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(54) **Production of overbased calcium sulphonate, product thus obtained and lubricating oil containing it.**

(57) The solubility of Overbased Calcium Sulphonate in based oils is improved by controlling water content and extent of carbonation to minimise the formation of crystalline material so resulting in lower sediment and improved filtration.

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The present invention relates to the production of overbased calcium sulphonates and to the overbased calcium sulphonates thereby produced.

Overbased calcium sulphonates which consist of colloidal calcium carbonate dispersed in calcium sulphonate have been known as lubricant additives for some time. They act as dispersants and their basicity neutralises acids formed in the lubricant thus reducing corrosion. One problem with the use of overbased calcium sulphonates in lubricating oils has been that the colloidal calcium carbonate has tended to form haze and sediment in the oil. In addition the materials can be difficult to filter after manufacture.

Various proposals have been made to overcome this problem for example, United States patent 3,714,042 suggests that the overbased sulphonate be reacted with an alkenyl succinic acid or a derivative thereof. This adds to the cost of the overbased sulphonate, requiring an extra reactant and an additional processing step.

Overbased calcium sulphonates are generally produced by carbonating mixtures of an oil soluble sulphonic acid or an alkaline earth metal sulphonate, an alcohol, often methanol, calcium oxide and oil. In some processes second solvents, promoters and alkaline earth metal halides are used. Processes for the production of overbased calcium sulphonates are described in United Kingdom patent specifications 1,299,253 and 1,309,172.

We believe that the development of haze and sediment in lubricating oils is due to the morphology of the calcium carbonate. The calcium carbonate present generally contains both crystalline and amorphous material and it appears that the greater the amount of crystalline material present in the final product the more difficult it is to filter and the greater the tendency for haze and sediment formation.

The present invention therefore provides a process for the production of highly basic calcium sulphonates comprising the following steps.

(i) Forming a mixture of

(a) an oil-soluble sulphonic acid or an alkaline earth metal sulphonate,

(b) an aromatic or aliphatic hydrocarbon solvent,

(c) a C_1 to C_5 alcohol,

(d) oil,

(e) an excess of calcium oxide over that required to react with the sulphonic acid,

(ii) adjusting the water content to between 0.50% and 4% of the weight of excess calcium oxide,

(iii) carbonating the mixture of (i) until the pH of the mixture is in the range 6.0 to 7.5 or until the Infra-Red Spectrum first indicates the formation of vaterite as shown by a peak at 872 cm^{-1},

(iv) removing the volatiles.

Component (a) of the reaction mixture includes oil-soluble sulphonic acids and these may be natural or synthetic sulphonic acids, e.g. a mahogany or petroleum alkyl sulphonic acid; an alkyl sulphonic acid; or an alkaryl sulphonic acid. The alkyl sulphonic acid should preferably have at least 18 carbon atoms in the alkyl chain. Most suitable are sulphonic acids of molecular weight from 300 to 700, preferably from 400 to 500, suitable sulphonates are the salts of such sulphonic acids.

Instead of a sulphonic acid, an alkaline earth metal sulphonate can be used, for example, a calcium sulphonate.

Component (a) can be conveniently used as a mineral oil solution, e.g. one consisting of 70% by weight by sulphonic acid or sulphonate and 30% by weight of oil.

Component (b) of the reaction mixture is an aromatic or aliphatic hydrocarbon solvent. Aromatic hydrocarbons are preferred, and examples of these are toluene, xylene and ethyl benzene. Suitable aliphatic hydrocarbons include paraffinic hydrocarbons such as n-hexane, n-heptane, n-decane, n-dodecane, white spirit, naphtha or iso-paraffins.

Component (c) is preferably methanol although other C_1 to C_5 alcohols such as ethanol can be used.

Additional reaction promoters may be used and these may be the ammonium carboxylates such as those described in United

Kingdom patent 1,307,172 where the preferred ammonium carboxylates are those derived from C_1 to C_3 saturated monocarboxylic acids, e.g. formic acid, acetic acid or propionic acid. The preferred ammonium carboxylate is ammonium formate.

Alternatively alkali metal salts of a C_1 to C_3 carboxylic acid may be used, the preferred being those of C_1 to C_3 saturated monocarboxylic acids. The preferred alkali metals are sodium and potassium.

An an alternative promoter a metal halide or sulphide may be used. The preferred metals are alkali metals or alkaline earth metals, e.g. sodium, potassium, lithium, calcium, barium and strontium. Salts of aluminium, copper, iron, cobalt and nickel may also be used.

The water content of the initial reaction mixture is critical to obtaining the desired product and should not be more than 4 wt % and not less than 0.50 wt % based on weight of the excess calcium oxide, we prefer to use from 1 wt % to 3 wt % based on the weight of the excess calcium oxide. The reactants which are used are therefore preferably anhydrous, including the carbon dioxide and any calcium oxide which is added later to the reaction mixture. If they are not anhydrous the water level must be adjusted after formation of the reaction mixture to allow for water in the components and the water formed by neutralisation of the sulphonic acid, here we prefer that the C_1 to C_5 alcohol is not added until the

formation of the mixture of (a), (b), (d) and (e) since the presence of the alcohol at this stage could interfere with the removal of water.

