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3,444,191

NORMAL ALKENYL-1-SULFONATE DETERGENTSWalter David Nielsen, Richmond, Calif., assignor to
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2 Claims

ABSTRACT OF THE DISCLOSURE

Alkenyl-1-sulfonic acids and alkenyl-1-sulfonates are prepared from C₁₂-C₂₂ α-olefin mixtures having an average molecular weight in the range 220-245 in which 50 to 75 weight percent of the olefin is a C₁₆-C₁₈, inclusive, α-olefin mixture and from 5 to 30 weight percent of the olefin feed is above or below the C₁₆-C₁₈ range. These materials are wholly biodegradable and are satisfactory replacements for alkylbenzene sulfonate detergent actives.

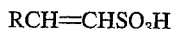
This invention concerns novel aliphatic compositions useful for the formulation of detergents. More particularly, this invention concerns novel aliphatic compositions comprised of normal alkenyl sulfonic acids useful in the formulation of detergents.

Alkylbenzene sulfonates have for a long time been a primary commercial detergent material. These detergents are benzene sulfonates with relatively long alkyl side chains and have excellent washing properties as well as sudsing ability. The phenyl ring is considered to significantly contribute to the desirable detergency properties of the sulfonates. However, detergents which can be made directly from available aliphatic hydrocarbons and have good detersive properties are particularly desirable because the presence of the phenyl ring in the alkylbenzene sulfonate requires an extra process step of alkylating benzene with an alkyl group, and the phenyl ring diminishes the biodegradability of the alkyl group.

Pursuant to this invention, novel compositions of alkenyl sulfonic acids useful in the formulation of detergents have been made which show excellent detergency properties, comparable to the best commercial detergents, while being readily biodegraded under ordinary sewage treatment.

The novel compositions of this invention are mixtures of C₁₂-C₂₂ alkenyl-1-sulfonic acids. The compositions of this invention can be divided into three fractions: a first fraction of normal alkenyl sulfonic acids having fewer than 16 carbons; a second fraction of normal alkenyl sulfonic acids of from 16 to 18 carbons; and a third fraction of normal alkenyl sulfonic acids of greater than 18 carbons. The major fraction will be the fraction of from C₁₆-C₁₈, and will usually vary from about 50 to 70 weight percent of the total composition. The other two fractions, those normal alkenyl sulfonic acids having fewer than 16 carbons and those normal alkenyl sulfonic acids having greater than 18 carbons will vary from about 5 to 30 percent.

The normal alkenyl-1-sulfonic acids can be further exemplified by the following formula:



wherein R is a straight-chain alkyl group of from 10 to 20 carbons, more usually of from 12 to 18 carbons.

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Each fraction of the composition, e.g., C₁₆-C₁₈, may have 1 or more homologs. That is, for example, the C₁₆-C₁₈ fraction need only have the C₁₈ homolog or may have the C₁₈ homolog in combination with the C₁₆ and C₁₇. It is preferred that the C₁₆-C₁₈ fraction have at least 2 homologs—2 to 3—the homologs being present in relatively equal amounts by weight. It is also preferred that the other two fractions, i.e., the fraction having alkenyl sulfonic acids of fewer than 16 carbons and the fraction having alkenyl sulfonic acids of greater than 18 carbons, have not more than 3 homologs—1 to 3—and preferably not more than 2 homologs—1 to 2.

The average molecular weight for the novel compositions is in the range of about 300 to 325.

The compositions of this invention can be prepared by sulfonating with sulfur trioxide the individual olefins and then combining them in the proper amounts or by sulfonating a mixture of the 1-olefins, the composition of the mixture of the 1-olefins being the desired composition of the final detergent product, or by a combination of the two methods.

The alkenyl sulfonic acids can be prepared by bubbling sulfur trioxide diluted with an inert gas into the α-olefin in the liquid phase at moderate temperatures. Inert gas is defined as a gas that will not significantly coordinate with the sulfur trioxide. Common inert gases are air, oxygen, nitrogen, helium, argon, methane, ethane, trifluorochloromethane, etc.

Various forms of sulfur trioxide can be used. These include stabilized forms, e.g., Sulfan, the liquid γ-modification, etc. The sulfur trioxide can be vaporized by passing the inert gas over the sulfur trioxide at elevated temperatures or by injecting the sulfur trioxide into the gas stream and then passing the mixture into a vaporizer. Or, it can be vaporized by other means known in the art.

