

1 **ISOMERIZED ALPHA OLEFIN SULFONATE AND METHOD OF MAKING**
2 **THE SAME**

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4 This application claims priority from U.S. Provisional Application No. 60/982,847
5 filed on October 26, 2007, the entire contents of which are incorporated herein by
6 reference.

7
8 The present invention is directed to an isomerized alpha olefin sulfonate and a method
9 of making the same.

10
11 BACKGROUND OF THE INVENTION

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13 Alpha-olefins, especially those containing about 6 to about 20 carbon atoms, are
14 important items of commerce, with about 1.5 million tons reportedly being produced
15 in 1992. Alpha-olefins are also used as intermediates in the manufacture of detergents,
16 as monomers (especially in linear low density polyethylene), and as intermediates for
17 many other types of products. Alpha-olefins may also be employed in the oilfield
18 drilling fluids market. The use of alpha-olefins as such, and alpha-olefins isomerized
19 to internal olefins, has increased in recent years. As a consequence, improved
20 methods of making these compounds are of value.

21
22 Most commercially produced alpha-olefins are made by the oligomerization of
23 ethylene, catalyzed by various types of compounds, see for instance B. Elvers, et al.,
24 Ed. Ullmann's Encyclopedia of Industrial Chemistry, Vol. A13, VCH
25 Verlagsgesellschaft mbH, Weinheim, 1989, p. 243-247 and 275-276, and B. Cornils,
26 et al., Ed., Applied Homogeneous Catalysis with Organometallic Compounds, A
27 Comprehensive Handbook, Vol. 1, VCH Verlagsgesellschaft mbH, Weinheim, 1996,
28 p. 245-258. The major types of commercially used catalysts are alkylaluminum
29 compounds, certain nickel-phosphine complexes, and a titanium halide with a Lewis
30 acid such as diethylaluminum chloride (DEAC). In all of these processes significant
31 amounts of vinylidene and/or tri-substituted and/or internal olefins and/or diolefins,
32 can be produced depending on the carbon number of the olefin and the specific

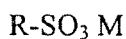
process. Since in most instances these are undesired, and often difficult to separate from the desired linear alpha-olefins, minimization of these byproducts is sought. Small, U.S. Patent No. 6,911,505 discloses processes for the production of alpha-olefins, including dimerization and isomerization of olefins using a cobalt catalyst complex are provided herein. The olefins so produced are described in this patent as being useful as monomers in further polymerization reactions and useful as chemical intermediates.

Eaton, et al., U.S. Patent No. 6730750, is directed to improved drag reducing agents and methods of forming improved drag reducing agents comprising the steps of isomerizing olefin monomers to form isomerized olefin monomers, polymerizing the isomerized olefin monomers in the presence of at least one catalyst to form a polyolefin drag reducing agent having unexpectedly superior drag reduction properties when combined with liquid hydrocarbons, such as viscous crude oil. This patent further discloses that the drag reducing agents may be introduced into conduits, such as pipelines, to increase the flow of the hydrocarbons through the conduit.

SUMMARY OF THE INVENTION

The present invention is directed to an isomerized alpha olefin sulfonate. The present invention is also directed to a method of making the isomerized alpha olefin sulfonate.

In one embodiment, the present invention is directed to an isomerized alpha olefin sulfonate having the general formula:



wherein R is an aliphatic hydrocarbyl group having from about 12 to about 40 carbon atoms, having from about 20 to 98 weight percent branching, and containing one or more olefin or alcohol moieties or mixtures thereof; and R is derived from a partially isomerized alpha olefin containing a residual alpha olefin content, wherein when the percent branching in the partially isomerized alpha olefin is less than or equal to 25

1 weight percent, then the residual alpha olefin content in such partially isomerized
2 alpha olefin is greater than or equal to 8 weight percent; and M is a mono-valent
3 cation.

4

5 In one embodiment, the present invention is directed to a method of making an
6 isomerized alpha olefin sulfonate comprising the steps of

7

8 (a) sulfonating an isomerized alpha olefin with sulfur trioxide in the presence of
9 air thereby producing primarily an isomerized alpha olefin sulfonic acid,
10 wherein the isomerized alpha olefin is derived from the isomerization of C₁₂-
11 C₄₀ normal alpha olefins;

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13 (b) optionally thermally digesting the product from step (a);

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15 (c) neutralizing the product from step (b) with a source of alkali or alkaline earth
16 metal or amines such as ammonia; and

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18 (d) optionally, hydrolyzing the product from step (c) with additional base or
19 caustic.

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21 In one embodiment, the present invention is directed to an isomerized alpha olefin
22 sulfonate having the general formula:

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24
$$R-SO_3 M$$

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26 wherein R is an aliphatic hydrocarbyl group having from about 12 to about 40
27 carbon atoms, having from about 20 to 98 weight percent branching, and
28 containing one or more olefin or alcohol moieties or mixtures thereof; R is
29 derived from a partially isomerized alpha olefin containing a residual alpha
30 olefin content, wherein if the percent branching in the partially isomerized
31 alpha olefin is greater than or equal to 15 weight percent, then the residual
32 alpha olefin content in such partially isomerized alpha olefin is less than or

1 equal to 15 weight percent and wherein if the percent branching in the
2 partially isomerized alpha olefin is less than or equal to 15 weight percent,
3 then the residual alpha olefin content in such partially isomerized alpha olefin
4 is greater than or equal to 15 weight percent.; and M is a mono-covalent
5 cation.