The reaction mixture is an oil solution of components (a), (b), (c) and (e) and suitable oils include hydrocarbon oils, particularly those of mineral origin. Oils which have viscosities of 15 to 30 cS at 100°F are very suitable. Alternatively other oils which may be used are the lubricating oils which are described later in the specification.

Regarding the quantities of components (a), (b), (c), (d) and (e) the volume ratio of components (b) and (c) should preferably be between 30:70 and 80:20, otherwise if there is too much of component (b) the resulting product will be greasy, whereas with too much of component (c) the reaction mixture will be too viscous during addition of carbon dioxide and any calcium oxide. Preferred volume ratios of (b) and (c) are between 50:50 and 70:30.

If a promoter is used we prefer to use less than 10%, e.g. between 3.0% and 7.0% by weight based on the total weight of calcium oxide in the reaction mixture, (i.e. including any calcium oxide which is added at a later stage in the reaction).

The relative quantities of the other components of the reaction mixture are not so critical, but it is preferred that the weight of component (a) is 40% to 220% of the total

weight of oil in the reaction mixture; and that the amounts by weight of components (b) and (c) are each between 30% and 160% of the total weight of oil, in the reaction mixture. The calcium oxide may be added in several batches but we prefer than the weight of each charge is preferably between 20 and 30% by weight based on the total weight of oil plus component (a).

The carbon dioxide is introduced until the pH of the reaction mixture is in the range 6.0 to 7.5, preferably 6.5 to 7.0, as is indicated by monitoring with narrow-range pH paper. Alternatively the Infra-Red Spectrum of the reaction mixture may be monitored and stopped on appearance of the 872 cm^{-1} peak in the Spectrum which corresponds to the crystalline calcium carbonate. If carbonation is continued without removal of methanol at this point the peak at 872^{-1} grows rapidly whilst the peak at 865 cm-1 declines to result in a predominatly crystalline product giving haze and sediment problems. The peak at 872 cm^{-1} tends to appear when the pH of the reaction mixture is in the range 6.5 to 7.0 and we find that if excess methanol is removed at this point and carbonation continued the peak at 865 cm^{-1} is retained giving a final product with peaks at both 865 cm^{-1} and 872 cm^{-1} and does not give haze and sediment problems.

When the carbon dioxide has been added, if desired further calcium oxide up to the specified maximum quantity may be added and carbon dioxide introduced into the reaction

mixture in the same manner as previously. If a sulphonic acid was used initially as the component (a) it will not be necessary to use so much calcium oxide as was originally present in the reaction mixture before the first addition of carbon dioxide. However, in practice, it is convenient to use the same amount of calcium oxide for each charge.

If desired a still further addition or additions of calcium oxide followed by carbon dioxide may be carried out using similar reaction conditions as with the previous addition. Before adding calcium oxide in a further addition step, the carbon dioxide treatment of the previous step should be complete, i.e. the reaction mixture should not be capable of absorbing any more carbon dioxide.

After the last treatment with carbon dioxide, the reaction mixture should be heated to an elevated temperature, e.g. above 130°C, to remove volatile materials (components (b), water and any remaining alcohol) and thereafter filtered, a filter aid is generally used. The desired overbased detergent additive usually having a TBN of 300 or more, is obtained as the filtrate.

As a further preferred embodiment of the process water is added to the reaction mixture after introduction of carbon dioxide is complete and before removal of the volatile materials. Although the water is generally removed with the other volatiles we have found that this addition of water reduces the tendency of the product to form a skin on storage.

The above process can be varied by including in the reaction mixture a sixth component (f) and that is a long-chain monocarboxylic acid, or anhydride, or a long-chain di-carboxylic acid or anhydride. By long-chain we mean that the molecular weight of the acid is at least 500. Preferred carboxylic acids are those having a molecular weight of between 600 and 3000, e.g. between 800 and 1800. These carboxylic acids are conveniently derived from a polymer of a mono-olefin, e.g. a C_2 to C_5 mono-olefin, such as polyethylene, polypropylene or polyisobutene.

The quantity of component (f) which is used is preferably from 20 to 55 wt % of the weight of component (a). The combined weight of components (a) and (f) are then preferably 40% to 220% of the total weight of oil in the reaction mixture.

Also as a further modification, to minimise the production of greasy products, the reaction mixture can include small amounts (e.g. between 4% and 15% by weight of oil) of an alkyl phenol containing at least 7 carbon atoms in the alkyl chain. Suitable examples are n-decyl phenol, cetyl phenol and nonyl phenol. Alkyl phenols act as copromoters and also enhance the speed of reaction.

The overbased detergent of this invention is suitable for use in lubricating oils, both mineral and synthetic. The lubricating oil may be an animal, vegetable or mineral oil, for

example petroleum oil fractions ranging from naphthas or spindle oil to SAE 30, 40 or 50 lubricating oil grades, castor oil, fish oils or oxidised mineral oil.

Suitable synthetic ester lubricating oils include diesters such as di-octyl adipate, dioctyl sebacate, didecyl azelate, tridecyl adipate, didecyl succinate, didecyl glutarate and mixtures thereof. Alternatively the synthetic ester can be a polyester such as that prepared by reacting polyhydric alcohols such as trimethylolpropane and pentearythritol with monocarboxylic acids such as butyric acid, caproic acid, caprylic acid and pelargonic acid to give the corresponding tri- and tetra-esters.

Also complex esters may be used as base oils such as those formed by esterification reactions between a dicarboxylic acid, a glycol and an alcohol and/or a monocarboxylic acid.

Blends of diesters with minor proportions of one or more thickening agents may also be used as lubricants. Thus one may use blends containing up to 50% by volume of one or more water insoluble polyoxyalkylene glycols, for example polyethylene or polypropylene glycol, or mixed oxyethylene/oxypropylene glycol.

The amount of overbased detergent added to the lubricating oil should be a minor proportion, e.g. between 0.01% and 10% by weight, preferably between 0.1% and 5% by weight.

The final lubricating oil may contain other additives according to the particular use for the oil. For example, viscosity index improvers such as ethylene propylene copolymers may be present as may succinic acid based dispersants, other metal containing dispersant additives and the well known zinc dialkyldithiophosphate antiwear additives.

The present invention is illustrated but in no way limited by reference to the following example in which the following charge was placed in the reaction vessel.

Sulphonic Acid	89.9 grams
Calcium Oxide	5.2 grams
Anhydrous Calcium Chloride	1.9 grams
Toluene	115.9 grams
Oil (solvent 150 Neutral)	80.6 grams

The water of neutralisation and any other water present was removed azeotropically. The reaction mixture was then cooled to below 60°C, 41.0 grams of methanol, 50.6 grams calcium oxide and varying amounts of water as specified in Table 1 added. The mixture was then carbonated at 60°C until the end point according to the following table was reached.

The reaction mixture was stripped at 150°C liquid temperature to remove the volatiles, 40.1 grams of oil being added during stripping.

	Added Water % wt on Excess CaO	Carbonation End Point	Filtration USG/hr/ft^2	TNB mg KOH/g	Kinematic Viscosity (100°C) (Centistokes)	Solubility at 5 wt % in solvent 600 oil
	0	pH 6.8	0.2	271	*	Clear after 6 days
5	0.50	pH 6.8	0.5	266	1218	Clear - no sediment after 8 days
	1.02	pH 6.5	1.3	303		)
	3.06	CO_2 break-through + 30 minutes	1.0	297		) Clear blends after 21 days
10	5.11	pH 7.1 (IR showed some vaterite)	Very slow	204		)
	7.11	pH 7.1 (IR showed some vaterite)	So slow no product obtained			

* Almost solid at Room Temperature.

WHAT WE CLAIM IS:

1. A process for the production of highly basic calcium sulphonates comprising the following steps.

(i) Forming a mixture of

(a) an oil-soluble sulphonic acid or an alkaline earth metal sulphonate,

(b) an aromatic or aliphatic hydrocarbon solvent,

(c) a C_1 to C_5 alcohol,

(d) oil,

(e) an excess of calcium oxide over that required to react with the sulphonic acid.

(ii) Adjusting the water content to between 0.50% and 4% of the weight of excess calcium oxide.

(iii) Carbonating the mixture of (1) until the pH of the mixture is in the range 6.0 to 7.5 or until the Infra-Red Spectrum first indicates the formation of vaterite as shown by a peak at 872 cm^{-1}.

(iv) Removing the volatiles.

2. A process according to claim 1 wherein the sulphonic acid is an alkylaryl sulphonic acid of molecular weight from 300 to 700.

3. A process according to claim 1 or claim 2 wherein the hydrocarbon solvent is toluene, xylene or ethyl benzene.

4. A process according to any of the preceding claims in which the volume ratio of components (b) and (c) is from 30:70 to 80:20.

5. A process according to any of the preceding claims in which the weight of component (a) is from 40 to 200 wt % of the total weight of oil in the mixture.

6. A process according to any of the preceding claims in which water is added to the reaction mixture after introduction of carbon dioxide is complete.

7. A process according to any of the preceding claims in which from 4% to 15% by weight based on the weight of oil of an alkyl phenol is added to the reaction mixture.

8. A highly basic calcium sulphonate whenever produced by a process according to any of the preceding claims.

9. Lubricating oil containing from 0.01 to 10% by weight of a highly basic calcium sulphonate according to claim 8.

European Patent Office

EUROPEAN SEARCH REPORT

Application number EP 80 30 3029

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US - A - 3 429 811 (MAX L. ROBBINS et al.) * Column 6, example 1 * --	1
	EP - A - 0 000 264 (EXXON CO.) * Complete document * --	1
A	DE - A - 1 444 550 (BRAY OIL CO.) * Page 34, lines 6-18 * ----	1

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 07 C 143/00
C 10 M 1/40

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 07 C 143/00
C 10 M 1/08

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	27-11-1980	GRAMAGLIA