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(54) Preparation of overbased calcium sulphonates.

(57) The problem of sludge formation is avoided in the preparation of high base number calcium sulphonates in good yields by carbonating a mixture of:

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

b) a hydrocarbon solvent

c) a C₁₋₁₈ alcohol, preferably methanol,

d) oil, and

e) excess calcium hydroxide,

at a temperature not exceeding 35°C, heat soaking the carbonated mixture, and then separating the heat soaked product into an alcohol/water phase and a solvent/oil phase. The alcohol/water phase is removed before stripping the solvent/oil phase to yield the overbased product.

EP 0 121 024 A1

PREPARATION OF OVERBASED CALCIUM SULPHONATES

1 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.

5 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;
10 thereby reducing corrosion, and the dispersent 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
15 diluent oil. In US 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
20 sulphonate to give an emulsion which separates into two phases, the methanol phase being removed from the oil phase containing the dispersed product.

US 3318809 describes a similar process in which finely powdered calcium oxide is slurried in methanol and carbonated in a counter - current carbonation unit before

1 being mixed with oil and calcium sulphate. After
mixing the methanol and oil phases are separated, and
following stripping the oil phase is treated with water
to decompose any methanol complex.

5 US 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-dispersable surfactant such as a calcium sulphate
to form an emulsion. The emulsion breaks on standing and
10 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
15 impossible to handle. Bray describes the addition of
water to break this gel, but acknowledges that this may
result in filtration problems.

US 3 258 426 describes an alternative process for preparing
calcium carbonate dispersions in oil in which an emulsion
20 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.

1 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
5 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
10 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 0000264, which also describes a soaking
15 period in which, after carbonation and before stripping
and filtration, the reaction mixture is held at 20°C to
35°C for at least 1/2 hour.

We have found that a conventional stripping step to remove
an alcohol such as methanol from the product of the low
20 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.
25 The sludge has a grease-like consistency and also contains
a considerable amount of the overbased calcium sulphonate

1 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
5 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
10 tendency to sludge formation may be remarkably diminished
or even eliminated.

GB 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
15 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
20 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
25 advantages in viscosity and/or stability and/or haze.

Thus, in one aspect the invention provides a process of

- 1 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,
 - 5 c) a C₁₋₅ 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% CO₂ based on the excess calcium hydroxide;
 - 10 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
15 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
20 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
25 metal salts of these most suitable sulphonic acids, and a calcium sulphonate is the preferred sulphonate.

- 1 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.
- 5 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,
- 10 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
- 15 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
- 20 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.

1 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
5 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
10 the ammonium carboxylates such as those described in
United Kingdom patent 1 307 172 where the preferred
ammonium carboxylates are those derived from C₁ to C₃
saturated monocarboxylic acids, e.g. formic acid, acetic
acid or propionic acid. Alternatively alkali metal salts
15 of a C₁ to C₃ carboxylic acid may be used, such as
those of a C₁ to C₃ 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
20 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

1 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
5 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
10 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
15 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
20 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
25 temperature carbonation promotes the reduction of sediment
resulting from formation of insoluble carbonates.

1 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
5 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
10 (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
15 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
20 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
25 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

1 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.

10 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 -
15 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
20 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
25 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.

1 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
5 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
10 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,
15 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
20 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
90cSt, more preferably less than 70 cSt. More particularly,
the process enables such products to be prepared such
25 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,

- 1 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.

- 5 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.

- 10 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
15 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
20 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
25 one may use blends containing up to 50% by volume of one or more water-insoluble polyoxyalkylene glycols, for

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1 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
5 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
10 dispersants, other metal containing dispersant additives
and the well known zinc dialkyldithiophosphate antiwear
additives. The invention extends to an additive concen-
trate comprising an oil solution of an overbased calcium
sulphonate of the invention and preferably one or more
15 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

20 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:

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

- 1 Notes: 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

- 5 In the carbonation step, unless otherwise indicated, the amount of carbon dioxide added to the above mixture was 356g - 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
- 10 for CO₂ is the same.

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

Comparative Example A

- 15 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

20 to 25 ± 2°C.

