

"PROCESS FOR THE PREPARATION OF SULPHURISED ALKALINE EARTH
METAL ALKYLPHENATES WHICH CAN BE USED AS ADDITIVES FOR
LUBRICATING OILS"

The present invention relates to the preparation of sulphurised alkaline earth metal, in particular calcium, alkylphenates of high alkalinity, and to the use of these sulphurised alkylphenates as detergent-dispersant additives
5 for lubricating oils.

It is known that sulphurised calcium alkylphenates of high alkalinity can be prepared by sulphurisation-neutralisation of dodecylphenol with sulphur and lime in the presence of an oil and glycol (or neutralisation of a
10 sulphurised alkylphenol with lime in the presence of an oil and glycol), carbonation and then filtration of the oily solution of the sulphurised calcium alkylphenate, after distillation of the glycol. A large amount of glycol must be used for carrying out this process, since it serves both
15 as the diluent solvent and also as the dispersant for the calcium carbonate in the mixture.

It has been found that about 50% of the glycol used remains in the finished product, which has an adverse effect on engines; that the viscosity of the mixture is
20 increased, especially at the end of the sulphurisation-neutralisation; that redox reactions occur between the sulphur and the glycol, which has an adverse effect on the performance of the finished product (in particular on its

antioxidant properties); and that a large excess of sulphur is required for sulphurising the alkylphenol, which causes powerful evolution of H_2S and a significant redox phenomenon with the glycol.

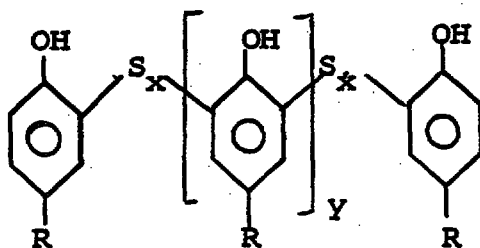
5 The present invention provides a novel process in which the amount of glycol used is reduced, which reduces the viscosity of the mixture, especially after the sulphurisation-neutralisation, and thus reduces the amount of diluent oil; reduces the amount of residual glycol;
10 reduces the evolution of H_2S ; and reduces the significance of the redox reaction between the sulphur and the glycol.

 The new process for the preparation of a sulphurised alkaline earth metal alkylphenate of high alkalinity comprises neutralising a sulphurised alkylphenol
15 with an alkaline earth metal base in the presence of diluent oil, glycol and an alcohol of boiling point greater than $150^\circ C$; filtering, after distillation of water, alcohol and glycol and carbonating the filtrate, followed by distilling off glycol, alcohol and, if present, water, and then filtering
20 to remove sediment, the neutralisation and carbonation being carried out in the presence of halide ions and the following amounts of reactants being used: the amount of alcohol corresponds to a molar ratio of alcohol/glycol greater than or equal
25 to 0.4:1, generally of the order of 0.4:1 to 10:1; the ratio between the amount of alkaline earth metal base used, expressed in mols, and the amount of sulphurised alkylphenol,

expressed in mols of alkylphenol, is from 0.4:1 to 3:1, preferably from 0.6:1 to 2.5:1; the amount of glycol used corresponds to a molar ratio of alkaline earth metal base/glycol of from 2.6:1 to 8:1, preferably from 2.7:1 to 6:1; 5 the amount of halide ions corresponds to a ratio of gram atoms of halide/mols of alkaline earth metal base of from 0.01:1 to 0.15:1, preferably from 0.015:1 to 0.09:1; and the amount of CO_2 used corresponds to a ratio of mols of CO_2 to gram-atoms of alkaline earth metal of from 0.2⁵:1 to 0.75:1.

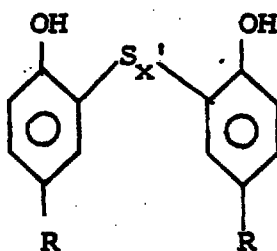
10 By "sulphurised alkylphenol" is meant the mixture obtained by sulphurisation of an alkylphenol with sulphur or sulphur chloride, this mixture chiefly consisting of non-sulphurised alkylphenol and sulphurised alkylphenol represented by the formula:

15



in which R represents an alkyl radical with 9 to 30 carbon atoms (preferably 9 to 22 carbon atoms), x is from 1 to 3 and y is from 0 to 6.

A simplified representation of this mixture of 20 "sulphurised alkylphenol" is given by the following average formula:



in which x' is from 1 to 3, and in general has an average value from 1.4 to 2.5.

Alkaline earth metal bases which can be used include oxides and hydroxides of calcium, barium and strontium, and especially lime.

The diluent oils which can be used include, preferably, paraffin oils, such as 100 Neutral oil.

Naphthenic oils and mixed oils are also suitable. The amount of diluent oil which can be used is such that the amount of oil contained in the end product makes up 25 to 65% by weight, preferably 30 to 50% by weight, of the said product.

Alcohols of boiling point greater than 150°C include alkanols with 6 to 14 carbon atoms, oxo-alcohols, and alkoxy-alkanols, such as the products sold commercially under the names ethyl-hexanol, decyl alcohol, tridecyl alcohol, 2-butoxyethanol, butoxypropanol and dipropylene glycol methyl ether.

The halide ions are preferably Cl^- ions; these can be used in the form of ammonium chloride or a metal chloride, such as calcium chloride or zinc chloride.

The neutralisation is advantageously carried out at a temperature from 120 to 180°C, preferably from 130 to 170°C, under a pressure slightly less than atmospheric pressure ($930 \times 10^2 \text{ Pa}$ to $960 \times 10^2 \text{ Pa}$).

- 5 The neutralisation can also be carried out in the presence of an amine in a molar ratio of amine/alkaline earth metal base up to 0.2:1. Amines which can be used include polyalkylene amines, such as the polyethyleneamines and oxyamines, and especially ethylenediamine and tris-(3-oxa-6-amino-hexyl)amine. This operation can also advantageously be carried out in the presence of acetic acid in an amount corresponding to a molar ratio of acetic acid/alkaline earth metal base up to 0.2:1, preferably up to 0.1:1.
- 10
- 15 The two distillations which follow the neutralisation and carbonation respectively are carried out to remove water, glycol and alcohol.

The carbonation is carried out at a temperature from 145 to 180°C under a pressure less than or equal to 20 atmospheric pressure ($930 \times 10^2 \text{ Pa}$ to $1,010 \times 10^2 \text{ Pa}$).

The sulphurised alkylphenol may be prepared in situ in the neutralisation mixture, from the alkylphenol and sulphur. The amount of sulphur used corresponds to a molar ratio of sulphur/alkylphenol of from 0.8:1 to 2:1.

- 25 The sulphurisation-neutralisation operation is advantageously carried out at a temperature from 145 to

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175°C, preferably from 155 to 170°C, if necessary in the presence of an amine, such as those indicated above for the general neutralisation stage.

The carbonation is then carried out at a temperature from 155 to 180°C, preferably from 165 to 175°C, in the presence of halide ions, as indicated above.

The product of the new process described above is useful as an additive for improving the detergent and dispersant properties of lubricating oils. The amount of additive used depends on the intended use of the said oils. Thus, the amount of additive to be added to an oil for a petrol engine is usually 1 to 2.5%; the amount added to an oil for a diesel engine is usually 1.8 to 4%; and the amount added to an oil for a marine engine can be up to 30%.

15 The lubricating oils which can be improved in this manner can be any of a wide range of lubricating oils, such as naphthenic lubricating oils, paraffinic lubricating oils, and mixed such oils. Other hydrocarbon lubricants, for example lubricating oils derived from coal products, 20 and synthetic oils, for example alkylene polymers, polymers of the alkylene oxide type and derivatives thereof, including alkylene oxide polymers prepared by polymerising an alkylene oxide in the presence of water or an alcohol, for example ethyl alcohol, dicarboxylic acid esters, liquid 25 esters of phosphorus acids, alkylbenzenes and dialkyl benzenes, polyphenyls, alkyl-biphenyl ethers and polymers of

silicon, can also include the new additive.