Alternatively, rather than using an inert gas-SO₃ mixture, the SO₃ may be coordinated with a complexing agent. Various complexing agents have been reported in the art. A few of these are dioxane, thiooxane, alkyl phosphates, etc. Numerous studies have appeared describing the use of these coordinating agents and their effect on product distribution; the addition of sulfur trioxide to olefins can yield polymers, carbyl sulfates, hydroxyalkylsulfonic acids, β-alkenyl sulfonic acids, γ-sultones, etc. Therefore, the coordinating agent and reaction conditions should be chosen to maximize the yield of alkenyl sulfonic acids.

When using coordinating agents, it is necessary to separate them from the reaction mixture in order to isolate the product. This may frequently be expensive and time consuming, and a method of preparation avoiding coordinating agents is preferred. Therefore, only the method using inert gas-SO₃ mixtures will be described, because it avoids the difficulties created by the presence of the coordinating agents and is consequently the preferred method.

When using an inert gas, the percent by volume of the sulfur trioxide in the gas led into the reaction vessel will generally be in the range of about 0.5 to 20%, preferably in the range of about 1 to 8%.

Because of the high exothermicity of the addition of sulfur trioxide to an olefin, it is necessary to introduce the sulfur trioxide so that only low localized concentrations are obtained. The dilution of sulfur trioxide with the inert gas helps to reduce the localized concentration. Localized concentrations can be further reduced by intro-

ducing the SO₃-gas mixture as small bubbles and by efficient stirring with high shear rates.

The 1-olefins can be used neat or in the presence of solvent. Aliphatic hydrocarbons and halo-hydrocarbons can be used as solvents. Usually, the aliphatic 1-olefin will not be less than 25% by volume of the solution. Preferably, the aliphatic olefin will be used by itself, i.e., 100% of the initial reaction medium.

The mole ratio of sulfur trioxide to olefin will generally be in the range of about 0.1 to 1.3 moles of sulfur trioxide per mole of olefin. More usually, the mole ratio will be in the range of about 0.5 to 1.2. Large excesses of sulfur trioxide are to be avoided.

While the localized temperature at the site of reaction is difficult to measure accurately because of the great rapidity and exothermicity of the reaction, the temperature of the gas introduced and of the gross reaction medium can be measured. The temperature of the gas stream will generally be in the range of about 50° to 100° C. The temperature of the gross reaction mixture will generally be in the range of about -50° to +85° C., more usually in the range of about -25° to 50° C. The temperature of the gross reaction within the above limits does not appear to significantly affect the yield of alkenyl-1-sulfonic acids.

Pressure is not significant in affecting the results of the process. Usually, the pressure will be in the range of about 1/2 to 1 1/2 atmospheres.

The rate of addition of sulfur trioxide to the olefin will depend on a variety of factors, mainly, the ability to dissipate the heat of reaction. In a particular piece of apparatus, a convenient rate can be quickly determined.

After the addition of SO₃ is finished, the reaction mixture is usually treated with strong base, e.g., sodium hydroxide, in order to convert any compounds, which may be converted, to alkenyl sulfonic acid salts. Stirring with an aqueous or aqueous-alcoholic solution of a base at elevated temperatures is usually sufficient.

The novel detergent compositions will generally be used with a variety of additives common in the art. Inorganic builders commonly employed include polyphosphates, such as sodium tripolyphosphate, tetrasodium pyrophosphate, alkali metal sulfates, sodium silicate, alkali metal carbonates, and the like. Other conventional additives to detergent formulations may also be used. These include anticaking agents, optical bleaches, extenders and preventives of soil redeposition (e.g., carboxymethylcellulose or derivatives of oxidized cellulose), skin emollients and anti-irritants, perfume and coloring matter.

The active ingredient—alkenyl sulfonic acid salts—will comprise at least 10 weight percent of the final detergent composition and may be 100 percent. More usually, the alkenyl sulfonic acid salts will vary from 15 to 50% of the total weight of the composition. Preferred cations are the alkali metal cations, particularly sodium and potassium, although lithium may also find specialized uses.

