United States Patent Office 3,705,113 Patented Dec. 5, 1972

3,705,113

HYDROGENATED OLEFIN SULFONATE-ALKYL-1,2-GLYCOL DETERGENT COMPOSITIONS

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No Drawing. Filed Oct. 24, 1968, Ser. No. 770,386
Int. Cl. C11d 1/12
U.S. Cl. 252—555 7 Claims

ABSTRACT OF THE DISCLOSURE

High performance detergent compositions comprise a mixture of hydrogenated olefin sulfonates and an alkyl-1, 2-glycol.

BACKGROUND OF INVENTION

Recent concern over water pollution has resulted in significant changes in the active ingredient of modern detergents. Extensive and expensive research has been directed at discovering suitable detergent compounds which are both readily biodegradable and possess high detersive properties.

Heretofore, however, known commercial detergent compounds which possessed high detersive properties were not as biodegradable as desired; and, on the other hand, the readily biodegradable detergent compounds were not as desirable in terms of detersive properties.

In direct contrast to the aforementioned commercially available detergents the novel compositions of the present invention are both readily biodegradable and exhibit excellent detergent properties. In addition, the novel detergent compositions as described herein are readily and economically produced on a commercial scale basis.

DESCRIPTION OF INVENTION

It has now been found that superior detergent compositions comprise a mixture of straight-chain hydrogenated olefin sulfonates containing from 10 to 24 carbon atoms, and straight-chain alkyl 1,2-glycols wherein the alkyl radical contains from 10 to 20 carbon atoms. In particular, the performance of the described mixture is significantly greater than would be predicted from a knowledge of the performance of the individual components as well as other compounds.

The term "hydrogenated 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, hydrolysis and hydrogenation of the sulfonation reaction product. This complex mixture may contain hydroxyalkane, alkane 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 characteristics are exhibited by a hydrogenated olefin sulfonate 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 .95 to 1.15; 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; treatment of the sulfonate product with oxygen or hydrogen peroxide; and hydrogenation in the presence of Raney nickel or palladium on carbon catalysts at temperatures of from 70 to 120° C.

In addition to the preferred 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, and preferably 15 to 18 carbon atoms per molecule. Olefin mixture 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 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 reaction product from the sulfonation step may be neutralized with aqueous basic solutions containing compounds such as hydroxides, carbonates and oxides of the alkali metals, alkaline earth metals and ammonium. In the preferred method, sufficient neutralizing solution may be added to provide for neutralization of the hydroxyalkane sulfonic acids formed by sulfone hydrolysis. Generally, one equivalent of base 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 hydrolysis at temperatures below 100° C. Suitable hydrolysis temperatures range from about 100 to 200° C.

The straight-chain alkyl 1,2-glycols suitable for producing the excellent detergent compositions of the present invention may be represented by the formula

$$R_1\text{—}\underset{\underset{OH}{|}}{CH}\text{—}\underset{\underset{OH}{|}}{CH_2}$$

wherein R_1 is a straight-chain alkyl radical containing from 8 to 18 carbon atoms and preferably 9 to 12 carbon atoms. The alkyl glycol component need not be limited to compounds containing alkyl radicals of a single set carbon number but may include mixtures thereof, such as a mixed C_{11}–C_{14} alkyl 1,2-glycol. As used in the present specification the notation C_{11}–C_{14}, etc. refers to the total number of carbon atoms in the alkyl 1,2-glycol.

Suitable straight-chain glycols include, but are not limited to alkyl 1,2-glycols where the alkyl radical is selected from the following: n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, and mixtures thereof.

The selected glycols or mixtures thereof may comprise from 1 to 40 parts per hundred parts by weight of hy-

drogenated olefin sulfonate of the detergent composition. The most desirable ratio is usually from 5 to 30 parts per hundred parts by weight of olefin sulfonate.

The following examples describe the preparation of hydrogenated olefin sulfonates, their precursor olefin sulfonates and the novel detergent compositions of the present invention.

