# United States Patent

[11] **3,609,076**

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| [21] | Appl. No. | **767,833** |
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| [45] | Patented | **Sept. 28, 1971** |
| [73] | Assignee | **Standard Oil Company**<br>**Chicago, Ill.** |

[54] **METHOD OF PREPARING OVER-BASED ALKALINE EARTH SULFONATES**

**8 Claims, No Drawings**

[52] **U.S. Cl.** .......... **252/33.3,** 44/51, 44/57, 44/66, 252/33.2, 252/34, 252/18

[51] **Int. Cl.** .......... **C10m 1/40,** C10m 1/24, C10m 1/10

[50] **Field of Search** .......... 252/33.2, 34, 33.3; 44/51, 57, 66

[56] **References Cited**

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|---|---|---|---|
| 2,739,125 | 3/1956 | Myers | 252/33 |
| 2,961,403 | 11/1960 | Blumer | 252/33 |
| 3,033,889 | 5/1962 | Chiddix et al. | 252/49.8 |
| 3,170,879 | 2/1965 | Butcosk | 252/33.2 |

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**ABSTRACT:** Overbased, i.e., highly basic, alkaline earth sulfonates are prepared by reacting a preferentially oil-soluble sulfonic acid with a basic alkaline earth compound in the presence of small amounts of an ammonium salt of a $C_1$ to $C_7$ aliphatic acid.

# METHOD OF PREPARING OVER-BASED ALKALINE EARTH SULFONATES

## BACKGROUND OF THE INVENTION

It has become increasingly important, in order to meet the requirements of the operation of internal combustion engines, of both the spark ignition and the diesel types, to increase the alkalinity reserve of detergent-type additives employed in such engines. Highly basic alkaline earth sulfonates are particularly effective additives for spark ignition internal combustion engine lubricating oils; they are also well suited as diesel fuel additives to decrease excessive smoking of diesel engine exhaust.

Increasingly the alkalinity of alkaline earth sulfonates to provide an alkaline reserve is commonly referred to as "overbasing" or "superbasing." Many methods have been proposed for obtaining sulfonates having an alkaline reserve. In general, such prior art methods provide for controlled carbonation of an alkaline earth oxide or hydroxide in the presence of a neutral sulfonic acid soap. The preparation of overbased magnesium sulfonates is particularly difficult because of long reaction time, poor metal utilization and difficult filtration.

## SUMMARY

The process of the present invention comprises treating a neutral alkaline earth sulfonate with a mixture comprising, an excess amount of a basic alkaline earth compound, e.g., an alkaline earth oxide or hydroxide, a lower alkanol, water and a catalytic amount of an ammonium salt of a $C_1$ to $C_7$ aliphatic acid at a temperature of from about 50° F. to about 130° F. while introducing gaseous carbon dioxide at the rate of from about 0.5 to about 3.0 cubic feet per hour per mol of sulfonic acid. The ammonium salt promoter is employed in amounts of from about 0.05 to about 0.5 mols per mol of the basic alkaline earth compound, and the water in amounts of from about 1 to about 10 mols, preferably from about 2 to about 7 mols per mol of the basic alkaline earth compound charged.

The basic alkaline earth compounds are well known and include the hydroxides, and preferably the oxides of calcium, barium, strontium and magnesium; the present invention is particularly suitable for the preparation of overbased magnesium sulfonates. The basic alkaline earth compound, as stated above, is used in amounts in excess of that necessary to neutralize the sulfonic acid; in amounts in excess of about 0.5 mols, preferably from about 1 to about 6 mols, of the basic compound per mol of the sulfonic acid can be employed.

Suitable preferentially oil-soluble alkaline earth sulfonates are the alkaline earth salts of preferentially oil-soluble sulfonic acids ($RSO_3H$), such as the preferentially oil-soluble petroleum sulfonic acids, commonly referred to as "mahogany acids," of about 350 to about 750 molecular weight, alkyl sulfonic acids, aryl sulfonic acids, and alkaryl sulfonic acids. Illustrative of such sulfonic acids are dilauryl benzene sulfonic acid, lauryl cetyl benzene sulfonic acid, paraffin-substituted 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 2,500, and 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 1,500. Examples of other suitable sulfonic acids are monoparaffin wax-substituted naphthalene sulfonic acids, diparaffin wax-substituted phenol sulfonic acids, wax sulfonic acids, petroleum naphthalene sulfonic acids, diphenyl ethel sulfonic acids, diphenyl ether disulfonic acids, naphthalene disulfide sulfonic acids, naphthalene disulfide disulfonic acids, diphenyl amine disulfonic acids, diphenyl amine sulfonic acids, thiophene sulfonic acids, alpha-chloronaphthalene sulfonic acids, cetyl chlorobenzene sulfonic acids, cetyl sulfonic acids, cetyl-phenol disulfide sulfonic acids, cetyl-phenol monosulfide sulfonic acids, cetoxy capryl-benzene sulfonic acids, dicetyl thianthrene sulfonic acids, dilauryl beta-naphthol sulfonic acids, dicapryl nitronaphthalene sulfonic acids; hydroxy-substituted paraffin wax sulfonic acids, tetra-isobutylene sulfonic acids, tetra-amylene sulfonic acids, chloro-substituted paraffin wax sulfonic acids, nitroso paraffin wax sulfonic acids, cetyl-cyclopentyl sulfonic acids, lauryl-cyclohexyl sulfonic acids, mono- and polywax substituted cyclohexyl sulfonic acids. Other suitable oil-soluble sulfonic acids are well described in the art, such as for example, U.S. Pat. No. 2,616,604; U.S. Pat. No. 2,626,207; and U.S. Pat. No. 2,767,209, and others.

As noted above, the ammonium salt promoter is an ammonium salt of a $C_1$ to $C_7$, preferably a $C_1$ to $C_4$, aliphatic acid. Examples of such salts are ammonium formate, acetate, proportionate, butyrate, valerate, caproate, heptylate, etc.

The process of the present invention comprises diluting the sulfonic acid with an aliphatic or aromatic hydrocarbon solvent, e.g., xylenes, hexane, etc., and neutralizing the sulfonic acid with the basic alkaline earth compound in the presence of a small amount of water, i.e., 1 mol of $H_2O$ per mol of the basic compound. To facilitate the handling of the resultant sulfonate it is preferably diluted with a low-viscosity hydrocarbon oil, e.g., a S.A.E.5 or 5W grade mineral oil. The amount of diluent oil used can be any desired amount; an amount sufficient to give an oil solution containing about 40 percent of the sulfonate has been found suitable. The oil-diluted product is heated to a temperature sufficient to remove the water.

The diluted neutral sulfonate product is then cooled to a temperature below about 200° F., for example, about 160°-170° F., and there are added to the water-free product from about 5 mols to about 20 mols of a lower alkanol, e.g., methanol, ethanol, isopropyl alcohol, butyl alcohol, etc., per mol of the basic alkaline earth compound, from about 0.5 to about 6 mols of the basic compound per mol of the sulfonic acid in excess of that required to neutralize the sulfonic acid; from about 1 to about 10 mols of water per mol of the basic compound; and from about 0.05 to about 0.5 mols of the ammonium salt promoter per mol of the basic compound. The mixture is then preferably agitated with a high-speed stirrer and then blown with gasseous carbon dioxide at the rate of from about 0.5 to about 3 cubic feet per hour per mol of sulfonic acid at a temperature of about 40° F. to about 175° F. for a time sufficient to convert the excess basic compound to the carbonate.

The carbon dioxide treated mixture may be heated to a temperature sufficiently high to remove the alkanol, and, if desired, a portion of the hydrocarbon solvent. The alkanol-free mixture is maintained at a temperature of from about 170° F. to about 210° F., preferably about 180°-190° F., and then from about 0.5 to about 5 mols, preferably about 1 to 2 mols of water per mol of the basic alkaline earth compound slowly added to the heated reaction mixture. After the addition of the water, the temperature of the mixture is raised to from about 220° to about 400° F. to remove the water and the product filtered. If the filtration temperature is not sufficiently high to remove the hydrocarbon solvent, if employed, the filtrate may be heated to remove such solvent.

If the sulfonic acid contains an appreciable amount of free sulfuric acid, it is preferable to remove such sulfuric acid by treating the sulfonic acid-sulfuric acid mixture with a sufficient amount of CaO, and a small amount of water, to neutralize the sulfuric acid, and the water-insoluble calcium sulfate precipitate removed by filtration or by other suitable means.

Although in the foregoing the sulfonic acid is first neutralized and the neutralized product subsequently subjected to treatment with the excess basic compound, the process can be conducted by treating the sulfonic acid with an amount of the basic compound in excess of that required to neutralize the sulfonic acid.

## PREFERRED EMBODIMENT

The following examples are illustrative of the preferred embodiment of the present invention.

### PREPARATION I

#### PART 1

0.25 mols of a $C_{60}$ polypropylene alkylated benzene sulfonic acid having a molecular weight of 865 and containing less than 0.5 percent sulfuric acid was dissolved in hexane, and the hexane solution treated with sufficient CaO, in the presence of 1 mol of $H_2O$ per mol of CaO, to just neutralize the free sulfuric acid. The mixture is stirred and heated under reflux conditions to convert the sulfuric acid to water-insoluble calcium sulfate which is precipitated and removed from the hexane solution of the sulfonic acid.

#### PART 2

The sulfuric acid-free sulfonic acid solution of Part 1 was neutralized with MgO (0.125 mol per 0.25 mol of sulfonic acid), and sufficient S.A.E. 5 W hydrocarbon oil added to give a solution containing 40 percent sulfonate.

#### PART 3

The oil-diluted product of Part 2 was heated to 240° F. to remove water and hexane.

#### PART 4

The product of Part 3 was cooled to 160° F., diluted with 500 cc. xylene and 50 cc. $H_2O$ (1 mol per mol MgO), and to the xylene solution were added 110 grams MgO (2.875 mols per 0.25 mol sulfonic acid), 700 cc. methanol (5.22 mol per mol MgO) and 0.2 mol ammonium acetate, and the mixture rapidly agitated for 1 hour.

#### PART 5

The mixture of Part 4 was then blown with gaseous $CO_2$ at the rate of 1.6 cubic feet per hour for 3 hours. The heat of reaction during the $CO_2$ blowing was as follows:

| Time-Hrs. | Temperature, °F. |
|---|---|
| 0 | 94 |
| 0.5 | 120 |
| 1.0 | 127 |
| 2.0 | 125 |

#### PART 6

The $CO_2$-blown product of Part 5 was heated at 210° F. to remove the methanol and a portion of the xylene.

#### PART 7

To the product of Part 6 were added 150 cc. $H_2O$ and the mixture maintained at a temperature of 180° F. for 1 hour.

#### PART 8

The product of Part 7 was then heated at 240° F. to remove water and xylene, and then filtered. Filtration was rapid and accomplished without difficulty.

The resultant filtrate from Part 8 had a total base number (TBN) of 288.4.

### PREPARATION II

Preparation II was similar to Preparation I, except that in Part 4, 100 cc. $H_2O$ (2 mol per mol MgO) were used.

The heat of reaction during the $CO_2$ blowing (Part 5) was as follows:

| Time, Hrs. | Temperature °F. |
|---|---|
| 0 | 92 |
| 0.25 | 102 |
| 0.5 | 112 |
| 1.0 | 128 |
| 1.5 | 123 |
| 1.75 | 120 |

The recovered filtrate (Part 8) had a TBN of 386.4; the MgO utilization was about 94 percent.

The following Preparation III demonstrates the need to employ water in the treatment of the neutral sulfonate with excess basic alkaline earth compound and blowing with gaseous $CO_2$.

### PREPARATION III

This preparation was similar to Preparations I and II, except that in Part 4, water was not employed.

During the $CO_2$ blowing the heat of reaction observed was as follows:

| Time, Hrs. | Temperature °F. |
|---|---|
| 0 | 92 |
| 1.0 | 98 |
| 2.0 | 108 |
| 3.0 | 112 |

To the product, after removal of water and xylene (Part 6) water in amount of 10 mols per mol MgO was added and the mixture heated at 180° F. for 1 hour (Part 7). The product was then heated to 240° F. to remove $H_2O$ (Part 8) and the product from Part 8 subjected to filtration. Filtration was difficult and filter cake penetration was poor, indicating large amounts of $Mg(OH)_2$ present in the product.

The data presented by the foregoing preparation examples demonstrate that the use of an ammonium salt of a $C_1$ to $C_7$ aliphatic acid promoter and with $CO_2$ in the presence of water in the preparation of overbased alkaline earth sulfonates in accordance with the hereindescribed invention results in improved metal utilization, improved filterability and increased total base number of the sulfonates.

Percentages given herein and in the appended claims 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 includes such modifications and variations as come within the spirit and scope of the appended claims.

We claim:

1. The process of preparing an overbased alkaline earth metal sulfonate comprising the steps of:
   I. forming, in an inert hydrocarbon solvent, a reactant mixture consisting essentially of
      A. neutral alkaline earth metal sulfonate,
      B. at least 0.5 mol of a basic alkaline earth metal compound of the group consisting of an alkaline earth metal oxide or hydroxide per mol of (A),
      C. about 1–10 mols of water per mol of (B),
      D. about 5–20 mols of methanol per mol of (B),
      E. about 0.05–0.5 mol of an ammonium salt of a $C_{1\text{-}7\ 7}$ aliphatic monocarboxylic acid per mol of (B);
   II. passing carbon dioxide through said reactant mixture, at atmospheric pressure, at the rate of about 0.5–3 cubic feet of gaseous carbon dioxide per hour per mol of (A) at a temperature of about 40–175° F. for a time sufficient to convert said component (B) to carbonate; and
   III. recovering from the reaction mixture of step (II) said overbased alkaline earth sulfonate.
2. The process of claim 1 wherein (A) is an alkaryl sulfonate.
3. The process of claim 1 wherein (E) is ammonium acetate.
4. The process of claim 1 wherein (B) is magnesium oxide.
5. The process of claim 1 wherein (A) is magnesium polybutenyl-benzene sulfonate in which the polybutenyl substituent has a molecular weight of at least about 200; (B) is magnesium oxide; and (E) is ammonium acetate.
6. The process of claim 1 wherein (A) is magnesium polypropenyl-benzene sulfonate in which the polypropenyl substituent has a molecular weight of at least 250; (B) is magnesium oxide; and (E) is ammonium acetate.
7. The process of preparing an overbased magnesium sulfonate comprising the steps of:

I. reacting, in an inert hydrocarbon solvent, an oil-soluble alkyl-benzene sulfonic acid with a stoichiometric amount of magnesium oxide to form an oil-soluble neutral magnesium sulfonate in said solvent;

II. forming in the solvent/sulfonate mixture of step (I) a reactant mixture consisting essentially of

A. said neutral magnesium sulfonate,

B. at least 0.5 mol of magnesium oxide per mol of (A),

C. about 1–10 mol of water per mol of (B),

D. about 5–20 mols of methanol per mol of (B),

E. about 0.05–0.5 mol of ammonium acetate per mol of (B);

III. passing carbon dioxide through the reactant mixture of step (II), at atmospheric pressure, at the rate of about 0.5–3 cubic feet of gaseous carbon dioxide per hour per mol of (A) at a temperature of about 40–175° F. for a time sufficient to convert said magnesium oxide to carbonate; and

IV. recovering from the reaction mixture of step (III) said overbased alkaline earth sulfonate.

8. The process of claim 7 wherein said sulfonic acid is $C_{60}$ polypropenyl-benzene sulfonic acid.

PO-1050
(5/69)

# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,609,076 Dated September 28, 1971

Inventor(s) Albert R. Sabol, Eli W. Blaha and Cecil G. Brannen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 15, the word "Increasingly" should read --Increasing--;
line 68, the word "ethel" should read --ether--.

Column 2, line 9, the Patent No. "2,616,604" should read --2,616,904--;
line 41, the word "gasseous" should read --gaseous--.

Column 4, line 32, after "and" insert --blowing--;
line 54, "$C_{1-7\ 7}$" should read --$C_{1-7}$--.

Signed and sealed this 21st day of March 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents