

POLYALKENYL SULFONATES
BACKGROUND OF THE INVENTION

Sulfonates are a class of chemicals used in household, industrial, and institutional cleaning applications, personal care and agricultural products, metalworking fluids, industrial processes, emulsifying agents, corrosion inhibitors and as additives in lubricating oils. Some of the desirable properties of sulfonates for use in lubricating oil applications include their low cost, compatibility, water tolerance, corrosion inhibition, emulsion performance, friction properties, high temperature stability, rust performance, and light color.

Sulfonates that are used in lubricating oil applications have been classified as either neutral sulfonates, low overbased (LOB) sulfonates, or high overbased (HOB) sulfonates.

In the past, natural sulfonates, made as a by-product of white oil and process oil production, dominated the sulfonate market. However, as refineries switched to hydrotreating processes, which gave improved yields of process oils and white oils, and the desire for higher utilization of raw materials and thus improved economics grew, synthetic sulfonates have become more readily available. Many synthetic sulfonates have been produced from sulfonate polyalkyl aromatic compounds. Unfortunately, many synthetic sulfonates provide properties that are inferior to the properties of the natural sulfonates. Thus, there is a need for low cost synthetic sulfonates that have good performance properties and can serve as a replacement for the natural sulfonates.

SUMMARY OF THE INVENTION

A first aspect of the present invention provides a polyisobutenyl sulfonic acid composition comprising a mixture of polyisobutenyl sulfonic acids derived from a mixture of polyisobutenes comprising greater than 20 mole percent of alkyl vinylidene and 1,1-dialkyl isomers. An embodiment may provide such a composition wherein the alkyl vinylidene isomer can be a methyl vinylidene isomer, and the 1,1-dialkyl isomer can be a 1,1-dimethyl isomer. Also provided may be such a composition wherein the number average molecular weight of the polyisobutenes may be about 168 to about 5000. In a preferred embodiment, the

the molecular weight distribution of the polyisobutenyl sulfonic acids may be such that at least 80% of the molecular weights of polyisobutenyl sulfonic acids can be separated by even multiples of 56 daltons. Another embodiment may further provide such a composition
5 wherein less than 20% of the polyisobutenyl sulfonic acids in the molecular weight distribution of the polyisobutenyl sulfonic acids may contain a total number of carbon atoms that may not evenly be divisible by four.

A second aspect of the present invention provides a method of making polyisobutenyl sulfonic acid composition of the present invention, which comprises
10 sulfonating a mixture of polyisobutenes comprising greater than 20 mole percent of alkyl vinylidene and 1,1-dialkyl isomers.

A third aspect of the present invention further provides a polyisobutenyl sulfonate composition having a TBN of about 0 to about 60 wherein the polyisobutenyl sulfonate is an alkali metal or alkaline earth metal salt of a polyisobutenyl sulfonic acid composition of the
15 present invention. Further provided in accordance with a fourth aspect of the present invention is a polyisobutenyl sulfonate composition having a TBN of greater than 60 to about 400 wherein the polyisobutenyl sulfonate is an alkali metal or alkaline earth metal salt of a polyisobutenyl sulfonic acid composition of the present invention. An embodiment may provide a polyisobutenyl sulfonate composition wherein the alkali metal or alkaline
20 earth metal can be calcium.

In accordance with a fifth aspect of the present invention, there is also provided a method of making polyisobutenyl sulfonate composition which comprises making a sulfonic acid by a method of the present invention and reacting the resulting polyisobutenyl sulfonic acid composition with an alkali metal or alkaline earth metal.

Also provided by a sixth aspect of the present invention is a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount of a polyisobutenyl sulfonate composition of the third aspect of the present invention. A seventh aspect of the present invention also provides a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount of a polyisobutenyl sulfonate composition of the fourth aspect of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a negative ion electrospray ionization mass spectrum of a polybutene sulfonic acid of a polybutenyl sulfonic acid made in accordance with the present invention.

