salts of water-soluble salt-forming cations, at least 80 mol percent of the salts being calcium olefin sulfonates. In the preferred materials at least 90 mol percent of the sulfonates are calcium salts.

The balance of the salt-forming cations, which may be optionally present, may be any of numerous materials such as alkali metal, alkaline earth metal, ammonium or various nitrogen-containing cations, etc. Examples of suitable organic cations include amino materials such as those of the following structure:

$$NH_2^+(CH_2CH_2OH)_2 \text{ or } NH^+(CH_2CH_2OH)_3$$

The alkali metal cations are preferred, and sodium ions are particularly preferred.

These bars have excellent latherability and, due to their low solubility compared with other metal salts of similar olefin sulfonates, may be formed into bars which have extremely low slough loss.

Not only do nonsoap detergent bars based on olefin sulfonate as the major active detergent material have excellent physical properties, they also have a pH in the range 6.5 to 7, the pH being measured in a 1% solution of the active material in water. In this respect bars based on olefin sulfonate are markedly superior to soap and to combination soap-synthetic detergent bars. The importance of the pH property is clearly shown by Dr. Irwin Kantor's paper entitled, "Value of a Neutral Detergent Bar Instead of Alkaline Soap in the Routine Care of Aging Skin", Journal of the American Geriatric Society, March 1962, pp. 242–246. In addition to the superior physical and chemical properties of nonsoap synthetic detergent bars based on olefin sulfonate, it should be noted that these properties are found not in an esoteric chemical compound but in a material that can be easily and cheaply produced in large volume from readily available and inexpensive starting materials.

The term "olefin sulfonates" as used in the present invention defines the complex mixture obtained by the SO_3 sulfonation of straight-chain olefins containing 10 to 24 carbon atoms and subsequent neutralization and hydrolysis of the sulfonation reaction product. This complex mixture contains hydroxyalkane sulfonates and alkene sulfonates as its major components and a lesser proportion of disulfonated product.

While the general nature of the major components of the complex mixture is known, the specific identity and the relative proportions of the various hydroxy, sulfonate and disulfonate radicals and double bond locations are unknown. Accordingly, a determination of the entire chemical makeup is exceedingly difficult and has not heretofore been successfully accomplished. The mixture is best defined by the process used for producing it.

Optimum detergent bar properties are exhibited by an olefin sulfonate product which contains from about 25 to 75% by weight alkene sulfonates, from about 25 to 65% by weight hydroxyalkane sulfonates and not more than 20 weight % disulfonates. These optimum compositions are obtained by SO_3-air sulfonation of C_{10-24} straight-chain olefins with an SO_3:air volume ratio of about 1 to 50–100 and an SO_3:olefin mol ratio of 0.95 to 1.15, and neutralization and hydrolysis of the sulfonation reaction product at temperatures of 145° to 200°C using one equivalent of base per mol of SO_3 consumed in the sulfonation step.

In addition to the straight-chain alpha-olefins from wax cracking suitable olefin starting materials include straight-chain alpha olefins produced by Ziegler polymerization of ethylene, or internal straight-chain olefins prepared by catalytic dehydrogenation of normal

paraffins or by chlorination-dehydrochlorination of normal paraffins. The olefins may contain from 8 to 20 carbon atoms, usually 10 to 15 carbon atoms, and preferably 11 to 14 carbon atoms per molecule. Olefin mixtures must have an average molecular weight of at least about 165 but not more than 200.

The amount of SO_3 utilized in the sulfonation reaction may be varied but is usually within the range of 0.95 to 1.25 mols of SO_3 per mol of olefin and preferably in the range 1:1 to 1:1.15. Greater formation of disulfonated products is observed at higher SO_3:olefin ratios. Disulfonation may be reduced by carrying the sulfonation reaction only to partial conversion of the olefin—for example, by using SO_3:olefin ratios of less than 1 and removing the unreacted olefins by a deoiling process. The unreacted olefins may be removed by extracting the reaction product with a hydrocarbon such as pentane.

In order to obtain a product of good color, the SO_3 employed in the sulfonation reaction is generally mixed with an inert diluent or with a modifying agent. Inert diluents which are satisfactory for this purpose include air, nitrogen, SO_2, dichloromethane, etc. The volume ratio of SO_3 to diluent is usually within the range of 1:100 to 1:1.

