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The present invention relates to a viscosity additive for lubricating oils, with an alkyl polymethacrylate and an olefin copolymer base, the process for its preparation and also the lubricating compositions containing said additive.

Polymethacrylates (PMA) and olefin copolymers (OCP) are two families of additives of well known viscosity.

The patent US-A-3 506 574 also discloses viscosity additives which are constituted by alkyl polymethacrylate on which N-vinyl pyrrolidone has been grafted.

Each of these two families has advantages and disadvantages inherent to them. The PMA family makes it possible for rheological properties to be obtained at low temperatures above those of the OCP family; they also affect the flow point of the lubricating bases. On the other hand, their thickening effect is inferior to that of the OCP family; for this reason, they must be used in greater concentrations when lubricating formulae are being realised.

Therefore, attempts have been made to combine these two additives into one single additive in order to simply unite the advantages of each of these polymers.

Attempts have been made to make an additive of this kind, the simplest method consisting of a mixture of two polymers based on commercially available additives; but as patents US No. 4.290.925 and BE 870.329 state, such mixtures are not stable over time when one of the polymers has less than 5% total weight of polymers. For this reason, more complex methods have been envisaged. By way of example, it is possible to cite the grafting of a PMA on a OCP stock (patents BE No. 870.329, US No. 4.229.311 and US No. 3.923.930). A more complex technique consists in grafting an OCP with PMA and then in using that copolymer as a compatibility agent to stabilise the mixtures in emulsion of OCP and PMA (EP Patent No. 193.272 and US No. 4.290.925).

The Applicant has found a viscosity additive which is particularly economical and stable over time, whilst also comprising high proportions of PMA, on the one hand, and of OCP, on the other hand.

According to the invention, this is an additive with an olefin copolymer and an alkyl polymethacrylate base in solution in the oil for dilution, characterised in that it contains:

- 6 to 15 parts by weight, preferably 7.5 to 12.5 parts by weight of at least one ethylene-propylene copolymer with a weight average molecular mass of between about 155.000 and about 250.000, preferably in the order of 155.000 to 190.000, and having an ethylene/propylene weight ratio of between 60/40 and 54/46, preferably of between 58/42 and 54/46.

- 2 to 8 parts by weight, preferably 2.5 to 7.5 parts by weight of at least one C_1 - C_{20} alkyl polymethacrylate grafted per 1 to 8% of its weight, preferably from 1 to 4% of its weight, with a "dispersing" monomer, said polymethacrylate having a weight average molecular mass which can vary between 30.000 and 150.000, preferably in the order of 60.000 to 120.000, the weight ratio of grafted polymethacrylate/ethylene-propylene copolymer ranging from 1/5 to 1,

- and the complement with 100 parts of the oil for dilution.

One variant of the additive which is the object of the invention is characterised in that said additive also contains from 0 to 10% of its weight, preferably from 0.1 to 0.4% of its weight of an anti-oxidising agent.

The polymers, both the olefinic and methacrylic polymers, which make up said additive have as low as possible a dispersivity index; an index of less than 3.5 is particularly advantageous.

The alkyl polymethacrylate present is usually a mixture constituted by from 0 to 10% by weight of light polymethacrylates, the alkyl group of which is less than C_4 and from 10 to 100% by weight of heavy polymethacrylates, the alkyl group of which goes from C_{10} to C_{20} , preferably from C_{10} to C_{18} .

"Dispersing" monomers, that is to say the monomers which give said additive motifs which disperse the sludges in the lubricating oil can be cited as the

usual nitrogenous vinyl monomers, in particular N-vinylpyrrolidone, N-vinylimidazole, N-vinylpyridine...

The oil for dilution can be an oil with any commercial base, such as a petroleum oil with a paraffinic tendency, a mineral oil, a synthetic oil of the alkylene polymer type, diacid esters, polyol esters...