Figure 2 is a negative ion electrospray ionization mass spectrum of a polybutene sulfonic acid made from a polybutene with less than 10% methylvinylidene isomer content, i.e., not a polybutenyl sulfonic acid of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The polyalkenyl sulfonic acids of this invention are prepared by reacting a mixture of polyalkenes comprising greater than 20 mole percent alkyl vinylidene and 1,1-dialkyl isomers with a source of sulfur trioxide $-SO_3-$. The source of $-SO_3-$ can be a mixture of sulfur trioxide and air, sulfur trioxide hydrates, sulfur trioxide amine complexes, sulfur trioxide ether complexes, sulfur trioxide phosphate complexes, acetyl sulfate, a mixture of sulfur trioxide and acetic acid, sulfamic acid, alkyl sulfates or chlorosulfonic acid. The reaction may be conducted neat or in any inert anhydrous solvent. The conditions for sulfonation are not critical. Reaction temperatures can range from $-30^{\circ}C.$ to $200^{\circ}C.$ and depends on the particular sulfonating agent employed. For example, acetyl sulfate requires low temperatures for reaction and elevated temperatures should be avoided to prevent decomposition of the product. Reaction time can vary from a few minutes to several hours depending on other conditions, such as reaction temperature. The extent of the reaction can be determined

1 by titration of sulfonated polyalkene after any free sulfuric acid has been washed out.
2 Typical mole ratios of sulfonating agent to polyalkene can be about 1:1 to 2:1.

3 The preferred sulfonating agent is acetyl sulfate (or a mixture of sulfuric acid
4 and acetic anhydride which forms acetyl sulfate *in situ*) which produces the
5 polyalkenyl sulfonic acid directly. Other sulfonating agents, such as a mixture of
6 sulfur trioxide and air, may produce a sultone intermediate that needs to be hydrolyzed
7 to the sulfonic acid. This hydrolysis step can be very slow.

8 The polyalkenes used to prepare the polyalkenyl sulfonic acid are a mixture of
9 polyalkenes having 12 to 350 carbon atoms. The mixture comprises greater than 20
10 mole percent, preferably greater than 50 mole percent, and more preferably greater
11 than 70 mole percent alkylvinylidene and 1,1-dialkyl isomers. The preferred
12 alkylvinylidene isomer is a methyl vinylidene isomer, and the preferred 1,1-dialkyl
13 isomer is a 1,1-dimethyl isomer.

14 The polyalkenes have a number average molecular weight in the range of
15 about 168 to about 5000. Polyalkenes having number average molecular weights of
16 about 550, 1000 or 2300 are particularly useful.

17 The preferred polyalkene is polyisobutene. Especially preferred are
18 polyisobutenes made using BF_3 as catalyst.

19 U. S. Patent No. 5,408,018, which issued on April 18, 1995 to Rath and which
20 is incorporated by reference in its entirety, and the references cited therein describe a
21 suitable process for the production of polyisobutenes that contain greater than 20 mole
22 percent alkylvinylidene and 1,1-dialkyl isomers.

23 Typically, when polyisobutenyl sulfonic acids or sulfonates are prepared from
24 polyisobutene having a low mole percent of alkylvinylidene and 1,1-dialkyl isomers,
25 the product has a molecular weight distribution similar to that shown in Figure 2.
26 Since polyisobutene is used to prepare the sulfonic acid or sulfonate, it should be
27 expected that the mass spectrum of the product would show compounds separated by
28 even multiples of 56 daltons, i.e., a C_4H_8 fragment. However, Figure 2, which is the
29 mass spectrum of a polyisobutenyl sulfonate prepared from a polyisobutene having a
30 mole percent of methylvinylidene isomers of less than 20%, clearly shows compounds
31 which are separated by less than 56 daltons.

