

1

3,076,841

PREPARATION OF ALKALINE EARTH
PETROLEUM SULFONATES

Le Roi E. Hutchings, Crystal Lake, and Gifford W. Crosby, River Forest, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio
No Drawing. Filed Dec. 28, 1959, Ser. No. 862,079
4 Claims. (Cl. 260—504)

This invention relates to a method for preparing basic metal salts of oil-soluble petroleum sulfonic acids. More specifically, the invention relates to the preparation of mineral oil solutions of weakly-basic, alkaline earth metal petroleum sulfonates from refined mineral lubricating oils which are characterized by their increased detergency and alkaline reserve, ability to pass the water susceptibility test, compatibility with compositions containing polyvalent metal dialkyl dithiophosphates, and ability to suppress varnish formation under conditions of use.

The art of preparing salts or soaps of organic acids recognizes that the use of an excess of neutralizing agent may result in a product containing an excess over that amount of neutralizing base theoretically required to react with and replace all of the acidic hydrogens of the acid. As far as petroleum sulfonates are concerned, the formation of these basic salts is necessary to impart thereto an "alkaline reserve" and increased detergency properties when the sulfonates are used in lubricants. The alkaline reserve acts to neutralize the sulfur- and oxy-acids formed in the oil from the combustion of fuel, and the increased detergency acts to solubilize the oxidation products and sludge so formed.

The art teaches several methods of obtaining increased basicity. In one method described in the prior art, it is only necessary to react an alkaline earth metal petroleum sulfonate with an excess of alkaline earth metal base, generally in the form of an oxide, hydroxide or carbonate, and the resulting product after separation of any unreacted base is said to have the desired properties. In another method, "alkaline reserve," as represented by the base number obtained by electrometric titration (ASTM D-664-58), is obtained by reacting the alkaline earth metal petroleum sulfonate with excess base and at least 2% by weight of water, followed by blowing the reaction mixture with carbon dioxide. The alkaline reserve obtained by this method of preparation is represented by ASTM base numbers of over 10 or 11.0 and as high as about 200. In still another prior art method of preparing alkaline earth metal petroleum sulfonates, it is taught that the reaction of an excess of base with the petroleum sulfonate must be carried out in the presence of a promoter, such as certain enolic compounds. Although the highly basic petroleum sulfonates prepared by this last method are cited as being excellent detergents, the end products are more than alkaline earth metal petroleum sulfonates and are described as complexes containing carbonates of the alkaline earth metal.

This invention is directed primarily to the problem of preparing alkaline earth metal petroleum sulfonates which exhibit the required detergency and "alkaline reserve," but are not strongly basic as defined by "strong base numbers." It has been discovered that alkaline earth metal petroleum sulfonates can be prepared which are completely oil-soluble and storage-stable by treating the

2

alkaline earth metal petroleum sulfonate, after the separation of all oil-insoluble components, with a weakly acidic inorganic reagent, i.e., carbon dioxide, carbon disulfide and carbonyl sulfide in the presence of substantially no water, or at most no more than about 0.3 weight percent of water based on the weight of the alkaline earth metal petroleum sulfonates, and in the absence of a promoter.

Accordingly, it becomes a primary object of this invention to prepare weakly-basic, polyvalent metal, petroleum sulfonates having the desired oil solubility and detergency in oil compositions containing polyvalent dialkyl dithiophosphates.

Another object of this invention is to provide a method of preparing weakly-basic, polyvalent metal, petroleum sulfonates from sulfonic acids obtained from the treatment of solvent-refined oils with sulfur trioxide, including the steps of separating the oil-insoluble materials from the initially neutralized sulfonate, followed by blowing with an inorganic acidic material in the absence of water (or less than about 0.3 weight percent of water based on the amount of the sulfonate).

A further object of the invention is to provide a method of preparing weakly-basic, alkaline earth metal, petroleum sulfonates by reacting the oil-soluble portion of a neutralized petroleum sulfonate with carbon dioxide under conditions substantially devoid of complex or carbonate formation, and in the absence of water.