Example 1.—Preparation of olefin sulfonate

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_2 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% hexadecane, 28% heptadecene, 14% octadecene and 1% nonadecene. This material was charged to the top of the above described reactor at a rate of 206 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 temperatuure 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 sulfones to hydroxy sulfonic acids and neutralized the hydroxy 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, hydroxy alkane sulfonic acids, and disulfonic acids. These three major components were present in a weight ratio of about 50/35/15.

Example 2.—Preparation of C_{15-20} olefin sulfonates

A straight-chain 1-olefin mixture produced by cracking a highly paraffinic wax and containing 1% tetradecene, 18% pentadecene, 17% hexadecene, 16% heptadecene, 16% octadecene, 14% nonadecene, 13% eicosene, and 5% heneicosene was processed following the procedure in Example 1.

Example 3.—Preparation of hydrogenated 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 and 100 parts of 30% hydrogen peroxide was 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 was 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. The hydrogen pressure was maintained constant at 100 p.s.i.g. throughout the run. After one and one-half 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 4.—Preparation of hydrogenated olefin sulfonates

The product of Example 2 was reduced as in Example 3 to give a substantially 100% reduction of double bonds in the olefin sulfonate.

The hydrogen peroxide treating step prior to hydrogenation increases hydrogenation efficiency. The olefin sulfonate prior to such treatment contains unidentified compounds which poison hydrogenation catalysts. Without the hydrogen peroxide pretreat catalyst consumption is much higher. 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.

In addition to the Raney nickel exemplified, a wide variety of known hydrogenation catalysts may be used in the hydrogenation step. These include the noble metals and various forms of nickel other than Raney nickel such as 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% 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 from about 20° C. to 200° C. and preferably 70° C. to 120° C. At temperatures appreciably above 200° C. unnecessary 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 5000 p.s.i.g., but preferably from 30 to 200 p.s.i.g.

In Examples 3 and 4 above hydrogenation of the alkene sulfonate component of the neutralized sulfonation reaction mixture to alkane sulfonate was essentially complete. Partial hydrogenation of the olefin sulfonate to the extent that at least 50% of the alkene sulfonate is converted to alkane sulfonate yields a hydrogenated olefin sulfonate suitable for use in producing high quality non-soap detergent bars. Partial hydrogenation may be accomplished by proceeding as in Example 3 but discontinuing the hydrogenation reaction before hydrogen take up ceases. Partial hydrogenation can also be carried out by subjecting the olefin sulfonate to hydrogenation after neutralization but prior to hydrolysis.

Example 5.—Preparation of partially hydrogenated olefin sulfonate

The procedure of Example 3 was followed except that reduction was allowed to continue for only 30 minutes. The product was worked up as before. Analysis of a small aliquot by bromine number titration showed that 55% of the double bonds originally contained had been saturated.

Example 6.—Hydrogenation of an unhydrolyzed olefin sulfonate

1-hexadecene was sulfonated in a continuous falling-film reactor with SO_3/olefin mol ratio of about 1.2. The product from this reaction, 184 g. was dissolved in 198 g. of dioxane to give a 48% solution.

50 g. of this 48% solution was heated with stirring to 60° C. Then 2.1 g. of 34% hydrogen peroxide was added. Stirring was continued at this temperature for

one hour. The solution was allowed to cool to room temperature.

Of the hydrogen peroxide treated material, 17.3 g. was diluted to 50 ml. with dioxane and charged to a 200 ml. Fischer-Porter bottle along with 0.80 g. of 5% palladium-on-carbon hydrogenation catalyst. The mixture was heated to 24–26° C. and pressured to 50.5 p.s.i.g. with hydrogen. After 30 minutes of reaction, the pressure had dropped 18.4 p.s.i.g. No further drop in pressure occurred after this time. This pressure drop corresponds to hydrogenation of 31% of the original olefin-SO_3 reaction product.

The hydrogenated material was filtered to remove the catalyst. The dioxane was removed by evaporation at temperatures below 40° C. under reduced pressure. In this way, there was obtained 8.3 g. of a low melting solid. A portion of this solid, 6.4 g. was mixed with 2.0 g. of 50% aqueous sodium hydroxide in 35 ml. of water and heated at 150–155° C. for two hours. The water was then removed by evaporation. A bromine number analysis of the final product indicated that about 25% of the product was unsaturated. Accordingly, the calculated weight ratio of hydroxyalkane, alkene and alkane sulfonates would be 44/25/31, respectively.

