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HYDROGENATED OLEFIN

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ABSTRACT OF THE DISCLOSURE

Novel nonsoap detergent toilet bars are formed from water and a detergent prepared from a solution of a complex mixture of hydrogenated olefin sulfonates containing from 10 to 24 carbon atoms by cooling the solution to a temperature in the range of from 0° C. to 35° C. and subsequently filtering the solution to recover the improved hydrogenated olefin sulfonates as the precipitate.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of U.S. application Ser. No. 833,801, filed June 16, 1969, now Pat. No. 3,652,662.

BACKGROUND OF THE INVENTION

The present invention is concerned with the field of synthetic nonsoap detergent bars and, more particularly, with the preparation of bars or cakes for toilet or bath use from improved mixtures of hydrogenated 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 percent of the bar market is satisfied by all synthetic detergent bars.

As disclosed in copending application, U.S. Ser. No. 748,188, filed July 29, 1968 now Pat. No. 3,625,910, it has been discovered that superior nonsoap synthetic detergent bars can be formed employing hydrogenated linear olefin sulfonates as the major active detergent component. In particular, mixtures of straight-chain hydrogenated olefin sulfonates containing from 10 to 24 carbon atoms constitute a superior detergent component for nonsoap detergent toilet bars. Although these hydrogenated olefin sulfonate bars comprise a significant advance over the nonsoap detergent bars of the prior art, they are not as low in slough loss and wear rate as may be desirable.

SUMMARY OF THE INVENTION

It has now been discovered that superior nonsoap synthetic detergent bars low in slough loss and wear rate can be formed employing improved hydrogenated alpha-olefin sulfonates as the major active detergent component. In particular, the desired characteristics are exhibited by hydrogenated alpha-olefin sulfonates containing reduced amounts of highly water-soluble components.

In general, the hydrogenated alpha-olefin sulfonates of reduced solubility may be prepared by recovering the precipitate obtained from filtering or centrifuging an aqueous solution of hydrogenated alpha-olefin sulfonates at a temperature of from 0° C. to 35° C. By moderating the temperature at which the solution is filtered, the slough loss rate of detergent bars prepared from the present compositions may be controlled. That is, by increasing the temperature of the solution, less precipitate will be obtained. Surprisingly, the compositions of the present invention exhibit excellent slough loss and wear rate characteristics with little or no appreciable effect on the other outstanding properties of hydrogenated alpha-olefin sulfonate detergent bars.

In particular, the present invention includes the discovery that hydrogenated alpha-olefin sulfonates, mixtures and slurries thereof are effectively adapted to separation by filtration, centrifugation and the like to give selected components. Such ease of separation is in direct contrast to previously known alpha-olefin sulfonates and alkyl benzene sulfonates which do not lend themselves to separation by filtration, centrifugation and the like. Furthermore, the less soluble components which are obtained as filter cake may be washed with ease for even more efficient separation.

DESCRIPTION OF THE INVENTION

The term "alpha-olefin sulfonates" as used in the present invention, defines the complex mixture obtained by the SO_3 sulfonation of straight-chain alpha-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 and the major components of the complex mixture is known, the specific identity and the relative proportions of the various sulfonate, disulfonate and hydroxy 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 the composition obtained by hydrogenating an aqueous solution of an alpha-olefin sulfonate product which contains from about 25 to 75 percent by weight alkene sulfonates, from about 25 to 65 percent by weight hydroxyalkane sulfonates, and not more than 20 weight percent disulfonates; cooling to a temperature of from 0° to 35° C.; and filtering to recover the precipitate. The optimum alpha-olefin sulfonate compositions are obtained by SO_3-air sulfonation of C_{10}–C_{24} straight chain alpha-olefins with SO_3:air volume ratio of about 1:50–100 and an SO_3:olefin mole ratio of 0.95:1 to 1.25:1, and neutralization and hydrolysis of the sulfonation reaction product at temperatures of 145–250° C. using 1 equivalent of base per mole of SO_3 consumed in the sulfonation step.

