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ETHYLENE / VINYL ACETATE / UNSATURATED ESTERS TERPOLYMER
AS ADDITIVES ENCHANCING THE LOW-TEMPERATURE RESISTANCE
OF LIQUID HYDROCARBONS SUCH AS MIDDLE DISTILLATES AND
MOTOR FUELS OR OTHER FUELS

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Technical Field.

The invention relates to the use of copolymers of alpha-olefin, vinyl ester, and alpha, beta-unsaturated carboxylic acid ester as additives improving the resistance to cold of motor fuels and lubricants as well as fuel-oils and the packages containing these
10 copolymers.

Prior art.

At a reduced temperature, hydrocarbon compositions, in particular those with a medium distillate type base containing paraffin waxes, such as for example diesel fuels and heating fuel oils exhibit a significant reduction in their rheological properties. It is
15 well known that the crystallization of paraffins is a factor limiting the use of the middle distillates. It is thus important to prepare diesel fuels which are suitable for the temperatures at which they are used in motor vehicles, i.e. for the ambient climate. Generally, cold operability of motor fuels at -10°C is sufficient in numerous hot or temperate countries. However, in countries with a cold climate, such as the Scandinavian
20 countries, Canada and the countries of Northern Asia, motor fuel use temperatures well below -20°C can be reached. The same is true for domestic fuel oils stored outside buildings (houses, blocks of flats etc.). This adequacy of the cold operability of the middle distillate type motor fuels is important, in particular during cold engine start. If paraffins are crystallized at the bottom of the tank, they may be carried along in the fuel
25 system during starting and block in particular the filters and pre-filters arranged upstream of the injection systems (pump and injectors). Similarly, for the storage of domestic fuel oils, the paraffins precipitate at the bottom of the tank and can be carried along and obstruct the pipes upstream of the pump and the boiler fuel system (nozzle and filter). It is evident that the presence of solids, such as paraffin crystals, prevents the
30 normal circulation of the middle distillate.



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In order to improve their circulation either in the engine, or towards the boilers, several types of additives have appeared.

Initially, the oil industry applied itself to the development of cold flow improvers or CFIs promoting the dispersion of the paraffin crystals and thus preventing them from becoming organized into large networks responsible for obstructing the filter pores. These additives essentially act on the cold filter plugging point (CFPP) and the pour point, but do not modify the cloud point.

The prior art has described numerous CFI additives (see for example US 3,038,479, US 3,627,838, US 3,790,359, US 3,961,961, EP 261957) which are generally copolymers of ethylene and unsaturated ester, such as ethylene/vinyl acetate (EVA), ethylene/vinyl propionate (EVP), ethylene/vinyl ethanoate (EVE), ethylene/methyl methacrylate (EMMA), and ethylene/alkyl fumarate copolymers.

In order to improve the properties of conventional CFIs, the prior art also proposes mixtures of conventional CFI additives of ethylene/unsaturated ester type with lubricants (mono- or polycarboxylic acid and mono- or polyalcohol esters (see for example EP 721492), with anti-sedimentation agents (see for example FR 2490669), or with ethers (see for example US 3,999,960, EP 187488)

Improved CFI additives are also found which are terpolymers or copolymers deriving from more than 3 separate monomers.

For example, US 6,509,424 describes a process for the preparation of terpolymers of ethylene and at least two compounds containing ethylene unsaturations, such as vinyl esters, (meth)acrylic esters, vinyl alkyl ethers in a tubular reactor. These terpolymers can be used as additives improving the cold flow of petroleums and petroleum distillates.

US 3,642,459 describes terpolymers comprising 40 to 89% by weight of ethylene, 10 to 40% by weight of vinyl ester derived from short-chain carboxylic acid (C2-C4), such as vinyl acetate, and unsaturated monoesters having a C10-C22 alkyl chain); these terpolymers are used as additives to lower the pour point of petroleum distillates and as anti-wax agents and to improve their filterability.

US 4,156,434 describes terpolymers of ethylene, vinyl acetate and acrylic ester deriving from C12-C24 alcohol which lower the pour point of the motor fuels in which

they are incorporated but says nothing about the improvement of the cold filterability of these additives.

WO 2005/054314 describes useable terpolymers of alpha olefin, vinyl ester and alpha-beta unsaturated mono carboxylic acid ester. Examples are given of terpolymers, particularly preferred by the applicant, which contain more than 80% in moles of ethylene and less than 9% in moles of vinyl acetate. Although these terpolymers containing less than 9% in moles of vinyl acetate have an effect on the reduction of the CFPP for middle distillates containing more than 18% n-paraffins, they are not satisfactory as regards solubility on the one hand and blocking tendency (or filterability at ambient temperature) on the other hand: harmful filter blocking is noted.