6 7 DETAILED DESCRIPTION OF THE INVENTION

8 9 Definitions

10
11 As used herein, the following terms have the following meanings unless expressly
12 stated to the contrary:

13
14 The terms "active" or "actives" as used herein refers to the concentration of the metal
15 salt of the sulfonate as described herein.

16
17 The term "isomerized alpha olefin (IAO)" as used herein refers to an alpha olefin that
18 has been subjected to isomerization conditions which results in an alteration of the
19 distribution of the olefin species present and/or the introduction of branching along
20 the alkyl chain. The isomerized olefin product may be obtained by isomerizing a
21 linear alpha olefin containing from about 12 to about 40 carbon atoms, and more
22 preferably from about 20 to about 28 carbon atoms.

23
24 The term "branching" as used herein refers to alkyl groups along a hydrocarbon chain
25 as measured by infrared spectroscopy.

26
27 The term "alkali metal" as used herein refers to Group IA metals of the Periodic
28 Table.

29
30 Unless otherwise specified, all percentages are in weight percent and the pressure is
31 atmospheric pressure.

32 The present invention is directed to an isomerized alpha olefin sulfonate.

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2 The Isomerized Alpha Olefin Sulfonate

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4 The isomerized alpha olefin sulfonate of the present invention has the general
5 formula:

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9 wherein R is an aliphatic hydrocarbyl group having from about 12 to about 40 carbon
10 atoms, having from about 20 to 98 weight percent branching, and containing one or
11 more olefin or alcohol moieties or mixtures thereof; and R is derived from a partially
12 isomerized alpha olefin containing a residual alpha olefin content, wherein when the
13 percent branching in the partially isomerized alpha olefin is less than or equal to 25
14 weight percent, then the residual alpha olefin content in such partially isomerized
15 alpha olefin is greater than or equal to 8 weight percent; and wherein M is a mono-
16 valent cation. Preferably, M is an alkali metal or ammonium or substituted
17 ammonium ion. Preferably, the alkali metal is sodium.

18

19 Examples of substituted ammonium include ammonium independently substituted
20 with from about 1 to about 4 aliphatic or aromatic hydrocarbyl groups having from
21 about 1 to about 15 carbon atoms, such as alkyl, aryl, alkaryl and aralkyl, and
22 optionally having one or more heteroatoms, such as nitrogen, oxygen or sulfur, which
23 may be present in aliphatic or aromatic heterocyclic rings. Examples of suitable
24 heterocyclic ring substituents include pyrrole, pyrrolidine, pyridine, pyrimidine,
25 pyrazole, imidazole and quinoline. The heterocyclic ring substituent may be
26 substituted on the ammonium moiety through a carbon atom in the heterocyclic ring,
27 such as in a C-pyridyl-substituted ammonium, or, alternatively, the quaternary
28 ammonium nitrogen itself may be a nitrogen atom in the heterocyclic ring, such as in
29 a pyridinium ion.

30

31 The present invention is directed to a sodium isomerized olefin sulfonate (IOS) made
32 by the sulfonation of an isomerized alpha olefin (IAO) in which the IAO is made by

1 the isomerization of C₁₂-C₄₀ normal alpha olefins (NAO), preferably C₂₀-C₂₈ normal
2 alpha olefins, most preferred C₂₀-C₂₄ normal alpha olefins.

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4 The IAO is composed of between from about 20 to about 98 wt% branching,
5 preferably from about 45 to about 80 wt% branching and most preferred from about
6 60 to about 70 wt% branching and between from about 0.1 to about 30 wt% residual
7 alpha olefin, preferably between from about 0.2 to about 20 wt% residual alpha olefin
8 and most preferably between from about 0.5 to about 10 wt% residual alpha olefin
9 species.

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11 In one embodiment, the IAO is composed of at least about 23% branching, at least
12 about 9% residual alpha olefin, and having from about 20 to about 24 carbon atoms.

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14 In another embodiment, the IAO is composed of at least about 65% branching, at least
15 about 0.5% residual alpha olefin and having from about 20 to about 24 carbon atoms.

16 Sulfonation of the IAO may be followed by thermal digestion and then neutralization
17 and, optionally hydrolysis, with caustic, in which the resulting sodium isomerized
18 olefin sulfonate (IOS) is composed of between from about 1 to about 50 wt% alcohol
19 sodium sulfonate, preferably from about 3 to about 40 wt% alcohol sulfonate and
20 most preferably from about 5 to about 20 wt% alcohol sulfonate species with the
21 remainder of the sodium sulfonate species being the sodium olefin sulfonate species.