1 It has now been discovered that when polyisobutene having a mole percent of
2 alkyl vinylidene and 1,1-dialkyl isomers greater than 20% is used to prepare
3 polyisobutenyl sulfonic acids or sulfonates, the molecular weight distribution of the
4 resulting product has at least 80% of the polyisobutenyl sulfonic acids or sulfonates
5 whose molecular weights are separated by even multiples of 56 daltons (see Figure 1).
6 In other words, less than 20% of the polyisobutenyl sulfonic acids or sulfonates in the
7 molecular weight distribution of the sulfonic acids or sulfonates contain a total
8 number of carbon atoms that is not evenly divisible by four.

9 The polyalkenyl sulfonates of this invention are prepared by reacting the
10 polyalkenyl sulfonic acid (prepared as described above) with a source of an alkali or
11 alkaline earth metal. The alkali or alkaline earth metal can be introduced into the
12 sulfonate by any suitable means. One method comprises combining a basically
13 reacting compound of the metal, such as the hydroxide, with the polyalkenyl sulfonic
14 acid. This is generally carried out in the presence of a hydroxylic promoter such as
15 water, alcohols such as 2-ethyl hexanol, methanol or ethylene glycol, and an inert
16 solvent for the sulfonate, typically with heating. Under these conditions, the basically
17 reacting compound will yield the metal sulfonate. The hydroxylic promoter and
18 solvent can then be removed to yield the metal sulfonate.

19 Under certain circumstances, it may be more convenient to prepare an alkali
20 metal polyalkenyl sulfonate and convert this material by metathesis into an alkaline
21 earth metal sulfonate. Using this method, the sulfonic acid is combined with a basic
22 alkali metal compound such as sodium or potassium hydroxide. The sodium or
23 potassium sulfonate obtained can be purified by aqueous extraction. Then, the sodium
24 or potassium sulfonate is combined with an alkaline earth metal salt to form the
25 alkaline earth metal sulfonate. The most commonly used alkaline earth metal
26 compound is a halide, particularly a chloride. Typically, the sodium or potassium
27 sulfonate is combined with an aqueous chloride solution of the alkaline earth metal
28 and stirred for a time sufficient for metathesis to occur. Thereafter, the water phase is
29 removed and the solvent may be evaporated, if desired.

30 The preferred sulfonates are alkaline earth metal sulfonates, especially those of
31 calcium, barium and magnesium. Most preferred are the calcium and magnesium
32 sulfonates.

1 The polyalkenyl sulfonates of this invention are either neutral or overbased
2 sulfonates. Overbased materials are characterized by a metal content in excess of that
3 which would be present according to the stoichiometry of the metal cation in the
4 sulfonate said to be overbased. Thus, a monosulfonic acid when neutralized with an
5 alkaline earth metal compound, such as a calcium compound, will produce a normal
6 sulfonate containing one equivalent of calcium for each equivalent of acid. In other
7 words, the normal metal sulfonate will contain one mole of calcium for each two
8 moles of the monosulfonic acid.

9 By using well known procedures, overbased or basic complexes of the sulfonic
10 acid can be obtained. These overbased materials contain amounts of metal in excess
11 of that required to neutralize the sulfonic acid. Highly overbased sulfonates can be
12 prepared by the reaction of overbased sulfonates with carbon dioxide under reaction
13 conditions. A discussion of the general methods for preparing overbased sulfonates
14 and other overbased products is disclosed in U. S. Patent No. 3,496,105, issued
15 February 17, 1970 to LeSuer, which is incorporated by reference in its entirety.

16 The amount of overbasing can be expressed as a Total Base Number ("TBN"),
17 which refers to the amount of base equivalent to one milligram of KOH in one gram
18 of sulfonate. Thus, higher TBN numbers reflect more alkaline products and therefore a
19 greater alkalinity reserve. The TBN for a composition is readily determined by ASTM
20 test method D664 or other equivalent methods. The overbased polyalkenyl sulfonates
21 of this invention can have relatively low TBN, i.e., about 0 to about 60, or relatively
22 high TBN, i.e., greater than 60 to about 400.

23 The polyalkenyl sulfonates of this invention are useful as additives in
24 lubricating oils. They have good tolerance to water, a light color and provide good
25 performance characteristics.