The following examples describe the preparation of calcium olefin sulfonates and of detergent bars employing these materials as the major active component.

EXAMPLE 1

Preparation of C_{15}–C_{18} Sulfonates

The reactor used for this sulfonation consisted of a continuous falling film-type unit in the form of a vertical water-jacketed tube. Both the olefin and the SO_3-air mixture were introduced at the top of the reactor and flowed concurrently down the reactor. At the bottom the sulfonated product was separated from the air stream.

The feed was a straight-chain 1-olefin blend produced by cracking highly paraffinic wax and having the following composition by weight: 1% tetradecene, 27% pentadecene, 29% hexadecene, 28% heptadecene, 14% octadecene and 1% nonadecene. This material was charged to the top of the above-described reactor at a rate of 306 pounds/hour. At the same time 124.2 pounds/hour of SO_3 diluted with air to 3% by volume concentration of SO_3 was introduced into the top of the reactor. The reactor was cooled with water to maintain the temperature of the effluent product within the range of 43-46°C. The average residence time of the reactants in the reactor was less than two minutes.

After passing out of the reactor the sulfonated product was mixed with 612 pounds/hour of 11.2% aqueous caustic and heated to 145°–150°C. in a tubular reactor at an average residence time of 30 minutes. This step neutralized the sulfonic acids contained in the sulfonation reaction product, hydrolyzed the sultones to hydroxy sulfonic acids and alkene sulfonic acids and neutralized the hydroxy alkane sulfonic and alkene sulfonic acids. Olefin sulfonates were produced at the rate of 463 pounds per hour as an aqueous solution having 45% by weight solids content and a pH of 10.8.

A portion of this product was analyzed and shown to be made up of the sodium salts of alkene sulfonic acids, hydroxy alkane sulfonic acids, and disulfonic acids. These three major components were present in a weight ratio of about 50/35/15.

The calcium salt was prepared in the same way, using a 5% calcium hydroxide solution for neutralization and hydrolysis. Other salts were prepared in essentially the same way using aqueous solutions of potassium hydroxide and magnesium hydroxide.

EXAMPLE 2

Preparation of Other Olefin Sulfonates

The above reaction was repeated using 1-undecene as the feed stock at a 1-undecene:SO_3 mol ratio of 1.85. The reactant temperature was maintained at 25°C throughout the run. The reaction product was neutralized and hydrolyzed with a 5% calcium hydroxide solution. The product was then desalted by adding isopropyl alcohol and filtering. It was deoiled by extraction with n-pentane and then dried to give calcium undecene sulfonate.

Essentially the same procedure was followed in preparing calcium olefin sulfonates from 1-dodecane, 1-tridecene and 1-tetradecene. Then equal amounts of each of the C_{11}, C_{12}, C_{13}, and C_{14} calcium salts were dissolved in water and then dried to give the C_{11}–C_{14} bar forming material.

The reaction product from the sulfonation step may be neutralized with aqueous slurries or solutions containing hydroxides, carbonates, oxides, chlorides, etc., of calcium. In the preferred method sufficient neutralizing slurry or solution may be added to provide for neutralization of the alkene and hydroxy alkane sulfonic acids formed by sultone hydrolysis. Generally, one equivalent of calcium for each mol of SO_3 consumed in the sulfonation reaction is added to the sulfonation reaction product.

The proportion of hydroxyalkane sulfonates to alkene sulfonates in the hydrolyzed neutralized product may be varied somewhat by the manner in which neutralization and hydrolysis are carried out. Thus reduced amounts of hydroxyalkane sulfonates are obtained by carrying out the neutralization and hydrolysis at temperatures in the range of 145°–200°C while higher yields of hydroxy sulfonate are favored by carrying out the neutralization and hydrolyses at temperatures below 100°C. Suitable hydrolysis temperatures range from about 100° to 200°C.

Olefin sulfonates with mixed cations, such as calcium and magnesium, were prepared by dissolving the requisite amount of each salt in water, stirring well, and then drying to obtain the bar forming material.

EXAMPLE 3

Preparation of Detergent Bars from Various Olefin Sulfonate Salts

Following the general procedure of Example 2, calcium, magnesium, sodium, potassium, and mixed sodium and calcium, potassium and magnesium, and potassium and calcium sulfonates were prepared and made into bars. The following procedure was utilized for bar preparation: In the first step, the particular olefin sulfonate mixture and from 2 to 15% of water were milled into ribbons to provide a homogenous composition. It was then formed into a bar by molding it into a conventional soap bar mold. The bars formed in this manner are about 2⅛ inches by 1⅜ inches by ⅝ inch in size. These bars are aged by exposure to air in a room at ambient temperature and humidity for one week. The bars then weigh between 23 and 28 grams.

The bars prepared in Example 3 were tested for wear rate, slough loss and lather rating. The lather rating and wear rate are average values obtained from washing pre-washed hands by a panel of 12 to 15 people. The wear rate, which is a measure of the solubility characteristics of the detergent bar in actual use, is expressed in grams weight loss per wash (g/wash). The lather rate is a measure of the amount of lather produced in ordinary hand washing with a rating of 1 being slight lather, 2, moderate lather, and 3, copious lather.

The slough loss test is run by placing the bar in a 3½ inch I.D. Petri dish containing 30 ml. of water having 50 ppm hardness. After 18 hours the bar was removed and any loose gel was rubbed off. Then the bar was allowed to dry for 24 hours and weighed. The loss in weight of the bar in percent is reported as slough loss.

TABLE

Properties of Detergent Bars
Prepared from Calcium Olefin Sulfonates

Test No.	Olefin Sulfonate Type (Cation) % by Weight of Active	Alkyl Carbons	Slough Loss, %	Wear Rate, g./wash	Lather Rating
1	Calcium, 100%	12	0	0.22	2.6
2	do.	14	0.2	0.08	2.5
3	do.	11–14	0	0.17	3.0
4	do.	15–18	0	0.11–0.22	1.5
5	Calcium, 80% Potassium, 20%	do.	4	0.29	1.6
6	Calcium, 60% Potassium, 40%	do.	13	0.60	2.3
7	Calcium, 40% Potassium, 60%	do.	31	0.84	3.0
8	Calcium, 40% Sodium, 60%	do.	54	0.59	2.9
9	Magnesium, 100%	do.	61	0.55	2.7
10	Potassium, 100%	do.	51	0.83	2.9
11	Potassium, 50% Magnesium, 50%	do.	60	0.55	2.8
12	Sodium, 100%	15–18	100	0.99	2.8

These data show that the slough loss of detergent bars prepared from calcium olefin sulfonates of 11 to 14, 12, and 14 carbon atoms are remarkably superior to those prepared from other salts. The bars thus show negligible slough loss and a very small wear rate, yet they retain good and even excellent lather ratings. Bars prepared from materials having a higher molecular weight (15-18 carbons), while showing excellent slough loss, have insufficient lathering properties and are thus not acceptable bars.

In addition to the calcium olefin sulfonate detergent component of the bars of this invention, other conventional actives may be included in the bars. For example, superfatting agents, oxidation inhibitors, opacity-producing material such as titanium dioxide, bactericides such as trichlorocarbanilide and hexachlorophene, plasticizers, chelate forming materials such as versene, propiones, oils, dyes, may be included in the bars.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the following claims.

We claim:

1. Nonsoap synthetic detergent bar having improved slough loss characteristics, said bar consisting essentially of olefin sulfonates the hydrocarbon portions of which have from 8 to 20 carbon atoms and molecular weights in the range of about 165 to 200, said sulfonates being the salts of water-soluble salt-forming cations, at least 80 mol percent of said salts being calcium olefin sulfonates.

2. Synthetic detergent bar according to claim 1 wherein at least 90 mol percent of the olefin sulfonates are calcium olefin sulfonates.

3. Synthetic detergent bar according to claim 1 wherein the olefin sulfonates are alpha olefin sulfonates.

4. Synthetic detergent bar according to claim 1 wherein the hydrocarbon portions of the olefin sulfonates contain from 10 to 15 carbon atoms.

5. Synthetic detergent bar according to claim 4 wherein the hydrocarbon portions of the olefin sulfonates contain from 11 to 14 carbon atoms.

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