22

23 In one embodiment of the present invention, the normal alpha olefins are isomerized
24 using at least one of a solid or liquid catalyst. The NAO isomerization process can be
25 either a batch, semi-batch, continuous fixed bed or combination of these processes
26 using homogenous or heterogenous catalysts. A solid catalyst preferably has at least
27 one metal oxide and an average pore size of less than 5.5 angstroms. More preferably,
28 the solid catalyst is a molecular sieve with a one-dimensional pore system, such as
29 SM-3, MAPO-11, SAPO-11, SSZ-32, ZSM-23, MAPO-39, SAPO-39, ZSM-22 or
30 SSZ-20. Other possible solid catalysts useful for isomerization include ZSM-35, SUZ-
31 4, NU-23, NU-87 and natural or synthetic ferrierites. These molecular sieves are well
32 known in the art and are discussed in Rosemarie Szostak's Handbook of Molecular

1 Sieves (New York, Van Nostrand Reinhold, 1992) which is herein incorporated by
2 reference for all purposes. A liquid type of isomerization catalyst that can be used is
3 iron pentacarbonyl ($\text{Fe}(\text{CO})_5$).
4

5 The process for isomerization of normal alpha olefins may be carried out in batch or
6 continuous mode. The process temperatures may range from about 50°C to about
7 250°C. In the batch mode, a typical method used is a stirred autoclave or glass flask,
8 which may be heated to the desired reaction temperature. A continuous process is
9 most efficiently carried out in a fixed bed process. Space rates in a fixed bed process
10 can range from 0.1 to 10 or more weight hourly space velocity.
11

12 In a fixed bed process, the isomerization catalyst is charged to the reactor and
13 activated or dried at a temperature of at about 150°C under vacuum or flowing inert,
14 dry gas. After activation, the temperature of the isomerization catalyst is adjusted to
15 the desired reaction temperature and a flow of the olefin is introduced into the reactor.
16 The reactor effluent containing the partially-branched, isomerized olefins is collected.
17 The resulting partially-branched, isomerized olefins contain a different olefin
18 distribution (i.e., alpha olefin, beta olefin; internal olefin, tri-substituted olefin, and
19 vinylidene olefin) and branching content that the unisomerized olefin and conditions
20 are selected in order to obtain the desired olefin distribution and the degree of
21 branching.
22

23 Sulfonation

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25 Sulfonation of the IAO may be performed by any method known to one of ordinary
26 skill in the art to produce an IAO sulfonic acid intermediate. The sulfonation reaction
27 is typically carried out in a continuous falling film tubular reactor maintained at about
28 30°C to about 75°C. The charge mole ratio of sulfur trioxide to olefin is maintained
29 at about 0.3 to 1.1: 1.
30

1 Other sulfonation reagents, such as sulfuric acid, chlorosulfonic acid or sulfamic acid
2 may also be employed. Preferably, the isomerized alpha olefin is sulfonated with
3 sulfur trioxide diluted with air.

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5 Optionally, the product from the sulfonation process may then be thermally digested
6 by heating.

7 8 Neutralization of the Isomerized Alpha Olefin Sulfonic Acid

9
10 Neutralization of the IAO sulfonic acid may be carried out in a continuous or batch
11 process by any method known to a person skilled in the art to produce the IOS.

12 Typically, an IAO sulfonic acid is neutralized with a source of a mono-covalent
13 cation. Preferably, the mono-covalent cation is an alkali metal or ammonium or
14 substituted ammonium ion. Preferably, the alkali metal is sodium.

15
16 Optionally, the neutralized isomerized alpha olefin sulfonate may be further
17 hydrolyzed with additional base or caustic.

18 19 Method of Making an Isomerized Alpha Olefin Sulfonate

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21 A method of making an isomerized alpha olefin sulfonate comprises the steps of (a)
22 sulfonating an isomerized alpha olefin with sulfur trioxide in the presence of air
23 thereby producing primarily an isomerized alpha olefin sulfonic acid, wherein the
24 isomerized alpha olefin is derived from the isomerization of C₁₂-C₄₀ normal alpha
25 olefins; (b) optionally thermally digesting the product from step (a); (c)
26 neutralizing the product from step (b) with a source of an alkali metal or ammonium;
27 and (d) optionally, hydrolyzing the product from step (c) with additional base or
28 caustic.

29
30 The isomerized alpha olefin has from about 12 to about 40 carbon atoms, and from
31 about 20 to 98 weight percent branching, and comprises a partially isomerized alpha
32 olefin containing a residual alpha olefin content, wherein when the percent branching

1 in the partially isomerized alpha olefin is less than or equal to 25 weight percent, then
2 the residual alpha olefin content in such partially isomerized alpha olefin is greater
3 than or equal to 8 weight percent.

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5 The partially isomerized alpha olefin is composed of at least about 23 wt% branching,
6 at least about 9% residual alpha olefin, and having from about 20 to about 24 carbon
7 atoms.

