

"PROCESS FOR PREPARING A DETERGENT-DISPERSANT ADDITIVE
FOR LUBRICATING OILS"

The present invention relates to the preparation of additives which improve the detergency and dispersion properties of lubricating oils.

According to the present invention, a detergent-
5 dispersant additive for lubricating oils, having a TBN
(i.e. total basic number determined in accordance with
ASTM Standard D2896) of at least 225, and containing more
than 3.8% by weight of magnesium and, generally, of the
order of 2 to 3% by weight of calcium, and which provides,
10 in addition to detergency and dispersion characteristics,
good anti-wear properties, is prepared by a process which
comprises:

a) carbonating (in a first carbonation) a mixture
of: a magnesium alkylbenzenesulphonate with a TBN which is
15 less than or equal to 20, a sulphurised alkylphenol, a
diluent oil, and a magnesia "milk" comprising active
magnesium oxide, a glycol and an amine, until the amount of
sediment is less than 1.5% by weight relative to the weight
of the mixture,

20 b) neutralising and superalkalising with lime the
sulphurised alkylphenol present in the carbonated mixture
obtained,

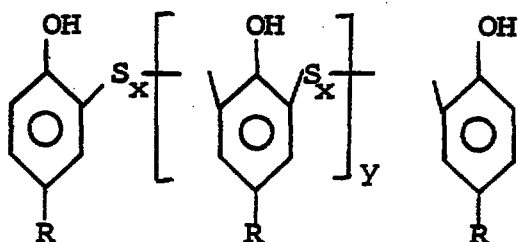
- 2 -

- c) optionally carbonating (in a second carbonation) the mixture obtained after removal of the water,
- d) distilling off the glycol, and
- e) removing the sediment.

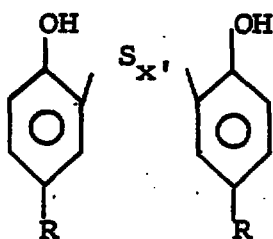
5 The magnesium alkylbenzenesulphonate used is a solution containing preferably from 25 to 80% by weight, more preferably from 30 to 70% by weight, of a magnesium alkylbenzenesulphonate in a diluent oil which may or may not be the same as that used to prepare the new additive. Suitable magnesium alkylbenzene-
10 sulphonates are the magnesium salts of sulphonic acids obtained by sulphonating alkylbenzenes derived from $C_{15}-C_{30}$ olefins or polymers thereof.

 The diluent oil used is preferably a paraffin oil such as 100 Neutral oil. Naphthenic or mixed oils are also
15 suitable. The amount of diluent oil which can be used is such that the amount of oil contained in the final product (including that originating from the initial magnesium alkylbenzenesulphonate) represents from 20 to 60% by weight of the said product, preferably from 25 to 55% and especially
20 from 30 to 45% by weight of the said product.

 The sulphurised alkylphenol is generally a mixture obtained by sulphurising an alkylphenol with sulphur or sulphur chloride, the mixture consisting mainly of non-sulphurised alkylphenol and of sulphurised alkylphenol
25 which can be represented by the following formula:



in which R represents a C_9-C_{30} (preferably C_9-C_{22}) alkyl radical, x varies from 1 to 3 and y varies from 0 to 6. A simplified representation of this formula is



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

By "active" magnesium oxide is meant magnesium oxide (MgO) with a specific surface area which is 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 DF" with a specific surface area of the order of $140 \text{ m}^2/\text{g}$, marketed by Merck, and "Ferumag" with a specific surface area of the order of $160 \text{ m}^2/\text{g}$, marketed by Rhone-Poulenc.

The glycol is preferably ethyleneglycol.

Suitable amines which can be used are polyalkyleneamines such as polyethyleneamines and especially ethylenediamine; and ether-amines and especially tris-

(3-oxa-6-aminohexyl)-amine. The amine used can be present in the magnesia "milk" from the start of the first carbonation or it can be added to the mixture during the carbonation.

The process for preparing the new additive can be carried out with good results by using amounts of reactants such that:

the ratio of the amount of magnesium alkylbenzenesulphonate, expressed in mols of alkylbenzenesulphonic acid, to the amount of sulphurised alkylphenol, expressed in mols of alkylphenol, is from 0.15 to 5.5 and preferably from 0.25 to 2;

the amount of active MgO corresponds to a "base ratio", that is to say to a ratio of mols of basic magnesium not fixed to the alkylbenzenesulphonic acid/mols of non-basic magnesium fixed to the alkylbenzenesulphonic acid, of from 5 to 14 and preferably from 7 to 11;

the amount of glycol corresponds to a molar ratio of MgO/glycol of from 0.1 to 0.7 and preferably of from 0.3 to 0.65;

20 the amount of amine corresponds to a ratio of mols of amine/mols of basic magnesium (i.e. unneutralized magnesium oxide) of from 0.01 to 0.4 and preferably from 0.04 to 0.25; and

the ratio of the amount of lime, expressed in mols of lime, to the amount of sulphurised alkylphenol, expressed in mols of alkylphenol, is from 0.2 to 2.5 and preferably from 0.4 to 2.

The first carbonation is advantageously carried out at a temperature from 90 to 140°C and preferably from 110 to 140°C, in one or more stages, with introduction of the magnesia "milk" into the medium containing the magnesium alkylbenzenesulphonate, the sulphurised alkylphenol and the dilution oil in one or more stages, each introduction of the magnesia "milk" being followed by a carbonation. It has been found that it is advantageous to carry out the first carbonation in two stages, the first stage in the presence of about 2/3 of the total amount of the magnesia milk and then a second stage by adding the remaining amount of the magnesia milk. It has also been found that the addition of an amount of water corresponding to a weight ratio of H₂O/MgO of from 0.1 to 0.9, towards the end of the first carbonation, helps the process to run satisfactorily.

The operation of neutralisation-superalcalisation of the sulphurised alkylphenol with lime is advantageously carried out at a temperature of 110 to 145°C and preferably from 120 to 140°C.

The optional second carbonation is advantageously carried out at a temperature of from 120 to 170°C and preferably from 130 to 150°C, using a slight excess of CO₂.

The new additive of the present invention has the advantage of being perfectly compatible with viscous oils, of containing a small proportion of sediments and of having a low viscosity. When added to lubricating oils, the new additive improves their detergent, dispersant and anti-wear properties.

The amount of additive used depends on the intended use of the lubricating oils. Thus, for a petrol engine oil, the amount of additive added is generally between 1 and 3.5%, for a diesel engine oil, it is generally between 1.8 and 5%, 5 and for marine engine oils, it can range up to 25%.

The lubricating oils which can be thus improved can be chosen from among a very wide variety of lubricating oils, such as lubricating oils with a naphthenic base, a paraffinic base or a mixed base, other hydrocarbon lubricants, for
10 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 the alkylene oxide in the presence of water or alcohols, for example ethyl
15 alcohol, dicarboxylic acid esters, liquid esters of phosphorus acids, alkylbenzenes and dialkylbenzenes, polyphenyls, alkyl-biphenyl ethers and silicon polymers.

Additional additives can also be present in the lubricating oils in addition to the new additive, e.g. anti-
20 oxidant additives, anti-corrosion additives, ashless dispersant additives and the like.

The Examples which follow are given by way of illustration.

Description of the general method of preparation

A) Preparation of the magnesium alkylbenzene-sulphonate

The following are introduced into a 3 litre round-bottomed flask:

an approximately 70% solution, in 100 Neutral oil, of an alkylbenzene sulphonic acid with a molecular weight of about 470 (weight of the sodium salt), 100 Neutral oil, an approximately 50% aqueous solution of calcium chloride, active 10magnesium oxide, "Maglite DE", to give a magnesium alkylbenzenesulphonate with a TBN of the order of 3, and then ethylene glycol over a period of five minutes.

