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3,708,437

2-OLEFIN SULFONATE FOR LIQUID DETERGENTS

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5 Claims

ABSTRACT OF THE DISCLOSURE

Detergent active materials having low cloud points in aqueous solutions of inorganic salts, the active materials comprising olefin sulfonates of substantially linear monoolefin of 10 to 24 carbon atoms and in which at least 40 percent by weight of the sulfonates are 2-olefin sulfonates.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention is concerned with the field of biodegradable sulfonate detergents and more particularly with sulfonates which provide good detergency characteristics and when combined in aqueous solution with inorganic salts provide compositions having particularly low cloud points.

In the past, alkyl benzene sulfonates have been employed in great quantities as heavy duty powdered detergents and in compounding light-duty aqueous liquid detergents. The light-duty materials in contrast to heavy-duty detergents do not depend substantially upon detergency builders, sequestering agents, etc., to achieve their performance. They are thus usually employed in light-duty application such as handwashing of dishes and lightly soiled fine fabrics. These materials cannot as a rule withstand the vigorous treatment of machine laundry.

The characteristics required of the light-duty detergents include satisfactory washing ability in those applications which are employed, mildness to skin, and possession of a low cloud point. The cloud point, as the name implies, is the temperature at which upon cooling the solution develops a hazy cloudy appearance. Market surveys have shown that this characteristic is quite important to the housewife, and consequently, the solution should remain clear at quite low temperatures, e.g., at least down to 40° F. and preferably to about 32° F.

Maintenance of a low cloud point is particularly difficult when a liquid heavy duty product is formulated containing the usual inorganic salt builders.

Prior art

In the past, the cloud points of liquid detergents compounded with materials such as the alkyl benzene sulfonates have been reduced to low levels by various means. For example, U.S. Pat. 3,175,978, discloses a method of reducing the cloud point of alkyl benzene sulfonate in aqueous solution containing inorganic sulfates to acceptable levels (under 40° F.), by the inclusion in the composition of ammonium salts of the sulfate esters of alkyl phenoxy polyethylene ethanols. The addition of these compounds result in clear points as low as 29° F. by additionally replacing some 25–75% by weight of the sodium alkyl benzene sulfonate with ammonium alkyl benzene sulfonate.

Because of the importance of biodegradability, linear alkyl benzene sulfonates now comprise the major active ingredient of household detergents. Although alpha olefin sulfonates are more biodegradable than linear alkyl benzene sulfonates, they have not found extensive use in

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replacing the alkyl benzene material in liquid detergent formulations because of their higher clear points. They have been employed, however, in certain combinations, particularly for light-duty application. For example, U.S. Pat. No. 3,444,087 discloses the use of straight chain sulfonates of monoolefins in liquid detergent concentrates.

Additionally, U.S. Pat. No. 3,332,874 discloses as one component of the detergent active of a light-duty detergent composition, a mixture of double-bond positional isomers of water-soluble salts of alkene-1 sulfonic acids. The other components comprise hydroxy alkane sulfonates and alkene disulfonates.

Light-duty detergent compositions prepared from the alpha-olefin sulfonates in the absence of inorganic sulfates (particularly sodium sulfate) have cloud points which barely meet the acceptable standards. The internal olefin sulfonates, which generally comprise an equilibrated mixture of the double-bond isomers, are somewhat better in respect to cloud points. These materials are disclosed in U.S. Pat. No. 3,444,087.

In many conventional processes for producing the olefin sulfonates, a significant amount of inorganic sulfate, particularly sodium sulfate, is retained in the product mixture and its removal entails considerable difficulty. When the inorganic sulfates are present in substantial amounts, i.e., from 5 to 20% by weight, relative to the olefin sulfonates, the cloud points of liquid formulations prepared from these materials are significantly increased. In these cases the alpha-olefin sulfonate based formulations become only nominally acceptable, and the internal olefin sulfonate formulations become completely unacceptable, having cloud points close to room temperature (70° F.). Therefore, it is desirable that light-duty detergent compositions be provided having acceptably low cloud points even in the presence of significant quantities of inorganic sulfates.

