

Description

This invention relates to the production of overbased calcium sulphonates, and in particular to the reduction of handling problems in the preparation and processing of overbased calcium sulphonates.

Overbased calcium sulphonates consist of colloidal calcium carbonate dispersed in an oil, with sulphonate acting as the surfactant. They have been known for some time as additives for automotive crankcase lubricants, their basicity neutralises acids formed in the lubricant; thereby reducing corrosion, and the dispersant effect of the additive helps to inhibit the formation of harmful deposits in the oil.

Early preparations of overbased calcium sulphonates comprised first forming a gel of calcium carbonate in an aqueous medium, and thereafter dispersing the gel in a diluent oil. In US—A—3 105 049 calcium oxide or hydroxide is reacted with carbon dioxide in the presence of methanol to form solvated calcium carbonate, which is then mixed with an oil and a dispersant such as calcium mahogany sulphonate to give an emulsion which separates into two phases, the methanol phase being removed from the oil phase containing the dispersed product.

US—A—3318809 describes a similar process in which finely powdered calcium oxide is slurried in methanol and carbonated in a counter-current carbonation unit before being mixed with oil and calcium sulphonate. After mixing the methanol and oil phases are separated, and following stripping the oil phase is treated with water to decompose any methanol complex.

US—A—3 342 733 describes a similar process in which a colloidal gel of an alkaline earth metal carbonate in an aqueous medium is mixed with a hydrocarbon oil containing an oil-dispersible surfactant such as a calcium sulphonate to form an emulsion. The emulsion breaks on standing and the water phase is removed.

"Dispersions of Insoluble Carbonates in Oils" by Bray *et al*, Ind. Eng. Chem. Prod. Res. Dev., Vol 14, No. 4, 1975, pp. 295—8 also describes that the removal of methanol by evaporation may yield a gel which is impossible to handle. Bray describes the addition of water to break this gel, but acknowledges that this may result in filtration problems.

US—A—3 258 426 describes an alternative process for preparing calcium carbonate dispersions in oil in which an emulsion is formed of calcium carbamate in oil and the carbamate is then converted to the carbonate by heating. Coarse particles formed in the formation of calcium carbonate are retained in an emulsion which is separated from the oil phase containing the calcium carbonate dispersion.

In more recent processes for preparing overbased calcium sulphonates in an attempt to produce products of higher base number (typically of 300 Total Base Number —TBN, as measured by ASTM 2896-80) which have good stability, it is more usual to use a process in which a mixture of an oil-soluble sulphonic acid or an alkaline earth metal sulphonate, an alcohol such as methanol, calcium hydroxide and oil is carbonated, and the temperature of carbonation is reduced below the reflux temperature normally used in early calcium oxide based processes. In such processes it is also possible to employ a second solvent, typically a hydrocarbon such as toluene and/or a promoter and/or an alkaline earth metal halide. An example of such a process is given in EP—A—0000264, which also describes a soaking period in which, after carbonation and before stripping and filtration, the reaction mixture is held at 20°C to 35°C for at least half-an-hour.

BE 785268 describes a similar process using methanol and a second, volatile hydrocarbon solvent in the mixture that is carbonated at a temperature of up to 35°C. Following carbonation, the mixture is optionally heated to reflux for a short time. After removing volatiles the mixture is again blown with carbon dioxide to complete carbonation.

We have found that a conventional stripping step to remove an alcohol such as methanol from the product of the low temperature carbonations of these processes tends to result in the formation of a product from which a heavier layer separates out. When the product is subsequently filtered this heavier layer forms a sludge on top of the filter cake which can tend to slow the filtering operation.

The sludge has a grease-like consistency and also contains a considerable amount of the overbased calcium sulphonate product but in a form which is clearly unsuitable for use as a lubricating oil additive. This reduces the yield of usable product from the preparation. Furthermore, the accumulation of sludge presents a considerable problem in a commercial process since it requires frequent cleaning operations to keep filters and centrifuges operable, while the sludge itself presents considerable disposal problems.

It has now been found that, by modifying the removal of alcohols such as methanol from the carbonated product, the tendency to sludge formation may be remarkably diminished or even eliminated.

GB—A—2097417 describes a process for the preparation of highly basic alkaline earth metal salts in which an alkaline earth metal hydroxide is carbonated in methanol and mixed with a dispersant (as in the early prior art) but then further carbonated, and water and methanol separated from the product.

However, by employing a low temperature carbonation and then separating methanol from the carbonated reaction mixture after a period of heat soaking a surprising improvement in overbased calcium sulphonate production is achieved, with reduced sediment and sludge formation resulting in improved filtration properties of the product and better yields. Moreover, the product shows advantages in viscosity and/or stability and/or haze.

Thus, in one aspect the invention provides a process of preparing an overbased calcium sulphonate comprising:

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_{1-5} alcohol,
- d) oil, and
- e) an excess of calcium hydroxide over that required to react with sulphonic acid present;

ii) carbonating the mixture at a temperature not exceeding 35°C with from 75 to 95 wt% CO_2 based on the excess calcium hydroxide;

iii) heating the reaction mixture after carbonation to a temperature not exceeding 60°C over a period of not less than 15 minutes;

iv) separating the carbonated mixture into a first phase comprising at least a major part of the alcohol and a second phase comprising at least a major part of the hydrocarbon solvent and the oil, and removing the first phase;

v) removing volatile material from the second phase to yield a dispersion of overbased calcium sulphonate in oil.

