

PROCESS FOR THE PREPARATION OF DETERGENT-DISPERSANT
ADDITIVES OF VERY HIGH ALKALINITY BASED ON CALCIUM, AND
PRODUCTS THUS OBTAINED

The present invention provides a process for the preparation of detergent-dispersant additives of very high alkalinity for lubricating oils, as well as the products obtained.

5 It has already been proposed in European Patents Nos. 3,694, 6,796, 7,260 and 7,257, granted in the name of the Applicant Company, to prepare additives of the alkaline-earth metal alkylphenoxides-alkylbenzenesulphonates type, of TBN (Total Basic Number - ASTM Standard D2896) higher
10 than 200 or 250.

Experience shows that the processes described therein do not permit additives to be obtained which could reach a TBN of 300.

A process has now been found which permits the
15 preparation of calcium alkylphenoxides-alkylbenzenesulphonates of TBN equal to at least 300.

The present invention provides a process for the preparation of detergent-dispersants, which comprises:

- a) mixing together an alkylbenzenesulphonic acid, an
20 alkylphenol, dilution oil, halide ions, and lime
- b) eliminating the water formed
- c) sulphurizing the product formed with sulphur in the presence of ethylene glycol and at least one heavy

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alcohol other than ethylene glycol of boiling point higher than 155°C.

d) carbonating the sulphurized product.

e) eliminating the ethylene glycol and heavy alcohol
5 of high boiling point.

f) recovering the liquid detergent-dispersant formed.

Preferably the liquid detergent-dispersant in step f) is recovered by filtration.

An improved variant of the said process consists in
10 carrying out the first stage in the presence of a C_1-C_4 carboxylic acid, possibly hydroxylated, such as formic acid, acetic acid, glycolic acid or oxalic acid.

By "alkylbenzenesulphonic acid" is meant the acids obtained by sulphonation of alkylbenzenes, the alkyl
15 radical or radicals of which contain 15 to 30 carbon atoms and are derived from linear olefins or olefin oligomers, as well as the acids obtained by sulphonation of petroleum cuts; their molecular mass, expressed as the sodium salt, is generally from 430 to 560. They are
20 generally used in solution at about 70% strength in dilution oil.

By "alkylphenols" are understood the alkylphenols bearing one or more C_9-C_{15} alkyl substituents, and preferably nonyl-, decyl-, dodecyl- or tetradecylphenol.

25 Among the dilution oils which can be employed, there may be mentioned paraffinic oils such as 100 Neutral

oil, and also naphthenic or mixed oils. The quantity of oil favourably employed is such that the quantity of oil contained in the final product (including that which comes from the alkylbenzenesulphonic acid used at the start)

5 represents from 20 to 60% by weight of the said product, or preferably 25 to 55% and most especially 30 to 40% by weight of the said product.

Among the halide ions, there may preferably be mentioned Cl^- ; they are used in the form of ammonium or 10 metal salts, such as ammonium chloride, calcium chloride, zinc chloride, etc.

The first stage is favourably carried out at a temperature above 70°C and below 130°C , in the presence of quantities of reagents corresponding to the following 15 molar ratios:

. alkylphenol/alkylbenzenesulphonic acid of from 0.4 to 10, and preferably from 0.8 to 5

. lime/(alkylphenol + alkylbenzenesulphonic acid) of from 2.6 to 8, and preferably from 2.8 to 6

20 . halide ion/lime of from 0.005 to 0.15, and preferably from 0.015 to 0.09

. optionally hydroxylated $\text{C}_1\text{-C}_4$ carboxylic acid/lime of from 0 to 0.2, and preferably from 0.01 to 0.2.

This first stage can last from a few minutes to 1 25 hour, generally about half an hour.

The stage involving elimination of the water formed

is generally carried out at a temperature of 110-150°C, and preferably of 130-140°C.

Among the alcohols of boiling point higher than 155°C (designated below "heavy alcohols") employed in the third 5 stage, there may be mentioned; the C_6-C_{14} alkanols or cycloalkanols such as ethylhexanol, the oxo alcohols, decyl alcohol, tridecyl alcohol, trimethylcyclohexanol....; the ethers of the alkylene glycols such as 2-butoxyethanol, 2-butoxypropanol, 2-(hexyloxy)ethanol, the methyl ethers of 10 dipropylene glycol; the alkylene glycols other than ethylene glycol such as propylene glycol, hexylene glycol and the butanediols.