The reaction medium is heated for 30 minutes at 110°C. under atmospheric pressure and then for 30 minutes in vacuo 15to distil off the water formed in the reaction.

B) 1st carbonation

The sulphurised dodecylphenol (DDP) containing about 11% by weight of sulphur is then introduced.

A magnesia milk is prepared in a beaker by mixing 20 active magnesium oxide, ethylene glycol and a polyamine, with agitation, and the milk is added to the medium to be carbonated.

Carbon dioxide is introduced at 110-120°C and then, after 3 hours of carbonation at 135°C, water is introduced and the carbonation is continued for 1 hour 30 minutes.

25 A vacuum is applied to the carbonated medium for 30 minutes.

C) Neutralisation-superalcalisation of the sulphurised alkylphenol with lime

After the vacuum has been broken, slaked lime is introduced at 120°C, a progressively increasing vacuum
5 (120 x 10²Pa) is then applied to the medium, and the medium is heated to 130°C. The vacuum is then broken and the medium is heated to 145°C.

D) Optional 2nd carbonation

The mixture obtained is carbonated for 2 hours
10 at 145°C.

E) The glycol is distilled off for 2 hours at 190°C under 66.5 x 10²Pa

F) The product is then filtered off

Characteristics of the product

15 Measurement of the proportion of sediment.

The % of sediment is measured according to ASTM Standard D 2273-67, but with the following modifications:
speed of rotation of the centrifuge: 6,000 rpm; relative centrifugal force: 10,000; the product to be analysed is
20 diluted fourfold in petrol E (25 cm³ of product to be analysed + 75 cm³ of petrol E); and the centrifugation time is 10 minutes.

Petrol E is a special aliphatic petroleum spirit containing less than 5-10% of aromatic components. Its volatility measured according to ASTM Standard D1078 is: initial point, 104°C; 5% point, 110°C; 50% point 119°C; 5 95% point, 135°C; end point, 139°C. Its density is 0.734 g/ml at 15°C, and its aniline point according to ASTM Standard D611 is 55°C.

Compatibility tests

No. 1

- 10 This test is carried out by adding 10% by weight of product to be tested to a SAE 30 mineral oil, storing the solution obtained for 1 month at 20°C and studying the appearance of the solution after that time.

The following grades are applied:

- 1 for a clear, bright product
- 2 for a very slightly turbid product
- 3 for a turbid product.

5 No. 2

The finished product is added to an SAE 50 oil of paraffinic character, so as to give a solution containing 125 millimols of calcium + magnesium. The solution is stored for 24 hours and then centrifuged under the following 10 conditions:

speed of rotation 6,000 rpm;

relative centrifugal force 10,000;

centrifugation time 1 hour;

and the proportion of sediment is measured and given as a percentage.

15 Examples 1 to 9

The amounts of reactants used in the various steps are indicated in Tables I and II, and the results obtained are shown in Table II.

Example 10

20 The various steps described in Examples 1-9 are carried out with the ethylenediamine being replaced by an equivalent amount of tris-(3-oxa-6-aminoethyl)-amine, called "TOA".

Examples 11 and 12 (comparison Examples)

25 The various operations are carried out in the absence of amine. The % of sediment obtained before neutralisation cannot be less than 5 and 4 respectively, even after increasing the carbonation time.

TABLE I

EXAMPLES	1	2	3	4	5	6	7	8	9	10	11	12
Step A												
Sulphonic acid solution	500	500	500	500	500	500	700	400	500	500	500	500
Oil	g											
	615	615	615	615	615	615	700	615	615	615	615	832
MgO	g	19	19	19	19	19	27	10	19	19	19	19
CaCl ₂ solution	g	4	4	4	4	4	12	4	4	4	4	7.7
Glycol	g	38	38	38	38	38	81	20	38	38	38	38
Step B												
Sulphurised DDP	g	419	419	419	419	419	138	550	419	419	419	730
MgO	g	129	129	129	129	129	200	129	160	129	129	180
Glycol	g	390	390	390	390	390	500	390	460	390	390	800
Ethylenediamine	g	16.5	16.5	16.5	33	8.5	26	16.5	19.5	-	-	-
TOA	g	-	-	-	-	-	-	-	-	16.5	-	-
CO ₂	g	180	180	180	180	180	240	190	212	180	180	300
H ₂ O	g	24	100	85	85	85	112	85	100	24	85	110
% of sediments		0.8	0.8	0.6	0.6	0.8	1.3	1	1	1.1	5	4