Component (a) of the reaction mixture includes one or more 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. Particularly suitable sulphonates are the alkaline earth metal salts of these most suitable sulphonic acids, and a calcium sulphonate is the preferred sulphonate.

Component (a) may be conventionally used as a mineral oil solution. A suitable mineral oil solution comprises from 50 to 90% by weight, preferably 70% by weight, of sulphonic acid or sulphonate.

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 very preferably methanol, although other C_1 to C_5 alcohols such as ethanol can be used.

When component (a) is introduced as an oil solution it may be unnecessary to introduce additional oil—thus, the oil solvent for (a) acts as component (d)—and this is preferred. Alternatively oil may be introduced separately into the reaction mixture. The reaction is thus an oil solution of components (a), (b), (c) and (e). Suitable oils for component (d) include hydrocarbon oils, particularly those of mineral origin. Oils which have viscosities of 15 to 30 cSt at 38°C are very suitable. Alternatively the lubricating oils described later in the specification may be used.

Calcium hydroxide used as component (e) will generally be derived from a natural source such as lime or gypsum.

The calcium hydroxide (component (e)) may be added in one stage or in two stages. In two stage addition first sufficient calcium hydroxide is added to neutralize the sulphonic acid, and then secondly the excess calcium hydroxide is added. However single stage addition is preferred.

Additional reaction promoters may be used and these may be the ammonium carboxylates, such as those described in United Kingdom patent GB—A—1 309 172 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. Alternatively alkali metal salts of a C_1 to C_3 carboxylic acid may be used, such as those of a C_1 to C_3 saturated monocarboxylic acid.

A further alternative promoter is a metal halide or sulphide such as a halide or sulphide of an alkali metal, alkaline earth metal, aluminium, copper, iron, cobalt or nickel.

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 tends to be greasy, whereas with too much of component (c) the reaction mixture may tend to be too viscous during addition of carbon dioxide and any further calcium hydroxide. 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 hydroxide in the reaction mixture, (i.e. including any calcium hydroxide 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 carbon dioxide is introduced into the mixture while it is at a temperature below 35°C , preferably not more than 30°C , and more preferably in the range to 23°C to 30°C , in an amount up to from 75 to 95

wt%, preferably 80 to 90 wt%, of that stoichiometrically required to neutralize the excess calcium hydroxide. When used in conjunction with the other steps of the process of the invention this low temperature carbonation promotes the reduction of sediment resulting from formation of insoluble carbonates.

Very preferably step ii) comprises:

ii) carbonating the mixture with an amount of from 80 to 90 wt% CO₂ based on the excess calcium oxide or hydroxide at a temperature of 25±2°C.

When the carbon dioxide has been added, if desired further calcium hydroxide, but preferably only up to the preferred maximum quantity described above, may be added and then further carbon dioxide introduced into the reaction mixture in the same manner as previously. If sulphonic acid was used initially as the component (a) it will not be necessary to use so much calcium oxide or calcium hydroxide in this second charge as was originally present in the reaction mixture before the first addition of carbon dioxide.

The heating step (iii), hereinafter referred to as "a heat soak" or "heat soaking", is preferably carried out over a period of from 1/2 to 3 hours, and most preferably over 1 to 2 hours. The temperature preferably does not exceed 55°C, and more preferably does not exceed 45°C and most preferably in the range of 30°C to 45°C. During the heat soak the reaction mixture is desirably stirred. It is believed that the heat soak results in more lime going into solution, which results in greater lime utilization and an increase TBN in the product. In addition lower viscosity products may be obtained for a given TBN. Better yields and/or a reduced skinning tendency and/or a reduction in the problems of sediment resulting from unreacted materials may also be obtained.

Diluent oil may be added either to the reaction mixture following heat soaking in step iii) or to the recovered second phase of step iv) to give the required dilution to the additive product or at both stages. Addition of at least part of the oil following step iii) is believed to improve subsequent centrifugation steps. Oil is preferably added to give a product containing from 25 to 75 wt% overbased calcium sulphonate.

Following heat soak, and optionally diluent oil addition, the reaction mixture is separated into two phases in step iv) and this is found to reduce the tendency to sludge formation in the product. The separation may be done by gravity—thus, by leaving the reaction mixture to stand—or by mechanical means such as centrifugation or decantation in a scroll decanter. This separation is preferably carried out between ambient temperature and 60°C, more preferably at a temperature not exceeding 45°C. The first, upper layer comprises alcohol and water formed during the reaction, with possible minor amounts of the hydrocarbon solvent and neutral calcium sulphonate. The second, lower layer comprises the desired overbased calcium sulphonate in the oil with possible minor amounts of alcohol and water and any sediment. The phases are separated and the second phase is treated further to recover the desired product. The first phase may be treated to recover the alcohol, which may then be recycled.

After the separation step the second phase may be heated to an elevated temperature, e.g. above 130°C, and/or reduced pressure to remove volatile materials (components (b), water and any remaining alcohol) and is preferably thereafter filtered and/or centrifuged to remove solids. Filtering may be enhanced using conventional filter aids. The desired overbased detergent additive is obtained as the filtrate.

It is possible for a single centrifugation step to be employed to carry out the phase separation of step (iv) with a simultaneous solids removal. Three phase centrifuges are available capable of carrying out such a liquid-liquid-solid separation.