SUMMARY OF THE INVENTION

Detergent active materials are provided which comprise olefin sulfonates of substantially linear monoolefins of 10 to 24 carbon atoms and in which at least 40% by weight of the sulfonates are 2-olefin sulfonates, that is the olefins from which the sulfonates are derived are the 2-ene isomers. These materials which are suitable in liquid formulations provide excellent detergency and have cloud points below the freezing point of water even in the presence of substantial amounts of inorganic sulfates. The sulfonates will preferably contain from 14 to 20 carbon atoms, most preferably they will contain from 14 to 18 carbon atoms.

The olefin sulfonates which comprise the detergent active of this invention are the water-soluble salts of sulfonic acids which are derived by conventional processes from substantially linear olefins. The term "2-olefin sulfonates" as used in the present invention thus defines the complex mixture obtained by the SO₃ sulfonation of straight-chain monoolefins (at least 40% by weight of which have their double bonds at the 2 position) containing 10 to 24 carbon atoms, followed by subsequent neutralization and hydrolysis of the sulfonation reaction product. This complex mixture contains hydroxy alkane sulfonates and the 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 sulfonates and disulfonate radicals and the precise double-bond locations are unknown. Accordingly, a determination of the entire chemical makeup is extremely difficult and has not heretofore been successfully accomplished. The mixture is best defined by the process used for producing it.

The olefin feed for sulfonation can be prepared by a variety of known methods which yield olefins containing predominantly the 2-isomer. Various 2-substituted alkanes, for example 2-halides, when subjected to elimination by the Saytzeff route (see "Organic Chemistry," 2nd ed., Cram and Hammond, page 330) yield predominantly 2-olefins. Simple dehydration of 2-alcohols yields 2-olefins. Various 2-alcohol derivatives, for example xanthate esters as in the Chugaev elimination (ibid, page 339) can be thermally decomposed to predominantly 2-olefin.

A particularly convenient route for preparing a suitable feed for the present invention is the controlled isomerization of the commercially available alpha olefins. The isomerization of the 1-olefins to internal olefins is accomplished by conventional techniques employing typical isomerization catalysts such as silica, alumina, etc. This process wherein equilibrated mixtures of the olefins are obtained is described in detail in U.S. Pat. No. 2,620,365. In this process the olefins are isomerized by contacting them with a solid catalyst having alumina as its active component at a temperature in the range of about 300 to 650° F. under pressure of about 50 lbs. per square inch with a Liquid Hourly Space Velocity (LHSV) of about 1 to 100. The isomerization can be accomplished with an LHSV between about 0.1 and 200.

In preparing the compositions of the current invention, since isomerization to equilibrium is not desired, the process is modified by decreasing the reaction temperature or preferably by raising the LHSV. Thus, in a typical example the temperature is maintained within the low range of the process limit described above (e.g., 300 to 400° F.) and/or the LHSV is raised to a range between 200 and 300. The product of the isomerization when properly prepared will have a minimum of 40% by weight of the 2-ene isomers and varying amounts of the other double-bond isomers including the 1, 3, 4, 5, etc.

In the previously described process for isomerizing the olefins the reaction is carried out by contacting the 1-olefin with the catalyst in a reactor tube. However, the process may also be carried out by a batch method which involves simply stirring the olefins in a reaction vessel containing a suitable amount of catalyst. In this case it is impossible to define an LHSV; but the reaction variable of time, catalyst concentration, and temperature can be adjusted to produce an olefin mixture having the requisite proportion of the 2-olefin isomer. It will be recognized that the isomerization processes in general are well known in the art and do not constitute a part of the present invention except that careful control is required.

In practice, the product isomer distribution must be closely watched and the temperature adjusted in a flow system or the batch time set in a batch system to obtain the highest 2-olefin content. Otherwise the unchanged 1-olefin content will be too high or the isomerization will have proceeded too far giving too much 3- and higher-olefins.

As previously noted, the sulfonate is obtained by conventional techniques as described, for example, in U.S. Pat. No. 3,428,654.