Of the anti-oxidising agents which may be present, it is possible to cite: dialkylamines whose alkyl group is greater than C_{12} , alkyl diphenyl amines which may be sulphurised, alkyl phenols which may be sulphurised.

The viscosity additive which is the object of the invention can be prepared by mixing, in the proportions noted hereinabove, a solution in the oil for dilution of an ethylene-propylene copolymer as defined hereinabove and a solution in an oil for dilution which is similar to or different from polymethacrylate which may have been grafted as defined hereinabove.

Said solutions of olefinic and methacrylic polymers can be commercial or non-commercial solutions.

Polymers with molecular masses greater than those claimed can be used; pre-cutting is then carried out, thereby making it possible for polymers of the desired molecular mass to be obtained.

When an anti-oxidising agent is present in said additive, this latter is preferably pre-mixed with the olefinic copolymer solution.

The present invention also relates to lubricating compositions obtained by adding to lubricating oils, in particular engine oils and oils for mechanical boxes and axles, from 0.1 to 10% by weight, preferably from 1 to 5% by weight in relation to the lubricating oil of the above-described additive.

These compositions can also contain other customary additives such as dispersants, detergents, anti-corrosion, extreme-pressure additives...

The following examples are given by way of example, and are not to be considered as limitative of the domain and sense of the invention.

Example 1

The following are introduced in succession into a beaker with a capacity of 250 cm³:

- 75 g of a solution with 10% by weight in a 150 N oil (oil with a paraffinic tendency of kinematic viscosity at 40°C of between 28 and 32.5 mm²/s) of an ethylene-propylene copolymer ("OCP") having an ethylene motif/propylene motif weight ratio of 58/42, a molecular mass by weight of 230.000 and a polydispersivity index of 3.1
- 4.3 g of a solution with 58% by weight in a 150 N oil of an alkyl copolymethacrylate ("PMA") (whose average length of the alkyl chains is 10 carbon atoms) grafted with 3.5% by weight of N-vinyl pyrrolidone (% by weight in relation to the total amount of copolymethacrylate) with a molecular mass by weight of 114.000 and a polydispersivity index of 2.5
- and 20.7 g of 150 N oil.

This mixture is stirred for one hour at 100°C; after cooling a mixture is obtained which is still stable after 300 days.

(The operation of determining stability is effected by visual observation; mixtures which are considered as instable are those in which a strong opalescence is observed, an oil type emulsion in oil or a demixing).

The following characteristics of the product are shown in Table I:

- thickening power (TP) : amount of active material (a.m.), that is to say the dry mixture of polymers necessary to obtain a kinematic viscosity of 13.8 mm²/s at 100°C (measured according to the standard ASTM D 445) in a 200 N oil (paraffinic oil whose kinematic viscosity at 40°C is from 37.5-43.5 mm²/s)
- viscosity index (VIE) : measured according to the standard ASTM D 2270 using 5% by weight of the above mixture in a 200 N oil
- cold cranking simulation (C.C.S.) : according to the standard ASTP D 2602 at -15°C.

Example 2

The same procedure is followed as that in Example 1 to prepare a mixture constituted by:

- 87.5 g of the OCP solution described in Example 1
- 6.5 g of the "PMA" solution described in Example 1

- 6 g of 150 N oil

The properties of the mixture are shown in Table I.

Example 3

The same procedure is followed as that in Example 1 to prepare a mixture constituted by:

- 76.5 g of a solution with 9.8 % by weight in a 150 N oil of a OCP having an ethylene/propylene weight ratio of 58/42, a weight molecular mass of 177.400 and a polydispersivity index of 2.3
- 0.2 g phenolic anti-oxidant (GARBANOX 150 marketed by the Société Française d'Organo Synthèse)
- 4.3 g of the "PMA" solution described in Example 1
- 19.2 g of 150N oil

The properties of the mixture are given in Table I.

Example 4

The procedure of Example 1 is followed to prepare a mixture constituted by:

- 89.3 g of the OCP solution described in Example 3
- 0.2 g of the anti-oxidant in Example 3
- 6.5 g of the PMA solution described in Example 1
- 4.2 g of 150 N oil.