The following tests were carried out to compare applicant's novel detergent compositions with a commercial sodium polypropylenebenzene sulfonate. One method for determining the deterative effectiveness of a detergent, and the one used in obtaining the data below, is the so-called "hand dishwashing test."

According to this test, dinner dishes or plates having a diameter of 9" are washed under conditions simulating home dishwashing, the total number of plates washed before the foam collapses being determined.

In this test, the dishes are smeared with molten, partially hydrogenated vegetable oils, melting point of 110-115° F. (Crisco), treated with a dye, such as Sudan red dye, to impart a uniform appearance to the grease. Using a syringe, 2.2 cc. of the molten soil is placed in the center of each clean, dry dinner plate. With the fingers, the soil is spread over a space of about 6.5" in diameter on each plate.

Six liters of washing water are adjusted to the desired hardness and at a temperature of 170° F. are placed in an 8,000 ml. container having a faucet outlet in the base (Scientific Glass, item P-2350). Samples of the detergent to be tested are made up into 6% solutions and 15.3 cc. of each solution are added to a dishpan 13.5" in diameter and 5.75" deep, thereby giving a final concentration of 0.15% by weight.

The water container is then placed above the dishpan in such a position that the distance between faucet outlet and bottom of the dishpan is 18". Further, the dishpan is so placed that the stream of water strikes the center of the dishpan with the water faucets fully open. This requires about 45-60 seconds. When a dishpan is completely charged, washing of the dishes is begun.

Five soiled plates and a clean dishcloth are placed in the dishpan. The dishes are washed in a circular manner to remove the grease from the front of the plate, then turned over and the grease clinging to the back is removed in the same way. During the washing, each plate is held at an angle so that almost 1/2 of the plate is kept under the washing solution. This is repeated until the five plates are washed. Another set of five plates is then placed in the dishwater and washing continued, the procedure being repeated until the foam collapses in the dishpan. At this point the surface is nearly devoid of foam. The number of plates washed before foam disappearance is reported.

Three different detergent compositions were tested. Two of them were derived from mixtures of sodium alkenyl-1-sulfonates (I and II), while the third (III) was a commercially available sodium polypropylenebenzene sulfonate of about 352 molecular weight. The following table indicates the relative amounts by weight of the various homologs as the sodium salts present in the alkenyl sulfonate compositions:

TABLE I

| | I | II |
|-----------------------|----|----|
| C ₁₄ | | 17 |
| C ₁₅ | 14 | 8 |
| C ₁₆ | 19 | 17 |
| C ₁₇ | 18 | 17 |
| C ₁₈ | 18 | 17 |
| C ₁₉ | 17 | 15 |
| C ₂₀ | 14 | 9 |

The average molecular weight of composition I was 355, and of composition II, 335.

The following table presents the data obtained as described above of three formulations having the following composition: 25% of the sodium salts of the sulfonic acids, 40% of sodium tripolyphosphate, 7% "N" silicate, 1% carboxymethylcellulose, 19% of sodium sulfate and 8% of water by weight.

TABLE II.—COMPOSITIONS

| Sample: | Plates |
|-----------|--------|
| I | 23, 23 |
| II | 23, 23 |
| III | 12, 13 |

¹ Indicates sodium sulfonate present in detergent compositions.

The deterativeness of the novel compositions of this invention was further investigated using the Terg-O-Tometer test and Foster D. Snell soiled cotton, as described in Detergency Evaluation and Testing, by J. C. Harris, Interscience Manual IV, Interscience Publishers, Inc., New York.

Using the compositions described above, the following results were obtained using the sodium polypropylenebenzene sulfonate composition for comparison.

TABLE III

| Concentration of formulation percent..... | Hardness ¹ | | | | | | | |
|---|-----------------------|------|------|------|------------|------|------|------|
| | 50 p.p.m. | | | | 180 p.p.m. | | | |
| | 0.05 | 0.10 | 0.15 | 0.20 | 0.05 | 0.10 | 0.15 | 0.20 |
| Detergent composition: | | | | | | | | |
| I..... | 1.4 | 4.9 | 5.6 | 6.0 | 1.0 | 1.7 | 3.5 | 5.9 |
| II..... | 1.5 | 3.0 | 3.7 | 4.3 | 1.2 | 1.4 | 2.6 | 4.4 |
| III..... | 0.5 | 0.8 | 1.3 | 3.6 | 0.4 | 0.5 | 1.4 | 3.7 |

¹ Hardness is expressed in parts per million of a mixture of $\frac{3}{4}$ calcium carbonate and $\frac{1}{4}$ magnesium carbonate. NOTE.—The numbers in the table are relative detergencies based on the scale at a concentration of 0.15%. A relative detergency of 2.0 is a poor performing commercial detergent in hard water, while a relative detergency of 6.0 represents an outstanding performance of a commercial detergent in soft water.

