

"PROCESS FOR PREPARING NOVEL METAL-BASED DETERGENT-  
DISPERSANT ADDITIVES FOR LUBRICATING OILS"

The present invention relates to the preparation of metal-based detergent-dispersant additives for lubricating oils.

According to the present invention, a detergent-  
5 dispersant additive for lubricating oils which has a TBN  
(i.e. total basic number determined in accordance with  
ASTM Standard 02896) of at least 225 and contains more  
than 3.8% by weight of magnesium and, usually, about 2 to  
3% by weight of calcium, which imparts to the said additive,  
10 besides detergent and dispersion characteristics, good  
anti-wear activity, is prepared by a process which  
comprises: a) carbonating a mixture of a magnesium alkyl-  
benzenesulphonate having a TBN of less than or equal to 20,  
a sulphurised calcium alkylphenate having a TBN of up to  
15 200 and a diluent oil, in the presence of a magnesia "milk"  
containing an activated magnesium oxide, a glycol and an  
amine, b) removing the water and the glycol, and c) removing,  
e.g. by filtering the mixture, the sediment.

By "magnesium alkylbenzenesulphonate" is meant  
20 any solution containing 25 to 80% by weight, preferably  
30 to 70% by weight, of a magnesium alkylbenzenesulphonate  
in a diluent oil, which may or may not be the same as that  
used in the preparation of the novel additive.

Magnesium alkylbenzenesulphonates which can be used include magnesium salts of sulphonic acids obtained by sulphonation of alkylbenzenes derived from olefins or polymeric olefins having 15 to 30 carbon atoms.

5           Diluent oils which can be used include, preferably, paraffin oils, such as 100 Neutral oil. Naphthenic oils or mixtures can also be suitable. The amount of diluent oil which can be used is such that the amount of oil contained in the end product (including that  
10 originating from the starting magnesium alkylbenzene-sulphonate) generally makes up to 20 to 60%, preferably 25 to 55% and especially 30 to 45%, by weight of the said product.

The term "sulphurised calcium alkylphenate" means any solution containing 25 to 70% by weight, preferably  
15 30 to 55% by weight, of a sulphurised calcium alkylphenate in a diluent oil, which may or may not be the same as that used in the preparation of the novel additive.

Sulphurised calcium alkylphenates which can be used include those obtained by the action of lime on a  
20 sulphurised alkylphenol having preferably one or more alkyl substituents of 9 to 30 carbon atoms (preferably 9 to 22 carbon atoms), such as sulphurised nonyl-, decyl-, dodecyl- or tetradecyl-phenol, followed, if appropriate, by carbonation; and those obtained by sulphurisation, with  
25 sulphur, of an alkylphenol<sup>9</sup> having preferably one or more alkyl substituents of 9 to 30 carbon atoms (preferably 9 to

22 carbon atoms) in the presence of lime and glycol, followed, if appropriate, by carbonation.

In an advantageous embodiment of the new process, a sulphurised calcium alkylphenate having a molar ratio of 5 lime:alkylphenol of from 0.2:1 to 2.5:1, preferably from 0.4:1 to 2:1, and ~~by~~ a molar ratio of sulphur/alkylphenol of from 1.1:1 to 2.2:1, preferably from 1.3:1 to 1.8:1, can be used.

The term "activated magnesium oxide" means 10 magnesium oxide, MgO, having a specific surface area greater than or equal to  $80 \text{ m}^2/\text{g}$ , for example between 100 and  $170 \text{ m}^2/\text{g}$ . Examples which may be mentioned are "Maglite DE" (registered Trade Mark), which has a specific surface area of about  $140 \text{ m}^2/\text{g}$  and is marketed by Merck, 15 and "Ferumag", which has a specific surface area of about  $160 \text{ m}^2/\text{g}$  and is marketed by Rhone-Poulenc.

Amines which can be used include polyalkylene- amines, such as the polyethylenamines, especially ethylene- diamine; and ether-amines, especially tris-(3-oxa-6-amino- 20 hexyl) amine (TOA).