A feature of this invention is the discovery that the detergency and "alkaline reserve" specifications attaching to alkaline earth metal petroleum sulfonates are not limited to preparation in the presence of a promoter during blowing with an inorganic acidic material, and are not limited to conditions of alkaline earth carbonate formation.

More particularly, this invention relates to a process wherein the petroleum sulfonic acids are initially neutralized in the presence of water, using an excess of alkaline earth metal base, the oil-insoluble portions formed or present during the neutralization are removed, and the resulting clear, strongly-basic, alkaline earth metal sulfonate product is reacted with an inorganic acidic material, such as carbon dioxide, in the absence of water (or less than about 0.3 weight percent of water, based on the amount of said sulfonate), to yield a weakly-basic product of improved detergency and dithiophosphate compatibility.

These and other objects and features of the invention will be described or become apparent as the specification proceeds.

The starting material for the process of this invention comprises oil-soluble organic sulfonic acid compounds derived from the sulfonation of petroleum hydrocarbons and fractions of petroleum hydrocarbons. The sulfonation of the petroleum hydrocarbons may be carried out by any of the known methods, followed by neutralization with an alkaline earth metal base. The neutralized mixture of alkaline earth metal petroleum sulfonates is preferably purified by centrifuging in the presence of a non-polar solvent in order to remove any sludge present as a result of the sulfonation reaction. The processes of sulfonation and neutralization described in the following United States patents may be used, with certain modifications: 2,514,733; 2,815,370; 2,802,026; 2,828,331; 2,800,503; 2,834,803, and 2,834,802.

In the preferred method of preparing the petroleum

sulfonate, the following procedure is used. An oil feed comprising any Mid-Continent solvent-refined neutral oil, ranging in viscosity from 170 to 600 SUS at 100° F., is passed through a drier containing alumina, an adsorbent clay, or rock salt, to remove traces of water that may be present. The physical properties of specific examples of feed oils contemplated are given in the following Table I:

Table I.—Feed Oils

Stock	200/90 Neutral	350/100 Neutral	500/100 Neutral
Gravity, ° API	29.1	30.0	29.6
Flash, COC, ° F	440	470	500
Fire, COC, ° F	485	530	565
Vis. at 100° F., SUS	202.3	350.9	515.5
Vis. at 130° F., SUS	105.3	166.6	233
Vis. at 210° F., SUS	46.3	55.8	65.2
Viscosity Index	93	101	100
Pour Point, ASTM, ° F	0	0	0
Color, NPA	+2	1½+	1½+
Carbon Residue, Con. percent	0.01	0.02	<0.1
VGC	0.83	0.81	0.81
Mol Wt. (cryoscopic)	395	490	530

The dry oil is sent to a sulfonator, i.e., a mechanically-agitated reactor such as a Votator, which is equipped with a cooling jacket to control the reaction temperature. In the reactor the dry oil mixes and reacts with a vapor-phase mixture of air and sulfur trioxide which is prepared by passing dry air and liquid sulfur trioxide into a vaporizer. The vaporizer may be of the falling-film type wherein a thin film of liquid sulfur trioxide flows downward along the inner surface of a steam-heated tube and the vaporized sulfur trioxide mixes with air flowing upward through the tube. This type of vaporizer also acts as a dehydrator in that any water vapor present in the recycle air stream combines with sulfur trioxide to form sulfuric acid which is collected and withdrawn at the bottom of the vaporizer. The effluent reaction mixture from the sulfur trioxide reaction with oil passes to a vapor-liquid separator where the sulfonic acids, along with unreacted oil, are separated from the air stream which latter is recycled to the reactor blowing system. The recycle air is treated by passage through a filter or demister to remove any entrained oil before recycling in the system.

The reaction is carried out using sulfur trioxide-to-oil weight ratios ranging from about 0.02 to 0.08, with an SO₃/oil weight ratio of about 0.06 preferred. The volume of sulfur trioxide to air entering the reactor may range from about 0.02 to 0.50, with 0.05 being preferred. The oil solution of petroleum sulfonic acids passes directly to the neutralization reactor. The base used in the neutralization may be purified to remove carbonates and other extraneous salts therefrom. The base, e.g., barium oxide, is sent to a hydrator or melter where sufficient water is added to form hydrated hydroxide. The resulting liquid product may be filtered to remove impurities. In this case, the quantity of water added to the hydrator is sufficient to form the octahydrate of the base, and any more than a slight excess of water is to be avoided because of the increased heat requirements in the remainder of the operation.

