United States Patent Office

3,260,670

Patented July 12, 1966

3,260,670

ALKALINE METAL SULFONATES

Eugene E. Richardson, Highland, Ind., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

No Drawing. Filed Nov. 29, 1962, Ser. No. 241,052
4 Claims. (Cl. 252—33)

This invention relates to the preparation of oil-soluble metal sulfonates and more particularly to the preparation of low alkaline oil-soluble metal sulfonates.

Lubricating oils, such as petroleum lubricating oil, are effective within certain defined limits of engine operating conditions, and when these limits are exceeded, such lubricants frequently fail to give the desired performance demanded of them. During the operation of an internal combustion engine, sediment, sludge and varnish are produced and a lubricating oil alone does not have properties to enable it to suspend such sludge, sediment and varnish. The sediment may collect in lines, foul oil filters and generally decrease the effectiveness of the lubricating oil. Sludge and varnish accumulate and form deposits, as well as coatings on cylinder and piston walls of an engine. Thus, it is necessary to prevent the formation of sludge and varnish deposits and sediment and/or suspend sludge, varnish and sediment in the oil by adding an addition agent thereto such as a dispersant. Dispersants are normally termed "detergent-type" addition agents and have the property of maintaining clean engines by suspending sediment and inhibiting deposition of sludge and varnish.

Alkaline earth metal sulfonates obtained by neutralization of sulfonic acids formed by the action of oleum on heavy alkyl aromatic hydrocarbons are particularly effective dispersants for use as lubricating oil additives. In general for applications where sediment, sludge and varnish accumulate in large amounts, it is desirable to increase the alkaline earth metal content of sulfonate dispersants as high as possible over and above that needed to neutralize the corresponding sulfonic acids because the increased alkaline earth content results in increased ability of the sulfonate to impart detergency characteristics to a lubricating oil. In many applications, however, where internal combustion engine deposits are formed in relatively smaller amounts, it is unnecessary to maintain a high-level of alkaline earth metal concentration in sulfonate dispersants and it becomes advantageous to control the alkaline earth metal concentration within a predetermined range to provide a low alkaline earth metal oil-soluble sulfonate. Low alkaline sulfonates require smaller amounts of alkaline earth metal and this smaller metal requirement gives an economic benefit.

Alkaline earth metal sulfonates for use in lubricating oils generally can be obtained by alkaline earth metal neutralization of sulfonic acids formed by the action of oleum on heavy alkyl aromatic hydrocarbons. Sulfonic acids formed in this manner usually contain from 1 to 10 percent free sulfuric acid even after withdrawal of spent acid. During neutralization the free sulfuric acid present precipitates alkaline earth metal sulfates which the neutralized sulfonate suspends because of its detergency power. Suspension of these undesirable sulfates interferes with subsequent filtration of the product by plugging up filters and reducing effective filter rate. Suspended sulfates which pass through the filters make the product hazy and by their very presence have adverse effects on engine performance, thus weakening its effect as a "detergent-type" addition agent for use in lubricating oils.

Accordingly, an object of this invention is a process for the production of alkaline earth metal sulfonates having substantially no alkaline earth metal sulfates suspended therein, such result being accomplished in a straightforward manner using conventional equipment and readily available materials. A further object is a process for production of an alkaline earth metal sulfonate having a controlled low alkaline earth metal content.

According to the present invention it has now been found that an alkaline earth metal sulfonate having a controlled low alkaline earth metal content is obtained substantially free of suspended undesirable alkaline earth metal sulfates by selectively neutralizing oil-soluble heavy alkylated sulfonic acids having free sulfuric acid entrained therewith which selective neutralization comprises first selectively removing the entrained free sulfuric acid by contacting the sulfonic acid-sulfuric acid mixture with an alkaline earth base material in an amount sufficient to neutralize the more reactive free sulfuric acid without neutralizing substantial amounts of the sulfonic acids which neutralization forms a sulfuric acid-free sulfonic acid phase. The sulfuric acid-free phase is then further contacted with an alkaline earth base material in excess of that necessary to neutralize the sulfonic acids present in the presence of a promoter having solubility for the acids and also for alkaline earth base materials to form a neutralized alkaline earth metal sulfonate phase having an excess of alkaline earth base material. The neutralized sulfonate phase is then heated in the presence of a heat-decomposable carbonate of ammonia such as ammonium bicarbonate and/or ammonium carbonate, at a temperature sufficient to decompose the carbonate and form a neutralized alkaline earth metal sulfonate phase having a controlled low alkaline earth metal content in the form of an alkaline earth metal carbonate.