26 The lubricating oil compositions of this invention comprise a major amount of
27 an oil of lubricating viscosity and a minor amount of the polyalkenyl sulfonates of this
28 invention. The oils can be derived from petroleum or be synthetic. The oils can be
29 paraffinic, naphthenic, halosubstituted hydrocarbons, synthetic esters, or combinations
30 thereof. Oils of lubricating viscosity have viscosities in the range from 35 to 55,000
31 SUS at 100°F., and more usually from about 50 to 10,000 SUS at 100°F. The
32 lubricating oil compositions contain an amount of the polyalkenyl sulfonates of this

1 invention sufficient to provide dispersant properties, typically from about 0.1 weight
2 percent to 10 weight percent, preferably from about 0.5 weight percent to about 7
3 weight percent.

4 Other conventional additives that can be used in combination with the
5 polyalkenyl sulfonates of this invention include oxidation inhibitors, antifoam agents,
6 viscosity index improvers, pour point depressants, dispersants and the like.

7 The lubricating oil compositions of this invention are useful for lubricating
8 internal combustion engines and automatic transmissions, and as industrial oils such
9 as hydraulic oils, heat transfer oils, torque fluids, etc.

10

11

EXAMPLE 1

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PREPARATION OF A POLYISOBUTENE SULFONIC ACID FROM A 13 HIGH METHYLVINYLDENE POLYISOBUTENE THAT HAS 14 A M_n OF 550 AND ACETYL SULFATE

15 To a beaker is added 5.5g (0.01 mol) of Glissopal 550 polyisobutene (which
16 has greater than about 80% methylvinyldene content with a number average
17 molecular weight of about 550) dissolved in 20mL hexane. To this is added 1.63g
18 acetic anhydride (0.016 mole) and then 0.98g sulfuric acid (0.01 mole). The resulting
19 mixture is stirred at room temperature for one hour. Then some methanol is added to
20 quench the reaction and the solvents are removed in vacuo. A total of 7.16g of crude
21 polyisobutene sulfonic acid is obtained.

22

EXAMPLE 2

23

PREPARATION OF A LOB POLYISOBUTENE SODIUM SULFONATE 24 FROM THE PRODUCT OF EXAMPLE 1

25 To 5.91g of the sulfonic acid from Example 1 is added 20 mL isopropyl
26 alcohol and 1 g sodium hydroxide in 1 mL of water. The resulting mixture is refluxed
27 for 6 hours and then held at room at room temperature overnight. Two layers form
28 and the bottom layer is decanted. The top layer contains sodium polyisobutene
29 sulfonate (5.67g) which contains 88% actives. The lower layer is stripped in vacuo
30 and contains 1.14g of a mixture of sodium hydroxide and sodium polyisobutene
31 sulfonate.

EXAMPLE 3

PREPARATION OF CALCIUM LOB POLYISOBUTENE SULFONATE

To a 2L round bottom flask is added 500g of Glissopal 550 polyisobutene (0.91 mol), 140.3g acetic anhydride (1.38 mol), and 84.7g concentrated sulfuric acid (0.86 mol) at room temperature. The resulting mixture is stirred 4 hours at room temperature. Then to this mixture is added 50 mL methanol to quench the reaction, and 500g of 100 neutral diluent oil. To this is then added 32.0g calcium hydroxide (0.43 mol) and 20 mL water. The resulting mixture is heated to 175°F and then 100 mL water is added. This is then heated to 225-230°F for 30 minutes, and then heated at 330°F for 1 hour to strip off the water. A calcium polyisobutene sulfonate is obtained.

EXAMPLE 4

PREPARATION OF POLYISOBUTENE SULFONIC ACID USING SO₃ AND AIR

A thin film of Glissopal 550 polyisobutene is sulfonated using SO₃ and air under the following conditions: temperature 60°C, SO₃ flow 16L/hr, air flow 192L/hr, feed rate 4.5g/min. The product from this reaction is a mixture of polyisobutene sulfonic acid and polyisobutene sultone. The product contains 2.04% sulfonate as calcium sulfonate and 0.70% sulfuric acid as determined by hyamine titration.