TABLE II

EXAMPLES	1	2	3	4	5	6	7	8	9	10	11	12
<u>Step C</u> Lime	100	100	100	100	100	100	70	100	100	100	100	165
<u>Step D</u> CO ₂	60	60	60	-	60	60	50	60	60	60	60	60
% of sediment	1	0.8	0.8	1.5	0.6	1	1.5	1.3	1	1.4	6	5
<u>Analysis of</u> <u>finished product</u>												
% of sediment	0.07	0.04	0.04	0.1	0.04	0.04	0.04	0.12	0.08	0.04	0.2	0.15
% of Mg	4.5	4.5	4.5	4.4	4.55	4.4	5.3	4.4	5.2	4.35	3.6	3.8
% of Ca	3	3	3	2.95	3	3	2.4	3	2.9	2.9	2.8	2.8
Viscosity at 100°C (cst)	420	350	350	550	370	360	430	381	390	334	460	550
TBN	270	270	270	264	271	268	272	268	283	262	220	228
<u>Compatibility</u>												
Test No. 1	1	1	1	1	1	1	1	1	1	1	2	1
Test No. 2	traces	traces	traces	0.1	0.01	0.01	0.1	0.003	traces	0.1	2	0.1

Example 13

Preparation of the magnesium alkylbenzenesulphonate
with a TBN of the order of 16

The following are introduced into a 3 litre round-
5 bottomed flask:

500 g of an approximately 70% solution, in 100
Neutral oil, of an alkylbenzene sulphonic acid with a
molecular weight of 470,

615 g of 100 Neutral oil, and

10 4 g of an approximately 50% aqueous solution of
calcium chloride.

151.5 g of Maglite DE and 432 g of ethylene glycol
are mixed in a beaker. 87 g of the said mixture are
introduced into the round-bottomed flask, which is heated.
15 When the temperature reaches 110°C , the maximum vacuum is
applied and the mixture is heated to 130°C . At this stage,
the % of sediment is 0.3.

Carbonation

The vacuum is broken and 411 g of a sulphurised
20 dodecylphenol containing about 11% of sulphur are introduced,
followed by the remaining 496 g of MgO + glycol mixture.
The introduction of CO_2 is started. After 2 hours of
carbonation under atmospheric pressure, the % of sediment
is 4. 19 g of ethylenediamine are then introduced.

25 When the carbonation has ended (after 5 hours 30
minutes in total), the % of sediment is 1.2. A vacuum is

applied to the carbonated medium.

Neutralisation-superalcalisation

The vacuum is broken and 100 g of slaked lime are introduced. The flask is heated to 115°C under 346×10^2 Pa and then heated for 1 hour at 140°C under 346×10^2 Pa.

The glycol is distilled off for 2 hours at 190°C under 66.5×10^2 Pa. The gross % of sediment is 0.8.

The product is filtered

Analysis of the finished product

10	% of sediment	0.04
	% of Ca	3
	% of Mg	4.6
	TBN	270
	viscosity at 100°C	500 cst
15	compatibility: test 1	1
	test 2	0.1% of sediment after centrifugation.

Example 14

The operations described in Example 13 are carried out, but the 19 g of ethylenediamine are introduced into the 496 g of MgO + glycol mixture.

The magnesia "milk" thus obtained is introduced in 3 portions into the medium to be carbonated, each introduction being followed by a carbonation and the interval between each introduction being about 1 hour.