The amine used can be added to the magnesia "milk" at the start of, or during, the carbonation.

In an advantageous embodiment of the new process, the novel additive can be obtained using amounts of 25 reactants such that: the ratio of the amount of magnesium alkylbenzenesulphonate, expressed in mols of alkylbenzene-sulphonic acid, to the amount of sulphurised calcium

alkylphenate, expressed in mols of alkylphenol, is from about 0.15:1 to 5.5:1, preferably from 0.25:1 to 2:1; the amount of activated MgO corresponds to a "base ratio", that is to say a ratio of mols of basic magnesium not 5 bonded to the alkylbenzenesulphonic acid/mols of non-basic magnesium bonded to the alkylbenzenesulphonic acid, of from 5:1 to 14:1, preferably 7:1 to 11:1; the amount of glycol corresponds to a molar ratio of MgO/glycol of from 0.1:1 to 0.7:1, preferably from 0.3:1 to 0.65:1; and the 10 amount of amine corresponds to a ratio of mols of amine/mols of basic magnesium of from about 0.01:1 to 0.4:1, preferably from 0.04:1 to 0.25:1.

The carbonation is advantageously carried out at a temperature of from 90 to 140°C, preferably from 110 to 15 140°C, in one or more stages, by introducing the magnesia "milk" into a mixture containing the magnesium alkylbenzenesulphonate, the sulphurised calcium alkylphenate and the diluent oil in one or more stages, each introduction of the magnesia "milk" being followed by a carbonation. The 20 carbonation described is continued or repeated until the amount of sediment remains constant; this takes at most 6 hours.

It has been found that the process is particularly advantageously carried out if an amount of water corresponding 25 to a weight ratio of  $H_2O/MgO$  of from about 0.1:1 to 0.9:1 is added towards the end of the carbonation.

In a variant of the new process, the carbonation is preceded by a stage in which a mixture of the magnesium alkylbenzenesulphonate, the sulphurised calcium alkylphenate and the diluent oil is precarbonated in the presence of 5 glycol and, optionally sulphur.

The precarbonation is advantageously carried out at a temperature of 150 to 180°C, preferably 160 to 175°C, in the presence of an amount of glycol corresponding to a molar ratio of calcium/glycol of from 0.15:1 to 0.77:1, 10 preferably 0.2:1 to 0.6:1; an amount of sulphur corresponding to a molar ratio of sulphur/calcium of from 0:1 to 1.5:1, preferably 0:1 to 1:1; and an amount of carbon dioxide corresponding to a molar ratio of CO<sub>2</sub>/calcium of from 0.2:1 to 0.8:1, preferably 0.4:1 to 0.65:1.

15        The novel additive produced in accordance with the invention has the advantages of being perfectly compatible with viscous oils, of containing a low level of sediment, and of having a low viscosity.

The present invention includes within its scope 20 lubricating oils comprising the new additive and having improved detergent, dispersant and anti-wear properties. The amount of additive used depends on the intended use of the oil. Thus, the amount of additive to be added to an oil for a petrol engine is usually between 1 and 3.5%; the 25 amount to be added to an oil for a Diesel engine is usually between 1.8 and 5%; and the amount to be added to an oil for a marine engine can be up to 25%.

The lubricating oils which can be improved in this manner can be chosen from a very diverse range of lubricating oils, such as lubricating oils having a naphthenic basis, a paraffin basis, or a mixed basis, 5 other hydrocarbon lubricants, for example lubricating oils derived from coal products, 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 10 presence of water or an alcohol, for example ethyl alcohol, esters of dicarboxylic acids, liquid esters of phosphorus acids, alkylbenzenes and dialkylbenzenes, polyphenyls, alkylbiphenyl ethers and silicon polymers.

Other additives can also be present in the 15 lubricating oils in addition to the novel additive of the invention. Examples of additives which may be mentioned are antioxidants, anticorrosion agents, and ashless dispersants.