The mixture of base material and the oil solution of petroleum sulfonic acids is next brought into intimate admixture in the neutralizer reactor and heated to about 300° F., using steam coils. A preferred method of obtaining intimate contact is to pass the reaction mixture into a recycle pump connected to a heat exchanger, whereby the mixture is circulated through the heat exchanger and back to the pump in such a manner that the mixture remains in the system about five minutes and is raised to a temperature of about 450° F. Electric heaters may be used for this purpose. The extent of alkalization in the finished product is controlled by regulating the temperature maintained in this reaction system in the

300–500° F. range, and the higher the temperature, the better the utilization of the excess barium hydroxide and the higher the base number of the finished product.

The resulting reaction mixture is a two-phase mixture consisting of barium sulfonates and unreacted oil in the oil phase, and water with small quantities of water-soluble sulfonates in the aqueous phase. This two-phase mixture is passed to a water-flash vessel wherein the water is flashed off as vapor, along with a small quantity of oil, in what may be described as essentially a steam distillation. The oil phase is separated from the overhead water phase and recycled to the neutralization reaction. The liquid, bottom phase in the water-flash vessel is withdrawn as dry, basic barium sulfonate containing a minor proportion of suspended solids.

At this point, a non-polar solvent, such as hexane, is added to the bottoms from the water-flash vessel to increase the fluidity thereof and to aid in the separation of suspended solids. Between about 100 to 400% by volume of non-polar solvent, e.g., hexane pentane, naphthas and the like, is added, based on the volume of the sulfonate bottoms. The resulting hexane-oil-sulfonate mixture is passed through a centrifuge where suspended solids are removed as sludge, leaving an entirely oil-soluble solution of sulfonates, including excess base in oil-soluble form. The hexane is removed in a solvent-recovery tower. The resulting clear, dry-product is then treated with an acidic material, such as carbon dioxide, while at a temperature ranging from about 150° F. to 400° F. The acidic material in gaseous form is introduced at the rate of 1.5 weight percent on the sulfonate basis. During this period, the pH of the sulfonate solution is decreased to less than about 11, indicating the attainment of substantially complete neutralization of strongly basic constituents. Because of the elevated temperatures used, no free carbon dioxide remains in the finished product. The product is then ready for use in compounding lubricating oil compositions, and for other uses where a detergent of weak basicity and high detergency is indicated. An important feature of the invention is conducting the blowing with the acidic material in the substantial absence of any excess, unreacted base material such as barium hydroxide, either in hydrated or oxide form. Any small amount of base present, amounting to less than 0.1 weight percent based on the total mixture, is present in oil-soluble amounts or in oil-soluble form. The product from this reaction is not highly basic but has a high detergency value, as will be demonstrated.

The invention is illustrated by the following examples.

EXAMPLE I

A Mid-Continent solvent-refined neutral oil was used as a sulfonation stock. This oil had the following properties:

Gravity, ° API	30.0
Viscosity at 100° F., SUS	350.9
Viscosity index	101

Dry oil was charged to one port of a Votator reaction vessel at the rate of 0.90 lb./min. A mixture of 17 volumes of air and 1 volume of SO₃ was charged to another Votator injection port so that the SO₃ charge rate was 0.056 lb./min. The sulfonation reaction took place in the annular space between the water-jacketed outer cylinder and the rotating shaft of the Votator. The dimensions of the Votator were as follows:

Votator shaft diameter	in.	2.9
Votator shaft length	in.	12
Votator annulus	in.	0.06
Votator shaft speed	r.p.m.	1080