- b) Carbonation:

Carbonation commenced at a rate of 97.8g/hour CO₂, and the temperature was maintained at 25 ± 2°C until 69% CO₂

1 was added. Then the temperature was raised to 55°C over
the remaining carbonation time.

c) Stripping:

A nitrogen sparge was commenced and the reflux condenser
5 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.

10 d) Filtration:

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
15 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.

TABLE 1

	A	B	C	D	E
<u>Charging</u>					
Lime addition (stages)	one	one	one (over 1 hour)	one (over 1 hour)	two (30 min + 10 min)
<u>Carbonation</u>					
Temperature (°C)	25-55	25-55	25-55	25-55	25-30
% Stoichiometric CO ₂	88	88	88	88	80
<u>Heat Soak</u>					
Temperature (°C)	-	-	-	-	-
Time (hour)	-	-	-	-	-
<u>Phase Separation</u>					
	No	No	Gravity	Gravity	Gravity
<u>Stripping</u>					
Temperature (°C)	80	150	150	-	150
Centrifuge	Yes	Yes	Yes	Yes	Yes
Temperature (°C)	150	-	-	Thin film evaporator	-
<u>Filtration</u>					
SSF precoat + (i)	+2% SPLJUS	(i) 2% SPLJUS	2.5% SSF	1.5% SSF	3.0% SSF
admix * (%)	ii)	+2% SDX	(ii) 2% SDX		

*SPLJUS = Speedplus
SDX = Speedex
SSF = Sp Speedflow

TABLE 1

F G H I J 1

Charging					
Line addition (stages)	two (30 min+10min)	two (30 min+10min)	two (30min+10min)	one (over 1 hour)	one (1 hour)
Carbonation					
Temperature (°C)	25-30	25-30	25-30	25-55	25-30
% Stoichiometric CO ₂	88	92	96	88	88
Heat Soak					
Temperature (°C)	-	-	-	-	30-55
Time (hour)	-	-	-	-	1
Phase Separation	Gravity	Gravity	Gravity	Gravity	Gravity
Stripping					
Temperature (°C)	-	150	150	-	-
Centrifuge	Yes	Yes	Yes	Yes	Yes
Temperature (°C) Thin film evaporator	-	-	150	150	150
Filtration					
SSF precoat + admix (%)	3.0% SSF	1.5% SSF	3.0% SSF	(i)1.5% SSF (ii)3.0% SSF (iii)3.0% SPLUS	1.5% SSF

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TABLE 1

	2	3	4	5	6
<u>Charging</u>					
Lime addition	one (1 hour)	one (1 hour)	one (1 hour)	one (1 hour)	two (30 min+30 min)
<u>Carbonation</u>					
Temperature (°C)	25-30	25-30	25-30	25-30	25-30
% Stoichiometric CO ₂	88	92	92	92	88
<u>Heat Soak</u>					
Temperature (°C)	30-55	30-55	30-55	30-55	30-55
Time (hour)	1	1	1	1	1
<u>Phase Separation</u>					
Gravity	Gravity	Gravity	Gravity	Gravity	Gravity
<u>Stripping</u>					
Temperature (°C)	-	-	-	150	-
Centrifuge	-	Yes	-	Yes	Yes
Temperature (°C)	150	150	150	-	150
<u>Filtration</u>					
SSF precoat + admix (%)	1.5% SSF	(i) 1.5% SSF (ii) 3.0% SSF	3.0% SSF	(i) 1.5% SSF	(i) 1.5% SSF (ii) 3.0% SSF

1 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
5 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
10 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 appea-
15 rance 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 sulphonate and which are deposited
from the product as hard or soft precipitates. On fil-
20 tering 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.

- 1 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.

- 5 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
- 10 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.

Example		A		B	C
After carbonation	Process Results	Units			
	sediment sludge	Vol % Vol %	1.6 -	1.6 -	2.0 -
After stripping	sediment	Vol %	0.12	0.8	3.0
	sludge	Vol %	8.0	6.0	1.0
After centrifugation	sediment	Vol %	0.06	0.3	
	sludge	Vol %	0.1	6.0	
Centrifugate flow rate g/min			220	220	-
Filterability* 1/hm ²			i) 69 ii) 102	i) 0 ii) 0	102
<u>Analytical Results</u>					
Total base no.		mgKOH/g	325.0 326.9	325.0 326.9	354.9
Kinematic viscosity at 100°C		cSt	62.1	67.7	253.8 (TEN 354.9) 49.5 (TEN 300)
% soap		mass %			35.8
% calcium		mass %			14.3
Water plus solvent content		mass %			35.8
Foaming tendency		ml/ml			0-0 (TEN 300) 49.5-30 (No. A/F)
Blend stability (initial/24 hr sediment)		vol %			0.4/1.0

Example	D	E	F
<u>Process Results</u>		Units	
After carbonation	sediment	Vol %	2.0
	sludge	Vol %	3.0
			-
After stripping	sediment	Vol %	0.2
	sludge	Vol %	3.0
			none
After centrifugation	sediment	Vol %	-
	sludge	Vol %	-
			-
Centrifugate flow rate		g/min	250
			200
Filterability		1/hm ²	33
			0
			85
<u>Analytical Results</u>			
Total base no.		mgkOH/g	315.8
			326.2
Kinematic viscosity at 100°C		cSt	55.5
			166.1
			178.2
% soap		mass %	-
			32.3
			28.4
% calcium		mass %	-
			12.89
			11.86
Water plus solvent content		mass %	-
			-
			2.40
Foaming tendency		ml/ml	-
			-
			190-90 (No A/F)
Blend stability (initial /24 hr sediment)		vol %	0.5/1.8
			1.8/1.4

Example	G		H	I
Process Results		Units		
After carbonation	sediment	Vol %	1.8	1.2
	sludge	Vol %	none	none
After stripping	sediment	Vol %	0.3	0.1 hard/0.1 soft
	sludge	Vol %	none	none
After Centrifugation	sediment	Vol %	0.1	-
	sludge	Vol %	none	-
Centrifugate flow rate		g/min	205	-
Filterability		l/hm ²	55	i) 47 ii) >119 iii) >142
Analytical Results				
Total base no.		mgKOH/g	317.1	327
Kinematic viscosity at 100°C		cSt		166.1
% soap		mass %	30.3	30.8
% calcium		mass %	12.55	12.77
Water plus solvent content		mass %		0.64
Foaming tendency		ml/ml	0-0	0-0
Blend stability (initial/24 hr sediment)		vol %	0.4/1/6	0.14/0.40

Example		J	1	2
Process Results		Units		
After carbonation	sediment	Vol %	0.8	3.0
	sludge	Vol %	none	(0.8 after heat up)
After stripping	sediment	Vol %	0.3	0.8
	sludge	Vol %	none	none
After Centrifugation	sediment	Vol %	-	-
	sludge	Vol %	none	none
Centrifugate flow rate g/min			-	80
Filterability		l/m ²	476	i) 35 ii) 102
Analytical Results				
Total base no.		mgKOH/g	324.5	325.0 324.0
Kinematic viscosity at 100°C		cSt	178.2	44.4 57.5
% soap		mass %	30.1	30.1 29.9
% calcium		mass %	12.99	13.04 12.93
Water plus solvent content		mass %	0.52	0.30 0.60
Foaming tendency		ml/ml	0-0	0-0 0-0
Blend stability (initial/24 hr sediment)		vol %	0.002/0.10	0.3/0.4 0.2/0.3

Example 3 4 5

Process Results		Units		
After carbonation	sediment	Vol %	2.8	2.8
	sludge	Vol %	none	none
After stripping	sediment	Vol %	0.50% hard	N/A
	sludge	Vol %	none	N/A
After Centrifugation	sediment	Vol %	-	0.02 hard/0.10 soft
	sludge	Vol %	-	none
Centrifugate flow rate		g/min	-	120-140
Filterability		1/hm ²	i) 286 ii) 274	93 107
Analytical Results				
Total base no.		mgKOH/g	333.6	-
Kinematic viscosity at 100°C		cSt	-	-
% soap		mass %	31.5	30.3
% calcium		mass %	13.17	13.05
Water plus solvent content		mass %	0.66	1.08
Foaming tendency		ml/ml	230-40 (No. A/F)	210-40 (No A/F)
Blend stability (initial/24 hr sediment)		vol %	0.4/1.8	0.2/0.10 after 3 days
				0.9/1.2

Example

6

	<u>Process Results</u>	<u>Units</u>	
After carbonation	sediment	Vol %	1.0
	sludge	Vol %	none
After stripping	sediment	Vol %	0.3 soft
	sludge	Vol %	none
After Centrifugation	sediment	Vol %	0.3
	sludge	Vol %	none
	Centrifugate flow rate	g/min	120
	Filterability	1/hm ²	i) 57 ii) 71

Analytical Results

Total base no.	mgKOH/g	306.0
Kinematic viscosity at 100°C	cSt	50.6
% soap	mass %	-
% calcium	mass %	-
Water plus solvent content	mass %	-
Foaming tendency	ml/ml	-
Blend stability (initial/24 hr sediment)	vol %	0.20/0.6

1 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,
5 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
10 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
15 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
20 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
25 also show that carbonation beyond 90% of stoichiometric

1 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.

5 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:

	Toluene	812g
10	Sulphonic Acid	812g
	Methanol	487g
	Lime	476g

The following procedure was employed:

a) Charging:

15 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.

20 b) Carbonation:

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

c) Heat soak:

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

1 d) Diluent oil addition:

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

e) Phase separation:

5 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:

10 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.

15 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
20 using a nephelometer (Coleman Photonephelometer available from Coleman Instruments Company of USA). The measurements are carried out on a 5wt% 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/24hr 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 (nephelos)	58	60	68	66	58

1 Example 12

The procedure of Examples 7 to 11 was repeated except for the following changes:

5 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.

10 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	<0.005/<0.01
(initial/24hr sediment)(vol%)	
Foaming tendency (ml/ml)	0/0
Haze (nephelos)	16

1 Example 13

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

a) Charging:

- 5 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 $25 \pm 2^\circ\text{C}$.

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	<0.01/<0.02
(initial/24hr sediment)(vol%)	
Foaming tendency (ml/ml)	0/0
Haze (nephelos)	17

1 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
<u>Process Results</u>			
After stripping			
sediment (vol %)	0.1	0.15	2.0
sludge (vol %)	none	none	none
Filterability (l/hm ²)	218	592	17
<u>Product Analysis</u>			
TBN (mgKOH/g)	332	299	334
kV at 100°C (cSt)	73.1	138.7	insufficient
Stability (initial/24hr sediment)(vol%)	(0.02/-)	trace/trace	product available after filtration
Foaming tendency (ml/ml)	0/0	0/0	0/0
Haze (nephalos)	58	12	22

1 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
5 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 300TBN additive
in view of its unacceptably high viscosity. Comparative
10 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 prepa-
ration of an additive on a commercial scale.

CLAIMS

1. 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 C₁₋₅ 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% CO₂ 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.

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)

4 A process as claimed in any of claims 1 to 3, in which in step iii) the carbonated reaction mixture is heated to a temperature not exceeding 55°C for 1/2 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. An overbased calcium sulphonate whenever prepared by a process as claimed in any of claims 1 to 5, and having a total base number (as defined herein) of at least 300.

7 An overbased calcium sulphonate as claimed in claim 6, having a viscosity measured at 100°C and a total base number of 300 or less than 90 cSt.

8. The use of an overbased calcium sulphonate as claimed in claim 6 or claim 7 as a lubricating oil additive.

9. A lubricating oil comprising an overbased calcium sulphonate as claimed in claim 6 or claim 7.

10 An additive concentrate for blending with lubricating oil comprising an oil solution of an overbased calcium sulphonate as claimed in claim 6 or claim 7.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	BE-A- 785 268 (CONTINENTAL OIL) * Page 16, example 1 - page 18; page 2, lines 1,2 *	1-10	C 10 M 1/40 C 07 C 143/00
D,A	EP-A-0 000 264 (EXXON) * Claims 1-12; page 6, paragraph 2 *	1-6,8-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17-02-1984	Examiner RO TSAERT L.D.C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	