Example 7.—Preparation of detergent composition

A sample of hydrogenated olefin sulfonates produced in accordance with Example 4 was formulated with an alkyl 1,2-glycol and other ingredients into a household detergent composition. The percentages of the various ingredients based on the total weight of the formulation were:

	Percent
Hydrogenated olefin (C_{15-18}) sulfonate	21
C_{11}–C_{14} alkyl 1,2-glycol	4
Sodium tripolyphosphate	40
Carboxy methyl cellulose	1
Sodium silicate	7
Sodium sulfate	19
Water	8
	100

The detergent formulation was dissolved in water to a 0.15% by weight concentration and evaluation by use of the "Hand Dishwashing Test." The "Hand Dishwashing Test" is an effective means for evaluating the detersive characteristics of detergent compositions and is based on a procedure presented at the ASTM D–12 Subcommittee on Detergents, Mar. 10, 1949, New York, N.Y. The test measures under simulated home washing conditions the number of plates or dishes washed before foam collapses.

The composition of Example 7 gave an excellent rating of 32 plates by this test. In comparison a sample of olefin sulfonates prepared in accordance with Example 1 was formulated as above, and tested, but gave a rating of only 25 plates.

Example 8

A sample of hydrogenated olefin sulfonates was prepared in accordance with Example 4 and separated into three portions. The first portion, 25 parts, was dissolved in 75 parts of water. This solution was evaluated at 0.15% concentration by the dishwashing test and gave a low rating of only 6 plates. A similar solution of olefin sulfonates prepared in accordance with Example 1 was dissolved in water in a similar manner and gave a rating of 20 plates.

Example 9

The second portion from Example 8 was combined with 19 parts of C_{11}–C_{14} alkyl 1,2-glycol per hundred parts of hydrogenated olefin sulfonate, and 25 parts of this mixture was dissolved in 75 parts of water. Evaluation of this composition at 0.15% concentration gave a rating of 11 plates, an improvement of almost 100%.

Example 10

The third portion from Example 8 was 19 parts of C_{15}–C_{18} alkyl 1,2-glycol per hundred parts of hydrogenated olefin sulfonate, and 25 parts of this mixture was dissolved in 75 parts of water. Evaluation of this composition at 0.15% concentration gave a rating of 12 plates, an improvement of 100%.

Detergent compositions were prepared in accordance with Example 7 except that different amounts of glycols were substituted. The results obtained in the dishwashing test are shown in Table I.

TABLE I

Example	Glycol	Amount [1]	Plates
11	C_{11}–C_{14}	4/98	30
12	C_{11}–C_{14}	20/105	32
13	C_{11}–C_{14}	30/95	29
14	C_{15}–C_{18}	20/105	24
15	C_{15}–C_{18}	30/95	30
16	None	0/100	24

[1] Parts of glycol/parts of hydrogenated olefin sulfonate.

Another effective means for measuring the properties of detergent compositions is known as the Bench Foam Test. In a representative test series solutions of .05% by weight concentration of formulations were prepared in aliquots of 1000 ml. The test consisted of mechanically stirring the test solutions, after heating to 120±10° F., in a 2000 ml. beaker for one minute, and measuring the foam height in mm. at 0 and after 10 minutes. Foam heights of 11 and 8 mm. at 0 and 10 minutes are considered satisfactory.

The Bench Foam Test correlates well with the dishwashing test. For example, a test on a sample prepared in accordance wtih Example 8 gave foam heights of 9 and 7 mm. at 0 and 10 minutes respectively. Foam heights of 13 and 11 mm. were observed for a sample prepared in accordance with Example 9 in a ratio of 20 parts of C_{11}–C_{14} alkyl 1,2-glycol per 80 parts of hydrogenated olefin sulfonate.

A sample prepared in accordance with Example 10 in a ratio of 10 parts of C_{15}–C_{18} alkyl 1,2-glycol per 90 parts of hydrogenated olefin sulfonate gave foam heights of 16 and 15 mm. respectively.