The charge-oil temperature was 95° F. and the acid-oil temperature at the Votator outlet was 126° F. The acid-oil was found to have a total acid number of 40 (ASTM D-974). The acid-oil was mixed with 15.0 wt. percent

of barium hydroxide octahydrate and the mixture heated to 260° F. at atmospheric pressure to remove the major portion of the water. The resulting, partially dried, neutral sulfonate was mixed with an additional 7.6 weight percent of barium hydroxide, and about 3 weight percent water, on an acid-oil basis. The product was heated with stirring to 450° F. at 350 p.s.i.g. for 50 minutes, and was then dried by removal of steam. Drying was completed by nitrogen-stripping the sulfonate product for ten minutes at 450° F. After cooling, the sulfonate containing suspended solids was diluted with 2 volumes of hexane and passed through a continuous centrifuge at the rate of 300 ml./min. The bowl diameter of the centrifuge was 1.75 inches and the rotational speed 24,000 r.p.m. The clarified sulfonate solution was distilled to remove hexane, and the dry, residual product was then blown with carbon dioxide at 250° F. until the strong base number (ASTM D-664) was reduced to zero. This product was found to have the following chemical analysis:

Ash as sulfate, wt. percent	11.9
Total base number, D-664	26.0
Strong base number, D-664	0.0
Ba(OH) ₂ , wt. percent	Not detectable
BaCO ₃ , wt. percent	Not detectable
Water, wt. percent	0.2

A lubricating oil blend was prepared from Mid-Continent solvent-refined neutral (89.8 wt. percent), basic barium sulfonate product (8.2 wt. percent), and commercial zinc dialkyl dithiophosphate (2.0 wt. percent). This blend remained clear after 24-hour storage at room temperature, indicating satisfactory compatibility of the sulfonate with the oxidation inhibitor and the mineral oil.

The sulfonate product was also subjected to water-susceptibility tests to determine the ability of the sulfonate and its mineral oil blends to be readily dried after water contamination without encountering cloudiness or precipitation in the dried product. The above sulfonate product successfully passed these tests.

The exceptionally good utility of the basic barium sulfonate of this example as a lubricating oil additive was demonstrated by performance tests in internal combustion engines.

A. Diesel engine detergency test—CRC Designation L-1-545.—The purpose of this test is outlined by the CRC Manual, 1946: "This procedure is intended for determining the effect of engine oils on ring-sticking, wear, and the accumulation of deposits under endurance conditions."

Test oil composition:	wt. percent
M-C, S-R, 200 vis., neutral oil	53.0
M-C, S-R, bright stock	36.9
Basic barium sulfonate, Example I	8.1
Zinc diaryl dithiophosphate	2.0

The one-cylinder Caterpillar engine was operated on the above oil blend under the specified L-1 condition using 1% sulfur fuel. The piston was rated after 480 hours of operation.

Top groove fill	19%.
2nd ring groove	Varnish.
3rd ring groove	Clean.
Top land	Varnish.
2nd land	Clean.
3rd land	Clean.

The small amount of carbon found in the top ring groove and the cleanliness and freedom from varnish of the lower parts of the piston indicated a high degree of lubricant detergency.

B. Gasoline engine test for oil oxidation stability and bearing corrosion.—The CRC Designation L-38 is a research technique for the study of oxidation characteristics of crankcase oils in the CLR oil-test engine. This test

procedure is published by the Oil Oxidation Tests Group of the Motor Vehicle Fuel, Lubricant and Equipment Research Committee of the Coordinating Research Council.

Test oil composition:	wt. percent
M-C, S-R, 170 vis. neutral oil	76.5
M-C, S-R, 85 vis. neutral oil	2.0
Extract from M-C, S-R neutral	5.0
Sulfonate, Example I	9.3
Zinc dialkyl dithiophosphate	0.9
Acrylic polymer	6.4

On completion of the test under the specified conditions, the bearing weight loss was determined and the piston cleanliness rated.

Bearing loss, mgm.	21.
Piston varnish	9.9 (10=clean).

These results indicate a very high order of freedom from varnish deposits and from copper-lead bearing corrosion.

C. Gasoline engine test for engine cleanliness and wear.—MS, sequences I, II and III using a dynamometer-coupled Oldsmobile engine, as published by Subgroup V-IV of Technical Committee B of ASTM D-2, were used to test lubricants containing the sulfonate of Example I.