8
9 The partially isomerized alpha olefin is composed of at least about 65% branching, at
10 least about 0.2% residual alpha olefin and having from about 20 to about 24 carbon
11 atoms.

12
13 In one embodiment, when the partially isomerized alpha olefin is less than or equal to
14 18 weight percent, then the residual alpha olefin content in such partially isomerized
15 alpha olefin is greater than or equal to 10 weight percent.

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17 Other embodiments will be obvious to those skilled in the art.

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19 The following examples are presented to illustrate specific embodiments of this
20 invention and are not to be construed in any way as limiting the scope of the
21 invention.

22
23 **Example 1**

24
25 **Measurement of % Branching and % Alpha-Olefin in C20-24 Isomerized Alpha**
26 **Olefins (IAO)**

27
28 Infrared spectrometry was used to determine the percentage methyl branching and
29 percentage residual alpha-olefin of isomerized C20-24 NAO or isomerized alpha
30 olefin (IAO). The technique involved developing a calibration curve between the
31 infrared absorption at 1378 cm⁻¹ (characteristic of the methyl stretch) measured by
32 attenuated reflectance (ATR) infrared spectrometry and the percent branching
33 determined by Generalized Last Principal Component (GLPC) analysis of the
34 corresponding hydrogenated IAO samples (hydrogenation converts the IAO to a

1 mixture of paraffin's in which the normal paraffin has the longest retention time for a
2 give carbon number). Similarly, a calibration curve was developed between the
3 infrared absorption at 907 cm⁻¹ (characteristic of alpha olefin C-H stretch)
4 determined by attenuated reflectance (ATR) infrared spectrometry and the percent
5 alpha-olefin determined by quantitative carbon NMR.

6

7 A linear least squares fit of data for the percent branching showed the following
8 equation:

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10 % Branching by Hydrogenation GC = 3.0658 (Peak Height at 1378 cm⁻¹, in mm, by
11 ATR Infrared Spectroscopy) - 54.679. The R² was 0.9321 and the branching content
12 of the samples used to generate this calibration equation ranged from approximately 9
13 % to 92 %.

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15 Similarly, a linear least squares fit of the percent alpha-olefin data showed the
16 following equation:

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18 % Alpha-Olefin by Carbon NMR = 0.5082 (Peak Height at 909 cm⁻¹, in mm, by ATR
19 Infrared Spectroscopy) - 2.371. The R² was 0.9884 and the alpha-olefin content of
20 the samples used to generate this calibration equation ranged from approximately 1%
21 to 75 %.

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24 **Example 2**

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26 **C20-24 Isomerized Alpha Olefin (IAO) - % Branching versus % Alpha Olefin**

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28 The primary olefinic species in Normal Alpha Olefins (NAO's) was normally alpha-
29 olefin. The isomerization of NAO's over the solid acid extrudate catalyst ICR 502
30 (purchased from Chevron Lummus Global) isomerized the alpha-olefin to other
31 olefinic species, such as beta-olefins, internal olefins and even tri-substituted olefins.
32 The isomerization of NAO's over ICR 502 catalyst also induced skeletal
33 isomerization in which methyl groups were introduced along the hydrocarbon chain

1 of the isomerized alpha olefin (IAO) which is referred to as branching. Both of the
2 alpha-olefin and branching content of IAO's were conveniently monitored by Infrared
3 spectrometry (Example 1). The degree of olefin and skeletal isomerization of an
4 NAO depends on the conditions of the isomerization process. Table 1 below shows
5 the % residual alpha-olefin vs. the % branching from the isomerization of the C20-24
6 NAO obtained from Chevron-Phillips Chemical Company in a tubular fixed bed
7 reactor (2.54-cm ID x 54 cm Length Stainless Steel) packed sequentially from the
8 bottom of the reactor to the top of the reactor as follows: 145 grams Alundum 24, 40
9 grams of ICR 505 mixed with 85 grams of Alundum 100, 134 grams of Alundum 24.
10 The reactor was mounted vertically in a temperature controlled electric furnace and
11 the NAO was pumped upflow at a weight hourly space velocity (WHSV) of 1.5 while
12 the catalyst bed was held at temperatures ranging between 130 °C and 230 °C at
13 atmospheric pressure and samples of IAO were collected at the outlet of the reactor.