Similar tests were run on different water concentrations, amounts of glycols and type of glycols and the results are given in Table II.

TABLE II

			Foam height after—	
Example	Glycol	Amount [1]	0 min.	10 min.
17		0/100	9	7
18	C_{11}–C_{14}	10/90	13	11
19	C_{11}–C_{14}	20/80	13	11
20	C_{15}–C_{18}	10/90	16	15
21	C_{11}–C_{14} [2]	10/90	17	15

[1] Parts of glycol/parts of hydrogenated olefin sulfonate.
[2] Made up to .10% concentration in water.

The individual C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17} and C_{18} alkyl 1,2-glycols when subjected to the dishwashing and Bench Foam tests exhibit improved detersive characteristics similar to the results of their respective mixtures.

Additional compatible ingredients may be incorporated into the detergent compositions prepared in accordance with the present invention to enhance their detergent properties. Particularly effective is the incorporation of certain pentavalent phosphoric acid salts. For example, suitable phosphates would include, but are not limited to: sodium tripolyphosphate, potassium tripolyphosphate, ammonium tripolyphosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, trisodium phosphate, tripotassium phosphate, ammonium phosphate, sodium hexametaphosphate, potassium hexametaphosphate, ammonium hexametaphosphate, monosodium orthophosphate, monopotassium orthophosphate, disodium orthophosphate, dipotassium orthophosphate and the like.

An effective amount of alkali pentavalent phosphoric acid salt usually comprises from about 0.2 to 3 parts per part by weight of hydrogenated olefin sulfonate. Preferably, the ratio is 1 to 2 parts per part by weight of hydrogenated olefin sulfonate.

Other compatible ingredients which may be incorporated into the detergent compositions of the present invention include anticorrosion, antiredeposition, chemical bleaching and sequestering agents; optical whiteners and certain inorganic salts other than phosphate, such as inorganic sulfates, carbonates or borates. The appropriate quantities and compositions of these additives, agents and builders are well described in the art.

As will be evident to those skilled in the art, various modifications on this process can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

I claim:

1. A detergent composition having improved detersive characteristics consisting essentially of

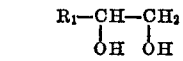
(a) a mixture of hydrogenated olefin sulfonates obtained by sulfonating straight-chain olefins containing from 10 to 24 carbon atoms with SO_3, wherein said sulfonated olefins are subsequently subjected to, in any desired sequence, the steps of:

(1) treating with an oxidizing agent selected from the group consisting of hydrogen peroxide, elemental oxygen, and air in an amount sufficient to improve the hydrogenatability thereof and hydrogenating said treated sulfonated olefins with a conventional hydrogenation catalyst at a temperature of from about 20° to 200° C., said catalyst being employed in an amount of from about 0.05 to 30% by weight based upon the olefin sulfonate content, the hydrogenation being allowed to proceed until from 50 to 100% of the unsaturated carbon-carbon double bonds therein are saturated;

(2) hydrolysis of the sultone content of said mixture at a temperature of from about 100° to 200° C.; and

(3) neutralization of said mixture; and

(b) a glycol, of the formula



wherein R_1 is a straight-chain alkyl radical containing from 8 to 18 carbon atoms, in a ratio of 1 to 40 parts per hundred parts of hydrogenated olefin sulfonate.

2. A detergent composition of claim 1 which contains as an additional adjuvant an alkali metal pentavalent phosphoric acid salt in an amount of from 0.2 to 3 parts by weight of hydrogenated olefin sulfonate.

3. A detergent composition as in claim 1 wherein the straight-chain olefins are alpha-olefins.

4. A detergent composition as in claim 3 wherein the straight-chain olefins contain from 15 to 20 carbon atoms.

5. A detergent composition as in claim 4 wherein the glycol is present in an amount of from 5 to 30 parts of hydrogenated olefin sulfonates.

6. A detergent composition as in claim 5 wherein from 75 to 100 percent of carbon-carbon double bonds are hydrogenated.

7. A detergent composition as in claim 5 wherein R_1 is selected from the group consisting of octyl, nonyl, undecyl, decyl, dodecyl, and mixtures thereof.

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U.S. Cl. X.R.

252—535, 536, 554