The process of the invention enables a high quality, high TBN calcium sulphonate product to be obtained in good yields with reduced amounts of material losses in sludge and/or sediment and reduced problems in waste disposal which can arise when large amounts of sludge or flocculent material are produced. The process of the invention in particular provides a means of preparing a preferred product with a TBN of at least 300 mg (KOH)/g at a kinematic viscosity measured at 100°C of less than 90 cSt, more preferably less than 70 cSt. More particularly, the process enables such products to be prepared such that in the final filtration of the product a preferred filtration rate of at least 200 l/hm², more preferably at least 400 l/hm², is achieved. In addition, preferred aspects of the process enable low haze, high stability products to be obtained.

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 to 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 pentaerythritol 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.

(14)

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 invention extends to an additive concentrate comprising an oil solution of an overbased calcium sulphonate of the invention and preferably one or more additional additives. It also extends to a lubricating oil containing the overbased calcium sulphonate.

The present invention is now described, though only by way of illustration, by reference to the following Examples.

Comparative Examples A to J and Examples 1 to 6

In these Examples, unless otherwise indicated, the initial reaction mixture comprising reactants in the following proportions, based on a five litre laboratory scale test comprised:

15	Toluene	1353 g
	Sulphonic acid ¹⁾	1353 g
20	Methanol	812 g
	Lime ²⁾	793 g

Notes:

- 25 ¹⁾ an oil solution containing 68.5 wt% active ingredient of 480 average molecular weight of which 25% is a C₁₈ straight chain sulphonic acid and 75% is a C₂₄ propylene oligomer sulphonic acid.
²⁾ lime obtained from Balthazard et Cotte of France which contains 95 wt% calcium hydroxide, and approximately 0.3 wt% magnesium.

30 In the carbonation step, unless otherwise indicated, the amount of carbon dioxide added to the above mixture was 356 g—i.e. 88 wt% of the stoichiometric amount required by the overbasing amount of lime—charged over 3.64 hours. Where different amounts are added the overall charge time for CO₂ is the same.

35 Diluent oil is added to the carbonated product, unless otherwise indicated, in an amount of 875 g. Stanco 150 is used as the diluent oil.

Comparative Example A

a) Charging:

40 The sulphonic acid and toluene were charged to a reactor fitted with a reflux condenser, stirrer and sparge tube, and stirred. The methanol was added, and then the lime. The temperature rose to 35°C, and the reactor was cooled to 25±2°C.

b) Carbonation:

45 Carbonation commenced at a rate of 97.8 g/hour CO₂, and the temperature was maintained at 25±2°C until 69% CO₂ was added. Then the temperature was raised to 55°C over the remaining carbonation time.

c) Stripping:

50 A nitrogen sparge was commenced and the reflux condenser replaced by a take-off condenser. The temperature was then raised to 80°C. Diluent oil was added during stripping at the rate that material was distilled off. The mixture was then centrifuged, and the centrifugate further stripped under vacuum at 150°C.

d) Filtration:

55 The stripped product was filtered using Dicalite Special Speedflow filter aid (available from General Refractory Co. of USA) as precoat and either 2% Speedplus or 2% Speedex (both available from General Refractory Co.) as an admix. Other filter aids used as admixes in the following Examples as shown in the Table.

For Comparative Examples B to J and Examples 1 to 6 the procedure was as described for Comparative Example A except where variations are shown in Table 1 below.

0 121 024

(15)

TABLE 1

	A	B	C	D
5	Charging Lime addition (stages)	one	one	one (over 1 hour)
10	Carbonation Temperature (°C) % Stoichiometric CO ₂	25—55 88	25—55 88	25—55 88
15	Heat soak Temperature (°C) Time (hour)	— —	— —	— —
	Phase separation	No	No	Gravity
20	Stripping Temperature (°C) Centrifuge Temperature (°C)	80 Yes 150	150 Yes —	150 Yes — Thin film evaporator
25	Filtration SSF precoat+(i) admix*(%) ii)	+2% SPLUS +2% SDX	(i) 2% SPLUS (ii) 2% SDX	2.5% SSF 1.5% SSF
30	*SPLUS=Speedplus SDX=Speedex SSF=Sp Speedflow.			

TABLE 1 (continued)

	E	F	G	H
35	Charging Lime addition (stages)	two (30 min+10 min)	two (30 min+10 min)	two (30 min+10 min)
40	Carbonation Temperature (°C) % Stoichiometric CO ₂	25—30 80	25—30 88	25—30 92
45	Heat soak Temperature (°C) Time (hour)	— —	— —	— —
50	Phase separation	Gravity	Gravity	Gravity
55	Stripping Temperature (°C) Centrifuge Temperature (°C)	150 Yes —	— Yes Thin film evaporator	150 Yes —
60	Filtration SSF precoat+(i) admix* (%) ii)	3.0% SSF	3.0% SSF	1.5% SSF 3.0% SSF
65	*SPLUS=Speedplus SDX=Speedex SSF=Sp Speedflow.			