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Table 1

Wt. % Branching	Wt. % Residual Alpha- Olefin	Wt. % Branching	Wt. % Residual Alpha- Olefin	Wt. % Branching	Wt. % Residual Alpha- Olefin	Wt. % Branching	Wt. % Residual Alpha- Olefin
4.4	68.8	20.5	14.5	33.4	1	65.7	0.3
7.7	40	20.5	13.1	33.6	0.8	66	1
8.1	47.5	20.6	17.1	34.3	1.1	67	1
8.1	43.2	20.7	12.6	34.5	2.5	67.2	1
8.3	55.3	20.7	14	36.9	1.1	67.5	1
8.9	45.3	20.7	14.2	40.6	1	67.5	0.3
9.1	40.4	20.8	16.8	41.8	0.8	67.7	0.4
10.9	41.2	20.9	12.5	42.8	0.8	67.8	1
12.7	34.4	20.9	14.1	43	0.8	68	1
12.8	26.2	21.2	8.7	43.2	1	68.5	0.3
12.8	26.9	21.3	13.6	44	1	68.6	1
14	22.3	21.8	14.4	44	1	68.6	1
14.6	19.4	22.2	11.1	48.8	1	68.6	1
14.8	15.5	22.2	12.6	50.8	0.4	69	1
14.8	17.7	22.2	12.9	51.8	0.6	69.3	1
15	19.2	22.4	11.4	52.3	1	69.4	1
16	17	22.4	4	52.4	2.5	70.2	0.4
16.4	15.1	22.6	3.7	52.8	0.5	70.4	1
16.6	13.8	22.6	10.7	54.9	1	70.6	0.4
16.9	14.8	22.6	11.6	55.4	1	71.6	1
17.3	12.3	23.6	9.8	55.5	1	71.8	1
17.5	13.6	23.6	9.5	55.5	0.4	72	1

Table 1 Continued

Wt. % Branching	Wt. % Residual Alpha- Olefin
17.6	15.3
18.7	6.7
18.9	8.7
18.9	16.5
19.1	7
19.1	8.2
19.7	9
19.8	10.8
20	16.5
20	16.3
20.3	7.7
20.3	13.3
20.5	10.2

Wt. % Branching	Wt. % Residual Alpha- Olefin
23.8	2.8
24.6	1.8
24.8	1.9
25	9.4
26.6	4.9
27.9	3.2
28.2	0.7
28.2	0.7
29	2.5
29.4	2
29.7	2.7
29.8	2.3
30.3	1

Wt. % Branching	Wt. % Residual Alpha- Olefin
57.7	1
59.2	1
61	0.4
61.2	1
61.5	1
61.6	1
61.6	1
62.3	1
62.8	1
63.5	1
63.6	1
64.7	1
64.8	0.3

Wt. % Branching	Wt. % Residual Alpha- Olefin
72	1
72.2	1
72.4	1
73.8	1
75.8	1
79.6	0.4
81.2	0.3
94.7	0.3
95.9	0.3
97.1	0.4

3 content and.

1 Example 3**2 Sulfonation of Branched C20-24 Isomerized Alpha Olefins (IAO's)**

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4 Isomerized C20-24 alpha olefin (IAO) feeds containing varying amounts of branching
5 and alpha-olefin obtained from Example 2, were sulfonated in a glass, water jacketed,
6 falling film tubular reactor (0.6 cm ID and three reactors in series, R1 = 30 cm, R2 =
7 30 cm and R3 = 70 cm) using SO₃/Air and the following conditions:

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9 IAO Feed Temperature = 50 °C

10 Reactor Temperature = 30 °C

11 Air Flow = 192 liters/hr

12 SO₂ Flow = 16 liters/hr

13 SO₂ to SO₃ conversion = 87 %

14

15 The IAO feed rate was varied to obtain the desired charge molar ratio of SO₃ to IAO.

16 The crude isomerized olefin sulfonic acid was then optionally digested in air at

17 varying temperatures and times with mechanical (magnetic stir bar) agitation in an

18 open beaker. The resulting isomerized olefin sulfonic acid was then analyzed by

19 cyclohexylamine titration. Table 2 illustrates the properties of IAO's and

20 corresponding olefin sulfonic acids obtained.

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Table 2

Entry	IAO Properties		Sulfonation	Digestion Conditions		IAO Sulfonic Acid Properties	
	Branching (%)	Alpha-Olefin (%)		Temperature (°C)	Time (minutes)	SO ₃ H (%)	H ₂ SO ₄ (%)
1	17.0	0.4	0.8	40	20	30.4	1.1
2	23.0	9.2	0.8	40	20	49.7	0.9
3	23.0	9.2	0.9	40	20	51.9	1.1
4	23.0	9.2	1.0	40	20	49.7	1.6
5	48.3	0.5	0.8	40	20	54.2	1.2
6	48.3	0.5	0.9	40	20	56.5	1.4
7	48.3	0.5	1.0	40	20	56.5	1.9
8	65.0	0.5	0.8	40	20	61.0	1.4
9	65.0	0.5	0.9	40	20	64.5	1.9
10	65.0	0.5	1.0	40	20	67.7	2.6
11	65.1	0.4	0.8	40	0	58.9	0.8
12	65.1	0.4	0.8	40	20	58.9	1.1
13	65.1	0.4	0.8	40	40	58.6	1.2
14	65.1	0.4	0.8	40	60	58.4	1.2
15	65.0	0.4	0.8	40	30	62.6	1.1
16	65.0	0.4	0.8	80	30	47.2	2.5
17	65.0	0.4	0.8	120	30	14.5	0.4
18	94.4	0.3	0.8	40	20	44.0	1.0
19	94.4	0.3	0.9	40	20	49.0	1.3
20	94.4	0.3	1.0	40	20	52.2	1.5