The properties of the mixture are given in Table I.

The properties of the mixture obtained in Examples 1 to 4 are compared to those of the prior art products, namely:

- test A: the PMA described in Example 1
- tests B, C: OCP (ethylene/propylene): ECA 6710 and ECA 8586 marketed by PARAMINS.
- tests D, E, F : OCP grafted with PMA: VISCOPLEX 5164C, VISCOPLEX 5067, VISCOPLEX 5962 marketed by ROHM.

The results given in Table I show that the mixtures of Examples 1 to 4 have:

- a thickening power which is equivalent to that of the OCP's and which is clearly greater than that of the PMA grafted OCP's
- a VIE greater than or equal to that of the OCP's

- a behaviour at low temperature which is greater than or equal to that of the OCP's, PMA's and PMA grafted OCP's.

The concentration of active material (polymer) of the mixtures of the invention is of the same order or less than those of commercial OCP's.

Example 5

The procedure of Example 1 is followed to prepare a mixture constituted by :

- 10 g of the OCP described in Example 1, taken in the pure state (and not in solution in a 150 N oil)
- 12.9 g of the PMA solution described in Example 1
- 77.1 g of the 150N oil.

Example 6 (not in accordance with the invention)

The procedure of Example 1 is followed to prepare a mixture constituted by:

- 75 g of the OCP solution described in Example 1
- 4.6 g of a solution with 54% by weight in a 150 N oil of a non-grafted alkyl copolymethacrylate having an average length of alkyl chains of 10 carbon atoms, a weight molecular mass of 114.000 and a polydispersivity index of 2.5
- 20.4 g of 150 N oil.

Example 7

The procedure of Example 1 is followed to prepare a mixture constituted by:

- 89.3 g of the OCP solution described in Example 3
- 0.2 g of anti-oxidant described in Example 3
- 10.4 g of a solution with 36% in the 150 N oil of an alkyl copolymethacrylate (mean length of alkyl chains: 10C) grafted with 1% N-vinylimidazole, having a weight molecular mass of 114.000 and a polydispersivity index of 2.5
- 0.3 g of 150 N oil.

Example 8

The procedure of Example 1 is followed to prepare a mixture constituted by:

- 76.5 g of the OCP solution described in Example 3
- 0.2 g of the anti-oxidant described in Example 3
- 4.3 g of a 58% solution in the 150 N oil of an alkyl copolymethacrylate (mean length of the alkyl chains: 10C) grafted with 3.5 % by weight of N-

vinylpyrrolidone, having a weight molecular mass of 63.700 and a polydispersivity index of 2.9.

Example 9

The procedure of Example 1 is followed to prepare a mixture constituted by:

- 89.3 g of the OCP solution described in Example 4
- 0.2 g of the anti-oxidant described in Example 4
- 6.5 g of the solution of PMA in Example 8.

Example 10

The procedure of Example 1 is followed to prepare a mixture constituted by:

- 12.5 g of OCP described in Example 1, taken in the pure state
- 4.3 g of the solution of PMA in Example 1
- 83.2 g of 150 N oil

Example 11

The procedure of Example 1 is followed to prepare a mixture constituted by:

- 75 g of the OCP solution described in Example 1,
- 12.9 g of the PMA solution of Example 3
- 12.1 g of the 150 N oil

The stability of the mixtures of Examples 1 to 11 is shown in Table II.

Comparative Example 12 (PMA/OCP weight ratio = 1.33)

The procedure of Example 1 is followed to prepare a mixture constituted by:

- 37.5 g of the OCP solution described in Example 1
- 8.6 g of the PMA solution of Example 1
- 53.9 g of 150 N oil

It is noted that the mixture demixes after 6 days.

Comparative Example 13 (PMA/OCP weight ratio = 0.17)

The procedure of Example 1 is followed to prepare a mixture constituted by:

- 75 g of the OCP solution described in Example 3
- 0.2 of the anti-oxidant of Example 3
- 2.2 g of the PMA solution of Example 3
- 22.8 g of 150 N oil

It is noted that the mixture forms grains after 90 days.

Lubricating Formulations

A lubricating formulation of grade 15 W 40 is prepared, introducing into a beaker:

- respectively:
 - 14.3 parts by weight of the mixture of Example 3
 - 10 parts by weight of the mixture of Example 4
 - 10.3 parts by weight of ECA 8685
 - 5.9 parts by weight of VISCOPLEX 5164C.
- 5 parts by weight of multifunctional package OLOA 4261 D marketed by OROGIL
- and the complement with 100 parts of a mixture of oils with a paraffinic base comprising 80% by weight of grade 175 N oil and 20% of 600 N grade oil.

It is stirred for 1 hour at 80°C.

For these four formulations, the following is determined:

- their kinematic viscosity at 100°C and at 40°C according to the standard ASTM D 445
- their VIE according to the standard ASTM D 2270
- their CCS at -15°C according to the standard ASTM 2602.

The results are shown in Table III.

TABLE I

EXAMPLE OR TEST	TP % a.m.	VIE	CCS	% ACTIVE MATERIAL
A	4.9	147	2450	58
B	1.51	123	2200	11
C	2.14	121	2100	17
D	2.68	136	2500	40
E	3.6	142	2100	60
F	2.04	137	2300	34
1	1.07	126	-	10
2	1.06	132	-	12.5
3	1.36	123	1500	10
4	1.45	125	2500	12.5

TABLE II

EXAMPLE		STABILITY (days)				
1		> 300				
2		> 300				
3		> 300				
4		> 300				
5		> 150				
6		> 150				
7		> 150				
8		> 150				
9		> 150				
10		> 150				
11		> 150				
12		6				
13		90				

ADDITIVE	%	a.m.%	V 100°C mm ² /s	V 40°C mm ² /s	VIE	CCS
ECA 8586	10.3	1.75	13.99	105.05	135	3300
VISCOPLEX 5164 C	5.9	3.36	14.32	102.19	144	3200
mixture of Example 3	14.3	1.43	14.51	104.9	142	3300
mixture of Example 4	10.0	1.25	14.18	103.7	139	3100

CLAIMS

1. A viscosity additive for engine oils, based on an olefin copolymer and an alkyl polymethacrylate in solution in the oil for dilution, characterised in that it contains:

- 6 to 15 parts by weight of at least one ethylene-propylene copolymer with a weight average molecular mass of between about 155.000 and about 250.000 and having an ethylene/propylene weight ratio of between 60/40 and 54/46,
- 2 to 8 parts by weight of at least one C_1 - C_{20} alkyl polymethacrylate grafted per 1 to 8% of its weight with a "dispersing" vinyl nitrogen monomer, said polymethacrylate having a weight average molecular mass which can vary between 30.000 and 150.000, the weight ratio of grafted polymethacrylate/ethylene-propylene copolymer ranging from 1/5 to 1,
- and the complement to 100 parts of the oil for dilution.

2. A viscosity additive for engine oils according to Claim 1, characterised by the fact that the dispersing monomer grafted onto the polymethacrylate is selected from the group comprising N-vinyl pyrrolidone, N-vinyl imidazole and N-vinyl pyridine.

3. An additive according to one of Claims 1 and 2, characterised in that it contains:

- 7.5 to 12.5 parts by weight of the ethylene-propylene copolymer,
- 2.5 to 7.5 parts by weight of alkyl polymethacrylate,
- and the complement to 100 parts of the oil for dilution.

4. An additive according to one of Claims 1 to 3, characterised in that it also contains 0 to 10% of its weight of an anti-oxidising agent.

5. Lubricating compositions based on lubricating oils containing 0.1 to 10% of their weight of an additive forming the object of one of Claims 1 to 4.