TABLE 1 (continued)

	I	J	1	2
5	Charging			
	Lime addition (stages)	one (over 1 hour)	one (1 hour)	one (1 hour)
10	Carbonation			
	Temperature (°C)	25—55	25—55	25—30
	% Stoichiometric CO ₂	88	88	88
15	Heat soak			
	Temperature (°C)	—	55	30—55
	Time (hour)	—	1	1
	Phase separation	Gravity	Gravity	Gravity
20	Stripping			
	Temperature (°C)	—	—	—
	Centrifuge	Yes	Yes	—
	Temperature (°C)	150	150	150
25	Filtration			
	SSF precoat+admix (%)	(i) 1.5% SSF (ii) 3.0% SSF (iii) 3.0% SPLUS	(i) 1.5% SSF (ii) 3.0% SSF (iii) 3.0% SPLUS	1.5% SSF 1.5% SSF
30	TABLE 1 (continued)			
		3	4	5
35	Charging			
	Lime addition (stages)	one (1 hour)	one (1 hour)	one (1 hour)
				two (30 min+30 min)
40	Carbonation			
	Temperature (°C)	25—30	25—30	25—30
	% Stoichiometric CO ₂	92	92	92
45	Heat soak			
	Temperature (°C)	30—55	30—55	30—55
	Time (hour)	1	1	1
	Phase separation	Gravity	Gravity	Gravity
50	Stripping			
	Temperature (°C)	—	—	150
	Centrifuge	Yes	—	Yes
	Temperature (°C)	150	150	—
55	Filtration			
	SSF precoat+admix (%)	(i) 1.5% SSF (ii) 3.0% SSF	3.0% SSF	(i) 1.5% SSF (ii) 3.0% SSF

The results of the above Examples and Comparative Examples are given in Table 2 below which indicates the analysis of the overbased calcium sulphonate product, and the amounts of sediment and sludge formed at various stages in carrying out the preparation. Also given are the critical processing parameters of filterability and centrifugate flow rate which indicate how readily the desired product may be isolated.

The process of the invention shows a remarkable reduction in the sludge formation, which gives a more efficient process with less processing problems and a greater yield of the desired product. In this connection it is pointed out that the term "sludge" is used to describe a heavy layer formed within the

product which is hazy in appearance and has a grease-like consistency when filtered off the product. It is to be distinguished from particulate sediments which generally comprise calcium carbonate and/or neutral calcium sulphate and which are deposited from the product as hard or soft precipitates. On filtering the sediments form a filter cake, while any sludge is deposited as a greasy layer on top.

The analytical results given are measured on the filtrate diluted to a nominal 300 TBN with diluent oil, unless otherwise indicated.

Kinematic viscosity was measured at 100°C by the technique described in ASTM D445-79.

The soap content was measured by the technique described in ASTM D3712.

10 Foaming tendency was measured on a solution of 2.0 wt% of the filtrate in diluent oil by the technique described in ASTM D892 Seq I using 400 ppm of Dow Corning D200 silicone as anti-foaming agent, unless otherwise indicated.

Blend stability was measured by observing a) the volume percentage of sediment formed after mixing the sample with heptane in a 1:1 (v/v) ratio and centrifuging for 20 minutes; and (b) the volume percentage of sediment formed after the sample/heptane mixture is left to stand for 24 hours.

15

	Process results	Units	Example		
			A	B	C
20	After carbonation	sediment sludge	Vol % Vol %	1.6 —	2.0 —
	After stripping	sediment sludge	Vol % Vol %	0.12 8.0	3.0 1.0
25	After centrifugation	sediment sludge	Vol % Vol %	0.06 0.1	0.3 6.0
30	Centrifugate flow rate	g/min	220	220	—
	Filterability*	l/hm ²	i) 69 ii) 102	i) 0 ii) 0	102
35	Analytical results				
	Total base No.	mgkOH/g	325.0 326.9	325.0 326.9	354.9
40	Kinematic viscosity at 100°C	cSt	62.1	67.7	253.8 (TBN 354.9) 49.5 (TBN 300)
	% Soap	mass %			35.8
	% Calcium	mass %			14.3
45	Water plus solvent content	mass %			35.8
	Foaming tendency	ml/ml			0—0 (TBN 300) 49.5—30 (No. A/F)
50	Blend stability (initial/24 hr sediment)	vol %			0.4/1.0

55

60

65

		Process results	Units	Example		
				D	E	F
5	After carbonation	sediment sludge	Vol % Vol %	2.0 —	3.0 —	3.0 —
	After stripping	sediment sludge	Vol % Vol %	0.2 trace	3.0 none	0.2 none
10	After centrifugation	sediment sludge	Vol % Vol %	— —	— —	— —
15		Centrifugate flow rate	g/min	250	—	200
		Filterability	l/hm ²	33	0	85
	Analytical results					
20	Total base No.		mgkOH/g	315.8	326.2	296.0
	Kinematic viscosity at 100°C		cSt	55.5	166.1	178.2
25	% Soap		mass %	—	32.3	28.4
	% Calcium		mass %	—	12.89	11.86
	Water plus solvent content		mass %	—	—	2.40
30	Foaming tendency		ml/ml	—	—	190—90 (No A/F)
	Blend stability (initial/24 hr sediment)		vol %		0.5/1.8	1.8/1.4

0 121 024

(19)

