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3,738,935

HYDROGENATED OLEFIN SULFONATE-SOAP COMBINATION TOILET BARS CONTAINING ALKANOLAMINES

Gar Lok Woo, Tiburon, Calif., assignor to Chevron Research Company, San Francisco, Calif.

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5 Claims

ABSTRACT OF THE DISCLOSURE

The inclusion of a minor portion of trialkanolamines in combination with sodium hydrogenated olefin sulfonate detergent and soap bars which contain more than 5% by weight of inorganic salt prevents blotching of the bar surfaces.

BACKGROUND OF THE INVENTION

Combination soap and detergent bars which offer substantial advantages over bars comprised of either of the materials alone have been disclosed in the art. For example, U.S. patent application Ser. No. 849,207 now Pat. No. 3,607,776 filed Aug. 11, 1969, discloses and claims "combars" comprising a certain mixture of soap and a particular detergent active that provides the desirable feel of soap bars and the noncurd-forming character inherent in detergent bars. The bars of the above-mentioned application consist essentially of a major proportion of one or more water-soluble salts of fatty acids having from about 10 to 20 carbon atoms and a minor proportion of C₁₀-C₂₄ hydrogenated olefin sulfonates sufficient to retain in suspension the insoluble lime soaps resulting from use of the bar in hard water.

While these combination bars have excellent lathering, slough loss, and feel characteristics, it has been found that they suffer an apparent disadvantage in that due to the inorganic salt content of the bars during storage their surfaces develop a mottled appearance. This appearance results from the formation upon the surface of the bar of visible white blemishes, possibly crystalline in structure, which decrease the commercial attractiveness of the bars.

SUMMARY OF THE INVENTION

It has now been found that surface blemishing may be prevented in combination sodium hydrogenated olefin sulfonate detergent and soap bars containing more than 5% by weight of inorganic salts by the inclusion in the bar of a minor amount of a trialkanolamine of 3 to 9 carbon atoms. The preferred trialkanolamine is triethanolamine. It is employed in minor quantities in the bar, i.e. from about 0.5 to 10 weight percent.

DESCRIPTION OF THE INVENTION

The soaps used in the compositions of this invention are any of the conventional soaps. These soaps are water-soluble salts of fatty acids having from about 10 to 20, preferably from 12 to 18, carbon atoms. The usual water-soluble salt is the sodium salt; but other salts, such as the potassium or ammonium salts, may also be used. The fatty acid portion of the soap is a straight-chain carboxylic acid. These acids are usually obtained by the saponification of fats, e.g. tallow, or of oils, e.g. coconut oil. However, suitable acids may also be obtained by the oxidation of normal paraffins. The fatty acid salts usually found in soaps include lauric, myristic, palmitic, oleic, and stearic.

The hydrogenated olefin sulfonates which comprise one component of the bars of this invention are mixed sulfonates obtained by

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- (2) Neutralizing and hydrolyzing the product of (1),
- (3) Hydrogenating from 50 to 100 percent of the unsaturated carbon-to-carbon double bonds in the product of (2).

5 The hydrogenated olefin sulfonates are present in amounts of at least about 5% of the total weight of soap and hydrogenated olefin sulfonate sufficient to retain in suspension the insoluble lime soaps resulting from use in hard water.

10 The trialkanolamines may comprise either mixed or nonmixed compounds—that is, the alkylol groups may be the same or different in each molecule. For example, suitable compounds include ethanol dipropanolamine, and propanol diethanolamine, etc. As previously mentioned, the preferred material is triethanolamine because of its commercial availability. The alkanolamine is employed in quantities of from 0.5 to 10% by weight of the bar and preferably from about 1.0 to 6% by weight.

20 The hydrogenated olefin sulfonates are obtained by the catalytic hydrogenation of olefin sulfonates. The term "olefin sulfonates," as used in the present invention, defines the complex mixture obtained by the SO₃ 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.

30 While the general nature and 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 general process used for producing it as herein described.

40 Optimum combar properties are exhibited by a composition obtained by hydrogenating 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 percent disulfonates. These optimum compositions are obtained by SO₃:air volume ratio of about 1:50–100, and an SO₃:olefin mole ratio of 1.05–1.25:1 followed by neutralization and hydrolysis of the sulfonation reaction product at temperatures of 145–250° C. using one equivalent of base per mole of SO₃ consumed in the sulfonation step.