Since sulfonic acids do not demonstrate the detergency power of the corresponding neutralized sulfonates, neutralization of the sulfonic acids only after precipitation of the undesirable sulfates prevents the sulfonate detergents from suspending the sulfates because the latter are first formed and are unavailable to the sulfonates at the time of and after sulfonate neutralization.

Sulfonic acids contemplated for use in the practice of this invention are generally derived from petroleum hydrocarbons. These petroleum hydrocarbons may be higher molecular weight olefins or polymers such as trimers, tetramers, and pentamers of C_3 and C_4 olefins and/or heavy alkylated aromatic hydrocarbons having molecular weight in the range of about 200 to about 900 such as products of the alkylation of benzene and toluene. Preferred are heavy alkylated aromatic hydrocarbons of the type obtained as bottoms from the distillation of detergent alkylate, for example, dodecylbenzene, pentadecylbenzene and hexadecylbenzene. These preferred materials are commonly referred to as detergent alkymer bottoms and they typically have molecular weights in the range of 330 to 450. In a typical operation, hydrocarbons as aforementioned are converted to sulfonic acids by reaction with oleum. In operations of this type even after withdrawal of spent acid the sulfonic acids will still have entrained therewith 1 to 10 percent free sulfuric acid. The process of the present invention is directed to sulfonic acids prepared in this manner as well as sulfonic acids derived from heavy petroleum hydrocarbons as herein described regardless of the manner of preparation wherein the result is a sulfonic acid product having sulfuric acid entrained therewith.

Neutralization of free sulfuric acid entrained with sulfonic acids is carried out by adding to the sulfonic acid-sulfuric acid mixture alkaline earth base material in an amount sufficient to neutralize the free sulfuric acid without neutralizing substantial amounts of the sulfonic acids. The sulfuric acid is neutralized as alkaline earth metal sulfates which are precipitated out of the sulfonic acid phase. Typically, the alkaline earth base material is an inorganic basic alkaline earth compound such as an oxide, hydroxide, etc., of an alkaline earth metal. Specific examples of such basic alkaline earth metal compounds are calcium oxide, calcium hydroxide, barium oxide, strontium oxide, etc., with calcium hydroxide being preferred.

The basic alkaline earth metal compound may be added to the reaction mixture, for convenience in handling, in the form of a slurry with a common diluent oil. Addition of such slurry may be made in one batch or intermittently over the reaction time. Amount of alkaline earth base material added in the first neutralization step is an amount sufficient to effectively neutralize free sulfuric acid present without neutralizing substantial amounts of sulfonic acids so that sulfuric acid may be precipitated out of the sulfonic acid phase as an inorganic alkaline earth metal sulfate. The amount of alkaline earth base material to be added has been found typically to be in the range of 1.1 to 1.6 mols of the alkaline earth base material per mol of sulfuric acid present with a ratio of 1.5 being preferred. For example, when the alkaline earth base material is calcium hydroxide, it is preferred that 1.5 mols of calcium hydroxide be added per mol of free sulfuric acid in the sulfonic acid-sulfuric acid mixture. The amount of sulfuric acid which must be neutralized normally will vary from 1 to 10 percent by weight and can be analyzed by any convenient method known to those skilled in the art such as the method of aniline titration.

Methods well known to those skilled in the art may be used to insure that neutralization of sulfuric acid is complete. For example, the reaction mixture may be stirred and blown with inert gas such as nitrogen at temperatures in the range of 150° F. for one hour to insure neutralization and removal of any sulfur dioxide present.

The sulfuric acid-free sulfonic acid phase is then neutralized by addition of an alkaline earth base material such as hereinbefore described along with a promoter having solubility for both sulfonic acids and the alkaline earth base material employed. The promoter may be an alkanol such as an alkyl alcohol having from 1 to 10 carbon atoms. Particular examples are: methanol, ethanol, isopropyl alcohol, n-butyl alcohol, amyl alcohol, hexanol, 2,3-dimethyl hexanol, isooctyl alcohol, 2,4-dimethyl octanol, etc., with methanol being preferred. Typically, the promoter is present in an amount from about 3 to about 4 mols per mol of sulfonic acid, however, the amount used is not critical. It is theorized that the function of the promoter is to provide a solvent for both the sulfonic acids and the alkaline earth base material so that intimate contact and complete reaction result.