		Process results	Units	Example		
				G	H	I
5	After carbonation	sediment sludge	Vol % Vol %	3.8 none	1.8 none	1.2 none
	After stripping	sediment sludge	Vol % Vol %	0.2 none	0.3 none	0.1 hard/0.1 soft none
10	After centrifugation	sediment sludge	Vol % Vol %	0.08+0.01 Gel none	0.1 none	—
		Centrifugate flow rate	g/min	180	205	—
15		Filterability	l/hm ²	67	55	i) 47 ii) >119 iii) >142
20	Analytical results					
	Total base No.		mgkOH/g	308.3	317.1	327
	Kinematic viscosity at 100°C		cSt			166.1
25	% Soap		mass %	31.4	30.3	30.8
	% Calcium		mass %	12.56	12.55	12.77
30	Water plus solvent content		mass %			0.64
	Foaming tendency		ml/ml	0—0	0—0	0—0
35	Blend stability (initial/24 hr sediment)		vol %	0.4/1.4	0.4/1/6	0.14/0.40

			Example		
	Process results	Units	J	1	2
5	After carbonation	sediment sludge	Vol % Vol %	0.8 none	3.0 (0.8 after heat up) (0.8 after heat up)
	After stripping	sediment sludge	Vol % Vol %	0.3 none	0.04 hard/0.15 soft none none
10	After centrifugation	sediment sludge	Vol % Vol %	— none	0.02 hard/0.02 soft— none none
		Centrifugate flow rate	g/min	—	80
15		Filterability	l/hm ²	i) 33 ii) 40 iii) 51	i) 35 ii) 102
20	Analytical results				
	Total base No.	mgkOH/g	324.5	325.0	324.0
	Kinematic viscosity at 100°C	cSt	178.2		
25				44.4	57.5
	% Soap	mass %	30.1	30.1	29.9
	% Calcium	mass %	12.99	13.04	12.93
30	Water plus solvent content	mass %	0.52	0.30	0.60
	Foaming tendency	ml/ml	0—0	0—0	0—0
35	Blend stability (initial/24 hr sediment)	vol %	0.002/0.10	0.3/0.4	0.2/0.3

			Example				
	Process results	Units	3	4	5	6	
5	After carbonation	sediment sludge	Vol % Vol %	2.8 none	2.8 none	2.8 none	1.0 none
	After stripping	sediment sludge	Vol % Vol %	0.50% hard none	N/A	N/A	0.3 soft none
10	After centrifugation	sediment sludge	Vol % Vol %	— —	— —	0.02 hard/ 0.10 soft none	0.3 none
15	Centrifugate flow rate	g/min	—	—	120—140	120	
	Filterability	l/hm ²	i) 286 ii) 274	93	107	i) 57 ii) 71	
20	Analytical results						
	Total base No.	mgkOH/g	333.6	—	—	306.0	
	Kinematic viscosity at 100°C	cSt	—	—	—	50.6	
25	% Soap	mass %	31.5	30.3	32.0	—	
	% Calcium	mass %	13.17	13.05	13.14	—	
30	Water plus solvent content	mass %	0.66	1.08	0.8	—	
	Foaming tendency	ml/ml	230—40 (No. A/F)	210—40 (No. A/F)	180—40 (No. A/F)	—	
35	Blend stability (initial/24 hr sediment)	vol %	0.4/1.8	0.2/0.10 after 3 days	0.9/1.2	0.20/0.6	

Comparative Examples A and B which do not employ a phase separation step form significant amounts of sludge. Comparative Examples C and D use a phase separation step but in conjunction with a high temperature carbonation, and the product still contains some sludge, has poor filterability and poor blend stability. Comparative Examples E—J show no sludge formation but the products have poor filterability and/or poor blend stability and/or high viscosity. Comparative Example J includes both phase separation and heat soaking step but employs a high temperature carbonation. The results are to be compared to those for Example 1, which is a similar process except that the low temperature conditions of the invention are employed. Whereas Comparative Example J gives poor filterability and an unacceptably high viscosity, Example 1 gives excellent filterability and a much lower viscosity. Examples 2 to 6 show the effect of variations from the preferred procedure of Example 1; in each case the product is free from sludge and where measured the viscosity is much lower than Comparative Example J. Examples 2 and 4 show reduced filterability but these results were obtained without a centrifugation step between phase separation and filtering and this would be expected to make filtration difficult. Examples 3 to 5 also show that carbonation beyond 90% of stoichiometric results in a less optimum product, and Example 6 shows that two part lime is less advantageous but the product of this Example shows improved blend stability as compared to Comparative Examples E—H which also use two part lime addition.

55 Examples 7 to 11

A further set of experiments was carried out using the same reactants as in the previous Examples, but on a 3 litre scale in the following amounts:

60	Toluene	812 g
	Sulphonic acid	812 g
	Methanol	487 g
65	Lime	476 g

The following procedure was employed:

a) Charging:

The sulphonic acid and toluene were charged to a reactor fitted with a reflux condenser, stirrer and sparge tube, and stirred. The methanol was added, and then the lime. The temperature rose to 35°C, and the reactor was cooled to 25±2°C.

b) Carbonation:

Carbonation was conducted at 25±2°C over 3.5 hours so that carbon dioxide was adsorbed to 90% of the stoichiometric amount required by the overbasing lime.

c) Heat soak:

The carbonated mixture was stirred at the temperatures and for the times shown in Table 3 below.

d) Diluent oil addition:

525 g of diluent oil were then added to the heat soaked product.

e) Phase separation:

The mixture was separated by centrifuging into a first liquid phase comprising a major part of the methanol, a second liquid phase comprising small amounts of solid phase which is discarded.

f) Stripping:

The second liquid phase was stripped by heating to 160°C under vacuum over 2 hours and then maintaining under vacuum at a temperature of 160°C for a further 2 hours.

g) Filtration:

The stripped product was filtered using Dicalite Special Speedflow filter aid as precoat and 1.5% Special Speedflow as an admix.