The examples which follow are given by way of 20 illustration.

Examples 1 to 9

A) Preparation of a magnesium alkylbenzenesulphonate of TBN 3

An approximately 70% solution of sulphonic acid 25 of approximate molecular weight 470 (weight of the sodium salt) in the diluent oil 100 Neutral oil, and 100 Neutral

oil are introduced into a 3 litre flask. The flask is heated to 80°C and magnesium oxide, "Maglite DE", to give a magnesium alkylbenzenesulphonate having a TBN of about 3, calcium chloride solution.

5 and then ethylene glycol are introduced in the course of five minutes. The reaction mixture is heated at 110°C under atmospheric pressure for 30 minutes and then in vacuo for 30 minutes so as to distil off the water of reaction.

A sample is taken to measure the amount of  
10 sediment.

B) Preparation of the sulphurised calcium alkylphenate

Sulphurised dodecylphenol (DDP) containing about 11% by weight of sulphur, slaked lime and ethylene glycol  
15 are added, at 110°C in the course of five minutes, to the product prepared above. The mixture is heated at 120°C for 2 hours (1 hour 30 minutes under atmospheric pressure and 30 minutes under a vacuum of  $120 \times 10^2$  Pa), and the vacuum is then broken.

20 C) Carbonation

A magnesia "milk" is prepared in a beaker by mixing activated magnesium oxide, ethylene glycol and an amine, with stirring. This milk is divided into three approximately equal fractions.

25 The first fraction of the milk is introduced into the flask, followed by CO<sub>2</sub> at 110°C, the second fraction of the milk and CO<sub>2</sub> are introduced 2 hours thereafter, and the third fraction of the milk and water are introduced 2

hours after the introduction of the second fraction. The carbonation operation is carried out for 2 hours.

D) Removal of the glycol

When the carbonation has stopped, the flask is  
5 put progressively under a vacuum ( $40 \times 10^2$  Pa), and is then heated at  $200^\circ\text{C}$  for 2 hours.

E) Filtration

Properties of the product

Measurement of the amount of sediment

10 The % of sediment is measured in accordance 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  
15 quarter-strength in spirit E (25 cc of the product to be analysed + 75 cc of spirit E); duration of centrifugation, 10 minutes. Spirit E is a special petroleum spirit containing less than 5-10% of aromatic components. Its volatility according to ASTM standard  
20 D1078 is initial point  $104^\circ\text{C}$ ; 5% point  $110^\circ\text{C}$ ; 50% point  $119^\circ\text{C}$ ; 95% point  $135^\circ\text{C}$ ; and point  $139^\circ\text{C}$ . Its density is 0.734 g/ml at  $15^\circ\text{C}$  and its aniline point according to ASTM standard D611 is  $55^\circ\text{C}$ .

Compatibility tests

25

No. 1

This test is carried out by adding 10% by weight of the product to be tested to a SAE 30 mineral

81

- 9 -

oil, storing the solution obtained at 20°C for 1 month and studying the appearance of the solution. The following ratings are given:

- 5                    1 for a clear and brilliant product;  
                     2 for a very slightly cloudy product;  
                     3 for a cloudy product.

No. 2

The finished product is added to SAE 50 oil of a paraffinic nature so as to give a solution containing 10 125 millimols of calcium + magnesium. 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; duration of centrifugation, 1 hour. The amount 15 of sediment is then measured and given as a percentage.

The quantities of the reactants used in the different stages are shown in Tables I and II. The results obtained are given in Table II.

Example 8 is a comparison Example.