In addition to the straight-chain alpha-olefins from wax cracking, suitable alpha-olefin starting material includes the straight-chain alpha-olefins produced by Ziegler polymerization of ethylene. The alpha-olefins may contain from 10 to 24 carbon atoms, usually 13 to 22 carbon atoms, and preferably 15 to 18 carbon atoms per molecule. These olefin mixtures should have an average molecular weight of at least about 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 moles of SO_3 per mole of olefin and, preferably, in the range 1:1 to 1.20:1. Greater formation of disulfonated products is observed at higher SO_3:olefin ratios and consequently should be avoided.

It is known that disulfonated products may be minimized by carrying the sulfonation reaction only to partial conversion of the olefin; for example, by using SO_3:olefin ratios of less than 1. However, unreacted olefins in the olefin sulfonate compositions have serious deleterious effects on the quality and effectiveness of the detergent

products. Removal of the unreacted olefins in other than only minor portions require expensive additional processing steps.

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 reaction product from the sulfonation step may be neutralized with aqueous basic solutions containing the sodium, potassium or magnesium 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, 1 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 hydroxylkane 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 100–200° C. The following examples describe the preparation of the precursor alpha-olefin sulfonates suitable for preparing hydrogenated alpha-olefin sulfonates within the scope of the present invention.

Example 1.—Preparation of alpha-olefin sulfonates

The reactor used for this sulfonation consisted of a continuous falling film-type unit in the form of 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, sulfonated product was separated from the air stream.

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 lbs./hour. At the same time, 124.2 lbs./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 2 minutes.

After passing out of the reactor, the sulfonated product was mixed with 612 lbs./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 sulfonic acids contained in the sulfonation reaction product, hydrolyzed the sultones to hydroxy sulfonic and alkene sulfonic acids and neutralized these sulfonic acids. Olefin sulfonates were produced at the rate of 463 lbs./hour as an aqueous solution having a 45 percent 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.

Prior to hydrogenation, the alpha-olefin sulfonates are treated with hydrogen peroxide to increase hydrogenation efficiency. The olefin sulfonate prior to such treatment contains unidentified compounds which poison hydrogenation catalysts. Without the hydrogen peroxide pretreat catalyst consumption is prohibitive. Other oxidizing agents may be used instead of hydrogen peroxide in the pretreating step, preferably, oxidizing agents which leave no solid residues in the product such as elemental oxygen or air.

A wide variety of known hydrogenation catalysts may be used in the hydrogenation step. These include the noble metals and various forms of nickel, such as Raney nickel, nickel on Kieselguhr, and other supported nickel catalysts. Palladium on carbon and ruthenium on alumina are effective noble metal catalysts, although Raney nickel and palladium on carbon are preferred catalysts. The amount of catalyst employed in the hydrogenation of olefin sulfonates may vary in a range from about 0.05 to 30 percent by weight, based on the olefin sulfonate present. Increasing the amount of catalyst will usually result in a shortening of the time necessary for complete hydrogenation. The hydrogenation reaction is usually carried out at temperatures of about 20° C. to 200° C. and, preferably 70 to 120° C. At temperatures appreciably above 200° C. unncessary hydrogenation of hydroxyalkane sulfonates and hydrogenative degradation of the product tend to occur. Hydrogen pressure during the reaction is not a critical variable. Reduction may be carried out at pressures varying from less than atmospheric to 5,000 p.s.i.g., or preferably from 30 to 200 p.s.i.g.

Example 2.—Preparation of hydrogenated alpha-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 sodium hydroxide used in the neutralization and hydrolysis step with H_2SO_4 and 100 parts of 30% hydrogen peroxide was added to 3,850 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 was charged to the previous 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. 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.

Example 3.—Preparation of filtered hydrogenated alpha-olefin sulfonates

Approximately 1,000 g. of 23% concentration in water of a C_{15}–C_{18} hydrogenated alpha-olefin sodium sulfonate was filtered at 24° C. to give a precipitate and a filtrate, which weighed 127 and 111 g. after drying, respectively.

Detergent bars were prepared from hydrogenated olefin sulfonates of Example 2 and from the precipitate and filtrate of Example 3 by the following procedure. In the first step, hydrogenated olefin sulfonate and 2–15 percent water are milled into ribbons to provide a homogeneous composition. It is then formed into a bar by molding in a conventional soap-bar mold. The bars formed in this way 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 g.