Ethylene glycol and the heavy alcohol can either be introduced in their entirety at the beginning of the third 15 stage, or preferably portion-wise during the third stage.

The sulphur needed for the sulphurization can be introduced at the beginning of the third stage, or else can already be present in the first stage.

The sulphurization procedure is carried out at a 20 temperature ranging from 155°C up to the boiling point of the heavy alcohol at normal pressure or under slightly reduced pressure; the procedure generally lasts from 1 to 2 hours.

The quantity of reagents which can be employed for 25 carrying out the sulphurization procedure corresponds to the following molar ratios:

. sulphur/alkylphenol ranging from 0.6 to 2, and preferably from 0.8 to 1.5 (corresponding to a molar ratio of sulphur/lime ranging from 0.04 to 0.8, and preferably from 0.06 to 0.5);

5 . ethylene glycol/lime ranging from 0.03 to 0.6, and preferably from 0.05 to 0.4;

. heavy alcohol/ethylene glycol ranging from 0.1 to 30, and preferably from 0.5 to 25.

The carbonation operation is favourably carried out
10 at a temperature ranging from 155°C up to the boiling point of the heavy alcohol, for a period of time ranging from 1 to 4 hours, and generally of about 2 hours; the quantity of CO₂ introduced is between that which can be completely absorbed by the reaction medium and an excess
15 of 30% above this quantity.

Since it is exothermic, this carbonation procedure can be performed in the presence of a supplementary quantity of cold ethylene glycol to compensate for ethylene glycol possibly vaporised.

20 The fifth stage is preferably carried out under vacuum at a temperature of 180-220°C for about 1 hour.

The present invention also provides detergent-dispersants of high alkalinity based on calcium obtained by the process described above. Thus the quantity of
25 detergent-dispersant of TBN 350 which can be added to lubricating oils is generally between 1.5 and 2% for a

petrol engine oil, between 3 and 4% for a diesel engine oil and between 7 and 20% for a marine engine oil.

The lubricating oils which can be improved in this manner can be various lubricating oils, such as the naphthene base, paraffin base and mixed base lubricating oils, 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 their derivatives, including the polymers of alkylene oxide prepared by polymerising alkylene oxide in the presence of water or alcohols such as ethyl alcohol, the esters of dicarboxylic acids, liquid esters of the phosphorus acids, alkylbenzenes and dialkylbenzenes, polyphenyls, alkyl biphenyl ethers, and polymers of silicon.

Supplementary additives may also be present in the said lubricating oils along with the detergent-dispersants obtained according to the process of the invention; there may be mentioned, for example, anti-oxidant additives, anti-corrosion additives, ashless dispersant additives.

The examples which follow illustrate the invention.

Examples 1 to 16

A) Stage A

The following are mixed with stirring:

- . the alkylbenzenesulphonic acid (sulphonic acid),
- the molar mass of the sodium salt of which is 480, in solution at 70% strength in 100 Neutral oil:

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- . dodecylphenol (DDP)
 - . 100 Neutral oil
 - . acetic acid
 - . ammonium chloride or calcium chloride.
- 5 . lime

The mixture is heated at 90°C for 30 minutes.

Sulphur is added and the mixture is heated at 155°C under slightly reduced pressure (930×10^2 Pa).

Ethylene glycol and a portion of butylglycol are
10 added over ten minutes, then the remainder of the butylglycol over fifty minutes. The mixture is heated at 160°C under slightly reduced pressure for 1 hour.

B) Carbonation

The mixture is heated at 165°C and carbonated for 2
15 hours at atmospheric pressure.

C) Elimination of the glycol and butylglycol

The vacuum is gradually raised to 66.5×10^2 Pa, and the mixture is then heated to 200°C for 1 hour.

D) Filtration

20 The quantities of reagents employed in the different stages are shown in Tables I to IV; the characteristics of the products obtained are shown in Tables I to IV.

Characteristics of the product

. Measurement of the sedimentation ratio

25 The percentages of sediments are measured according to the ASTM Standard D2273-67, introducing however the following modifications:

- . speed of rotation of the centrifuge 6,000 rpm

. relative centrifugal force 10,000

. the product to be analysed is diluted four-fold in petroleum spirit E (25 cm³ of product to be analysed + 75 cm³ of petroleum spirit E)

5 . duration of the centrifugation: 10 minutes.