TABLE I

| EXAMPLES                     | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
|------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| <u>Stage A</u>               |     |     |     |     |     |     |     |     |     |
| Sulphonic acid solution g    | 500 | 500 | 500 | 500 | 700 | 400 | 500 | 500 | 500 |
| Oil g                        | 615 | 615 | 615 | 615 | 700 | 615 | 615 | 615 | 615 |
| MgO g                        | 19  | 19  | 19  | 19  | 27  | 10  | 19  | 19  | 19  |
| CaCl <sub>2</sub> solution g | 4   | 4   | 4   | 4   | 12  | 4   | 4   | 4   | 4   |
| Glycol g                     | 38  | 38  | 38  | 38  | 81  | 20  | 38  | 38  | 38  |
| % sediment                   | 0.3 | 0.3 | 0.3 | 0.3 | 0.4 | 0.3 | 0.4 | 0.3 | 0.4 |
| <u>Stage B</u>               |     |     |     |     |     |     |     |     |     |
| Sulphurised DDP g            | 419 | 419 | 419 | 419 | 136 | 550 | 419 | 419 | 419 |
| Lime g                       | 100 | 100 | 100 | 100 | 70  | 100 | 100 | 100 | 100 |
| Glycol g                     | 100 | 100 | 100 | 100 | 80  | 100 | 100 | 100 | 100 |
| % sediment                   | 0.9 | 0.9 | 0.9 | 0.9 | 0.5 | 0.4 | 0.6 | 0.9 | 0.9 |

TABLE II

| EXAMPLES                                | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8   | 9      |
|-----------------------------------------|--------|--------|--------|--------|--------|--------|--------|-----|--------|
| <u>Stage C</u>                          |        |        |        |        |        |        |        |     |        |
| MgO                                     | g 129  | 129    | 129    | 129    | 200    | 129    | 129    | 129 | 160    |
| Glycol                                  | g 390  | 390    | 390    | 390    | 500    | 390    | 390    | 390 | 460    |
| Ethylenediamine                         | g 16.5 | 16.5   | 33     | 8.5    | 25     | 16.5   | -      | -   | 19.5   |
| TOA *                                   | g -    | -      | -      | -      | -      | -      | 16.5   | -   | -      |
| H <sub>2</sub> O                        | g 85   | 24     | 85     | 85     | 112    | 85     | 85     | 85  | 100    |
| CO <sub>2</sub>                         | g 180  | 180    | 180    | 180    | 260    | 190    | 180    | 190 | 212    |
| % sediment                              | 2.5    | 3      | 2.5    | 2.9    | 3.3    | 3.1    | 2.7    | 7   | 2.7    |
| <u>Analysis of the finished product</u> |        |        |        |        |        |        |        |     |        |
| % sediment                              | 0.08   | 0.08   | 0.08   | 0.08   | 0.08   | 0.06   | 0.09   | 0.2 | 0.15   |
| % Mg                                    | 4.4    | 4.36   | 4.44   | 4.35   | 5.2    | 4.3    | 4.38   | 3.5 | 5.1    |
| % Ca                                    | 3.0    | 3.0    | 3.0    | 3.0    | 2.4    | 2.95   | 3      | 2.8 | 2.9    |
| Viscosity at 100° C (cst)               | 310    | 304    | 340    | 325    | 430    | 322    | 296    | 410 | 380    |
| TBN                                     | 264    | 259    | 266    | 264    | 270    | 258    | 262    | 218 | 281    |
| Compatibility                           |        |        |        |        |        |        |        |     |        |
| Test No. 1                              | 1      | 1      | 1      | 1      | 1      | 1      | 1      | 2   | 1      |
| Test No. 2                              | traces | traces | traces | traces | traces | traces | traces | 2   | traces |

\* tris-(3-oxa-6-aminoethyl)amine.

Example 10

The operations described in Example 1 are repeated, replacing the 16.5 g of ethylene diamine by 8g of tris(3-oxa-6-amino-hexyl)amine, called "TOA". The 5 results are identical to those from Example 1.

Example 11

The operations described in Example 1 are repeated, the start of the carbonation stage being carried out at 130°C instead of at 110°C. The results are identical 10 to those from Example 1.

Example 12

A) Preparation of magnesium alkylbenzenesulphonate of TBN 18.

500 g of an approximately 70% solution of alkyl- 15 benzenesulphonic acid of molecular weight 470 in 100 Neutral oil, 615 g of 100 Neutral oil, 25 g of activated magnesium oxide and 7 g of an approximately 50% by weight aqueous solution of calcium chloride are introduced into a 3 litre flask. The flask is heated to 110°C and 112 g 20 of ethylene glycol are added in the course of 1 hour. Heating is continued up to 160°C.

B) Preparation of the sulphurised calcium alkyl-phenate

411 g of sulphurised dodecylphenol containing 25 about 10% of sulphur, 100 g of lime and 45 g of sulphur are added. The reactor is put under vacuum. 100 g of

glycol are introduced in the course of 1 hour, heating being continued. The mixture is kept at  $165^{\circ}\text{C}$  under  $345 \times 10^2 \text{Pa}$  for 1 hour.

C) Precarbonation

5 The vacuum is broken, heating is discontinued and carbonation is carried out for 1 hour at a rate of 0.5 g/minute.

D) Carbonation

A mixture of 129 g of  $\text{MgO}$  and 349 g of glycol 10 is prepared in a beaker and is introduced into the reactor in the course of 5 minutes. Carbon dioxide is introduced into the mixture. Two hours thereafter, 16.5 g of ethylenediamine are added, followed by 85 g of water after another two hours, and carbonation is then carried out for 15 a further 2 hours. During the 6 hours of carbonation, the rate of addition of  $\text{CO}_2$  is controlled such as to maintain a slight excess of  $\text{CO}_2$  over the amount absorbed.

E) Distillation

The mixture is distilled at  $200^{\circ}\text{C}$  under  $40 \times 10^2 \text{Pa}$  20 for 2 hours. 2.3% of crude sediment remains.

F) Filtration

Analysis of the product obtained

|    |                                    |         |
|----|------------------------------------|---------|
|    | % Ca                               | 3       |
|    | % Mg                               | 4.4     |
| 25 | % sediment                         | 0.06    |
|    | viscosity at $100^{\circ}\text{C}$ | 350 cst |
|    | TBN                                | 266     |

compatibility

|        |                                         |
|--------|-----------------------------------------|
| Test 1 | 1                                       |
| Test 2 | 0.01% of sediment after centrifugation. |

5 Example 12a) (Comparison Example)

The operations described in Example 12 are repeated in the absence of ethylenediamine. The results obtained are as follows:

|    |                                              |
|----|----------------------------------------------|
|    | 6.5% of crude sediment remains               |
| 10 | % Ca 2.9                                     |
|    | % Mg 3.2                                     |
|    | 0.1% of sediment after filtration            |
|    | viscosity 320 cst                            |
|    | TBN 210                                      |
| 15 | compatibility                                |
|    | Test 1 2                                     |
|    | Test 2 1.5% of sediment after centrifugation |

C L A I M S

1. Process for the preparation of an additive for lubricating oils which has a TBN of at least 225 and contains more than 3.8% by weight of magnesium which comprises: a) carbonating

5 a mixture of a magnesium alkylbenzenesulphonate having a TBN of less than or equal to 20, a sulphurised calcium alkylphenate having a TBN of up to 200 and a diluent oil, in the presence of a magnesia "milk" containing an activated magnesium oxide, a glycol and an amine; b) removing the  
10 water and the glycol; and c) removing the sediment.

2. Process according to claim 1, in which the sulphurised calcium alkylphenate has a molar ratio of lime/alkylphenol of from 0.2:1 to 2.5:1 and a molar ratio of sulphur/alkylphenol of from 1.1:1 to 2.2:1.

15 3. Process according to claim 2, in which the sulphurised calcium alkylphenate has a molar ratio of lime/alkylphenol of from 0.4:1 to 2:1 and a molar ratio of sulphur/alkylphenol of from 1.3:1 to 1.8:1.