EXAMPLE 5

PREPARATION OF POLYISOBUTENE SULFONIC ACID USING SO₃ AND AIR

A thin film of Glissopal 550 polyisobutene is sulfonated using SO_3 and air under the following conditions: temperature 60° , SO_3 flow 16L/hr, air flow 192L/hr, feed rate 4.2g/min. A total of 1354g product is obtained which is a mixture of polyisobutene sulfonic acid and polyisobutene sultone. The product contains 2.5% sulfonate as calcium sulfonate and 1.02% sulfuric acid as determined by hyamine titration. The acid number is determined by the ASTM D664 test to be 59.9 mg KOH/g sample.

EXAMPLE 6

PREPARATION OF SODIUM POLYISOBUTENE SULFONATE

The mixture of polyisobutene sulfonic acid and polyisobutene sultone from Example 5 is hydrolyzed using the following procedure. To a 100 mL three neck flask equipped with a reflux condenser and stirrer is added 20g of polyisobutene

1 sulfonic acid and the resulting mixture is heated to 100°C. To this is added 5 mL 49%
2 sodium hydroxide solution and the resulting mixture is stirred for four hours. The
3 product from this reaction is a mixture of sodium polyisobutene sulfonate and
4 polyisobutene sultone.

5 EXAMPLE 7

6 PREPARATION OF CALCIUM POLYISOBUTENE SULFONATE 7 FROM 550 MW POLYISOBUTENE (NEUTRAL SULFONATE)

8 To a 2 L round bottom flask is added 500g (0.91 mol) Glissopal 550 (550 M_n
9 polyisobutene containing about 85% methylvinylidene isomer), 140.3 g acetic
10 anhydride, (1.38 mol; 1.5 equivalents), and 84.7g sulfuric acid (0.864 mol; 0.95
11 equivalents) dropwise at room temperature. The resulting mixture is stirred 4 hours
12 at room temperature. Then to this is added 50 mL methanol and then 500g 100
13 neutral diluent oil is added. To this is then added 32.0g calcium hydroxide (0.43 mol)
14 and 20 mL water. This is heated to about 80°C and an additional 100 mL or water is
15 added. Then the volatile materials are removed at elevated temperatures. The product
16 is filtered to give 842.3 g of product which has a TBN of 3.4 mg KOH/g sample, a
17 viscosity @100°C of 72.4 cSt., 1.50% Ca, and 2.31% S.

18 EXAMPLE 8

19 PREPARATION OF CALCIUM POLYISOBUTENE SULFONATE 20 FROM 550 MW POLYISOBUTENE (LOB SULFONATE)

21 To a 4 L beaker is added 500g (0.91 mol) Glissopal 550 polyisobutene (550
22 M_n polyisobutene with about 85% methylvinylidene isomer content), 140.3 g acetic
23 anhydride (1.38 mol), and 84.7g sulfuric acid (0.864 mol). The resulting mixture is
24 stirred 1 hour at room temperature. To this is then added 50 mL methanol, 500g 100
25 neutral diluent oil, and 100 mL water. The resulting mixture is heated to 190°F and
26 48g (0.649 mol) calcium hydroxide is added. This is stirred for one hour and then the
27 temperature is raised to 212°F and maintained there until all the volatile material has
28 distilled. The resulting product is then filtered to give a LOB calcium polyisobutene
29 sulfonate which has a TBN of 12.3 mg KOH/g sample, 2.24 % S, 1.85% Ca, and a
30 viscosity @ 100°C of 79.4 cSt.

EXAMPLE 9

PREPARATION OF ADDITIONAL POLYISOBUTENE SULFONATES

Additional examples of calcium polyisobutene sulfonates are carried out using different conditions, charge mole ratios ("CMR's") and polyisobutene ("PIB") molecular weights as shown in Table 1.

