



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2051279 C 2003/05/27

(11)(21) **2 051 279**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(22) Date de dépôt/Filing Date: 1991/09/13

(41) Mise à la disp. pub./Open to Public Insp.: 1992/07/01

(45) Date de délivrance/Issue Date: 2003/05/27

(30) Priorité/Priority: 1990/12/31 (07/636,475) US

(51) Cl.Int.⁵/Int.Cl.⁵ C07C 303/32, C07C 309/31

(72) Inventeurs/Inventors:

JAO, TZE-CHI, US;
VACCARO, JAYNE MEISELBACH, US;
POWERS, WILLIAM JOSEPH III, US

(73) Propriétaire/Owner:

ETHYL ADDITIVES CORPORATION, US

(74) Agent: SMART & BIGGAR

(54) Titre : SULFONATE DE CALCIUM AVEC EXCES DE BASE

(54) Title: IMPROVED OVERBASED CALCIUM SULFONATE

(57) Abrégé/Abstract:

A method of preparing a calcium sulfonate having at least a TBN of 500 where the method comprises reacting CaO, Ca(OH)₂ and H₂O, and synthetic monoalkylbenzene sulfonate and synthetic dialkylbenzene sulfonate in certain molar ratios, respectively, for a sufficient length of time to produce the overbased calcium sulfonate.



2051279

IMPROVED OVERBASED CALCIUM SULFONATES

(D#79,502 -F)

5

ABSTRACT OF THE INVENTION

10

A method of preparing a calcium sulfonate having at least a TBN of 500 where the method comprises reacting CaO , Ca(OH)_2 and H_2O , and synthetic monoalkylbenzene sulfonate and synthetic dialkylbenzene sulfonate in certain molar ratios, respectively, for a sufficient length of time to produce the overbased calcium sulfonate.

15

20

IMPROVED OVERBASED CALCIUM SULFONATE

(D#79, 502 -F)

BACKGROUND OF THE INVENTION

5

This invention relates to overbased metal salts, and more particularly to an improved process for preparing overbased calcium sulfonates which are used as detergent and reserve alkalinity lubricating oil additives.

10

15

In the course of operation, internal combustion engines convert lubricating oil to acidic degradation products. Those acidic degradation products attack and corrode engine parts and catalyze the formation of sludge, thereby reducing lubricity and accelerating wear of moving parts in contact with the lubricating oil.

20

25

30

It is desirable to add basic substances to the lubricating oil which neutralize acids as they are formed in the engine before they reach concentrations sufficient to cause corrosion or to catalyze the sludge formation. Adding an alkalinity agent to the detergent in motor oil is known as overbasing. Colloidal carbonates of the alkaline earth metals have been found to be well suited for this purpose. These carbonate dispersions are stabilized by oil soluble surface active agents such as the sulfonates of the alkaline earth metals in which the sulfonic acid portion of the molecule has a molecular weight of preferably 350 to 600. The sulfonates are generally made by sulfonation of lubricating oil fractions from petroleum and/or by sulfonation of alkyl benzenes having the desired molecular weight for this purpose. Benzene alkylates with straight chain alkyl groups are especially desirable.

76621-10

5 There is an increasing demand for an overbased sulfonate having at least a 500 TBN in the marine lubricant product market. Because of the higher TBN content, less dosage of this product is required in the additive treatment to obtain equivalent or better diesel engine performance. The current sulfonate overbasing process cannot produce an acceptable 500 TBN overbased sulfonate, because it produces either an insuffi-
10 ciently overbased, too viscous, or base oil-incompatible product. By modifying the current sulfonate overbasing process, a cost-effective improved process can make a fluid and base oil-compatible 500 TBN overbased calcium sulfonate that provides an effective protection to marine diesel engines.

15 In general, the process of preparing oils which contain overbased calcium sulfonates comprises reacting a solution of alkarylbenzene sulfonic acids having a molecular weight greater than 400, in oil with calcium oxide or hydroxide and bubbling carbon dioxide through the reaction mixture; thereby incorpo-
20 rating an excess of calcium carbonate into the calcium sulfonate which confers reserve alkalinity to the product.

25 Thus, it is an object of the present invention to provide a method of producing effective overbased calcium sulfonates that contain only amorphous calcium carbonate and have a TBN of at least 500.

DISCLOSURE STATEMENT

30 U.S. Patent 4,997,584 discloses a method of preparing a calcium sulfonate having a TBN of 500 where the method comprises reacting CaO , Ca(OH)_2 and H_2O , and synthetic and petroleum sulfonates in certain molar ratios, respectively, for a sufficient length of time to produce the overbased calcium

sulfonate.

5 U.S. Patent 4,427,559 discloses that a mixture of calcium
oxide and calcium hydroxide can be used in the overbased
reaction to provide reserve alkalinity to neutral calcium
sulfonates. It is reported that when mixtures containing up to
30 percent CaO are used, satisfactory products were obtained.
When mixtures of 30 to 50 percent CaO were used, a gelatinous
material which plugged the filter were obtained. Concentra-
10 tions of CaO above 70 percent produced a fluid product contain-
ing finely divided particles which could not be filtered and
were reflective of light. In this regard, the patent teaches
the criticality of the ratio of the calcium oxide to calcium
hydroxide in the absence of a promoter in producing acceptable
15 product.

U.S. Patent 4,604,219 discloses that calcium oxide may be
used as the sole reserve alkalinity source in overbasing
calcium sulfonates. This patent teaches, in the absence of a
20 promoter, that water addition rate and amount are critical in
producing a low solids content, filterable product.

U.S. Patent 4,086,170 discloses that overbased calcium
sulfonates are prepared by reacting a solution of alkylbenzene
25 sulfonic acids with an excess of a calcium oxide having a
medium or low activity toward water and with carbon dioxide.
Improved overbasing and filterability of the overbased sulfo-
nate solution were obtained by the use of a promoter for the
conversion of the calcium oxide to calcium hydroxide. Recom-
30 mended promoters include ammonia or organic bases such as
monoamines or diamines, e.g. ethylene diamine.

U.S. Patent 4,954,072 discloses a method of preparing a
calcium sulfonate having a TBN of 325 where the method compris-

76621-10

es reacting CaO , Ca(OH)_2 and H_2O in certain molar ratios for a sufficient length of time to produce the overbased calcium sulfonate.

SUMMARY OF THE INVENTION

5 The present invention provides a process for preparing an improved overbased oil soluble calcium sulfonate having at least a TBN of 500. The process comprises:

 (a) diluting a synthetic monoalkyl
10 benzenesulfonate and a synthetic dialkylbenzene sulfonate in a petroleum solvent in a molar ratio of synthetic monoalkyl benzene sulfonate to synthetic dialkylbenzene sulfonate of about 40:60 to about 55:45;

 (b) adding to the diluted synthetic
15 monoalkylbenzene sulfonate/synthetic dialkylbenzene sulfonate solution, CaO and Ca(OH)_2 in molar ratios of $\text{CaO}:\text{Ca(OH)}_2$ of about 90:10 to about 20:80 and a charge molar ratios of total lime [CaO and Ca(OH)_2]:sulfonate of about 22:1 to about 27:1;

20 (c) heating the sulfonate mixture to a temperature ranging from about 100°F to about 170°F under a pressure ranging from about 0 to about 50 psig;

 (d) adding water to the heated sulfonate mixture of step (c) in a molar ratio of $\text{CaO}:\text{H}_2\text{O}$ of about 0.15:1 to
25 about 0.30:1, preferably between 0.2:1 to about 0.3:1;

 (e) passing CO_2 into and through the heated sulfonate mixture of step (d) for a period of about 60 to about 240 minutes, preferably between about 60 and about 180 minutes;

76621-10

(f) separating the solids from the liquid of the sulfonate mixture;

(g) adding a diluent oil to the CO₂ treated sulfonate mixture; and

(h) stripping the petroleum solvent from the resulting over-based oil soluble sulfonate product having at least a 500 TBN.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, there is provided a new process for making an overbased sulfonate of at least a 500 TBN has been developed. A critical ratio between a synthetic monoalkylbenzene sulfonate and a synthetic dialkylbenzene sulfonate ratio in the sulfonate feedstock coupled with the use of a low molecular weight pale oil diluent is essential to make a fluid product. The lime to sulfonate charge ratio is crucial to achieve at least a 500 TBN overbased sulfonate, and the critical ratio of synthetic monoalkylbenzene sulfonate to synthetic dialkylbenzene sulfonate is essential to successfully produce a base oil-compatible product. This process produces a clear product with low solid waste.

In the present process for overbasing calcium sulfonates a mixture of water, calcium oxide and calcium hydroxide are reacted with a synthetic monoalkylbenzene sulfonate and a synthetic dialkylbenzene sulfonate in specified molar ratios. The entire charge of water is added before the carbonation of the sulfonate mixture in an amount of 15 to 30 mole% of the calcium oxide. A clear product with a low solid waste is produced.

It is known to produce overbased sulfonates by means of calcium oxide alone or a mixture of calcium oxide and calcium hydroxide. The previously known invention is distinguished in the recognition that the petroleum derived monoalkylbenzene sulfonate to synthetic dialkylbenzene sulfonate molar ratio is critical to effectively produce a base oil compatible product. The calcium oxide:sulfonate charge molar ratio is essential to produce a clear, low solids content of at least a 500 TBN overbased sulfonate.

According to the present invention the improvement provided is by using synthetic monoalkylbenzene sulfonates in conjunction with the use of petroleum-derived alkylaryl-sulfonates so that a wider range of monoalkylarylsulfonate can be utilized in the sulfonate feedstock to prepare a 500 TBN or higher TBN overbased sulfonate. Greater use of the monoalkylaryl-sulfonate enhances the compatibility of the highly overbased sulfonate in engine oil blends. The expanded range of sulfonate feedstock mixture composition provides an increased flexibility for lubricant formulation.

Overbased sulfonates derived from alkaryl-sulfonate feedstocks are one of the most commonly used detergents in automotive and marine engine oils. Depending on their applications, overbased sulfonates of different overbasing levels are prepared. As the overbasing level increases, the selection of alkaryl-sulfonate feedstock becomes more critical. There are two criteria for the selection: 1) the feedstock must give a fluid overbased product, and 2) it must produce an overbased product that is soluble in common base oils.

According to the present invention, it has been found that the viscosity and solubility of the final overbased product are greatly influenced by the alkylate structure of the

76621-10

alkarylsulfonate feedstocks disclosed in U.S. Patent 4,997,584 which teaches the use of a blend of a petroleum-derived monoalkylarylsulfonate (commonly called petroleum sulfonate) sulfonate, which typically contains several
5 cyclic rings including one or two aromatic rings and a long chain alkyl group, and a synthetic di (C_{10} - C_{18}) alkylbenzene sulfonate as the sulfonate feedstock to control the viscosity and solubility of the final overbased product. However, the use of petroleum sulfonate limits the range of
10 petroleum sulfonate permissible between 25% and 35%. A higher amount of either petroleum-derived or synthetic monoalkylarylsulfonate is often desirable since it improves solubility in oils and offers greater flexibility for lubricant formulation.

15 Petroleum-based sulfonate may be used in addition to synthetic sulfonate where the molar ratio of synthetic sulfonate to petroleum-based sulfonate ranges from about 40:60 to about 55:45.

Also, it has now been found that a synthetic heavy
20 linear alkylbenzene sulfonate (C_{16} - C_{26}) can extend the range of monoalkylarylsulfonate in the sulfonate feedstock for the preparation of 500 TBN or higher overbased sulfonate from 25-35% to 25-55%. A wider range of monoalkarylsulfonate permissible in the sulfonate feedstock increases the
25 flexibility for lubricant formulation and improves the compatibility of the product with base oils.

In the process described herein, the charge molar ratio of CaO:sulfonate may range from about 23:1 to 25:1.

In the process described herein, the solid waste
30 volume of the solids separated in step (f) ranges from about

76621-10

10.0 percent to about 25.0 percent, preferably, about 20 percent.

In the process described herein, the petroleum solvent comprises a member selected from (C₅-C₁₅) alkane, preferably heptane, toluene, xylene and naphthalene. The petroleum solvent may also comprise a (C₁-C₄) alkanol, preferably methanol.

The advantages of the present invention are more clearly apparent when considering the following examples and results thereof.

5

EXAMPLE I

10

15

A blend containing 7.55g of synthetic monoalkylbenzene sulfonic acid (obtained from Enimont as MAPS), 15.44g synthetic dialkylbenzene sulfonate, 5.89g pale oil, 91.0g n-heptane, 7.9g methanol, and .086g calcium chloride was brought to reflux in a 500ml reaction flask for 15 minutes. To neutralize, .88g calcium hydroxide was added and allowed to mix for 30 minutes at 50°C. After neutralization, 12.79g calcium oxide and 11.27g calcium hydroxide was charged, and the reaction temperature was increased to 60°C. At this point, 1.10ml water was added, and carbon dioxide was immediately introduced, at a rate of 40 ml/minute, for 135 minutes.

20

The filtered and solvent-stripped final product had a TBN value of 509/513. Its infrared spectrum showed a symmetric band with a frequency maximum at 865 cm(-1), indicating amorphous calcium carbonate.

25

EXAMPLE II

30

A blend containing 45.30g of synthetic monoalkylbenzene sulfonic dialkyl acid (obtained from Enimont as MAPS), 92.64g synthetic dialkylbenzene sulfonate, 35.34g pale oil, 798.00 ml n-heptane, 47.40g methanol, and .516g calcium chloride was brought to reflux in a 3 liter reaction flask for 15 minutes. To neutralize, 5.28g calcium hydroxide was added and allowed to mix for 30 minutes at 50°C. After neutrali- zation, 76.74g

calcium oxide and 67.62g calcium hydroxide was charged, and the reaction temperature was raised to 60°C. At this point, 6.6 ml water was added, and carbon dioxide was immediately introduced at a rate of 250 ml/minute for 135 minutes.

5

The filtered and solvent-stripped final product had a TBN (ASTM D2896) value of 528.4. X-ray fluorescence showed the product to be 20.9% calcium. Its infrared spectrum showed a symmetric band with a frequency maximum at 865 cm⁻¹, indicating amorphous calcium carbonate.

10

EXAMPLE III

15

20

25

A blend containing 3.1 lbs of synthetic monoalkylbenzene sulfonic acid (obtained from Enimont as MAPS), 8.7 lbs synthetic dialkylbenzene sulfonate, 38 lbs heptane, 2.2 lbs 100 P pale oil, 5.6 lbs methyl alcohol, and 0.56 lb calcium hydroxide was brought to reflux (57°C) in a 10-gallon reactor. The reaction mixture was refluxed and stirred at 55-60°C for one hour to neutralize the sulfonic acid. After neutralization, the reaction mixture was cooled to 40°C. Then 6.4 lbs calcium oxide, 5.6 lbs calcium hydroxide, 25 grams calcium chloride and 0.5 lb water were added. The temperature of the reaction mixture was raised to 60°C and added a total of 6.6 lbs CO₂ at a constant rate over a period of 3 hours.

30

The crude product was filtered at 40°C. Stripped the solvents at 120°C. The stripped filtrate had 575 TBN. An appropriate amount of 100 P pale oil was added to obtain a final 500 TBN finished product. The finished product was clear and had a kinematic viscosity of 82 cSt at 100°C.

The effects of petroleum-derived and synthetic monoalkylaryl-sulfonates are summarized below in TABLE I.

TABLE I

Effects Of Petroleum-Derived and Synthetic Monoalkylarylsulfonates On The
Final Product's Kinematic Viscosity And Its Compatibility With Base Oils

Content of Mono- alkylaryl Sulfonate %	Petroleum-Derived Product		Synthetic-Derived Product	
	Kin Vis (1) at 100°C (cSt)	Compatibility with Bright Stock Base Oil	Kin Vis(1) at 100°C (cSt)	Compatibility With Bright Stock Base Oil
18.5	74.9	haze	-	-
20.0	--	Slightly haze		
25.0	--	Soluble		
30.0	164.2	Soluble		
35.0	206.0	Soluble		
40.0	206.0	Soluble	---(2)	Soluble
50.0			82	Soluble
55.0			less than 200	Soluble

(1) The kinematic viscosities at 100°C were obtained from
 products made by a 10-gallon reactor.

(2) The kinematic viscosity was estimated to be between 50 and
 80.

76621-10

CLAIMS:

1. A process for producing an overbased oil-soluble calcium sulfonate having at least a TBN of 500, said process comprising the following sequential steps:

- 5 (a) diluting a synthetic mono (C_{16} - C_{26}) alkylbenzene sulfonate and a synthetic di (C_{10} - C_{18}) alkylbenzene sulfonate with a petroleum solvent in a molar ratio of synthetic monoalkyl benzene sulfonate to synthetic dialkylbenzene sulfonate of 40:60 to 55:45;
- 10 (b) adding to the diluted synthetic monoalkylbenzene sulfonate/synthetic dialkylbenzene sulfonate solution, CaO and $Ca(OH)_2$ in molar ratios of $CaO:Ca(OH)_2$ of 90:10 to 20:80 and a charge molar ratios of total lime [CaO and $Ca(OH)_2$]:sulfonate of 22:1 to 27:1;
- 15 (c) heating the sulfonate mixture to a temperature of 100°F to 170°F under a pressure ranging from 0 to 50 psig;
- (d) adding water to said heated sulfonate mixture of step (c) in a molar ratio of $CaO:H_2O$ of 0.15:1 to 0.30:1;
- (e) passing CO_2 into and through said heated
- 20 sulfonate mixture of step (d) for a period of 60 to 240 minutes;
- (f) separating the solids from the liquid of the sulfonate mixture;
- (g) adding a diluent oil to the CO_2 treated
- 25 sulfonate mixture; and
- (h) stripping the petroleum solvent from the resulting over-based oil soluble sulfonate product having at least a TBN of 500.

76621-10

2. The process of claim 1, wherein petroleum derived sulfonate is used in addition to the synthetic sulfonate and wherein the molar ratio of synthetic sulfonate to petroleum derived sulfonate ranges from 40:60 to 55:45.

5 3. The process of claim 1 or 2, wherein the molar ratio of CaO:H₂O ranges from 0.2:1 to 0.3:1.

4. The process of any one of claims 1 to 3, wherein the charge molar ratio of CaO:sulfonate ranges from 23:1 to 25:1.

10 5. The process of any one of claims 1 to 4, wherein the petroleum solvent comprises a member selected from the group consisting of a (C₅-C₁₅) alkane, toluene, xylene and naphthalene.

15 6. The process of any one of claims 1 to 4, wherein the petroleum solvent comprises a (C₁-C₄) alkanol.

7. The process of any one of claims 1 to 6, wherein the CO₂ is passed into the sulfonate mixture for a period ranging from 60 to 180 minutes.

20 8. The process of any one of claims 1 to 7, wherein solid waste volume of the solids separated in step (f) ranges from 10.0 percent to 25.0 percent.

9. The process of claim 8, wherein the solid waste volume is 20 percent.

25 10. The process of claim 5, wherein said alkane is heptane.

11. The process of claim 6, wherein said alkanol is methanol.