1 **Example 4**2 **Neutralization of C20-24 Isomerized Alpha Olefin (IAO) Sulfonic Acids**

3

4 Isomerized alpha olefin (IAO) sulfonic acids obtained from Example 3 were
 5 neutralized by the successive addition of aliquots (typically between 1 and 3 grams
 6 each) of 50 wt % aqueous NaOH to the IAO sulfonic acid over approximately 45
 7 minutes to 80 minutes at between 25 and 40 °C with mechanical stirring
 8 (approximately 340 rpm). The resulting sodium alpha olefin sulfonates (IOS's) were
 9 analyzed and found to have the following properties as shown in Table 3:

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11
12

Table 3

Entry	IAO Sulfonic Acid from Example 3	Product pH	Wt. Average MW (1) (Daltons)	Activity(2) (%)	Hydroxy Sulfonate Content (3) (%)
A	Entry 1	10.5	385	-	27.7
B	Entry 2	10.9	410	30.3	28.1
C	Entry 3	7.8	413	34.5	37.9
D	Entry 4	10.1	408	37.3	27.9
E	Entry 5	11.2	410	42.3	15.7
F	Entry 6	10.4	406	43.9	11.1
G	Entry 7	11.2	405	44.3	10.9
H	Entry 8	10.2	402	47.2	2.6
I	Entry 9	10.7	402	49.4	3.7
J	Entry 10	10.6	401	50.4	4.1
K	Entry 18	10.8	405	35.2	5.2
L	Entry 19	10.6	408	38.9	5.6
M	Entry 20	10.4	406	40.7	5.7

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14 (1) Weight Average Molecular Weight was determined from Electro-Spray Ionization
 15 Mass Spectrometry (ESI-MS)

16

17 (2) Activity was determined by Hyamine Titration using the weight average
 18 molecular weight determined by ESI-MS

19

1 (3) The % Hydroxy Sulfonate was determined by Electro-Spray Ionization Mass
2 Spectrometry (ESI-MS).

3

4 **Example 5**

5 **Sulfonation of 65 % Branched C20-24 Isomerized Alpha - Olefin**

6

7

8 Isomerized C20-24 alpha-olefin containing 65 % branching and 0.5 % alpha-olefin
9 obtained from the isomerization of C20-24 normal alpha-olefin (purchased from
10 Chevron Phillips Company) in a fixed bed reactor containing the solid acid extrudate
11 catalyst ICR 502 (purchased from Chevron Lummnus Global) at atmospheric
12 pressure in up-flow mode at a WHSV of approximately 0.7. The C20-24 was pre-
13 heated by means of a heat exchanger and the catalyst bed temperature ranged between
14 187 °C and 190 °C was sulfonated in a vertical, falling film reactor (water jacketed
15 stainless steel, 0.6 inch ID, 5 feet long) using concurrent SO₃/Air down flow, a
16 cyclone separator where a portion of the acid is cooled acid and recycled to the
17 bottom of the falling film reactor. The crude acid is optionally digested by passing
18 through a water jacketed, plug flow vessel at 40 °C and neutralized by the addition of 50
19 wt. % aqueous NaOH by means of tee inlet followed by passing the neutralized acid
20 through a high sheer mixer at 85-90 °C. The following sulfonation and digestion
21 conditions were used (See Table 4):

22

Air / SO ₃ Temperature, °C	38
IAO Feed Temperature, °C	25
Reactor Temperature, °C	30
SO ₃ in Air Concentration, Vol %	2.5
SO ₃ Reactor Loading, kg/hr-cm	0.777

23

Table 4

Condition Number	MR SO ₃ /IAO	Digestion Time (minutes)	FLOWRATES	
			SO ₃ kg/hr	IAO Feed kg/hr
1	1.0	none	3.72	13.978
2	0.8	none	3.72	17.473
3	0.7	none	3.72	19.969
4	0.6	none	3.72	23.297
5	0.9	none	3.72	15.532
6	0.9	30	3.72	15.532

The following properties of the intermediate isomerized alpha olefin sulfonic acid (IAO Sulfonic Acid) and the corresponding sodium salt (IOS Sodium Salt) following neutralization were obtained (See Table 5):

Table 5

Condition Number	IAO Sulfonic Acid Properties			Sodium IOS Properties			
	RSO ₃ H (%)	H ₂ SO ₄ (%)	Acid Number (mg KOH / gm of Sample)	Hyamine Activity (%) (1)	Hydroxy Sulfonate, (%) (2)	pH(3)	Free Base (%)
1	60.9	2.1	113.5	70.4	25.7	9.7	0.77
2	59.8	1.1	101.1	71.8	23.0	9.8	0.69
3	55.4	0.6	88.7	66.2	12.0	9.7	0.69
4	55.9	0.4	88.9	68.3	8.7	9.5	0.80
5	61.4	1.5	107.4	73.9	20.5	9.5	0.69
6	60.9	1.6	108.4	65.5	12.9	9.7	0.69

(1) Calculated using a weight average molecular weight of 403.