Ex.	PIB M _n	% diluent oil	Ac ₂ O / PIB	H ₂ SO ₄ / PIB	H ₂ SO ₄ / Ca(OH) ₂	% Ca	% S	TBN	Vis @ 100°C
7	550	50	1.52	0.95	2.01	1.50	2.31	3.4	72.4
8	550	50	1.52	0.95	1.33	1.85	2.24	12.0	79.4
9	550	45	1.51	0.95	1.83	1.84	2.60	5.5	113.8
10	550	45	1.51	0.95	2.00	1.71	2.58	2.6	167.4
11	1000	45	1.51	0.95	1.81	1.08	1.50	3.1	153.8
12	1000	45	1.51	0.95	1.76	1.03	1.52	0.9	156.1
13	1000	45	1.50	0.95	1.83	1.08	1.49	3.9	163.8

EXAMPLE 14

PREPARATION OF CALCIUM ACETATE-FREE 550 M_n
CALCIUM POLYISOBUTENE SULFONATE

The sulfonic acid from 550 M_n polyisobutene is first prepared by reacting Glissopal 550 polyisobutene (2000 g, 3.64 mol), with 408.3 g acetic anhydride (4.0 mol), and 338.7 g sulfuric acid (3.46 mol). The resulting mixture is stirred for one hour at room temperature. Then 200 mL of methanol is added. The resulting product contains about 90% actives. Then 260 g of this product is diluted with 260 g of 100 neutral diluent oil and this is heated at 40°C with a nitrogen sparge to remove the unreacted acetic acid, methyl acetate, and methanol. Analysis by ¹H NMR spectroscopy indicates that only about 0.3% acetic acid remained. This product (448.2 g) is then placed in a 1000 mL beaker and heated to 190°F and to this is added 13.2g calcium hydroxide. The resulting mixture is stirred for 1 hour at 190°F, and then the temperature is increased to 330°F to remove any volatile material. The resulting product is then filtered to give a calcium acetate-free calcium polyisobutene

1 sulfonate which has a TBN of 5.4 mg KOH/g sample, 1.12%Ca, 1.82% S, and a
2 viscosity @ 100°C of 27.5 cSt.

3 COMPARATIVE EXAMPLE A

4 PREPARATION OF 950 M_n POLYISOBUTENE SULFONIC ACID
5 FROM PARAPOL 1000

6 200g Parapol 950 (950 M_n polyisobutene with less than 5% methylvinylidene
7 isomer content, 0.21 mol) is reacted with 22.46g acetic anhydride (0.22 mol) and
8 18.63g sulfuric acid (0.190 mol). The resulting product is stirred at room temperature
9 for 1 hour then 20 mL methanol was added. This product contains only about 67%
10 actives.

11 EXAMPLE 15

12 PREPARATION OF 1000 M_n POLYISOBUTENE SULFONIC ACID
13 FROM GLISSOPAL 1000

14 To 2000g (2.0 mol) of Glissopal 1000 polyisobutene (M_n 1000 with about
15 85% methylvinylidene isomer content) is added 224.6 g acetic anhydride (2.2 mol)
16 and 186.3 g of sulfuric acid (1.90 mol). The resulting product is reacted as in
17 Comparative Example A. The product contains about 90% actives. This shows the
18 improvement in yield that is obtained with the teachings of this invention.

19 COMPARATIVE EXAMPLE B

20 ELECTROSPRAY IONIZATION-MASS SPECTRUM OF SULFONIC ACID
21 FROM POLYISOBUTENE WITH LESS THAN 20% METHYLVINYLIDENE
22 CONTENT

23 Figure 2 shows the electrospray ionization mass spectrum of a polybutene
24 sulfonic acid from Hivis 5 (polybutene with less than 10% methylvinylidene isomer
25 content). The spectrum shows a molecular weight distribution with molecular ions
26 that are separated by 14 daltons. This indicates that the polyisobutene sulfonic acid
27 actually is not a mixture of C₁₂, C₁₆, C₂₀ etc. isomers, but is a mixture of C₁₂, C₁₃, C₁₄,
28 etc., isomers.

