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METHOD OF PREPARING ALKALINE EARTH SULFONATES OF HIGH ALKALINITY

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ABSTRACT OF THE DISCLOSURE

Preparation of oil-soluble alkaline earth sulfonates of high alkalinity is improved by using an amine promoter during the carbonation of a mixture comprising neutral alkaline earth sulfonate, excess basic alkaline earth compound, a lower alkanol, and water.

This invention relates to improvements in preparing alkaline earth sulfonates, in particular to an improved method of preparing highly basic alkaline earth sulfonates, and more particularly highly basic magnesium sulfonates.

It has become increasingly important, in order to suit the requirements of the operation of internal combustion engines, of both the spark-ignition and diesel types, to increase the alkalinity of the detergent-type additives used in such engines. Highly basic alkaline earth sulfonates are particularly effective lubricating oil additives. It has also been found that such sulfonates are well suited as diesel fuel additives to decrease excessive smoking of diesel engine exhaust.

Increasing the alkalinity of alkaline earth sulfonates to provide an alkaline reserve is commonly referred to as "over-basing" or "super-basing." Many methods have been proposed for obtaining compounds possessing an alkaline reserve. In general, such prior art methods make preparation by controlled carbonation of the alkaline earth oxide or hydroxide in the presence of the neutral sulfonic acid soap. The preparation of over-based magnesium sulfonates is particularly different because of long reaction time, poor metal utilization and difficult filtration.

It is an object of the present invention to provide an improved method of preparing over-based alkaline earth sulfonates. Another object of the invention is to provide an improved method of preparing over-based sulfonates which provides improved metal utilization, shorter reaction times, increased total base numbers and better filterability. Still another object of the invention is to provide an improved method of preparing over-based preferentially oil-soluble magnesium sulfonates. These and other objects and advantages of the present invention will become apparent as the description thereof proceeds.

In accordance with the present invention, the above objects ate attained by preparing over-based alkaline earth sulfonates, particularly over-based magnesium sulfonates, in the presence of an amine promoter. The amine promoter, used in concentrations of from about 0.05% to about 18% of the weight of the basic alkaline earth compound, may be introduced prior to or during the over-basing stage of the process, and may be retained in the final product or removed therefrom by suitable means.

Broadly stated, the process of the present invention comprises neutralizing at a temperature of from about 80° F. to about 212° F., a preferentially oil-soluble sulfonic acid, preferably in solution in a hydrocarbon solvent, which may be aromatic, e.g. xylenes or aliphatic, e.g. hexanes, with a basic alkaline earth compound, such as an alkaline earth oxide or hydroxide, adding to the neutral sulfonate an excess of the basic alkaline earth

compound, the amine, a lower alkanol, e.g. methanol, ethanol or propanol, and a small amount of water, and then blowing sufficient carbon dioxide through the mixture to convert the alkaline earth bases to carbonates at a temperature of from about 40° F. to about 175° F. The carbon dioxide-treated product may be heated to reflux for about 10 minutes to about 60 minutes. To the alcohol-free product, water is added and the mixture may be blown with carbon dioxide for about 15 to 180 minutes at about 70° F. to about 212° F. The mixture is then heated to remove water and solvent, and filtered. If desired, only the water may be removed prior to filtration, and the solvent removed after filtration. Although it is preferred to add the amine after the formation of the neutral alkaline earth sulfonate, the amine can be added during the formation of the neutral sulfonate.

Sulfonic acids suitably used in accordance with this invention are preferentially oil-soluble sulfonic acids. Such sulfonic acids include preferentially oil-soluble petroleum sulfonic acids, commonly referred to as "mahogany acids," alkyl sulfonic acids, aryl sulfonic acids, and alkaryl sulfonic acids. Illustrative of suitable sulfonic acids are the preferentially oil-soluble petroleum sulfonic acids, e.g. "mahogany acids" of about 350 to 750 molecular weight, dilauryl aryl sulfonic acid, laurylcetyl aryl sulfonic acid, paraffin wax-substituted benzene sulfonic acids, didodecyl benzene sulfonic acids, polyolefin alkylated benzene sulfonic acids, such as polybutylene alkylated benzene sulfonic acids, in which the polybutylene substituents have molecular weights of at least about 200, and preferably within the range of from about 300 to about 2500; polypropylene alkylated benzene sulfonic acids in which the polypropylene substituents have a molecular weight of at least about 250, and preferably within the range of from about 290 to about 1500; naphthalene sulfonic acids; alkyl-substituted naph thalene sulfonic acids; and the like.

The preparation of the sulfonic acid is well known to those skilled in the art. Such sulfonic acids can be prepared by reacting the material to be sulfonated with a suitable sulfonating agent, such as concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid or sulfur trioxide for a period of time sufficient to effect sulfonation, and thereafter separating insoluble acid sludge from the oil-soluble sulfonic acid.

The amine promoter used in accordance with the present invention can be an aliphatic amine, an aromatic amine, or heterocyclic amine.

Illustrative of specific suitable amines are methylamine, N-methyloctylamine, dibutylamine, cyclohexylamine, dodecylamine, octadecylamine, methylene amines, ethylene amines, butylene amines, propylene amines, hexylene amines, ethylene diamine, triethylene tetramine, propylene diamine, octylmethylene diamine, tetraethylene pentamine, dipropylene triamine, 1,3-diamino propanes such as compounds of the general formula $RNHCH_2CH_2CH_2NH_2$, in which "R" is the alkyl radical derived from tallow fatty acids and from cocoa fatty acids; such products are commercially marketed as Duomeen T and Duomeen C, respectively.

The following specific examples illustrate the process of the present invention.

EXAMPLE I

Part 1

Benzene alkylated with a polypropylene of about 730–800 molecular weight was sulfonated to obtain a polypropylene alkylated benzene sulfonic acid of 880 molecular weight containing about 2.3 weight percent sulfuric acid. To 700 grams of a 50% xylene solution of the polypropylene alkylated benzene sulfonic acid were added 15 grams

of calcium oxide (1.5 moles per mole H_2SO_4) and the mixture stirred and heated at 150° F. for one hour under reflux conditions to convert the free sulfuric acid to water-insoluble calcium sulfate which is precipitated and removed from the xylene solution of the sulfonic acid.

Part 2

To the sulfonic acid solution of Part 1, free of sulfuric acid, were added 460 grams of a solvent extracted SAE 5 petroleum oil, 450 grams of xylene, 16 grams of magnesium oxide and 200 cc. methanol, and the mixture stirred and heated at reflux temperature of about 160° F. for one hour to neutralize the sulfonic acid.

Part 3

To the neutral magnesium sulfonate were added 25 grams ethylene diamine, 160 grams magnesium oxide and 72 grams water (1 mole water per mole of magnesium oxide) and the mixture blown with 1.6 cubic feet per hour (CFH) CO_2 gas for 2.5 hours.

Part 4

The product of Part 3 was heated to 190° F. to remove the methanol, then 50 grams of water added and the mixture heated to 270° F. The mixture was then cooled to 190° F., 100 grams of water added and the mixture blown with CO_2 at 1.6 c.f.h. for one hour at 180° F.

Part 5

The product of Part 4 was heated to 320° F. to remove the water and xylene and then filtered through diatomaceous earth.

The recovered product had the following properties:

Percent sulfonate	30
Total base number	300
Viscosity at 80° F.	Fluid
Filterability	Excellent

EXAMPLE II

Part 1

A mixture of 275 grams of an alkylated benzene sulfonic acid of 463 molecular weight derived from detergent alkylate bottoms, 380 grams of a solvent extracted SAE 5 petroleum oil, 10 grams magnesium oxide powder and 5 cubic centimeters water was stirred in a flask provided with a reflux condenser for one-half hour at room temperature, i.e. about 160° F. to form the neutral magnesium sulfonate.

Part 2

To the product of Part 1 were added 500 grams xylene, 110 grams magnesium oxide powder, 400 grams methanol, 50 cubic centimeters water and 20 grams ethylene diamine and the mixture stirred and cooled to a temperature of 76° F. Carbon dioxide was then passed into the mixture at the rate of 1.6 cubic feet per hour for 1.5 hours. The temperature of the mixture rose to 114° F. after 55 minutes, and then fell to 104° F. at the end of 1.5 hours.

Part 3

The product of Part 2 was then heated to 210° F. to remove the methanol, then 50 cc. of water added, and the mixture heated, without the reflux condenser, to 240° F. to distill off most of the water.

Part 4

The product of Part 3 was then filtered at 240° F. through diatomaceous earth and the filtrate heated to 320° F. under reduced pressure to remove the xylene solvent.

EXAMPLE III

The product of this example was prepared substantially as in Example II, except that the ethylene diamine was omitted in Part 2.

The products of Examples II and III had the following properties.

	Example II	Example III
Percent Sulfonate	30	34
Total Base Number	350	105
MgO Utilization, percent	95+	33
Viscosity at 80° F	Fluid	Fluid
Filterability	Excellent	Fair

EXAMPLE IV

Part 1

A mixture of 820 grams of a hexane solution of a polypropylene alkylated benzene sulfonic acid (540 grams 80% active sulfonic acid of 865 molecular weight), 640 grams of a solvent extracted SAE 5 petroleum oil, 10 grams of magnesium oxide powder and 5 cubic centimeters of water was heated to 240° F. to neutralize the free sulfonic acid and form the neutral magnesium sulfonate. The hexane was then removed by distillation.

Part 2

The product of Part 1 was cooled to 80° F. and mixed with 700 grams of xylenes, 120 grams of magnesium oxide powder, 400 grams methanol, 50 cubic centimeters of water and 20 grams of ethylene diamine. The temperature of the mixture rose from 80° F. to 90° F. The mixture was then blown with CO_2 at the rate of 1.6 cubic feet per hour for 1.5 hours; after 90 minutes, the temperature rose to 124° F.

Part 3

The product of Part 2 was heated to 210° F. and 50 cubic centimeters of water added. The reflux condenser was removed and the mixture heated to 240° F. until substantially all of the water was distilled off.

Part 4

The product of Part 3 was filtered through diatomaceous earth and the filtrate heated to 320° F. under reduced pressure to remove the xylenes.

EXAMPLE V

Polypropylene alkylated benzene sulfonic acid was treated with magnesium oxide substantially as in Example IV, except that the ethylene diamine was omitted in Part 2.

The products of Examples IV and V had the following properties:

	Example IV	Example V
Percent Sulfonate	30	34
Total Base Number	250	97
MgO Utilization, percent	95	38
Viscosity at 80° F	Fluid	Fluid
Filterability	Excellent	Good

The data presented by the foregoing examples demonstrate that the use of amine promoters in the preparation of over-based alkaline earth sulfonates in accordance with the herein-described invention results in improved metal utilization, improved filterability, shorter reaction time and increase total base number of the sulfonates. While in the examples given we have employed magnesium oxide as the basic alkaline earth compound, similar results are attainable with the hydroxides, carbonates and oxides of the other members of the alkaline earth group, such as, for example, calcium and barium.

Percentages given herein are weight percentages unless otherwise stated.

While particular embodiments of the invention have been described, it is to be understood that the invention is not limited thereto, but covers such modifications and variations as come within the spirit and scope of the appended claims.

We claim:

1. The method of preparing an over-based oil-soluble magnesium sulfonate comprising the steps of:

(a) forming in a petroleum oil vehicle a reaction mixture of (i) neutral oil-soluble magnesium sulfonate, (ii) magnesium oxide, (iii) a lower alkanol, (iv) about 0.9–1 mol of water per mol of magnesium oxide, and (v) ethylene diamine in an amount of about 0.05–18% of the weight of the magnesium oxide;

(b) treating said reaction mixture at a temperature of about 40–175° F. with an amount of carbon dioxide sufficient to convert said magnesium oxide to magnesium carbonate;

(c) heating the carbonated product mixture to remove said alkanol;

(d) adding about 0.9–1 mol of water per mol of magnesium oxide to the alkanol-free mixture; and

(e) thereafter heating the aqueous mixture to remove water therefrom, and filtering the water-free product mixture.

2. The method of claim 1 wherein said sulfonate is an alkaryl sulfonate; and the lower alkanol is methanol.

3. The method of claim 2 wherein the aqueous mixture in step (d) is treated with additional carbon dioxide prior to removal of water therefrom.

4. The method of claim 2 wherein said alkaryl sulfonate is a polypropylene-alkylated benzene sulfonate in which the polypropylene substituent has a molecular weight of about 290–1500.

5. The method of claim 2 wherein the reaction mixture contains about 2.75–4 mols of magnesium oxide.

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