The analysis of the material was carried out as described hereinbefore with the addition of a haze test. Haze was measured as the amount of light scattering determined using a nephelometer (Coleman Photonephelometer available from Coleman Instruments Company of USA). The measurements are carried out on a 5 wt% solution in diluent oil and the results are expressed in nephalos.

TABLE 3

Example	7	8	9	10	11
Heat soak					
Temperature (°C)	25+40	25	25+40	25+40	40
Time (hours)	1.0+1.5	2.0	2.0+0.5	2.0+1.0	1.5
Process results					
After stripping					
sediment (vol %)	0.07	0.08	0.05	0.06	0.06
sludge (vol %)	none	none	none	none	none
Filterability (l/hm ²)	394	488	396	485	327
Product analysis					
TBN (mgKOH/g)	333	323	336	334	332
kV at 100°C (cSt)	69.5	83.6	62.4	71.5	71.5
Stability (initial/24 hr sediment (vol %))	trace/0.02	0.02/0.02	0.05/0.02	trace/trace	0.01/0.02
Foaming tendency (ml/ml)	0/0	0/0	0/0	0/0	0/0
Haze (nephalos)	58	60	68	66	58

Example 12

The procedure of Examples 7 to 11 was repeated except for the following changes:
Reactants: Lime from Company of USA US Gypsum was used in place of lime from Balthazard et Cotte.

b) Carbonation:

Carbonation was carried out over 3 hours, but still to 90% of the stoichiometric amount required by the overbasing lime.

23

c) Heat soak:

This was conducted at 40°C for 1.5 hours.

Six repeats were made of this test and the results in Table 4 below represent the average of the six runs.

TABLE 4

Process results	
After stripping	
sediment (vol %)	0.10
sludge (vol %)	none
Filterability (l/hm ²)	625
Product analysis	
TBN (mgKOH/g)	335
kV at 100°C (cSt)	60.8
Stability (initial/24 hr sediment) (vol%)	<0.005/<0.01
Foaming tendency (ml/ml)	0/0
Haze (nephelos)	16

Example 13

The procedure of Example 12 was repeated except for the following change:

a) Charging:

The lime, most of the toluene and methanol were charged to the reactor, and then the sulphonic acid and remaining toluene was added. The reactor was cooled to 25±2°C.

Again six repeats were carried out and the results are given in Table 5 below.

TABLE 5

Process results	
After stripping	
sediment (vol %)	0.1
sludge (vol %)	none
Filterability (l/hm ²)	806
Product analysis	
TBN (mgKOH/g)	333
kV at 100°C (cSt)	61.7
Stability (initial/24 hr sediment) (vol %)	<0.01/<0.02
Foaming tendency (ml/ml)	0/0
Haze (nephelos)	17

Example 14 and Comparative Examples K and L

The procedure of Example 12 was repeated using Balthazard Lime in place of US Gypsum lime. To provide a comparison this preparation was repeated without heat soaking (Comparative Example K) and without phase separation (Comparative Example L).

The results are given in Table 6 below.

TABLE 6

Example	14	K	L
Process results			
After stripping			
sediment (vol %)	0.1	0.15	2.0
sludge (vol %)	none	none	none
Filterability (l/hm ²)	218	592	17
Product analysis			
TBN (mgKOH/g)	332	299	334
kV at 100°C (cSt)	73.1	138.7	insufficient
Stability (initial/24 hr sediment) (vol %)	(0.02/—)	trace/trace	product available after filtration
Foaming tendency (ml/ml)	0/0	0/0	0/0
Haze (nephelos)	58	12	22

The results show that the process of the invention is advantageous in terms of giving a sludge-free product which is readily filtered, and shows high product quality in terms of TBN, viscosity, stability, foaming tendency and haze. In Comparative Example K the absence of a heat soak step leads to a low TBN product with high viscosity indicating a less efficient overbasing process. This product would be unsuitable for use as a 300 TBN additive in view of its unacceptably high viscosity. Comparative Example L shows that the omission of the phase separation step results in such a low filtration rate that product yield was minimal. A large amount of sediment was also formed. Such a process would be impractical for preparation of an additive on a commercial scale.