Alkaline earth base material is added to the sulfonic acid phase in an amount sufficient to neutralize sulfonic acids present and provide an excess alkaline earth metal content in the sulfonic acid phase. Typically, the amount of alkaline earth base material to be added has been found to be in the range of 1.1 to 2.0 mols of alkaline earth base material per mol of sulfonic acid with a ratio of 1.5 being preferred. For example, when the alkaline earth base material is calcium hydroxide, it is preferred that 1.5 mols of calcium hydroxide be added per mol of sulfonic acid. The amount of sulfonic acid to be neutralized can be analyzed by any convenient method known to those skilled in the art such as the method of aniline titration.

Neutralized alkaline earth metal sulfonates free of sulfuric acid are then heated in the presence of a carbonate of ammonia such as ammonia bicarbonate and/or ammonium carbonate to give carbon dioxide and ammonia. Heating takes place at a temperature sufficient to decompose the carbonate so that carbon dioxide released reacts with alkaline earth base material present to produce an alkaline earth metal sulfonate phase having a low alkaline earth content in the form of an alkaline earth metal carbonate. The purpose of this final step is to react carbon dioxide with the excess alkaline earth metal present in the sulfonate formed during the second neutralization step to form alkaline earth metal carbonates. Ammonium bicarbonate and ammonium carbonate are used because they decompose with heating in sulfonates of the type described herein to release carbon dioxide in small bubbles substantially uniform in size and evenly distributed throughout the sulfonate phase. Further, carbonates of ammonia are particularly advantageous because upon decomposition ammonia passes off as a vapor whereas other carbonates such as sodium carbonate and sodium bicarbonate, for example, decompose leaving an undesirable metal ion which must be removed later. Reaction of carbon dioxide with alkaline earth metal in this fashion provides an effective method to control the amount of carbonate formed and thus regulate the alkaline content of the sulfonate product. Thus, for operations where it is desirable to control the alkaline content of a sulfonate within a low range, it becomes particularly advantageous to employ one of the aforementioned ammonium compounds as a source of carbon dioxide. An excess of the carbonate of ammonia should be added to provide sufficient carbon dioxide for reaction with alkaline earth metal. The amount of ammonium compound added will depend upon the desired carbonate concentration of the product with a high carbonate concentration requiring use of larger amounts of the ammonium compound. For example, use of ammonium bicarbonate in the ratio from about 0.08 to about 0.12 mol per mol of sulfonic acid will produce a low alkaline product having a total base number (TBN) from about 20 to about 30.

Total base number is a measure of excess alkaline content in milligrams of potassium hydroxide per gram and is used herein to determine the amount of excess alkalinity in the alkaline earth metal sulfonate phase. Total base number is determined by non-aqueous perchloric acid titration in glacial acetic acid. Further details of this titration method are defined in the paper entitled The Non-Aqueous Titration of Alkalinity in Lubricating Oil Additives Using Glacial Acetic Acid, a paper presented by C. W. Parkert and W. L. Groves at the division of Petroleum Chemistry Meeting of the American Chemical Society in Chicago, Illinois, September 6–11, 1953.

Typically, a low alkaline earth metal sulfonate as described herein will have a TBN of less than 100. Optimally, the TBN will be less than about 60 with the range from about 20 to about 30 being preferred.

Heating of the carbonates of ammonia takes place at a temperature sufficient to decompose the particular carbonate employed and release carbon dioxide. For example, in an operation utilizing ammonium bicarbonate the temperature may range from about 95° F. to about 170° F. At temperatures outside of this range, ammonium bicarbonate either does not decompose or decomposes so rapidly that its use is of little value. In a preferred operation using ammonium bicarbonate the heating takes place at the reflux temperature of methyl alcohol. Although either ammonium compound is suitable for use in the practice of this invention, ammonium bicarbonate is preferred because it gives a greater yield of carbon dioxide per unit of weight than does ammonium carbonate.

Examples of the process of my invention are given below by way of illustration only. It should be understood that the process admits of variations over those specifically shown in the examples.