When the compounds of this invention are employed as light-duty, liquid detergent materials, they are dissolved in amounts of from about 10 to 30% by weight in solvent agents which normally comprise a mixture of urea, low molecular weight alcohol and water. As examples of suitable alcohols there can be mentioned methyl, ethyl, propyl and isopropyl alcohols. Formula 3a alcohol is preferred. The volume composition of this alcohol is 90.48% ethyl alcohol, 4.76% methyl alcohol and 4.76% water. In addition to the solvent, the detergent solutions may contain other materials. For example, there may be employed such materials as sulfated ethoxylated primary alcohols, amides of fatty acids such as lauric-isopropanol amide, lauric-diethanol amide, lauric-myristic diethanol amide, etc. These materials are employed optionally as foam boosting agents, and when employed are added in quanti-

ties of from about 1 to 3% by weight of the total solutions.

The light duty liquid formulations in which low cloud points are difficult to attain with other active materials will usually contain from about 5 to 20% by weight of an inorganic salt, especially the inorganic sulfates such as sodium sulfate, potassium sulfate, etc.

In addition to being employed in the light-duty detergent compositions, the 2-olefin sulfonate materials of this invention may be employed in heavy-duty applications. Thus, they may be combined in substantially dry form with conventional additives which enhance their detergent properties. These compositions may also be formulated advantageously into a liquid form. Such ingredients may include but are not limited to anti-corrosion, anti-redeposition, bleaching and sequestering agents, optical whiteners and organic and inorganic alkali and alkaline earth salts including phosphates, inorganic sulfates, carbonates or borates. In addition they may be combined with conventional phosphate builders and nonphosphate builders including such materials as trisodium nitrilotriacetic acid and other polycarboxylate materials such as the copolymers of ethylene and maleic anhydride.

The following examples illustrate the preparation of the compounds and compositions of this invention. The examples are illustrative and nonlimiting.

Example 1.—Isomerization of 1-olefin

A portion of a C₁₅–C₁₈ alpha olefin mixture (200 lbs.) was charged to a stainless steel kettle equipped with a stirrer, heating means, and a temperature recording device, along with 2½% by weight based on olefin of a commercial low alumina cracking catalyst (American Cyanamid Aerocat 75/85 having 85% SiO₂ and 14–15% Al₂O₃ and an average particle size of 60 microns). The resulting mixture was stirred at 365–380° F. for about 3 hours. It was redistilled leaving 5% bottoms.

The product gave the following analysis:

Bromine No. -----	70
Gravity ----- ° API	47.9
Refractive index, n _D ²⁰ -----	1.4445
GC analysis (percent):	
C ₁₄ -----	<1
C ₁₅ -----	30
C ₁₆ -----	33
C ₁₇ -----	29
C ₁₈ -----	7
Ave. mol. wt. -----	225

The olefin portion of this mixture contained 8% 1-olefin, 59% 2-olefin, 33% 3- and higher olefins.

Example 2.—Equilibrium isomerization of 1-olefins

The general procedure of Example 1 was followed employing a C₁₆, C₁₇, C₁₈ 1-olefin mixture in the ratio of 3/2/1, respectively. The same catalyst was used, but heating was continued at 400° F. for about 5 hours. The product was redistilled. In this case the olefin portion of the product had the following composition:

Component:	Wt. percent
1-olefin -----	1
2-olefin -----	20
3- and higher olefin -----	79

Example 3.—Sulfonation of olefins to produce 2-olefin sulfonate product

Portions of the product of Examples 1 and 2 were sulfonated by reaction with SO₃.

The reactor used for the sulfonation consisted of a continuous falling film type unit in the form of a vertical, 5 mm. I.D. 3-foot water-jacketed tube with an inlet weir for the olefin feed, a central 3 mm. O.D. SO₃-air inlet tube, followed by a 1¾ inch by 4 inch post reactor tube. Both the olefin and the SO₃-air mixture were introduced at the top of the reactor and flowed concurrently

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down the reactor. At the bottom the sulfonated product was separated from the air stream. The olefin was charged to the above-described apparatus at a rate of 4.21 grams/min. At the same time 1.87 grams/min. of SO_3 diluted with air to 5% by volume was introduced into the reactor. The apparatus was cooled with water in order to maintain the temperature of the product within the range of 40–50° C. Under these conditions the average residence time was less than 2 minutes.