(2) Determined by electro-spray ionization mass spectrometry (ESI-MS).

(3) Determined on approximately a 1 wt. % sodium IOS in water using a calibrated (pH 7 and 10) pH electrode.

The IOS sodium salts obtained following neutralization were then subjected to hydrolysis conditions. The general hydrolysis procedure involves weighing 30 grams of the IOS sodium salt into a 50 ml mechanically stirred pressure reactor (Parr Model 4590 Micro Bench Top Reactor equipped with a Parr Model 4843 temperature

1 controller), adding a specified amount of 50 wt. % aqueous NaOH, initiating stirring
 2 (approximately 200 rpm) and increasing the temperature to the desired hydrolysis
 3 temperature (typically over 15-25 minutes), holding the reactor contents at the desired
 4 temperature followed by cooling to room temperature and removing the contents of
 5 the reactor. Using this procedure to hydrolyze the sodium IOS's obtained above
 6 afforded products with the following properties (See Table 6):

Table 6

Hydrolyzed Sodium IOS Properties					
Condition Number	Hydrolysis Temperature (°C)	Hydrolysis Time (hours)	Amount of Base added per 30 grams of IOS Sodium Salt	Hydrolyzed Sodium IOS Hyamine Activity (%) (1)	Hydroxy Sulfonate, (%) (2)
1	120	0.5	2.0	75.8	27.4
2	120	0.5	2.0	73.1	19.8
3	120	0.5	2.0	67.3	13.8
4	120	0.5	2.0	60.1	11.7
5	120	0.5	2.0	72.4	22.6
5	140	0.5	2.0	67.3	27.6
5	160	0.5	2.0	67.7	22.7
5	120	0.5	1.0	70.1	24.6
5	120	0.5	1.5	73.4	23.5
5	120	1.0	2.0	72.3	23.7
6	120	0.5	2.0	73.8	15.4

Example 6

Isomerized C20-28 Alpha Olefin (IAO) – Fixed Bed Process

15 A mixture of C20-24/C26-28 NAO (70:30 blend by weight respectively obtained
 16 from Phillips Chemical Company) was isomerized by passing the NAO blend
 17 through a fixed bed reactor as described in Example 2 at a WHSV of 1.2. Product
 18 was collected with time and samples analyzed to approximate (since the data used in
 19 Example 1 is for C20-24 IAO) the percent branching using the method of Example 1.
 20 The temperature of the catalyst bed was gradually increased over 36 hours from 221

1 °C to 223 °C to maintain the branching at approximately 65 %. The final product
2 obtained contained 66.5 % branching and 0.5 % residual alpha-olefin.

3

4 **Example 7**

5 **Isomerized C20-28 Alpha Olefin (IAO) – Batch Process**

6

7 Four liters (approximately 3.2 kg) of a mixture of C20-24/C26-28 NAO (80:20 blend
8 by weight respectively obtained from Phillips Chemical Company) was added to a 10
9 liter, glass, round bottom flask fitted with a mechanical stirrer, reflux condenser and a
10 thermocouple under a dry nitrogen atmosphere. To this mixture was added 25 grams
11 of dry ICR 502 catalyst, as used in Example 2. The reaction temperature was
12 gradually raised from 150 °C to 180 °C using a temperature controller over
13 approximately 10 days. Aliquots from the reaction flask were analyzed with time to
14 determine the approximate (since the data used in Example 1 is for C20-24 IAO)
15 percent branching and alpha olefin by infrared spectroscopy using the method of
16 Example 1. Additional ICR 502 catalyst was added after approximately 7 days (40
17 grams). The final product contained approximately 85.1 % branching and 0.2 %
18 residual alpha-olefin by the method of Example 1.

19

20 **Example 8**

21 **Sulfonation of C20-28 IAO containing 85.1 % Branching and 0.2 % Alpha-Olefin**

22

23 Isomerized C20-28 alpha-olefin (IAO) containing 85.1 % branching and 0.2 % alpha-
24 olefin obtained from Example 7 was sulfonated as in Example 3 using the following
25 conditions:

26

27 IAO Feed Temperature = 30 °C

28 Reactor Temperature = 30 °C

29 Air Flow = 192 liters/hr

30 SO₂ Flow = 16 liters/hr

31 SO₂ to SO₃ conversion = 87 %

32

The resulting isomerized alpha-olefin (IAO) sulfonic acids obtained were then digested at 40 °C for 20 minutes with mechanical (magnetic stir bar) agitation in an open beaker and then analyzed by cyclohexylamine titration. The IAO sulfonic acids obtained were then neutralized by the successive addition of aliquots (typically between 1 and 3 grams each) of 50 wt % aqueous NaOH to the IAO sulfonic acid over approximately 45 minutes to 80 minutes at between 35 and 40 °C with mechanical stirring (approximately 340 rpm). The resulting sodium alpha olefin sulfonates (IOS's) were analyzed and found to have the following properties (See Table 7):