Other additives can also be present in the lubricating oils, besides the detergent-dispersants of the invention. Examples of such other additives include 5 antioxidants, anticorrosion agents, and ashless dispersants.

The examples which follow are given by way of illustration.

Examples 1 to 8

A) Sulphurisation, dehydration, neutralisation

10 Dodecylphenol (DDP), sulphur, lime, calcium chloride, zinc chloride or ammonium chloride and an oil are introduced into the reaction vessel, with stirring.

The mixture is heated to 160°C and a mixture of ethylene glycol and ethylhexanol is slowly added under 15 slightly reduced pressure in the course of 80 minutes. The mixture is kept at 165°C under slightly reduced pressure ($930 \times 10^2 \text{ Pa}$) for 1 hour.

A distillate D_1 is collected.

B) Carbonation

20 Carbonation is carried out at 165-175°C under atmospheric pressure for 100 minutes and the remaining diluent oil is then added.

C) Removal of the glycol

A vacuum is progressively applied up to $66.5 \times 25 \times 10^2 \text{ Pa}$. The mixture is heated at 190°C for one hour and subjected to stripping with nitrogen at 190°C for one hour.

A distillate D_2 is collected.

D) Filtration

Characteristics of the product

Measurement of the amount of sediment

The per cent of sediment is measured in accordance
5 with the standard ASTM D 2273-67, but with the following
modifications: speed of rotation of the centrifuge, 6,000
revolutions per minute; relative centrifugal force, 10,000;
the product to be analysed is diluted to one quarter in E
spirit (25 cc of the product to be analysed + 75 cc of E
10 spirit); and duration of centrifugation, 10 minutes. (E
spirit is a special aliphatic petroleum spirit containing
less than 5-10% of aromatic components. Its volatility
according to ASTM Standard D1078 is initial point, 104°C; 5%
point, 110°C; 50% point, 119°C; 95% point, 135°C; and end
15 point, 139°C. Its density at 15°C is 0.734g/ml, and its
aniline point according to ASTM Standard 611 is 55°C.)

Compatibility test

The finished product is added to an SAE 50 oil of
a paraffinic nature so as to give a solution containing 25%
20 of additive.

The solution is kept for 24 hours and is then
centrifuged under the following conditions: speed of
rotation, 6,000 revolutions per minute; relative centrifugal
force, 10,000; and duration of centrifugation, 1 hour; and
25 the amount of sediment is then measured.

The amounts of reactants used in the different
stages are shown in Tables I and II in which the figures
given correspond to weight in grams; the results obtained
are given in Tables III and IV.

30 Example 9 to 11

A) Neutralisation

Sulphurised dodecylphenol containing
about 11% of sulphur, lime, calcium chloride, and
a diluent oil are introduced into

the reaction vessel. The mixture is heated to 130°C and ethylene glycol, mixed with ethylhexanol or 2-butoxyethanol, is then added. The mixture is heated to 145°C and then kept under a vacuum of 345×10^2 Pa for 30 minutes.

5 A distillate D₁ is collected.

The vacuum is broken.

B) Carbonation

Carbonation is carried out under atmospheric pressure for 100 minutes. The temperature at the start
10 of the carbonation is 145°C. The mixture is then heated to a temperature of 170°C at the end of the carbonation. The remainder of the diluent oil is added.

C) Removal of the glycol

A vacuum is progressively applied up to $66.5 \times$
15 10^2 Pa, while heating to 190°C. The mixture is kept at 190°C for 1 hour and is then subjected to stripping with nitrogen at 190°C for 1 hour.

A distillate D₂ is collected.

D) The mixture is filtered

20 The amounts of reactants used in the various stages are shown in Table II; the results obtained are given in Table IV.