Test oil composition:	wt. percent
M-C, S-R, 170 vis., neutral oil	76.5
M-C, S-R, 85 vis., neutral oil	2.0
Extract from M-C, S-R neutral	5.0
Sulfonate, Example I	9.3
Zinc dialkyl dithiophosphate	0.9
Acrylic polymer	6.4

MS, sequences I, II and III results:

Cam and tappet scuffing	None.
Cam and tappet wear:	
Average, combined	0.0036".
Maximum, combined	0.0043".
Rust ratings:	
Tappet body	9.5 (10=rust free).
Engine average	9.7.
Ring sticking and plugging	None.
Sludge ratings:	
Top cover	9.2 (10=clean).
Engine average	9.5.
Varnish ratings:	
Piston skirt	9.8 (10=clean).
Engine average	9.5.

Additional gasoline engine testing of lubricants was carried out under simulated conditions of stop-and-go service conducive to the formation of low-temperature sludge. A 96-hour test in a 1958 Cadillac engine gave the following results when the lubricant used in the above L-38 and MS tests was employed.

Overall sludge rating	9.4 (10=clean).
3-point average sludge rating	8.8.
Piston varnish	9.8.
Average tappet wear	0.0004".
Average cam-nose wear	0.0009".

A 135-hour test was carried out on the same lubricant in a 1959 Oldsmobile engine operated under conditions which normally lead to low-temperature sludge and varnish.

Average sludge	9.7 (10=clean).
Average varnish	9.7.
Piston varnish	9.0.

The foregoing engine tests show the effectiveness of the basic barium sulfonate detergent of this invention in keeping internal combustion engines clean under a variety of conditions, without adversely affecting other lubricant properties, such as oxidation stability and ability to lubricate without allowing high wear rates.

EXAMPLE II

A Mid-Continent, solvent-refined neutral oil was used in the manufacture of basic barium sulfonate. Charge oil properties:

Gravity, ° API	29.6
Viscosity at 100° F., SUS	515.5
Viscosity index	100

Sulfonation took place in a Votator reaction vessel of the following dimensions:

Shaft diameter	in.	3.80
Shaft length	in.	27
Votator annulus	in.	0.10
Shaft speed	r.p.m.	1250

Dry oil was pumped to the reaction vessel at the rate of 3.03 lb./min. A 15/1 volume ratio of air to SO₃ was employed, and this gaseous mixture fed to a separate Votator port at the rate of 0.236 lb. of SO₃/min. The oil temperature at the reactor inlet was 80° F. and the acid-oil temperature at the reactor outlet was 131° F.

Acid-oil analysis:

Total acid number, ASTM D-974	50
Sludge, vol. percent	<1

Neutralization of the acid-oil was accomplished by adding 35.8 weight percent of barium hydroxide octahydrate (acid-oil basis) and heating to 200° F. with stirring. The neutral sulfonate product, containing water and excess barium hydroxide, was then heated to 450° F. in a stirred autoclave for 1 hour. Maximum pressure was 370 p.s.i.g. Steam was removed at 450° F. and the basic sulfonate product was dried by nitrogen-stripping for 10 minutes after reaching atmospheric pressure. The resulting sulfonate product was cooled to 80° F., diluted with 2 volumes of hexane and centrifuged in a Sharples laboratory model centrifuge with a bowl diameter of 1.75 in. A speed of 24,000 r.p.m. was employed. The hexane solution was fed to the centrifuge at the approximate rate of 300 ml./min. Hexane was removed from the clear centrifuge effluent by distillation to give a residual basic barium sulfonate product dissolved in the unsulfonated portion of the oil:

Ash as sulfate, wt. percent	12.8
Total base number, D-664	28
Strong base number, D-664	14
Ba(OH) ₂ , wt. percent	Not detectable
BaCO ₃ , wt. percent	Not detectable
Water, wt. percent	0.3

This product was found to be compatible with mineral oil and zinc dialkyl dithiophosphate in an SAE 10 formulation and was found to be capable of being reconstituted as clear, dry additive or oil blend on heating after water contamination.

This strongly basic barium sulfonate was tested as a lubricating oil detergent by the L-1 diesel engine test procedure using 1% sulfur fuel.

Lubricant composition:	Wt. percent
M-C, S-R, 200 vis., neutral oil	56.0
M-C, S-R, bright stock	34.5
Basic barium sulfonate, Example II	7.5
Zinc diaryl dithiophosphate	2.0

Observation of the piston after the usual 480-hour test showed good control of top ring-groove carbon deposition, but poor control of varnish deposition below the top ring-groove.

Top groove fill	5%.
Second ring groove	Clean.
Third ring groove	Varnish.
Top land	Varnish.
Second land	Varnish.
Third land	Varnish.

EXAMPLE III

A portion of the strongly basic barium sulfonate prepared in Example II was heated to 250° F., and carbon dioxide added through a sintered-glass inlet tube until the strong base number (ASTM D-664) was reduced to zero. The total base number remained unchanged at 28. An improved ability to prevent varnish deposition on an L-1 diesel piston compared to the lubricant containing the strongly basic barium sulfonate of Example II was demonstrated.

Lubricant composition:	Wt. percent
M-C, S-R, 200 vis., neutral oil	56.0
M-C, S-R, bright stock	34.4
Basic barium sulfonate, Example III	7.6
Zinc diaryl dithiophosphate	2.0

L-1, 480-hour piston rating (1% sulfur fuel):

Top groove fill	9%.
Second ring groove	Trace varnish.
Third ring groove	Trace varnish.
Top land	Varnish.
Second land	Clean.
Third land	Clean.

Although the combination of sulfonation, neutralization and finishing steps described herein is applicable to the preparation of weakly-basic polyvalent metal salts of oil-soluble petroleum sulfonic acids from the reactable portions of petroleum oils, the method has particular application in the preparation of alkaline earth metal petroleum sulfonates from refined oils. Refined oils as starting materials, although producing sulfonates of good yield, high detergency and oil-solubility are often deficient in the required ability to suppress varnish formation, alkaline reserve, water susceptibility and compatibility with other addends in lubricating compositions, particularly in crankcase lubricating compositions for use in modern high-compression engine as demonstrated by the tests herein. The method of this invention also may be applied to the preparation of sulfonates for use in any compositions where detergency is a prime requisite, and other properties, such as ability to suppress varnish formation, oil-solubility, alkaline reserve, water susceptibility, and compatibility, are not important. For this purpose, the method may be applied to any sulfonatable material, such as fatty oils, synthetic hydrocarbons or petroleum oils, whether refined or not, using any reactable metal, metal base, metal oxide or metal salt in the neutralization, including in particular metals of Groups I, II, IV, V, VI, and VIII of the Periodic Chart of the Atoms, W. M. Welch Manufacturing Company, Revised Edition 1941. Specific examples of base materials suitable for this application are the alkali metal hydroxides, alkaline earth metal oxides, alkaline earth metal hydroxides, magnesium hydroxide, aluminum hydroxide, zirconium hydroxide, vanadium hydroxide, molybdenum hydroxide, and cobalt hydroxide. The acidic material used in the finishing step may be carbon dioxide, carbon disulfide and carbonyl sulfide. Where alkaline reserve is not a desired property for the sulfonates, the method finds application in the preparation of alkali metal sulfonates for use in non-petroleum compositions, as an illustration.

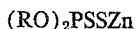
However, where it is desired to prepare sulfonates possessing the requisite combination of ability to suppress varnish formation, alkaline reserve, detergency, weak basicity, water susceptibility, oil-solubility, and compatibility with other addends for use in lubricating oil compositions, which sulfonates are best prepared using refined oils, particularly Mid-Continent solvent refined (MCSR) oils—e.g., neutral oils having viscosities in the range of 170 to 600 SUS at 100° F. or neutral oils preferably having viscosities in the range of 200 to 600 SUS at 100° F., the basic materials are restricted to alkaline earth metals, salts, oxides, hydroxides and their hydrated forms. The acidic material used in this instance is selected from the

group of carbon dioxide, carbon disulfide and carbonyl sulfide. The base materials used to obtain multi-characteristic sulfonates most suitable for use in lubricating oil compositions are the alkaline earth metal oxides, hydroxides and their hydrated forms, particularly barium oxide, barium hydroxide, barium hydroxide octahydrate, calcium oxide, calcium hydroxide, strontium oxide and strontium hydroxide. For some applications, magnesium oxide, magnesium hydroxide, aluminum oxide, molybdenum oxide, and zirconium hydroxide may be used. The alkaline earth metal petroleum sulfonates, namely those of barium, calcium and strontium, constitute the preferred products of this invention where water susceptibility, compatibility with salts of thiophosphorus acids, and varnish formation are problems.