Example 1

1730 grams of commercially obtained detergent alkymer bottoms having a molecular weight of 384 were reacted with 1800 grams of 20 percent oleum. After acid addition and a settling period, spent acid was drawn off and 13 milliliters of water and 400 grams of diluent oil were added and the mixture was permitted to settle. Spent acid which had separated was again drawn off, and the sulfonic acid phase was analyzed by aniline titration to contain 72 weight percent sulfonic acid and 5 weight percent sulfuric acid. To 2240 grams of this mixture was added 130 grams of calcium hydroxide slurried in 300 grams of diluent oil. The mixture was stirred and blown with inert gas at 150° F. for one hour to insure neutralization of sulfuric acid present and removal of sulfur dioxide. 490 milliliters of methyl alcohol were then added along with 385 grams of calcium hydroxide slurried in 1000 grams of diluent oil. The mixture was stirred and refluxed for one hour to insure neutralization of the sulfonic acids. 27 grams of ammonium bicarbonate were added, and the mixture was stirred and heated for three hours at the reflux temperature of methyl alcohol. The mixture was then heated to 300° F. to strip out methyl alcohol, and the product was filtered. The product had a total base number of 22.5.

Example 2

1640 grams of commercially obtained detergent alkymer bottoms having a molecular weight of 410 were reacted with 1620 grams of 20 percent oleum. After acid addition and a settling period, spent acid was drawn off and 7 milliliters of water and 400 grams of diluent oil were added and the mixture was permitted to settle. Spent acid which had separated was again drawn off, and the sulfonic acid phase was analyzed by aniline titration to contain 60 weight percent sulfonic acid and 3.55 weight percent sulfuric acid. To 2153 grams of this mixture was added 86 grams of calcium hydroxide. The mixture was stirred and blown with inert gas at 150° for one hour. 380 milliliters of methyl alcohol were then added along with 292 grams of calcium hydroxide slurried in 750 grams of diluent oil. The mixture was stirred and refluxed for one hour. 21 grams of ammonium carbonate were then added, and the mixture was stirred and heated for three hours at the reflux temperature of methyl alcohol. The resulting mixture was heated to 300° F. to strip out methyl acohol, and the product was filtered. The product has a total base number of 24.

Thus, having described the invention what is claimed is:

1. A process for making an alkaline earth metal sulfonate having a controlled low alkaline earth metal content, and substantially free of suspended alkaline earth metal sulfates, obtained by neutralizing oil-soluble heavy alkylated sulfonic acids having free sulfuric acid entrained therewith, which process comprises:

(a) first selectively removing said entrained free sulfuric acid by contacting said oil-soluble sulfonic acids having free sulfuric acid entrained therewith with an alkaline earth base material in an amount sufficient to neutralize said free sulfuric acid without neutralizing substantial amounts of said sulfonic acids to precipitate insoluble alkaline earth sulfate to obtain a phase containing oil-soluble sulfonic acid and precipitated insoluble alkaline earth sulfate;

(b) contacting said oil-soluble sulfonic acid and precipitated insoluble alkaline earth sulfate phase with an alkaline earth base material in excess of that necessary to neutralize said sulfonic acids in the presence of an alkanol of from 1 to about 10 carbon atoms to form an alkaline earth sulfonate phase containing a mixture of said precipitated neutralized alkaline earth sulfate and an excess of said alkaline earth base material;

(c) heating said sulfonate phase containing said mixture in the presence of a carbonate of ammonia at a temperature sufficient to decompose said carbonate of ammonia to form a neutralized alkaline earth sulfonate having a low alkaline earth carbonate content, and

(d) filtering to recover said alkaline earth sulfonate having a low alkaline earth carbonate content.

2. The process of claim **1** wherein (a) from about 1.1 to about 1.6 mols of alkaline earth base material per mol of free sulfuric acid is used.

3. The process of claim **1** wherein (b) from about 1.1 to about 2.0 mols of alkaline earth base material per mol of sulfonic acid is used.

4. The process of claim **1** wherein said alkaline earth base material is calcium hydroxide.

References Cited by the Examiner

UNITED STATES PATENTS

2,361,476	10/1944	Highbee et al.	260—504
2,402,325	6/1946	Griesinger et al.	260—504
2,865,956	12/1958	Ellis et al.	260—505
3,027,325	3/1962	McMillen et al.	260—504
3,031,498	4/1962	Pengilly	260—505
3,057,896	10/1962	Schlicht et al.	260—504
3,083,146	3/1963	Sweeney et al.	260—505

FOREIGN PATENTS

202,606	4/1955	Australia.

DANIEL E. WYMAN, *Primary Examiner.*

LEON ZITVER, *Examiner.*

B. M. EISEN, P. P. GARVIN, *Assistant Examiners.*