TABLE I

Examples	1	2	3	4	5	6	7
<u>Stage A</u>							
DDP	100	100	100	100	100	100	100
S	12.8	12.8	12.8	12.8	12.8	12.8	12.8
Lime	45	45	45	45	45	49.5	49.5
Sulphurised	-	-	-	-	-	-	-
DDP							
CaCl_2	1.4	1.4	-	-	1.4	1.4	-
ZnCl_2	-	-	1.4	-	-	-	-
NH_4Cl	-	-	-	1.4	-	-	-
Oil	35	35	35	35	35	35	35
Glycol	16	11	11	11	11	12.6	12.6
Ethylhexanol	44	20	20	20	20	20	20
Butoxyethanol	-	-	-	-	-	-	-
<u>D₁</u>							
H_2O	11	11	11	11	11	12.2	12.2
Glycol	1	1	1	1	1	2	2
Ethylhexanol	8	7	7	7	7	7	7
Butoxyethanol	-	-	-	-	-	-	-
<u>Stage B</u>							
CO_2	14.6	14.7	14.4	15	14.7	17	17
Oil	35	35	35	35	44	35	35
<u>D₂</u>							
Glycol	9	6	6	6	6	7	7
Ethylhexanol	35	12	12	12	12	12	12
Butoxyethanol	-	-	-	-	-	-	-
H_2S evolved	4.8	4.8	4.7	4.9	4.8	4.8	4.8

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TABLE II

Examples	8	9	10	11
<u>Stage A</u>				
DDP	100	-	-	-
S	12	-	-	-
Lime	25	45	45	44.5
Sulphurised DDP	-	110	110	110
CaCl ₂	1.4	1.4	1.4	1.4
ZnCl ₂	-	-	-	-
NH ₄ Cl	-	-	-	-
Oil	40	35	35	35
Glycol	7	11	11	7
Ethylhexanol	15	20	20	-
Butoxyethanol	-	-	-	20
<u>D₁</u>				
H ₂ O	6	11	11	11
Glycol	0.5	1	1	1
Ethylhexanol	5	7	7	-
Butoxyethanol	-	-	-	8
<u>Stage B</u>				
CO ₂	4.6	14.8	14.8	14.8
Oil	46	44	44	44
<u>D₂</u>				
Glycol	3.2	6	7	4
Ethylhexanol	9	12	12	-
Butoxyethanol	-	-	-	11
H ₂ S evolved	3.9	0.8	0.8	0.9

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TABLE III

Examples	1	2	3	4	5	6	7
<u>Stage D</u>							
Speed of filtration (kg/hours/ m ²)	130	120	140	110	160	120	40
% crude sediment	1.4	1.4	1.3	1.5	1.3	1.4	5
<u>Analysis of the finished product</u>							
% Ca	10.47	10.48	10.5	10.34	10.1	11.2	8.8
% S	3.6	3.6	3.65	3.55	3.42	3.3	3.6
Viscosity at 100°C (cst)	380	330	320	360	250	394	170
TBN *	281	281	282	277	270	302	240
% sediment	0.02	0.04	0.03	0.04	0.01	0.04	0.03
% CO ₂	5.05	5.1	5.3	5.2	5.2	5.6	4.8
% glycol	2	1.5	1.5	1.5	1.5	1.7	2
compati- bility	traces	traces	traces	traces	traces	traces	traces

* total basic number determined by ASTM Standard 2896.

TABLE IV

Examples	8	9	10	11
<u>Stage D</u>				
Speed of filtration (kg/hours/m ²)	210	120	120	120
% crude sediment	0.6	1.3	1.2	1.4
<u>Analysis of the finished product</u>				
% Ca	5.85	10.47	10.45	10.4
% S	3.45	3.5	3.7	3.7
Viscosity at 100°C (cst)	120	380	410	410
TBN (ASTM 2896)	161	280	280	279
% sediment	0.04	0.03	0.05	0.05
% CO ₂	2	5.3	5.3	5.3
% Glycol	1	1.4	1	0.5
compatibility	traces	traces	traces	traces

Examples 12 to 23 and 28

A) Sulphurisation, dehydration and neutralisation

Dodecylphenol, sulphur, lime, calcium

or ammonium chloride and an oil and in some

- 5 Examples acetic acid are introduced into the reaction vessel, while stirring. The mixture is heated to 155°C under slightly reduced pressure ($930 \times 10^2 \text{ Pa}$). A first batch of alcohol consisting of a mixture of ethylene glycol and 2-butoxyethanol or butoxypropanol is slowly added
- 10 in the course of 30 minutes, followed by a second batch of 2-butoxyethanol or butoxypropanol only in the course of 40 minutes. The mixture is kept at 165°C under slightly reduced pressure ($930 \times 10^2 \text{ Pa}$) for 1 hour.

A distillate D_1 is collected.

15 B) Carbonation

Carbonation is carried out at 165°C under atmospheric pressure for 120 minutes and the diluent oil is then slowly added.

C) Removal of the glycol

- 20 A vacuum is progressively applied up to $66.5 \times 10^2 \text{ Pa}$. The mixture is heated at 190°C for 1 hour and then subjected to stripping with nitrogen at 190°C for 1 hour.

A distillate D_2 is collected.

25 D) Filtration

The amounts of reactants used in the various stages are shown in Tables V to VIII; the results obtained are given in Tables VI and VIII.

Example 24

The operation described in Example 12 is carried out, introducing a mixture of 10 g of glycol and 10 g of 2-butoxyethanol (first batch) from the start (and not when the temperature reaches 155°C). Equivalent results are obtained.

Example 25

The operation described in Example 12 is carried out, introducing the 10 g of glycol at the start, followed by the 10 g of 2-butoxyethanol at 155°C. Equivalent results are obtained.

Example 26

The operations described in Examples 9 to 11 are carried out, starting from sulphurised dodecylphenol 15 containing about 8% of sulphur. The amounts of reactants used in the various stages are shown in Tables VII and VIII; the results obtained are given in Table VIII.

Example 27

The operation described in Example 26 is carried out, using sulphurised dodecylphenol containing 7% of sulphur and an additional amount of sulphur. The amounts of reactants used are given in Tables VII and VIII; the results obtained are given in Table VIII.

(24)

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TABLE V

Examples	12	13	14	15	16	17	18
<u>Stage A</u>							
DDP g	87.5	87.5	75	87.5	87.5	87.5	75
S g	10.9	10.9	9.2	10.9	10.9	9.5	13.5
Lime g	44	44	44	44	44	44	44
Sulphurised <u>DDP</u> g	-	-	-	-	-	-	-
NH ₄ Cl g	-	-	2	-	-	-	-
CaCl ₂ g	2	2	-	2	2	2	2
CH ₃ COOH g	-	-	-	-	-	-	-
Oil g	35	35	35	35	35	35	35
Glycol g	10	6.2	10	9.2	13.2	10	10
butoxyethanol g	10+70	10+70	10+70	10+70	10+70	10+70	10+70
butoxypropanol g	-	-	-	-	-	-	-
<u>D₁</u>							
H ₂ O g	11	11	11	11	11	11	11
Glycol g	4	1	4	3	4	4	4
butoxyethanol g	15	15	15	15	15	15	15
butoxypropanol g	-	-	-	-	-	-	-

[illegible]