The metal sulfonates of this invention may be used in any application where detergency is required, however, and find utility in rust-inhibiting compositions, metal-drawing compositions, resin compositions, foaming compositions, textile oils, penetrating oils, gum solvent oils, flushing oils, asphalt compositions and the like. The weakly-basic alkaline earth metal petroleum sulfonates of this invention may be used in lubricating oils, engine oils, greases, crankcase oils, diesel oils, transmission oils, gear oils, torque-converter oils, ATF compositions, and similar applications taking advantage of the multi-characteristics thereof.

The "water-susceptibility tests" used as one criterion for evaluating the end-product of this invention are well known. This test procedure is described in detail in United States Patents 2,828,331 and 2,856,422. The test results give a measure of the performance to be expected of the sulfonate when incorporated in a crankcase oil used under conditions of water contamination. The blend and concentrate test, so described, evaluate the sulfonate with regard to its propensity to form precipitates, haze, or cloudiness under the test conditions in the presence of 0.1 to 1.0% by weight of water.

The sulfonate products of this invention, particularly the multi-characteristic alkaline earth metal salts thereof, are compatible with mineral oil solutions containing various other addends. A feature of the invention is the compatibility of the instant sulfonates with metal salts of thiophosphorus acids, particularly heavy metal salts of dialkyl dithiophosphates and heavy metal salts of diaryl dithiophosphates. These materials have multi-functional properties which permit them to serve as corrosion inhibitors, anti-oxidants, detergents, anti-wear agents and E.P. agents, all of which properties are well known. Salts of esters of thiophosphoric acid having the general formula:



may be used wherein R is an organic radical and Zn is one equivalent of zinc. Although other techniques are available, in general, these addends are formed by reacting organic hydroxy compounds or mixtures of organic hydroxy compounds with phosphorus pentasulfide to form esters. The resulting esters or mixed esters are acidic and readily form salts with basic metallic compounds, usually a metal oxide, hydroxide, sulfide, or carbonate. The zinc salts of the higher-molecular-weight members are soluble in hydrocarbon oils and the commercial products, such as the zinc dialkyl dithiophosphate wherein the alkyl group is mixed C₄ to C₇, and the zinc diaryl dithiophosphate wherein the aryl group is butylphenyl, used herein are supplied as mineral oil solutions. It is preferred that the said organic radical have 4-40 carbon atoms in order to facilitate the dissolution of the zinc dithiophosphate in the oleaginous base. This organic radical may be alkyl, aryl, cycloalkyl, aralkyl, a combination of these, or others. Examples of suitable dithiophosphates include but are not limited to zinc salts of dihexyl dithiophosphate, dicapryl-dithiophosphate, dilauryl dithiophosphate, distearyl dithiophosphate, diphenyl dithiophosphate, dinaphthyl dithiophosphate, di(2,4-diethylphenyl)dithio-

phosphate, dicetylphenyl dithiophosphate, di(wax-substituted naphthyl)dithiophosphate, dicyclohexyl dithiophosphate, dicyclopentyl dithiophosphate, di(amylocyclohexyl)dithiophosphate, hexylcapryl dithiophosphate, naphthyl lauryl dithiophosphate, amyl cyclohexyl dithiophosphate, methyl cyclohexyl dithiophosphate.

Between about 0.02 to 0.5 weight percent of zinc, as the commercial dithiophosphate additive, is generally used for optimum anti-wear and E.P. properties. The 2.0 weight percent of zinc dibutylphenyl dithiophosphate used in the examples represents a zinc content in the total composition of about 0.07 weight percent.