50 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 10 to 24 carbon atoms, usually 13 to 22 carbon atoms, per molecule. Olefin mixtures should have an average molecular weight of at least about 200.

60 The amount of SO₃ utilized in the sulfonation reaction may be varied but is usually within the range of 0.95 to 1.35 moles of SO₃ per mole of olefin and, preferably, in the range of 1.05–1.25:1. Greater formation of disulfonated products is observed at higher SO₃:olefin ratios. Disulfonation may be reduced by carrying the sulfonation reaction only to partial conversion of the olefin—for example, by using SO₃: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.

70 In order to obtain a product of good color, the SO₃ employed in the sulfonation reaction is generally mixed

- (1) Sulfonating straight chain olefins containing from 10 to 24 carbon atoms with SO₃.

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 reaction product from the sulfonation step may be neutralized with aqueous basic solutions containing sodium, potassium or ammonium hydroxides, carbonates, or oxides. In the preferred method, sufficient neutralizing solution may be added to provide for neutralization of the sulfonic acids formed by sultone hydrolysis. Generally, one equivalent of base for each mole 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 hydrolysis at temperatures below 100° C. Suitable hydrolysis temperatures range from about 100 to 200° C.

The hydrogenated olefin sulfonates described above are very good lime-soap dispersants. That is, compositions of soap and hydrogenated olefin sulfonate give less insoluble curd in hard water than does the same soap alone. Any amount of the hydrogenated olefin sulfonate is beneficial in reducing curd formation. Thus, the amount of hydrogenated olefin sulfonate ranges upwards from about 1%, but preferably in excess of 5%, of the total weight of soap and hydrogenated olefin sulfonate. As the quantity of hydrogenated olefin sulfonate in the combination bar is increased, the amount of insoluble curd that forms when the composition is dissolved in hard water is decreased. At soap to hydrogenated olefin sulfonate ratios less than about 85:15, no curd is formed even in water containing 300 p.p.m. of hardness. It is generally preferred that the combars of this invention contain from 15 to 50% (by weight based on the two components) of hydrogenated olefin sulfonate.

The sodium hydrogenated olefin sulfonates usually have a residual sodium sulfate content of more than 5% by weight and if prepared for making into bars by bleaching with, for example, sodium hypochlorite, have an additional salt content (usually NaCl) of from about 5 to 6% by weight. The blotching problem can be overcome by very carefully controlling the reaction conditions during the sulfonation and neutralization reaction and during bleaching so that the total inorganic salt content in the mixture is less than about 4% by weight. However, the difficulty of accomplishing such controlled reaction makes such production impractical for commercial use.

Example 1.—Preparation of sodium olefin 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 hydroxyalkane and alkene sulfonic acids, and neutralized these sulfonic acids. Olefin sulfonates were produced at the rate of 463 pounds per hour as an aqueous solution having a 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, hydroxyalkane sulfonic acids, and disulfonic acids. These three major components were present in a weight ratio of about 50:35:15.

Example 2.—Preparation of hydrogenated sodium olefin sulfonates

The apparatus for this hydrogenation consisted of a 1-liter Magne-Drive autoclave equipped with an accumulator, a constant pressure regulator, and a temperature recording means. The product of Example 1 was diluted with water to a 26% solids concentration and was filtered to remove a trace amount of insoluble material. The pH was adjusted to a value of 6.5–7.5 by neutralizing the slight excess of NaOH used in the neutralization and hydrolysis step with H_2SO_4 . One hundred parts of 30% hydrogen peroxide was then added to 3850 parts of the filtered 26% solution in an open glass vessel. This mixture was heated to 80° C. and stirred for one hour at this temperature, after which time no hydrogen peroxide remained. After cooling this solution to room temperature, 650 g. of it were charged to the previously described autoclave along with 8.5 g. of Raney nickel. The system was purged with nitrogen and then with hydrogen. It was then pressured with hydrogen to 50 p.s.i.g. The autoclave was warmed to 100° C. at which temperature hydrogen was again introduced to bring the pressure up to 100 p.s.i.g. and then vigorous stirring commenced. The hydrogen pressure was maintained constant at 100 p.s.i.g. throughout the run. After 1½ hours of stirring at this temperature and pressure, and at which time there was no additional hydrogen uptake, the solution was cooled to about 70° C., filtered, and then allowed to cool. After cooling, the final product was drum dried.