TABLE VII

Examples	19	20	21	22	23	26	27	28
<u>Stage A</u>								
DDP g	87.5	87.5	87.5	87.5	87.5	-	-	75
S g	10.9	10.9	10.9	10.9	10.9	0	2.5	10
Lime g	44	44	44	44	44	44	44	50
sulphurised								
DDP g	-	-	-	-	-	82	82	-
NH ₄ Cl g	-	-	-	-	-	2	2	-
CaCl ₂ g	-	0.5	0.5	2	2	-	-	2
CH ₃ COOH g	-	-	1	-	-	-	-	1
oil g	35	35	35	35	35	35	35	35
glycol g	10	10	10	10	10	10	10	10
butoxy-ethanol g	10+70	10+70	10+70	-	-	10+70	10+70	10+70
butoxy-propanol g	-	-	-	10+70	-	-	-	-
<u>D₁</u>								
H ₂ O g	11	11	11	11	11	11	11	12
glycol g	4	4	4	4	4	4	4	4
butoxy-ethanol g	15	15	15	-	-	15	15	15
butoxy-propanol g	-	-	-	15	-	-	-	-

TABLE VIII

[illegible]



CLAIMS

1. Process for the preparation of a sulphurised alkaline earth metal alkylphenate of high alkalinity, which comprises neutralising a sulphurised alkylphenol with an alkaline earth metal base in the presence of a diluent oil, glycol, and an alcohol of boiling point greater than 150°C, filtering, after distillation of water, alcohol and glycol, and carbonating the filtrate, followed by distilling off glycol, alcohol and, if present, water, and then filtering to remove sediment, the neutralisation and carbonation being carried out in the presence of halide ions, and the following amounts of reactants being used: the amount of alcohol corresponds to a molar ratio of alcohol/glycol greater than or equal to 0.4:1, the ratio between the amount of alkaline earth metal base used, expressed in mols, and the amount of sulphurized alkylphenol, expressed in mols of alkylphenol, is from 0.4:1 to 3:1, the amount of glycol corresponds to a molar ratio of alkaline earth metal base/glycol of from 2.6:1 to 8:1, the amount of halide ions corresponds to a ratio of gram atoms of halide/mols of alkaline earth metal base of from 0.01:1 to 0.15:1 and the amount of CO₂ corresponds to a ratio of mols of CO₂ to gram-atoms of alkaline earth metal of from 0.25:1 to 0.75:1.



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2. Process according to claim 1, in which the molar ratio of alcohol/glycol is 0.4:1 to 10:1, the molar ratio of alkaline earth metal base/alkylphenol is 0.6:1 to 2.5:1, the molar ratio of alkaline earth metal base/5 glycol is 2.7:1 to 6:1 and the ratio of gram-atoms of halide/mols of alkaline earth metal base is 0.015:1 to 0.09:1.

3. Process according to claim 1 or 2 in which the alkaline earth metal base is calcium hydroxide.

10 4. Process according to any of the preceding claims, in which the alcohol of boiling point greater than 150°C is an alkanol with 6 to 14 carbon atoms or an alkoxyalkanol.

5. Process according to claim 4, in which the 15 said alcohol is ethylhexanol or 2-butoxyethanol.

6. Process according to any of the preceding claims, in which the halide ions are chloride ions.

7. Process according to claim 6, in which the chloride ions are introduced in the form of CaCl_2 , ZnCl_2 20 or NH_4Cl .

8. Process according to any of the preceding claims, in which the neutralisation is carried out in the presence of an amine, in an amount corresponding to a molar ratio of amine/alkaline earth metal base up to 0.2:1.

25 9. Process according to claim 8, in which the amine is ethylenediamine or tris-(3-oxa-6-amino-hexyl)amine.



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10. Process according to any of the preceding claims, in which the neutralisation is carried out in the presence of acetic acid in an amount corresponding to a molar ratio of acetic acid/alkaline earth metal base up to 0.2:1.

11. Process according to claim 10, in which the molar ratio of acetic acid/alkaline earth metal base is up to 0.1:1.

12. Process according to any of the preceding 10 claims, in which the sulphurised alkylphenol is prepared in situ in the neutralisation mixture from an alkylphenol and sulphur.

13. Process according to claim 1 substantially as described in any one of the foregoing Examples.

15 14. A sulphurised alkaline earth metal alkylphenate prepared by the process of any of the preceding claims.

15. A lubricating oil comprising a sulphurised alkaline earth metal alkylphenate prepared by the process of any of claims 1 to 13.