1 EXAMPLE 16
2 ELECTROSPRAY IONIZATION-MASS SPECTRUM OF SULFONIC ACID
3 FROM POLYISOBUTENE WITH MORE THAN 20% METHYL VINYLIDENE
4 CONTENT

5 Figure 1 shows the electrospray ionization mass spectrum of a polybutene
6 sulfonic acid from Glissopal 550 (polybutene with greater than 85% methylvinylidene
7 isomer content). The spectrum shows a molecular weight distribution with molecular
8 ions that are separated by 56 daltons. This indicates that the polyisobutene sulfonic
9 acid is a mixture of C₁₂, C₁₆, C₂₀, etc., isomers (i.e., the ions are multiples of four
10 carbon atoms).

CLAIMS:

1. A polyisobutenyl sulfonic acid composition comprising a mixture of polyisobutenyl sulfonic acids derived from a mixture of polyisobutenes comprising greater than 20 mole percent of alkyl vinylidene and 1,1-dialkyl isomers.
5
2. The composition of claim 1 wherein the mixture of polyisobutenes comprises greater than 50 mole percent of alkyl vinylidene and 1,1-dialkyl isomers.
- 10 3. The composition of claim 2 wherein the mixture of polyisobutenes comprises greater than 70 mole percent of alkyl vinylidene and 1,1-dialkyl isomers.
4. The composition of claim 1, 2 or 3 wherein the alkyl vinylidene isomer is a methyl vinylidene isomer, and the 1,1-dialkyl isomer is a 1,1-dimethyl isomer.
15
5. The composition of any one of claims 1-4 wherein the number average molecular weight of the polyisobutenes is about 168 to about 5000.
6. The composition of claim 5 wherein the number average molecular weight of the polyisobutenes is about 550.
20
7. The composition of claim 5 wherein the number average molecular weight of the polyisobutenes is about 1000.
- 25 8. The composition of claim 5 wherein the number average molecular weight of the polyisobutenes is about 2300.
9. The composition of any one of claims 1-8 wherein the polyisobutenes have been made using a BF_3 catalyst.
30
10. The composition of claim 1 wherein the molecular weight distribution of the polyisobutenyl sulfonic acids is such that at least 80% of the molecular weights of the polyisobutenyl sulfonic acids are separated by even multiples of 56 daltons.

11. The composition of claim 1 wherein less than 20% of the polyisobutenyl sulfonic acids in the molecular weight distribution of the polyisobutenyl sulfonic acids contain a total number of carbon atoms that is not evenly divisible by four.
- 5
12. A method of making polyisobutenyl sulfonic acid composition of any one of claims 1-11, which comprises sulfonating a mixture of polyisobutenes comprising greater than 20 mole percent of alkyl vinylidene and 1,1-dialkyl isomers.
- 10
13. A polyisobutenyl sulfonate composition having a TBN of about 0 to about 60 wherein the polyisobutenyl sulfonate is an alkali metal or alkaline earth metal salt of a polyisobutenyl sulfonic acid composition of any one of claims 1-11.
14. A polyisobutenyl sulfonate composition having a TBN of greater than 60 to about 400 wherein the polyisobutenyl sulfonate is an alkali metal or alkaline earth metal salt of a polyisobutenyl sulfonic acid composition of any one of claims 1-11.
- 15
15. A polyisobutenyl sulfonate composition of claims 13 or 14 wherein the alkali metal or alkaline earth metal is calcium.
- 20
16. A method of making polyisobutenyl sulfonate composition, which comprises making a sulfonic acid by a method of claim 12 and reacting the resulting polyisobutenyl sulfonic acid composition with an alkali metal or alkaline earth metal.
- 25
17. A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount of a polyisobutenyl sulfonate composition of claim 13.
- 30
18. A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount of a polyisobutenyl sulfonate composition of claim 14.