Table 7

Entry	IAO Sulfonation Conditions	Digested IAO Sulfonic Acid Properties		Neutralized IOS Properties			
		SO ₃ H (%)	H ₂ SO ₄ (%)	pH (4)	Wt. Average MW (1) (Daltons)	Activity (2) (%)	Hydroxy Sulfonate Content (3) (%)
1	0.8	41.4	4.1	10.1	417	33.5	2.5
2	0.9	40.8	5.3	10.1	415	32.0	2.2
3	1.0	35.7	6.5	9.3	416	28.0	2.3

(1) Weight Average Molecular Weight was determined from Electro-Spray Ionization Mass Spectrometry (ESI-MS)

(2) Activity was determined by Hyamine Titration using the weight average molecular weight determined by ESI-MS

(3) The % Hydroxy Sulfonate was determined by Electro-Spray Ionization Mass Spectrometry (ESI-MS).

(4) Determined on approximately a 1 wt. % sodium IOS in water using a calibrated (pH 7 and 10) pH electrode

1 WHAT IS CLAIMED IS:

2

3 1. An isomerized alpha olefin sulfonate having the general formula:

4

5 $R-SO_3 M$

6

7 wherein R is an aliphatic hydrocarbyl group having from about 12 to about 40
8 carbon atoms, having from about 20 to 98 weight percent branching, and
9 containing one or more olefin or alcohol moieties or mixtures thereof; and R is
10 derived from a partially isomerized alpha olefin containing a residual alpha
11 olefin content, wherein when the percent branching in the partially isomerized
12 alpha olefin is less than or equal to 25 weight percent, then the residual alpha
13 olefin content in such partially isomerized alpha olefin is greater than or equal
14 to 8 weight percent; and M is a mono-valent cation.

15

16 2. The sulfonate of Claim 1 wherein the partially isomerized alpha olefin is
17 composed of at least about 23 wt% branching, at least about 9% residual alpha
18 olefin, and having from about 20 to about 24 carbon atoms.

19

20 3. The sulfonate of Claim 1 wherein the partially isomerized alpha olefin is
21 composed of at least about 65% branching, at least about 0.2% residual alpha
22 olefin and having from about 20 to about 24 carbon atoms.

23

24 4. A method making an isomerized alpha olefin sulfonate comprising the steps of

25

26 (a) sulfonating an isomerized alpha olefin with sulfur trioxide in the
27 presence of air thereby producing primarily an isomerized alpha olefin
28 sulfonic acid, wherein the isomerized alpha olefin is derived from the
29 isomerization of C₁₂-C₄₀ normal alpha olefins;

30

31 (b) optionally thermally digesting the product from step (a);

32

- 1 (c) neutralizing the product from step (b) with a source of a mono-valent
2 cation; and
3
4 (d) optionally, hydrolyzing the product from step (c) with additional base
5 or caustic.
6
- 7 5. The method of Claim 4 wherein the isomerized alpha olefin has from about 12
8 to about 40 carbon atoms, and from about 20 to 98 weight percent branching;
9 and comprises a partially isomerized alpha olefin containing a residual alpha
10 olefin content, wherein when the percent branching in the partially isomerized
11 alpha olefin is less than or equal to 25 weight percent, then the residual alpha
12 olefin content in such partially isomerized alpha olefin is greater than or equal
13 to 8 weight percent.
14
- 15 6. The method of Claim 4 wherein the partially isomerized alpha olefin is
16 composed of at least about 23 wt% branching, at least about 9% residual alpha
17 olefin, and having from about 20 to about 24 carbon atoms.
18
- 19 7. The method of Claim 4 wherein the partially isomerized alpha olefin is
20 composed of at least about 65% branching, at least about 0.2% residual alpha
21 olefin and having from about 20 to about 24 carbon atoms.
22
- 23 8. The sulfonate of Claim 1 wherein when the percent branching in the partially
24 isomerized alpha olefin is less than or equal to 18 weight percent, then the
25 residual alpha olefin content in such partially isomerized alpha olefin is
26 greater than or equal to 10 weight percent.
27
- 28 9. An isomerized alpha olefin sulfonate having the general formula:
29
30 $R-SO_3 M$
31

1 wherein R is an aliphatic hydrocarbyl group having from about 12 to about 40
2 carbon atoms, having from about 20 to 98 weight percent branching, and
3 containing one or more olefin or alcohol moieties or mixtures thereof; and R is
4 derived from a partially isomerized alpha olefin containing a residual alpha
5 olefin content, wherein if the percent branching in the partially isomerized
6 alpha olefin is greater than or equal to 15 weight percent, then the residual
7 alpha olefin content in such partially isomerized alpha olefin is less than or
8 equal to 15 weight percent and wherein if the percent branching in the
9 partially isomerized alpha olefin is less than or equal to 15 weight percent,
10 then the residual alpha olefin content in such partially isomerized alpha olefin
11 is greater than or equal to 15 weight percent ; and M is a mono-valent cation.
12

13 10. The method of Claim 4 wherein the product from step (b) is
14 neutralized with a source of an alkali metal or ammonium or
15 substituted ammonium ion; and
16