Analysis of the finished product

	% of sediment	0.04
	% of Ca	3
	% of Mg	4.6
5	TBN	270
	viscosity at 100°C	350 cst.
	compatibility: test 1	1
	test 2	0.1% of sediment after centrifugation.

10 The word "Maglite" is a registered Trade Mark.



26

- 15 -

C L A I M S

1. Process for preparation of an additive useful in lubricating oils having a TBN of at least 225 and containing more than 3.8% by weight of magnesium which comprises:

a) carbonating in a first carbonation a mixture
5 of: a magnesium alkylbenzenesulphonate with a TBN which is less than or equal to 20, a sulphurised alkylphenol, a diluent oil, and a magnesia "milk" comprising active magnesium oxide, a glycol and an amine, until the amount of sediment is less than 1.5% by weight based on the weight
10 of the mixture,

b) neutralising and superalkalising with lime the sulphurised alkylphenol present in the carbonated mixture obtained,

c) optionally carbonating (in a second carbonation)
15 the mixture obtained after removal of the water,

d) distilling off the glycol, and

e) removing the sediment.

2. Process according to claim 1, in which the amine used is a polyethyleneamine.

20 3. Process according to claim 1, in which the amine used is ethylenediamine.

4. Process according to claim 1, in which the amine used is an ether-amine.

25 5. Process according to claim 4, in which the ether-amine used is tris-(3-oxa-6-aminoethyl)-amine.



- 16 -

6. 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 alkylbenzene-sulphonate, expressed in mols of alkylbenzenesulphonic acid, 5 to the amount of sulphurised alkylphenol, expressed in mols of alkylphenol, is from 0.15 to 5.5;

the amount of active magnesium oxide corresponds to a base ratio of from 5 to 14;

the amount of the glycol corresponds to a molar 10 ratio of magnesium oxide/glycol of from 0.1 to 0.7;

the amount of amine corresponds to a ratio of mols of amine/mols of basic magnesium of from 0.01 to 0.4; and

the ratio of the amount of lime, expressed in mols of lime, to the amount of sulphurised alkylphenol, expressed 15 in mols of alkylphenol, is from 0.2 to 2.5.

7. Process according to claim 6, in which the amounts of reactants are such that:

the ratio of the amount of magnesium alkylbenzene-sulphonate, expressed in mols of alkylbenzenesulphonic acid, 20 to the amount of sulphurised alkylphenol, expressed in mols of alkylphenol, is from 0.25 to 2;

the amount of active magnesium oxide corresponds to a base ratio of from 7 to 11;

the amount of glycol corresponds to a molar ratio 25 of magnesium oxide/glycol of from 0.3 to 0.65;

the amount of amine corresponds to a ratio of mols of amine/mols of basic magnesium of from 0.04 to 0.25; and



28

- 17 -

the ratio of the amount of lime, expressed in mols of lime, to the amount of sulphurised alkylphenol, expressed in mols of alkylphenol, is from 0.4 to 2.

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

9. Process according to any one of the preceding claims, in which the amine used is present in the magnesia "milk" at the start of the 1st carbonation or is added to the "milk" during the said carbonation.

15 10. Process according to any one of the preceding claims, in which an amount of water corresponding to a weight ratio of H₂O/MgO of from 0.1 to 0.9 is added to the mixture towards the end of the first carbonation.

11. Process according to any one of the preceding 20 claims, in which the neutralisation-superalkalisation of the sulphurised alkylphenol with lime is carried out at a temperature of 110 to 145°C.

12. Process according to any one of the preceding claims, in which the optional second carbonation is carried 25 out at a temperature of 120 to 170°C.

24



- 18 -

13. Process according to claim 1 substantially as described in any one of the foregoing Examples 1 to 10, 13 and 14.

14. An additive produced by the process of any 5 of the preceding claims.

15. A lubricating oil comprising an additive produced by the process of any of claims 1 to 13.