After passing out of the reactor, the air free sulfonated product was mixed with aqueous caustic solution. The resulting slurry was hydrolyzed by heating at 145–150° C., for 30 minutes.

In order to demonstrate the efficacy of the 2-olefin sulfonates in light-duty detergent applications, the products of Example 3 were examined for cloud point along with a C_{15} – C_{18} alpha-olefin sulfonate prepared by a similar technique. The sulfonation product from Example 1 material will be entitled 3a, and that from Example 2, 3b. The solutions are prepared by mixing the specified quantities in water and in aqueous solution with 10% added Na_2SO_4 based on sulfonate. The resulting mixtures were stirred at a gradually decreasing temperature until a cloudy solution was obtained. The results are given in Table I.

TABLE I.—CLOUD POINTS OF OLEFIN SULFONATES

Detergent	Cloud point (25% active conc.), ° F.	
	In water	With 10% added Na_2SO_4
3a	31	29
3b	30	68
Alpha-olefin sulfonate (C_{15} – C_{18})	35	37

It may be seen from these data that the 2-olefin sulfonate material yields a significantly lower cloud point in the sulfate-containing solution than either the alpha-olefin sulfonate or internal olefin sulfonate. It may further be noted that the internal olefin sulfonate having a cloud point of 68° F. would be entirely unsatisfactory for liquid detergent use. Further, in the water solution the internal olefin sulfonate and 2-olefin sulfonate each have substantially lower cloud points than the alpha-olefin sulfonate.

In order to demonstrate the detergent effectiveness of the compound of this invention, the above-mentioned sulfonates were placed in conventional liquid detergent formulations and tested in a standard hand dishwashing test.

The formulations were as follows with each ingredient being specified in percent by weight:

Sulfonate detergent active	18
Sulfated ethoxylated primary alcohol	12
Lauric-isopropyl amide	6
Formula 3a alcohol	14.4
Urea	2.5
Water	47.1

The deterative properties of the above compositions were determined by the following dishwashing test, as described in U.S. Pat. 3,349,141.

To six liters of water of 50 p.p.m. hardness at a temperature of 115° F. was added 150 g. of 6 percent solu-

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tion in water of the test detergent formulation. Plates soiled with 2 cc. of molten fat shortening evenly applied to the surface were then washed by hand. When the suds disappeared from the surface of the solution the test is deemed complete and the number of washed plates is counted. Using the indicated formulations of the present invention and the alpha-olefin and internal olefin sulfonates for comparative purposes, the following tabulated results were obtained.

TABLE II

Detergent:	Dishes washed
3a	32
3b	33
Alpha-olefin sulfonate (C_{15} – C_{18})	31

The foregoing data indicate that the 2-olefin sulfonate compositions are equal to the alpha-olefin and internal olefin sulfonate materials in detergency.

As will be evident to those skilled in the art, various modifications on this invention 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. An aqueous liquid detergent having a low cloud point, said formulation consisting essentially of:

(I) as a detergent active material, from 5 to 30% by weight of a mixture of olefin sulfonates produced by

(a) sulfonating substantially linear monoolefins of 10 to 24 carbon atoms, at least 40% by weight of said olefins being 2-olefin, with sulfur trioxide, and

(b) neutralizing and hydrolyzing the product of (a),

(II) from 5 to 20% by weight based on actives of an alkali metal sulfate, and

(III) water sufficient to make 100%.

2. The formulation of claim 1 in which the olefin sulfonate contains from 14 to 20 carbon atoms.

3. The formulation of claim 1 in which the sulfonates contain from 14 to 18 carbon atoms.

4. The formulation of claim 1 in which the inorganic sulfate is sodium sulfate.

5. The formulation of claim 1 which contains in addition minor amounts of urea and a lower alkanol.

References Cited

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