Bars prepared as above were tested for slough loss and wear rate and the results are given in Table I below. The Slough Loss Test was run by placing the bar in a 3½ inch I.D. Petri dish containing 30 ml. of water, having 50 p.p.m. 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 percentage of weight lost is reported as slough loss.

An important property of detergent bars is their solution rate under actual washing conditions. A convenient method of measuring the solubility characteristics of a detergent bar is by determining its loss in weight in g. per handwashing. This value is referred to as the bar wear rate. The values are obtained by averaging the weight loss from a number of handwashings by different individuals, using tap water at temperatures of about 110° F.

TABLE I.—COMPARISON OF BARS PREPARED FROM THE TWO COMPONENTS SEPARATED BY FILTRATION OF EXAMPLE 3

	Precipitate	Filtrate	Unfiltered HAOS
Recovery after drying, percent	54	46	
Bar slough loss:			
Grams	1.2	12.0	
Percent	5	45	34
Bar wear rate, g./wash	0.23	0.72	.80
Bar water content, percent	2.7	5.2	

The degree of soluble material allowed to be removed from the hydrogenated olefin sulfonates may be varied by controlling the concentration of the solution and temperature of filtration. In general, conducting the filtration at temperatures of from 0° C. to 35° C., and preferably 5° to 25° C., on a solution within the concentration range of 5 to 50 and preferably 20 to 30, produced significant improvement in the hydrogenated olefin sulfonate precipitate.

While completely satisfactory bars can be prepared from hydrogenated alpha-olefin sulfonates as shown above, the feel and appearance of the bars may be improved by incorporation of conventional emollients, superfatting agents, opacifiers, fillers, perfumes, dyes and the like. These additives may constitute up to about 40 percent by weight of the finished bar. Representative conventional additives are the polyethylene glycols, C_{12}–C_{16} fatty alcohols, stearic acid, mineral oil, fatty acid amides, mixed fatty acid alkanol amine compounds, lauric acid isopropanolamide, polyethylene glycol monostearate, and glycerol monostearate.

In addition, it may be desirable to have incorporated within the nonsoap synthetic bar other detergent-active materials compatible with the hydrogenated alpha-olefin sulfonates in an amount of from 0 to 25 percent by weight of the hydrogenated alpha-olefin sulfonates. Such detergent-actives would include straight-chain alkylbenzene sulfonates, straight-chain primary and secondary alkyl sulfates, polyoxyethylene alkylphenol sulfates, acylisethionates, alkylglycerylether sulfonates, and sulfated fatty acid monoglycerides.

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. A nonsoap detergent bar consisting essentially of (1) from about 2 to 15 percent by weight of water based on the total weight of the bar and (2) from about 85 to 98 percent by weight of improved hydrogenated alpha olefin sulfonate produced by
   (a) sulfonating straight-chain alpha olefins having from 10 to 24 carbon atoms with diluted SO_3;
   (b) neutralizing and hydrolyzing the product of (a);
   (c) hydrogenating from 50 to 100 percent of the unsaturated carbon-carbon double bonds in the product of (b);
   (d) cooling an aqueous solution of the product of (c) to a temperature of from 0° C. to 35° C.; and
   (e) filtering the cooled solution to recover an improved hydrogenated olefin sulfonate as a precipitate which is employed as the detergent active in the bar.

2. A nonsoap detergent bar as in claim 1, wherein the straight-chain alpha olefins contain from 13 to 22 carbon atoms.

3. A nonsoap detergent bar as in claim 2, wherein the hydrogenated alpha olefin sulfonates are prepared by sulfonating the olefins with an SO_3:olefin mole ratio of from 0.95 to 1.25 and hydrolyzing the sulfonated olefins at temperatures of from 100 to 200° C.

4. A nonsoap detergent bar as in claim 3, wherein from 75 to 100 percent of the unsaturated carbon-carbon double bonds in the alpha olefin sulfonates are hydrogenated.

References Cited

UNITED STATES PATENTS

3,186,948	6/1965	Sweeney	252—554
3,332,880	7/1967	Kessler	252—555 X

FOREIGN PATENTS

6,703,874	9/1967	Netherlands.

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