4. Process according to any one of the preceding  
20 claims, in which the amine used is a polyethyleneamine.

5. Process according to any one of claims 1 to 3 in which the amine is ethylenediamine.

6. Process according to any one of claims 1 to 3 in which the amine is an ether-amine.



- 16 -

7. Process according to claim 6, in which the ether-amine is tris-(3-oxa-6-amino-hexyl)amine.

8. Process according to any one of the preceding claims, in which the amounts of reactants used are such that the ratio of the amount of magnesium alkylbenzenesulphonate, expressed in mols of alkylbenzenesulphonic acid, to the amount of sulphurised calcium alkylphenate, expressed in mols of alkylphenol, is from about 0.15:1 to 5.5:1; the amount of activated MgO corresponds to a "base ratio" of 10 from 5:1 to 14:1; the amount of glycol corresponds to a molar ratio of MgO/glycol of from 0.1:1 to 0.7:1; and the amount of amine corresponds to a ratio of mols of amine/mols of basic magnesium of from 0.01:1 to 0.4:1.

9. Process according to claim 8, in which the 15 amounts of reactants are such that the ratio of the amount of magnesium alkylbenzenesulphonate, expressed in mols of alkylbenzenesulphonic acid, to the amount of sulphurised calcium alkylphenate, expressed in mols of alkylphenol, is from 0.25:1 to 2:1; the amount of activated MgO corresponds 20 to a "base ratio" of from 7:1 to 11:1; the amount of glycol corresponds to a molar ratio of MgO/glycol of from 0.3:1 to 0.65:1; and the amount of amine corresponds to a ratio of mols of amine/mols of basic magnesium of from 0.04:1 to 0.25:1.



\* C L M S \*

10. Process according to any of the preceding claims, in which the carbonation is carried out at a temperature of from 90 to 140°C, in one or more stages, by introducing the magnesia "milk" into a mixture  
5 containing the magnesium alkylbenzenesulphonate, the sulphurised calcium alkylphenate and the diluent oil, in one or more stages, each introduction of the magnesia "milk" being followed by a carbonation.

11. Process according to any of the preceding  
10 claims, in which the amine is added to the magnesia "milk" at the start of, or during, the carbonation.

12. Process according to any of the preceding claims, in which an amount of water corresponding to a weight ratio of H<sub>2</sub>O/MgO of from 0.1:1 to 0.9:1 is  
15 introduced towards the end of the carbonation.

13. Process according to any of the preceding claims, in which a mixture containing the magnesium alkylbenzenesulphonate, the sulphurised calcium alkylphenate and the diluent oil is precarbonated in the presence of  
20 glycol and, optionally, sulphur, before the carbonation in the presence of the magnesia milk.

14. Process according to claim 13, in which the precarbonation is carried out at a temperature of from 150 to 180°C.



- 18 -

15. Process according to claim 13 or 14, in which the precarbonation is carried out in the presence of an amount of glycol corresponding to a molar ratio of calcium/glycol of from 0.15:1 to 0.77:1; an amount of sulphur corresponding to a molar ratio of sulphur/calcium of from 0:1 to 1.5:1; and an amount of carbon dioxide corresponding to a molar ratio of CO<sub>2</sub>/calcium of from 0.2:1 to 0.8:1.

16. Process according to claim 15, in which the precarbonation is carried out in the presence of an amount of glycol corresponding to a molar ratio of calcium/glycol of from 0.2:1 to 0.6:1; an amount of sulphur corresponding to a molar ratio of sulphur/calcium of from 0:1 to 1:1; and an amount of carbon dioxide corresponding to a molar ratio of CO<sub>2</sub>/calcium of between 0.4:1 and 0.65:1.

17. Process according to claim 1 substantially as described in any one of Examples 1 to 7, and 9 to 12.

18. An additive useful for addition to lubricating oils when prepared by the process claimed in any of claims 1 to 17.

19. A lubricating oil comprising an additive produced by the process of any of claims 1 to 17.