. Test of compatibility

The finished product is added to an SAE 50 oil of substantially paraffin nature, so as to obtain a solution containing 25% of additive.

10 The solution is stored for 24 hours, and then centrifuged under the following conditions:

. speed of rotation: 6,000 rpm

. relative centrifugal force: 10,000

. duration of centrifugation: 1 hour

15 The sedimentation ratio is then measured.

Examples 2, 3, 11 and 12 are comparative examples.

Example 17

The quantities of reagents employed are those used in Example 1.

20 A) Stage A

The following are mixed with stirring:

. the sulphonic acid

. DDP

. 100 Neutral oil

25 . acetic acid

. lime.

The mixture is heated to 90°C, and then sulphur and ammonium chloride are added.

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The mixture is heated at 155°C under slightly reduced pressure (930×10^2 Pa).

Ethylene glycol and a portion of butylglycol are added over 20 minutes, and then the remainder of the 5 butylglycol over 1 hour.

The mixture is left for 2 hours at 160°C under the same slightly reduced pressure.

B) Carbonation stage

The mixture is heated to 165°C and then carbonated 10 for 2 hours at atmospheric pressure.

C) and D) Stages identical to those in Example 1

The characteristics of the product obtained are similar to those of the product of Example 1.

Example 18

15 The procedure described in Examples 1-16 is carried out, replacing the butylglycol by 1,3-butanediol.

The quantities of reagents employed and the characteristics of the product obtained are shown in Table V.

20 Example 19

The procedure described in Examples 1-16 is carried out, replacing the butylglycol by hexylglycol.

The quantities of reagents employed and the characteristics of the product obtained are shown in Table V.

25 Example 20

The procedure described in Examples 1-16 is carried out, replacing the butylglycol by hexylene glycol.

The quantities of reagents employed and the character-

istics of the product obtained are shown in Table V.

Examples 21-24

The procedure described in Examples 1-16 is carried out, replacing the butylglycol by 2-ethylhexanol.

- 5 The quantities of reagents employed and the characteristics of the product obtained are shown in Table VI.

Example 25

The procedure described in Example 21 is carried out, replacing the 18 g of acetic acid by 13.8 g of formic acid.

- 10 The results obtained are identical.

Example 26

- The procedure described in Example 1 is carried out, replacing the (100 + 560 g) of butylglycol by mixture of (100 + 193 g) of 1,4-butanediol and (100 + 400 g) of 15 2-ethylhexanol and reducing the quantity of ethylene glycol.

The results obtained are shown in Table VI.

TABLE I

<u>Example</u>		1	2	3	4
Sulphonic acid	g	440	440	440	440
DDP	g	261	261	261	261
Oil	g	432	432	432	432
Acetic acid	g	10	0	10	10
NH ₄ Cl	g	10	0	10	10
CaCl ₂	g	0	0	0	0
Lime	g	375	375	375	375
S	g	33	40	40	33
Ethylene glycol	g	66	204	204	66
Butylglycol	g	100 + 560	0 + 0	0 + 0	100 + 300
CO ₂	g	154	154	154	154
Crude sediment	%	1	6	5	1.2
<u>Analysis of the product</u>					
Ca	%	12.63	11.2	11.3	12.49
S	%	2.74	3.1	3.1	2.7
Viscosity (100°C)	cSt	330	460	470	302
CO ₂	%	9.6	8.1	8.2	9.8
TBN		321	280	285	316
% Sediments		0.01	0.1	0.1	0.02
Compatibility		trace	1	1.2	trace

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TABLE II

<u>Example</u>		5	6	7	8
Sulphonic acid	g	440	440	440	440
DDP	g	261	261	261	261
Oil	g	432	432	444	444
Acetic acid	g	10	10	11.8	15
NH ₄ Cl	g	10	10	0	15
CaCl ₂	g	0	0	25	0
Lime	g	375	375	442	430
S	g	33	40	33	33
Ethylene glycol	g	66	66	78	78
Bucylglycol	g	100 + 160	100 + 360	100 + 525	100 + 325
CO ₂	g	154	154	195	187
Crude sediment	%	1.5	1.1	1.3	1.5
<u>Analysis of the product</u>					
Ca	%	12.2	12.5	13.85	13.4
S	%	2.67	2.94	2.52	2.3
Viscosity (100°C) cSt		246	412	371	363
CO ₂	%	9.8	9.8	10.6	10.5
TBN		309	317	360	346
% Sediments		0.03	0.04	0.06	0.06
Compatibility		trace	trace	trace	trace

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TABLE III

<u>Examples</u>		9	10	11	12
Sulphonic acid	g	440	440	440	440
DDP	g	261	261	261	261
Oil	g	432	432	432	432
Acetic acid	g	15	20	0	10
NH ₄ Cl	g	15	0	0	0
CaCl ₂	g	0	25	0	0
Lime	g	570	715	375	375
S	g	33	33	33	33
Ethylene glycol	g	90	107	66	66
Butylglycol	g	100 + 680	100 + 560	100 + 560	100 + 560
CO ₂	g	206	225	155	140
Crude sediment	%	2	2.5	7	6.1
<u>Analysis of the product</u>					
Ca	%	15.4	16.7	10.1	11.0
S	%	2.35	2.2	3.1	3
Viscosity (100°C) cSt		478	522	132	158
CO ₂	%	12	14.3	7	8.3
TBN		414	451	252	275
% Sediments		0.1	0.12	0.12	0.08
Compatibility		trace	trace	0.1	trace

TABLE IV

<u>Examples</u>	13	14	15	16
Sulphonic acid g	440	490	525	280
DDP g	261	211	176	421
Oil g	432	432	432	444
Acetic acid g	0	11.8	11.8	11.8
NH ₄ Cl g	10	0	0	0
CaCl ₂ g	0	25	25	25
Lime g	375	442	442	442
S g	33	27	72	53
Ethylene glycol g	78	78	78	78
Bucylglycol g	100 + 560	100 + 525	100 + 525	100 + 525
CO ₂ g	140	196	200	194
Crude sediment %	1.6	1.2	1.2	1.3
<u>Analysis of the product</u>				
Ca %	12	13.9	13.8	13.7
S %	2.9	2.5	0.5	2.5
Viscosity (100°C) cSt	340	362	303	380
CO ₂ %	8.9	10.5	10.6	10.5
TBN	303	362	359	356
% Sediments	0.1	0.08	0.1	0.1
Compatibility	trace	trace	trace	trace

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TABLE V

<u>Examples</u>		18	19	20
Sulphonic acid	g	440	440	440
DDP	g	261	261	261
Oil	g	444	444	444
Acetic acid	g	11.8	11.8	11.8
NH_4Cl	g	0	0	0
CaCl_2	g	25	25	25
Lime.	g	442	442	442
S	g	33	33	33
Ethylene glycol	g	66	90	66
Heavy alcohol	g	100 + 525	100 + 525	100 + 525
CO_2	g	195	195	195
Crude sediment	%	1.5	2	1.5
<u>Analysis of the product</u>				
Ca	%	13.8	13.6	13.8
S	%	2.5	2.5	2.5
Viscosity (100°C)	cSt	410	365	340
CO_2	%	10.5	10.3	10.6
TBN		359	357	360
% Sediments		0.06	0.05	0.06
Compatibility		trace	trace	trace

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TABLE VI

<u>Examples</u>		21	22	23	24	26
: Sulphonic acid	g	492	525	534	513	440
: DDP	g	300	300	300	312	261
: Oil	g	510	477	510	494	432
: Acetic acid	g	18	18	22	19	10
: NH_4Cl	g	0	0	0	0	10
: CaCl_2	g	21	21	26	80	0
: Lime	g	480	480	591	500	375
: S	g	42	42	42	43	33
: Ethylene glycol	g	144	144	177	117	20.3
: Heavy alcohol	g	200+646	200+646	300+720	200+750	200+593
: CO_2	g	204	204	270	210	154
: Crude sediment	%	1	1	1.5	2	1
<u>Analysis of the product</u>						
: Ca	%	13.9	13.8	15	13.4	12.6
: S	%	2.8	2.7	2.5	2.7	3.1
: Viscosity (100°C)cSt		480	390	800	800	310
: CO_2	%	10.75	10.5	12.7	9.4	9.7
: TBN		353	357	386	350	320
: % Sediments		0.04	0.06	0.1	0.1	0.06
: Compatibility		trace	trace	trace	trace	trace



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CLAIMS

1. A process for the preparation of detergent-dispersants, which comprises

a) mixing together an alkylbenzenesulphonic acid, an alkylphenol, dilution oil, halide ions and lime

5 b) eliminating the water formed

c) sulphurizing the product formed with sulphur in the presence of ethylene glycol and at least one heavy alcohol other than ethylene glycol of boiling point higher than 155°C

10 d) carbonating the sulphurized product

e) eliminating the ethylene glycol and heavy alcohol of high boiling point

f) recovering the liquid detergent-dispersant.

15 2. A process according to Claim 1, wherein in step f) the liquid detergent-dispersant is recovered by filtration.

3. A process according to Claim 1, wherein a) is carried out in the presence of a C_1-C_4 carboxylic acid or a hydroxylated C_1-C_4 carboxylic acid.

20 4. A process according to Claim 3, wherein the carboxylic acid is formic acid, acetic acid, glycolic acid or oxalic acid.

5. A process according to Claim 1, 2, 3 or 4, wherein the halide ions are chloride ions.

25 6. A process according to Claim 5, wherein the chloride ion is employed in the form of ammonium



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chloride or a metal chloride.

7. A process according to any one of the preceding claims, wherein the heavy alcohol is a C_6-C_{14} alkanol or cycloalkanol, alkylene glycol ether, butanediol or 5 alkylene glycol other than ethylene glycol.

8. A process according to any one of the preceding claims, wherein stage a) is carried out at a temperature above $70^{\circ}C$ and below $130^{\circ}C$.

9. A process according to any one of Claims 1 to 8, 10 wherein stage a) is carried out in the presence of quantities of reagents corresponding to the following molar ratios:

. alkylphenol/alkylbenzenesulphonic acid of from 0.4 to 10.

15 . lime/(alkylphenol + alkylbenzenesulphonic acid) of from 2.6 to 8.

. halide ion/lime of from 0.005 to 0.15

. optionally hydroxylated C_1-C_4 carboxylic acid/lime from 0 to 0.2.

20 10. A process according to Claim 9, wherein stage a) is carried out in the presence of quantities of reagents corresponding to the following molar ratios:

. alkylphenol/alkylbenzenesulphonic acid of from 0.8 to 5.

25 . lime/(alkylphenol + alkylbenzenesulphonic acid) of from 2.8 to 6.

. halide ion/lime of from 0.015 to 0.09



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. optionally hydroxylated C_1-C_4 carboxylic acid/lime of from 0.01 to 0.2.

11. A process according to any one of the preceding claims, wherein the sulphurization stage c) is 5 carried out at a temperature of from 155°C up to the boiling point of the heavy alcohol.

12. A process according to any one of the preceding claims, wherein the sulphur is introduced in stage c).

10 13. A process according to any one of Claims 1 to 11, wherein the sulphur is present in stage a).

14. A process according to any one of the preceding claims, wherein the quantity of reagents employed for carrying out the sulphurization stage c) corresponds 15 to the following molar ratios:

- . sulphur/alkylphenol of from 0.6 to 2
- . ethylene glycol/lime of from 0.03 to 0.6
- . heavy alcohol/ethylene glycol of from 0.1 to 30.

15. A process according to Claim 14, wherein the 20 quantity of reagents employed for carrying out the sulphurization stage c) corresponds to the following molar ratios:

- . sulphur/alkylphenol of from 0.8 to 1.5
- . ethylene glycol/lime of from 0.05 to 0.4
- 25 . heavy alcohol/ethylene glycol of from 0.5 to 25.

16. A process according to any one of the



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preceding claims, wherein the carbonation stage d) is carried out a temperature of from 155°C up to the boiling point of the heavy alcohol.

17. A process according to any one of the 5 preceding claims, wherein the quantity of CO₂ introduced in stage d) is between that which can be completely absorbed by the reaction medium and an excess of 30% above this quantity.

18. A process according to any of the 10 preceding claims substantially as herein described in any one of Examples 1, 4 to 10 and 13 to 26.

19. A detergent-dispersant obtained by a process according to any one of the preceding claims.

20. A lubricating oil composition containing a 15 detergent-dispersant according to Claim 19.

21. A lubricating oil composition according to Claim 20 containing from 1.5 to 20% by weight of the detergent-dispersant.