10 Claims

1. A process of preparing an overbased calcium sulphonate comprising:
 - i) forming a mixture of
 - 15 (a) an oil-soluble sulphonic acid or an alkaline earth metal sulphonate,
 - (b) an aromatic or aliphatic hydrocarbon solvent,
 - (c) a C₁₋₅ alcohol,
 - (d) oil, and
 - (e) an excess of calcium hydroxide over that required to react with sulphonic acid present;
 - 20 ii) carbonating the mixture at a temperature not exceeding 35°C with from 75 to 95 wt% CO₂ based on the excess calcium hydroxide;
 - iii) heating the reaction mixture after carbonation characterised in that in step (iii) the reaction mixture is heated to a temperature not exceeding 60°C over a period of not less than 15 minutes; and subsequently
 - 25 the process comprises:
 - iv) separating the carbonated mixture into a first phase comprising at least a major part of the alcohol and a second phase comprising at least a major part of the hydrocarbon solvent and the oil, and removing the first phase; and
 - v) removing volatile material from the second phase to yield a dispersion of overbased calcium
 - 30 sulphonate in oil.
2. A process as claimed in claim 1, in which step (ii) comprises:
 - ii) carbonating the mixture at a temperature of not exceeding 30°C.
3. A process as claimed in claim 1 or claim 2, in which diluent oil is added following step (iii) and/or following step (v).
- 35 4. A process as claimed in any of claims 1 to 3, in which step (iii) the carbonated reaction mixture is heated to a temperature not exceeding 55°C for half to 3 hours.
5. A process as claimed in claim 4, in which the carbonated reaction mixture is heated to from 30°C to 45°C.
6. The use of an overbased calcium sulphonate dispersion as produced by the process of any of claims 1 to 5 as a lubricating oil additive.
- 40 7. A lubricating oil comprising an overbased calcium sulphonate dispersion as produced by the process of any of claims 1 to 5.
8. An additive concentrate for blending with lubricating oil comprising an oil solution of an overbased calcium sulphonate dispersion as produced by the process of any of claims 1 to 5.

45 Patentansprüche

1. Verfahren zur Herstellung eines überbasischen Calciumsulfonats, bei dem
 - i) eine Mischung aus
 - 50 (a) einer öllöslichen Sulfonsäure oder einem Erdalkalimetallsulfonat,
 - (b) einem aromatischen oder aliphatischen Kohlenwasserstofflösungsmittel,
 - (c) einem C₁₋₅-Alkohol,
 - (d) Öl und
 - 55 (e) Calciumhydroxid im Überschuß gegenüber derjenigen Menge, die für die Reaktion mit der vorhandenen Sulfonsäure erforderlich ist, gebildet wird,
 - ii) die Mischung bei einer Temperatur von nicht über 35°C mit 75 bis 95 Gew.% CO₂, bezogen auf das überschüssige Calciumhydroxid, carbonisiert wird und
 - 60 iii) die Reaktionsmischung nach der Carbonisierung erhitzt wird, dadurch gekennzeichnet, daß in Stufe (iii) die Reaktionsmischung über einen Zeitraum von nicht weniger als 15 Minuten auf eine Temperatur von nicht über 60°C erhitzt wird, anschließend
 - iv) die carbonisierte Mischung in eine erste Phase, die mindestens einen größeren Teil des Alkohols umfaßt, und eine zweite Phase, die mindestens einen größeren Teil des Kohlenwasserstofflösungsmittels und des Öls umfaßt, getrennt und die erste Phase entfernt wird und
 - 65

24

The results show that the process of the invention is advantageous in terms of giving a sludge-free product which is readily filtered, and shows high product quality in terms of TBN, viscosity, stability, foaming tendency and haze. In Comparative Example K the absence of a heat soak step leads to a low TBN product with high viscosity indicating a less efficient overbasing process. This product would be unsuitable for use as a 300 TBN additive in view of its unacceptably high viscosity. Comparative Example L shows that the omission of the phase separation step results in such a low filtration rate that product yield was minimal. A large amount of sediment was also formed. Such a process would be impractical for preparation of an additive on a commercial scale.

10. Claims

1. A process of preparing an overbased calcium sulphonate comprising:
 - i) forming a mixture of
 - 15 (a) an oil-soluble sulphonic acid or an alkaline earth metal sulphonate,
 - (b) an aromatic or aliphatic hydrocarbon solvent,
 - (c) a C₁₋₅ alcohol,
 - (d) oil, and
 - (e) an excess of calcium hydroxide over that required to react with sulphonic acid present;
 - 20 ii) carbonating the mixture at a temperature not exceeding 35°C with from 75 to 95 wt% CO₂ based on the excess calcium hydroxide;
 - iii) heating the reaction mixture after carbonation characterised in that in step (iii) the reaction mixture is heated to a temperature not exceeding 60°C over a period of not less than 15 minutes; and subsequently
 - 25 the process comprises:
 - iv) separating the carbonated mixture into a first phase comprising at least a major part of the alcohol and a second phase comprising at least a major part of the hydrocarbon solvent and the oil, and removing the first phase; and
 - v) removing volatile material from the second phase to yield a dispersion of overbased calcium
 - 30 sulphonate in oil.
 2. A process as claimed in claim 1, in which step (ii) comprises:
 - ii) carbonating the mixture at a temperature of not exceeding 30°C.
 3. A process as claimed in claim 1 or claim 2, in which diluent oil is added following step (iii) and/or following step (v).
 - 35 4. A process as claimed in any of claims 1 to 3, in which step (iii) the carbonated reaction mixture is heated to a temperature not exceeding 55°C for half to 3 hours.
 5. A process as claimed in claim 4, in which the carbonated reaction mixture is heated to from 30°C to 45°C.
 6. The use of an overbased calcium sulphonate dispersion as produced by the process of any of claims
 - 40 1 to 5 as a lubricating oil additive.
 7. A lubricating oil comprising an overbased calcium sulphonate dispersion as produced by the process of any of claims 1 to 5.
 8. An additive concentrate for blending with lubricating oil comprising an oil solution of an overbased calcium sulphonate dispersion as produced by the process of any of claims 1 to 5.