Example 3.—Preparation of combars

1130 g. of commercial raw soap (a mixture of coconut soap and tallow soap in a 20/80 weight ratio) containing about 7–10% water, 450 g. of the product of Example 2, 0.25% titanium dioxide, and a trace amount of a dye were added and mixed well. The resulting soap-detergent mixture was milled on a conventional milling apparatus and enough water was added during this milling operation to permit the composition to be milled into ribbons. The composition was then extruded and formed into bars using a conventional soap bar mold. The bars formed in this way were about 2½ inches by 1½ inches by ½ inch in size. They were stored for one week at ambient temperature and humidity. At the end of this time the bars weighed 26–27 grams and contained 5.6% water.

Other bars were prepared in essentially the same way as before but with a 60:40 ratio of soap and hydrogenated olefin sulfonate. Both types of bars were tested for hand-washing by a panel and were found to have excellent soap-type "feel," to form good lather, and to remove body soil satisfactorily.

Example 4.—Combination soap-hydrogenated olefin sulfonate toilet bars containing alkanolamines

Bars were prepared as in Example 3 employing 30% by weight of sodium hydrogenated olefin sulfonate in combination with 70% of the same soap containing 1.5% by weight (relative to the soap content) of triple pressed stearic acid as a superfatting agent and 7% water. The bars were stored at a temperature of 40° F. for a period

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of 7 days. Observation of the bars before and after storage indicated that white blemishes developed upon the surface of the bars. It was found that longer periods of storage at ambient temperature produced the same results.

Bars were prepared in the same manner using about 70% by weight of soap, the balance being sodium hydrogenated olefin sulfonate and a variety of additives, in particular glycerol, which is known to prevent crystal growth in transparent bars. Results from storage tests are set forth in the following table.

TABLE
Effect of additives upon the storage

Test	Percent Na HAOS	Soap		Additive	Percent	40° F. storage test	
		Type	Percent			Storage time	Degree of blotching
1	30		70				Severe.
2			100				None.
3	24		70	Sodium linear alkylbenzene sulfonate	6		Severe.
4	24		70	Triethanolamine	6		None.
5	24		70	C ₁₀ and C ₁₈ fatty alcohol	6		Severe.
6	24		70	Sodium lauryl alcohol sulfate	6		Do.
7	24		70	Sodium hydrogenated coconut monoglyceride sulfate	6		Do.
8	24		70	Carbowax 4000	6		Do.

Note that the triethanolamine completely eliminated the blotching while the use of the various other additives has no effect upon the problem.

Tests showed that the addition of as low as 1% of triethanolamine to bars having spotting or blotching problems eliminated the problem.

Combination bars prepared in the same manner but using hydrogenated olefin sulfonate which was prepared in such a manner that the bar contained less than 4% by weight of inorganic salt showed no blotching.

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.

I claim:

1. Soap and detergent bars consisting essentially of a major portion of one or more water-soluble soaps of fatty acids having from about 10 to 20 carbon atoms, a minor

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portion of C₁₀₋₂₄ hydrogenated olefin sulfonates sufficient to retain in suspension the insoluble lime soaps resulting from use of the soap and detergent bars in hard water, and from 0.5 to 10% by weight relative to the weight of the bars to inhibit blotching of the finished bars of a trialkanolamine of 3 to 9 carbon atoms, wherein said bars contain at least 5% by weight of sodium sulfate relative to the hydrogenated olefin sulfonates.

2. The bars of claim 1 wherein the trialkanolamine is triethanolamine.

3. The bars of claim 2 in which the trialkanolamine is present in the amount from about 0.5 to 6% by weight relative to the total weight of the bar.

4. The bar of claim 1 in which the water-soluble salts of the fatty acids have from 12 to 18 carbon atoms and are mainly sodium laurate, myristate, palmitate, stearate, and oleate.

5. The bar of claim 2 in which the cation in the hydrogenated olefin sulfonate is sodium.

References Cited

UNITED STATES PATENTS

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LEON D. ROSDOL, Primary Examiner

E. L. ROLLINS, Assistant Examiner

U.S. Cl. X.R.

252-121, 548, 555

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,738,935 Dated June 12, 1973

Inventor(s) Gar Lok Woo

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, following line 32, insert the following claims:

6. The bars of Claim 1 in which the hydrogenated olefin sulfonates contain from 13 to 22 carbon atoms.

7. The bars of Claim 1 in which the hydrogenated olefin sulfonates are derived from alpha olefin sulfonates.

Column 1, line 9, "5 Claims" should read -- 7 Claims --.

Signed and sealed this 7th day of May 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents