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(54) PREPARATION OF OVERBASED CALCIUM SULFONATES

(71) We, LABOFINA S.A, a Belgian Body Corporate of Rue de la loi 33, 1040 Brussels, Belgium, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a process for preparing overbased calcium sulfonates having a high degree of alkalinity. In this specification the term high degree of alkalinity is used to mean an alkalinity of at least 300 mgKOH/g.

Serious problems, especially concerning lubrication, can be encountered in internal combustion engines working under heavy load and using fuels which contain sulfur, sometimes in relatively high amounts. The strong acidity produced by the combustion of the fuel induces a corrosion of the engine and an intense oxidation of the lubricating oil which leads to a formation of varnish and sludge.

One preferred way to counteract these detrimental effects is to incorporate a calcium sulfonate having a high degree of alkalinity into the lubricating oil.

The detergent effect of such calcium sulfonates has been well known for a long time (see, for example U.S. Patent No. 2,270,577).

The degree of alkalinity or in other words the potential alkalinity of the calcium sulfonate serves to neutralize the strong acidity to which the lubricating oil is exposed during its use and to avoid or at least to strongly reduce the detrimental effects of that acidity. This action of overbased sulfonates has been known for a long time (see for instance U.S. Patents Nos. 2,418,894; 2,402,325; 2,485,861 and 2,501,731).

In general the process of preparing oils which contain overbased calcium sulfonates essentially consists of reacting a solution of alkylbenzene-sulfonic acids having a molecular weight higher than 400 in oil with calcium oxide or hydroxide and bubbling carbon dioxide through the reaction mixture. As a result, an excess of calcium carbonate is incorporated into the calcium sulfonate and this confers to the product a potential alkalinity.

The first products which were obtained in this manner had only a low potential of alkalinity; moreover, they formed more or less cloudy solutions which were difficult to filter because they caused clogging of the filters. Since then, the methods have been improved and the potential of alkalinity of the products has been increased up to values sometimes reaching 400 mg KOH/g. Nevertheless, the problems which are encountered during the filtration of these products remains the most limiting factor of their preparation. The efforts to improve that filtration have been obviously directed to additives which can improve the reaction of carbon dioxide with calcium oxide or hydroxide. For this purpose alcohols, amines or ammonia are frequently added to the reaction mixture. It has also been thought that the difficulties of filtration could be due to impurities in the calcium oxide, which are present in the commercial quicklime. Therefore the use of quicklimes which are as reactive as possible has also been attempted. However, these different factors have only a small influence on the filtration step which remains the most critical step of the process.

The preparation of oily concentrates of overbased calcium sulfonates having a high degree of alkalinity has been described in the literature and in various patents. This preparation comprises using a mixture containing a sulfonic acid, an oil, sometimes an aromatic diluent such as benzene or toluene, calcium oxide or hydroxide, an oxygenated solvent such as methanol, ethanol or even glycol and other additives such as ammonia and amines more or less hydrated which serve to optimize the absorption of carbonic acid which bubbles through the mixture. When the absorption of carbon dioxide is complete, the volatile solvents and additives are distilled off and the overbased sulfonate is filtered. This latter operation is usually very difficult when the desired alkalinities are high, i.e. of at least 300 mg KOH/g.

It has now been found that calcium oxide having a medium reactivity to water (as hereinafter defined) allows preparation of calcium sulfonates having a degree of alkalinity of at least 300 mg KOH/g, and that oily solutions of such overbased calcium sulfonates are perfectly limpid and easily filtrable.

According to the present invention there is provided a process for the preparation of an overbased calcium sulphonate having a high degree of alkalinity (as hereinbefore defined), which process includes the steps of:

a) preparing a mixture of at least one alkylbenzene-sulphonic acid which is essentially free of sulfuric acid and the alkyl group of which has an average molecular weight of from 250 to 2000 and an excess of a calcium oxide having a medium reactivity to water (as hereinafter defined), and

b) reacting the resultant mixture with gaseous carbon dioxide.

According to a preferred embodiment of the invention a solution of the alkyl-benzene-sulfonic acid in a solvent comprising a mineral oil is mixed with an excess of the said calcium oxide, then carbon dioxide is passed through the resultant mixture, and subsequently a concentrated solution of overbased calcium sulfonates in oil is recovered. Preferably, any insoluble ipurities, e.g. calcium sulfonates, are removed from the reaction mixture e.g. by filtration or centrifugation.

The process of the present invention provides overbased calcium sulfonates having a high degree of alkalinity and which form limpid solutions in organic solvents and/or lubricating oils.

The reactivity to water of the calcium oxide used in the process of the present invention is measured according to ASTM method C 110-67 (Physical testing of quicklime and hydrated lime-slaking rate of quicklime), which essentially consists in hydrating quicklime or calcium oxide and determining the temperature variation during that exothermal hydration reaction and tracing a curve of the reaction temperature relative to the reaction time. The activity of calcium oxide is characterised according to this method by the total reaction period. The medium reactivity to water of the calcium oxide or quicklime which is used in the process of the present invention is measured in accordance with this ASTM method, and is defined by a total reaction period of from 10 to 20 minutes.

For a calcium oxide having such a medium reactivity, the temperature rise ratio (i.e. the temperature rise after 30 seconds, expressed as a percentage of the total temperature rise) is from 15 to 45%. The temperatures measured for the determination of the temperature rise ratio are measured in accordance with the method described in ASTM-C1110 - 67.

The data for calcium oxide activity referred to in this specification are determined according to the said ASTM-C 110 method on calcium oxide samples previously heated at 700°C during 1 hour.

Calcium oxides having a medium reactivity to water have a lower reactivity to water than that of quicklimes or commercial calcium oxides for which the reaction period at the very most does not exceed 10 minutes.

The use of calcium oxide of medium reactivity to water is a particularly important feature; the chemical purity and the degree of fineness of the oxide granules play a less critical role. Generally a calcium oxide of good quality and which is carefully roasted in order that its reactivity be medium is perfectly convenient for the process of the invention.

However, in order not to have to use an excessive amount of calcium oxide and in order to obtain an overbased sulfonate of good quality, it is advantageous to use calcium oxide having a CaO content of at least 92%, and in the form of a powder which is as fine as possible, e.g. a powder in which the maximum amount of oversized particles retained on an ASTM 400 mesh sieve is 35%, based on the total amount of powder.

The calcium oxide which is preferably used fulfils the following specification:

CaO : minimum 92%
CO_2 : maximum 1%
SiO_2 : maximum 1.7%
MgO : maximum 1.4%
S : maximum 0.02%
Fe_2O_3 : maximum 1.5%
Ignition loss : maximum 1.5%

A calcium oxide having a medium reactivity to water can easily be obtained by extending the roasting time of the limestone or by carrying out this roasting at a temperature which is much higher than that which is usually required for the complete conversion of the limestone into calcium oxide. When an oily solution of overbased calcium sulfonates is prepared, preferably the solvent which is used to prepare the starting solution of alkyl-benzene-sulfonic acids further comprises oxygen-containing solvents, preferably C_{1-3} mono- or divalent alcohols, e.g. methanol and ethanol, and/or aromatic solvents, e.g. benzene or toluene. It has now been found that a small amount of water in methanol optimizes the reaction between calcium oxide and carbon dioxide, but if the calcium oxide is highly reactive towards water, it tends to agglomerate, thus reducing its surface area which is available for the contact with carbon dioxide, whereas in the present invention when a calcium oxide having a medium reactivity towards water (as hereinbefore defined) is used under the same conditions it remains finely suspended in the mixture and it absorbs the carbon dioxide easily. Further to the above mentioned solvents, alkaline additives, such as ammonia or organic amines, which are removable by evaporation and/or do not form insoluble products may be added during the reaction. The volatile solvents and other additives are removed by distillation after the reaction is completed. After evaporation of the solvents and additives, the concentrated oily solution of overbased sulfonates which is obtained from the calcium oxide having a medium reactivity to water is easily filtrable and has a high degree of alkalinity. In contrast, oily solutions of calcium sulfonates which are obtained from a calcium oxide highly reactive to water have a lower degree of alkalinity, and their filtration is difficult or even impossible.

The sulfonic acids which are used in the present invention have an alkyl group which has an average molecular weight of from 250 to 2000, which corresponds to a total molecular weight of the sulfonic acid of from 400 to 2150. The most convenient acids for preparing a calcium sulfonate having a high degree of alkalinity have a molecular weight which does not exceed 650 and which is advantageously from 480 to 580. The alkyl group may be straight or branched and may be of the polypropylene or poly-n-butene type; the polyisobutylene structure is to be avoided.

The alkyl benzene sulfonic acids are obtained in the conventional manner by sulfonating an alkylbenzene (which usually is a mixture of alkylbenzenes of the hereinabove described type) with oleum or with sulfuric anhydride, preferably in the presence of an inert solvent, such as for instance hexane. After sulfonation and mere decantation of the acidic sludges, the sulfonic acids are not pure enough for the manufacture of overbased calcium sulfonates having a high degree of alkalinity: indeed, they contain a percentage of free sulfuric acid and of sulfonic acids of lower molecular weight which are even more distubring. The sulfuric acid content induces difficulties during the filtration of oily solutions of overbased calcium sulfonates which are prepared from such a raw sulfonic acid mixture. Moreover, these calcium sulfonates contaminated with calcium sulfate give poor results as corrosion inhibiting and detergent agents in internal combustion engines.

Thus, a purified alkylbenzene-sulfonic acid is used, that is to say an alkyl-benzene-sulphonic acid which is free from sulfuric acid. A method for removing sulfuric acid consists in carrying out an extraction of the free sulfuric acid with water, in the presence of an organic oxygenated solvent (French patent No. 1,478,530). Another suitable purification method is described in our U.S. Patent No. 3,720,707. According to this method, the free sulfuric acid is neutralized with an excess of ammonia and converted into ammonium bisulfate, which is easily separated by filtration or centrifugation. The excess of ammonia neutralizes about 20% of the alkylbenzene-sulfonic acid, but the resultant, alkyl benzene-sulfonic acid containing some ammonium alkylbenzene-sulfonate can still be used for preparing overbased calcium sulfonates according to the process of the invention. Another purification method of sulfonic acids consists of using such an amount of calcium hydroxide which stoichiometrically neutralizes the free sulfuric acid which is present in the mixture, and thereafter separating the formed calcium sulfate by filtration (U.S. Patent No. 3,476,800). The major drawback of this process resides in the fact that the exact amount of sulfuric acid present in the mixture must be known, in order to calculate the amount of calcium hydroxide to be used. Any excess of calcium hydroxide results in a partial neutralization of the sulfonic acid, and thus increases its ash content. Another purification method consists of reacting the free sulfuric acid with calcium oxide and thereafter eliminating the formed calcium sulfate by filtration or centrifugation. The advantage of this method with regard to the preceeding is that the calcium oxide does not react with the sulfonic acids at the temperatures where this purification is carried out and thus the calcium oxide may be used in excess without any drawback. An embodiment of this purification process is described below in Part A of the Example.

The purified alkylbenzene-sulfonic acid, which is generally diluted with a mineral oil, is reacted with the calcium oxide of medium reactivity as hereinabove defined and carbon dioxide is then bubbled through the mixture, to confer to the final product its high alkalinity. It has been found that this high alkalinity as well as the filtration of the overbased sulfonate solution are made easy when, first, the bubbling through of the carbon dioxide, and, thereafter, the evaporation of the solvents are carried out in an alkaline medium. In order to obtain this alkaline medium, any basic compound which does not form insoluble products and/or is removable by evaporation, may be added, such as for instance ammonia or organic bases, typically mono- or diamines such as theylenediamine. It is possible, for example, for ammonia and carbon dioxide to be alternately bubbled through the reaction mixture. The selection of the basic compound principally depends on economic conditions, and therefore, ammonia is advantageously used. The above mentioned solvents may be used during the overbasing. By way of example, the solvent may consist of a mixture comprising a C_{1-3} aliphatic alochol such as methanol, ethanol or isopropanol, low amounts of water and an aromatic hydrocarbon, typically benzene, toluene and xylene.

The following Example illustrates the present invention.

EXAMPLE

Part A. *Preparation and purification of the sulfonic acid*

An alkylbenzene obtained from poly-n-butene and benzene is used as starting material. This alkylbenzene has the following characteristics:

Specific gravity 15/4°C	: 0.870
Viscosity at 100°F. (cS)	: 154.5
at 210°F. (cS)	: 10.46
Flash point Cleveland (°C.)	: 218
Refractive index n_D^{20}	: 1.4827
Average molecular weight	: 475

5 kg of this alkylbenzene are diluted, at room temperature, with 5 kg hexane and thereafter 5.5 kg (110 % by weight) of oleum containing 20% of SO_3 are added to the mixture. The temperature rises to about 55°C. and is maintained at this value by indirect cooling. After the addition of the oleum, the mixture is stirred during 3 minutes, and thereafter 640 ml water are added, while maintaining the temperature at 55°C. Then the acidic sludges are separated from the mixture, and 10.5 kg of a dilute mixture of alkylbenzene sulfonic acids having an average molecular weight of 555 are thus obtained.

These 10.5 kg of sulfonic acids are introduced into a vessel fitted with a reflux condenser and 210 g (2%) of a commercial calcium oxide are added while stirring. The mixture is heated to reflux temperature, that is to about 68°C. After 2 hours, the mixture is cooled and centrifuged. Hexane is then evaporated and a mixture of alkylbenzene-sulfonic acids having the following characteristics is thus obtained:

Alkylbenzene-sulfonia acid content	: 87%
Acidity (milliequivalent / g)	: 1.28
Viscosity at 210°F. (cS)	: 48.37

Part B - *Preparation of overbased calcium sulfonates*

The above alkylbenzene sulfonic acids are diluted with a mineral oil (tradename "Solvent Neutral") having a viscosity of 100 SSU at 100°F. in order to obtain a 39% active substance content in the mixture. To 1 kg of this solution (containing 0.71 mole of alkylbenzene sulfonic acids having an average molecular weight of 555), 300 g of toluene and 183 g of methanol containing 12.3% by weight water are added. The mixture is heated and when a temperature of 30°C is reached, 44 g (0.78 mole) of calcium oxide with a medium reactivity are added.

This calcium oxide had a total reaction time (measured in accordance with ASTM method C110) of 15 minutes. The ratio of the temperature rise in 30 seconds to the total temperature rise of this calcium oxide was measured as 29.41%.

The mixture is further heated to reflux temperature, that is to about 67°C. This temperature is maintained during 15 minutes. Thereafter 580 g toluol are added and the mixture is cooled to about 45°C.

Then, 312 g (5.57 moles) of calcium oxide of the same quality are added. Then there are bubbled through the mixture, first 4.4 g ammonia at a rate of 1 g per minute, thereafter 171 g carbon dioxide at a rate of 0.55 liter per minute, thereafter 10 g ammonia at a rate of 1 g per minute, while always maintaining the temperature near 45°C. Thereafter, the solvents are evaporated by progressively heating the mixture up to 160°C, and nitrogen is bubbled through the mixture at this temperature.

Thereafter, 8% by weight of coarse grained diatomaceous earth are added and the mixture is filtered on a Buchner filter loaded with coarse grained diatomaceous earth. An amount of 550 g is filtered within 6 minutes on a filter of 11.5 cm diameter without any tendency to clogging. The filtered product is perfectly limpid to the eye, even as a 10 cm thick layer. Its other characteristics are the following:

Viscosity at 210°F (cS)	: 65
Neutral calcium sulfonate (%)	: 28
Calcium carbonate (%)	: 23
Calcium (%)	: 12
Oil (%)	: 49
Alkalinity mg KOH/g	: 320
Molecular weight of the sulfonic acid	: 555

Other experiments which are carried out with calcium oxide samples from different origins but of medium activity towards water (total reaction time according to ASTM method C110 of from 10 to 20 minutes; temperature rise ratio of from 15 to 45%), always yield easily filtrable products having a high degree of alkalinity. The best results with regard to these characteristics and limpidity have been obtained with calcium oxide which has a medium reactivity to water and which gives rise to a temperature rise ratio of from 25 to 35%.

Comparative Examples

By way of comparison, the embodiment hereinabove described is repeated but by using in Part B, a highly active commercial calcium oxide or quicklime having a total reaction time to water of 6.5 minutes and a temperature rise ratio of 75.2%. It has been noted that this calcium oxide although it is very fine, is more poorly dispersed than the medium active calcium oxides. During the filtration, the filter is clogged after 3 minutes and only 53 g of a product which is not perfectly limpid are removed. However, its alkalinity is also 320 mg KOH/g.

Various other experiments which are carried out under similar conditions with calcium oxides from different origins and having a total reaction time to water lower than 8 minutes, in accordance with the ASTM method, always lead to products, the filtration of which is difficult or impossible.

These different experiments illustrate the favorable and quite unexpected effect which the use of a calcium oxide of reduced activity towards water has in facilitating the filtration of an oily solution of overbased calcium sulfonates prepared therefrom.

WHAT WE CLAIM IS:

1. A process for preparing an overbased calcium sulfonate having a high degree of alkalinity (as hereinbefore defined), which process includes the steps of:-

a) preparing a mixture of at least one alkylbenzene-sulfonic acid which is essentially free of sulfuric acid and the alkyl group of which has an average molecular weight of from 250 to 2000 and an excess of a calcium oxide having a medium reactivity to water (as hereinbefore defined), and

b) reacting the resultant mixture with gaseous carbon dioxide.

2. A process according to Claim 1, wherein in step (a) a solution of at least one alkyl-benzene-sulfonic acid in a solvent comprising a mineral oil is mixed with an excess of said calcium oxide, and after step (b) a concentrated oily solution containing overbased calcium sulfonate is recovered.

3. A process according to Claim 2, wherein the recovery of the oily solution comprises removing undissolved products from the oily solution.

4. A process according to Claim 3, wherein the removal of the undissolved products is effected by filtration.

5. A process according to Claim 2, 3, or 4, wherein the recovery of the oily solution comprises evaporating volatile components from the reaction mixture.

6. A process according to any one of Claims 2 to 5, wherein the solvent further comprises an aromatic hydrocarbon.

7. A process according to any one of Claims 2 to 6, wherein the solvent further comprises a C_{1-3} aliphatic alcohol.

8. A process according to Claim 7, wherein the solvent further comprises water.

9. A process according to any one of the preceding claims, wherein step (b) further comprises adding ammonia or an organic mono- or diamine to the reaction mixture.

10. A process according to Claim 9, wherein ammonia and carbon dioxide are alternately bubbled through the reaction mixture.

11. A process according to any one of the preceding claims, wherein residual sulfuric acid has been removed from the alkylbenzene-sulfonic acid by treatment with ammonia and removal of the resultant ammonium bisulfate.

12. A process according to any one of the preceding claims 1-10, wherein residual sulfuric acid has been removed from the alkyl-benzene-sulfonic acid by treatment with calcium oxide and removal of the resultant calcium sulfate.

13. A process according to Claim 1 substantially as hereinbefore described.

14. A process according to Claim 1 substantially as described in the Example.

15. Overbased calcium sulfonates when obtained by a process as claimed in any one of the preceding claims.

16. A concentrated oily solution of an overbased calcium sulfonate when obtained by a process as claimed in Claim 2, or any one of Claims 3 to 12 when appendant to Claim 2.

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