45 Patentansprüche

1. Verfahren zur Herstellung eines überbasischen Calciumsulfonats, bei dem
 - i) eine Mischung aus
 - 50 (a) einer öllöslichen Sulfonsäure oder einem Erdalkalimetallsulfonat,
 - (b) einem aromatischen oder aliphatischen Kohlenwasserstofflösungsmittel,
 - (c) einem C₁₋₅-Alkohol,
 - (d) Öl und
 - 55 (e) Calciumhydroxid im Überschuß gegenüber derjenigen Menge, die für die Reaktion mit der vorhandenen Sulfonsäure erforderlich ist, gebildet wird,
 - ii) die Mischung bei einer Temperatur von nicht über 35°C mit 75 bis 95 Gew.% CO₂, bezogen auf das überschüssige Calciumhydroxid, carbonisiert wird und
 - 60 iii) die Reaktionsmischung nach der Carbonisierung erhitzt wird, dadurch gekennzeichnet, daß in Stufe (iii) die Reaktionsmischung über einen Zeitraum von nicht weniger als 15 Minuten auf eine Temperatur von nicht über 60°C erhitzt wird, anschließend
 - iv) die carbonisierte Mischung in eine erste Phase, die mindestens einen größeren Teil des Alkohols umfaßt, und eine zweite Phase, die mindestens einen größeren Teil des Kohlenwasserstofflösungsmittels und des Öls umfaßt, getrennt und die erste Phase entfernt wird und
 - 65



25

v) flüchtiges Material aus der zweiten Phase entfernt wird, so daß eine Dispersion von überbasischem Calciumsulfonat in Öl erhalten wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß Stufe (ii) umfaßt:

ii) Carbonisieren der Mischung bei einer Temperatur von nicht mehr als 30°C.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß im Anschluß an Stufe (iii) und/oder Stufe (v) Verdünnungsöl zugesetzt wird.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die carbonisierte Reaktionsmischung in Stufe (iii) eine halbe bis 3 Stunden lang auf eine Temperatur von nicht mehr als 55°C erhitzt wird.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß die carbonisierte Reaktionsmischung auf 30 bis 45°C erhitzt wird.

6. Verwendung einer überbasischen Calciumsulfonatdispersion hergestellt nach einem der Ansprüche 1 bis 5 als Schmieröladditiv.

7. Schmieröl, das eine überbasische Calciumsulfonatdispersion hergestellt nach dem Verfahren gemäß einem der Ansprüche 1 bis 5 enthält.

8. Additivkonzentrat zum Mischen mit Schmieröl, das eine Öllösung einer überbasischen Calciumsulfonatdispersion hergestellt nach dem Verfahren gemäß einem der Ansprüche 1 bis 5 enthält.

Revendications

1. Procédé de production d'un sulfonate de calcium rendu surbasique, consistant:

i) à former un mélange

(a) d'un acide sulfonique ou d'un sulfonate de métal alcalino-terreux soluble dans l'huile,

(b) d'un solvant hydrocarboné aromatique ou aliphatique,

(c) d'un alcool en C₁ à C₅,

(d) d'une huile, et

(e) d'un excès d'hydroxyde de calcium par rapport à la quantité nécessaire pour réagir avec l'acide sulfonique présent;

ii) à carbonater le mélange à une température n'excédant pas 35°C avec 75 à 95% en poids de CO₂ sur la base de l'hydroxyde de calcium en excès;

iii) à chauffer le mélange réactionnel après carbonatation, caractérisé en ce que dans l'étape (iii), le mélange réactionnel est chauffé à une température ne dépassant pas 60°C pendant une période n'excédant pas 15 minutes; après quoi le procédé consiste:

iv) à diviser le mélange carbonaté en une première phase comprenant au moins une quantité dominante de l'alcool et une deuxième phase comprenant au moins une quantité dominante du solvant hydrocarboné et de l'huile, et à éliminer la première phase; et

v) à chasser la matière volatile de la seconde phase pour obtenir une dispersion dans l'huile de sulfonate de calcium rendu surbasique.

2. Procédé suivant la revendication 1, dans lequel l'étape (ii) consiste:

ii) à carbonater le mélange à une température n'excédant pas 30°C.

3. Procédé suivant la revendication 1 ou la revendication 2, dans lequel l'huile de dilution est ajoutée après l'étape (iii) et/ou après l'étape (v).

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans l'étape (iii) duquel le mélange réactionnel carbonaté est chauffé à une température n'excédant pas 55°C pendant 0,5 à 3 heures.

5. Procédé suivant la revendication 4, dans lequel le mélange réactionnel carbonaté est chauffé à une température de 30 à 45°C.

6. Utilisation d'une dispersion de sulfonate de calcium rendu surbasique telle qu'obtenue par le procédé suivant l'une quelconque des revendications 1 à 5 comme additif pour huile lubrifiante.

7. Huile lubrifiante comprenant une dispersion de sulfonate de calcium rendu surbasique telle que produite par le procédé suivant l'une quelconque des revendications 1 à 5.

8. Concentré d'additif destiné à être mélangé avec une huile lubrifiante, comprenant une solution dans l'huile d'une dispersion de sulfonate de calcium rendu surbasique telle que produite par le procédé suivant l'une quelconque des revendications 1 à 5.