Any of the known sulfonating agents may be used, particularly sulfur trioxide, and sulfur trioxide-producing materials are preferred. Mixtures of sulfur trioxide and sulfur dioxide, or sulfur trioxide and a mutual inert solvent, may be used, employing the techniques of the patents disclosed herein on the sulfonation reaction. For consistent results, high yields, and assurance that the product exhibits the desired multi-purpose characteristics, it is preferred that the sulfonating agent be a mixture of sulfur trioxide and air.

A feature of the invention is the substantial exclusion of water during the treatment with carbon dioxide, carbon disulfide and carbonyl sulfide or mixtures of same.

Elimination of water is accomplished by employing an efficient drying step following treatment with the metal base. The substantial absence of water (or less than about 0.3 weight percent of water based on the weight of the total sulfonate present in the clear solution) in combination with the substantial absence of any excess, unreacted base material leads to the excellent properties of the finished sulfonates of this invention. The attainment of these goals is followed by the pH of the CO₂-reaction mixture and the total base and strong base numbers (D-664) of the end product. In general, these conditions are concomitant with a nil barium hydroxide content (or less than about 0.1%) and a nil barium carbonate content (or less than about 0.1% on a weight basis). Also, the strong base number is essentially zero.

The sulfonates of this invention may be used with any desired amounts of other addends for the purpose of compounding a wide variety of compositions as herein disclosed. Foam depressants, corrosion inhibitors, rust inhibitors, pourpoint depressants, and various VI improvers may be used with the sulfonates of this invention in mineral oil or other carrier liquids to form solid, semi-solid or fluid compositions. The acrylic polymer used in the compositions tested herein was Acryloid 618, a trademark for an acrylic acid polymer used industrially as a combination VI improver and pour-point depressor. The "Acryloids" are polymers of the esters of methacrylic acid and a high-molecular-weight fatty alcohol, or fatty alcohol mixture. Another such product, under the trademark of Acryloid 150, having combination properties, is a methacrylate polymer and is described in United States Patents 2,509,620, 2,681,891 and 2,820,013. This product is a polymer having the following properties: specific gravity, 60/60, 0.89; viscosity at 210° F., 3100 SUS; and viscosity at 100° F. of 27,500 SUS. The polymeric esters of methacrylic acid and such higher fatty alcohols as lauryl, cetyl and octyl alcohols have molecular weights of 10,000-15,000 and higher. Since these addends are well known in this art, no further description is necessary.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The method of preparing weakly-basic metal petroleum sulfonates from Mid-Continent solvent refined neutral lubricating oils having viscosities in the range of about 170-600 SUS at 100° F. which comprises, sulfonating said refined lubricating oils with sulfur trioxide at a sulfur-trioxide-to-oil weight ratio of about 0.02 to 0.08 and a temperature of about 95 to 126° F. to

11

form sulfonic acids therefrom, reacting said sulfonic acid product with a hydrated melt of an alkaline earth metal compound of the group consisting of barium hydroxide, barium oxide, barium hydroxide octahydrate, calcium oxide, calcium hydroxide, strontium oxide and strontium hydroxide at a temperature of about 300–500° F. to form the alkaline earth metal salt thereof, drying the resulting salt product to a water content of less than about 0.3 weight percent, centrifuging said dried product from a hydrocarbon solvent to remove suspended solids, reacting the centrifuged product with an acidic component of the group consisting of carbon dioxide, carbon disulfide and carbonyl sulfide at a temperature of about 150–400° F. while maintaining said water content below about 0.3 weight percent until the sulfonate product has a pH of less than about 11 and the finished product is characterized by an alkaline earth metal hydroxide content and an alkaline earth metal carbonate content of less than about 0.1% by weight and exhibits a strong

12

base number of substantially 0, and recovering the weakly basic alkaline earth metal petroleum sulfonate so formed.

2. The method in accordance with claim 1 in which said alkaline earth metal compound is barium hydroxide octahydrate.

3. The method in accordance with claim 1 in which said acidic component is carbon dioxide.

4. The method in accordance with claim 1 in which the amount of water present during the reaction with said alkaline earth metal compound is sufficient to hydrate said metal compound and the neutralized mixture is dried and centrifuged from a hexane solution to remove water and suspended solids.

References Cited in the file of this patent

UNITED STATES PATENTS

2,916,451 Faust ----- Dec. 8, 1959