The following experiment describes a typical preparation of a novel composition of this invention.

The apparatus used for the reaction had three inlets for the sulfur trioxide situated at the periphery at the bottom of the vessel. The inlets had orifices about 1 mm. in diameter. The vessel was cylindrically shaped and was fitted with a stirrer which had numerous paddles along its length while the vessel itself was indented, providing high shearing. The reaction vessel was surrounded with a cooling jacket. At the top of the vessel was an inlet for the stirrer, and an exhaust for any gases.

Liquid SO₃ was added via syringe pump at a predetermined rate into the air stream, which then passed through a gas heater in which the air and SO₃ were heated to the desired temperature. The mixture was then led into the reaction vessel through the capillaries while the reaction mixture was vigorously stirred. Carrying out the reaction as described above, 16.7 grams (0.25 mole) of an olefin mixture having the composition of I indicated in Table I was introduced into the flask at about room temperature. Liquid SO₃ was added at a rate of about $\frac{1}{3}$ ml. per minute into the incoming air stream. The air was added at 9100 ml. per minute, and then both air and SO₃ were heated to about 90° C. A pressure of about 28 mm. mercury over atmospheric was applied to the reaction system. After 33 minutes, the addition of sulfur trioxide was stopped, the temperature of the reactor having varied between about 30 and 35° C. during most of the course of the reaction.

To the reaction mixture was then added 400 ml. of ethanol and sufficient 5.18 normal sodium hydroxide to obtain a pH of about 7. The mixture was then heated to reflux with stirring, cooled, and extracted with isopentane. The aqueous layer was concentrated to 207.3 grams and a cationic titration using methylene blue indicator was carried out to determine the milliequivalents of active material in the mixture.

The nuclear magnetic resonance (NMR) and infrared spectrums were taken of the product. The NMR spectrum indicated the presence of a double bond, while the infrared spectrum was consistent with the published spectra of analogous compounds. A. F. Turbak et al., I & EC Product Research and Development, 2, 229 (1963).

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. The improved normal alkenyl-1-sulfonate detergent composition obtained by sulfonation of an α -olefin feed which comprises introducing vaporized sulfur trioxide diluted with at least 80 volume percent of an inert gas into a mixture of normal acyclic α -olefins within the range of C₁₂ and C₂₂ and having an average molecular weight in the range 220–245; wherein from 50 to 75 weight percent of said feed is a mixture of C₁₆–C₁₈, inclusive, α -olefins and the fractions of said feed above and below the C₁₆–C₁₈ portion are each in the range 5–30 weight percent; wherein the sulfonation reaction is carried out at a gross reaction medium temperature in the range –50° C. to about +85° C.; wherein the amount of SO₃ reacted is in the range from 0.5 to 1.2 mols per mol of olefin feed and wherein the resulting sulfonation reaction mixture is converted to its corresponding detergent salt.

2. The process for the production of improved normal alkenyl-1-sulfonate detergent compositions by sulfonation of an α -olefin feed which comprises introducing vaporized sulfur trioxide diluted with at least 80 volume percent of an inert gas into a mixture of normal acyclic α -olefins within the range of C₁₂ and C₂₂ and having an average molecular weight in the range 220–245; wherein from 50 to 75 weight percent of said feed is a mixture of C₁₆–C₁₈, inclusive, α -olefins and the fractions of said feed above and below the C₁₆–C₁₈ portion are each in the range 5–30 weight percent; wherein the sulfonation reaction is carried out at a gross reaction medium temperature in the range –50° C. to about +85° C.; wherein the amount of SO₃ reacted is in the range from 0.5 to 1.2 mols per mol of olefin feed and wherein the resulting sulfonation reaction mixture is converted to its corresponding detergent salt.

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