EP 1391498 describes additives improving the low temperature fluidity of middle distillates, namely vinyl polymers (A), preferably ethylene-vinyl ester copolymers, in which the quantity of materials which are insoluble in hexane exceeds 60% by weight at -20°C and is less than 30% by weight at 10°C; the examples of EP 1391498 clearly show that the filterability temperature (CFPP) is lowered for copolymers and terpolymers in which the quantity of material which is insoluble in hexane exceeds 60% by weight at -20°C and is less than 30% by weight at 10°C in relation to the copolymers and terpolymers having the same repetition units present in the same proportions but in which the quantity of materials which are insoluble in hexane is outside the claimed range; the copolymers given as examples are EVA copolymers and ethylene-vinyl acetate-neodecanoate or vinyl 2-ethylhexanoate terpolymers.

There is an unresolved need for additives to improve the resistance to cold of motor fuels (CFPP and pour point) whilst reducing or even eliminating the risk of blocking, in order to avoid blocking the filters of the fuel systems of the engines or boilers (injection system and tanks).

Description of the invention

The present invention relates to the use of copolymers as additives improving the resistance to cold of motor fuels (CFI additives); these copolymers contain units derived from at least one alpha-olefin, at least one vinyl ester and at least one alpha-beta unsaturated mono carboxylic acid ester, and are preferably terpolymers of ethylene, vinyl acetate and ethyl-2,hexyl acrylate.

The copolymers according to the invention which can be used as CFI additives comprise

- 78 to 87% in moles of at least one alpha-olefin, preferably at least ethylene,
- 5 ▪ 12 to 18% in moles of at least one vinyl ester, preferably at least vinyl acetate,
- 1 to 4% in moles of at least one alpha-beta unsaturated mono carboxylic acid ester, preferably at least ethyl-2, hexyl acrylate.

Advantageously, the copolymers which can be used as CFI additives comprise:

- 10 ▪ 78 to 87% in moles of ethylene,
- 12 to 18% in moles of vinyl acetate, preferably 12 to 16 % in moles;
- 1 to 4% in moles of 2, hexyl-ethyl acrylate, preferably 1.5 to 3.5 % in moles.

The copolymers according to the invention which are random copolymers have a numerical molecular weight (Mw) measured by GPC generally comprised between
15 3,000 and 30,000, and an average numerical molecular weight (Mn) measured by GPC generally comprised between 1,000 and 15,000.

These copolymers can be prepared in a known manner by any polymerization process, (see for example, Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, "Waxes", Vol. A 28, p.146; US 3,627,838; EP 7590) in particular by radical
20 polymerization, preferably under high pressure, typically of the order of 1,000 to 3,000 bars (100 to 300 MPa), preferably 1,500 to 2,000 bars (150 to 200 MPa), the reaction temperatures generally ranging from 160 to 320°C, preferably from 200 to 280°C, and in the presence of at least one radical initiator generally chosen from the organic peroxides and/or the oxygenated or nitrogenated compounds, and a molecular weight regulator
25 (ketone or aliphatic aldehyde etc.). The copolymers can for example be prepared in a tubular reactor according to the process described in US 6,509,424.

The hydrocarbon-based compositions in which the copolymers according to the invention are incorporated are chosen from all types of fuel oils or motor fuels, such as diesel fuels, domestic fuel oils for heating installations (DF), kerosene, aviation fuels,
30 heavy fuel oils, etc.

Generally the sulphur content of the hydrocarbon compositions is less than 5,000 ppm, preferably less than 500 ppm, and more preferably less than 50 ppm, or even less than 10 ppm and advantageously sulphur-free.

5 The hydrocarbon-based compositions comprise middle distillates with a boiling temperature comprised between 100 and 500°C; their initial crystallization temperature ICT is often greater than or equal to -20°C, generally comprised between -15°C and +10°C. These distillates can for example be chosen from distillates obtained by direct distillation of crude hydrocarbons, distillates from vacuum distillation, hydrotreated distillates, distillates originating from catalytic cracking and/or hydrocracking of
10 distillates under vacuum, distillates resulting from conversion processes of ARDS (atmospheric residue desulphuration) type and/or visbreaking, distillates originating from upgrading of the Fischer-Tropsch cuts, distillates resulting from BTL (biomass to liquid) conversion of vegetable and/or animal biomass, taken alone or in combination and/or the esters of vegetable and animal oils or their mixtures.

15 The hydrocarbon compositions can also contain distillates originating from refining operations, which are more complex than those originating from the direct distillation of the hydrocarbons which can for example originate from cracking, hydrocracking and/or catalytic cracking processes and visbreaking processes.

They can also contain novel sources of distillates, among which there can in
20 particular be mentioned:

- the heaviest cuts originating from the cracking and visbreaking processes with a high concentration of heavy paraffins, comprising more than 18 carbon atoms,
- synthetic distillates originating from the conversion of gas such as those originating from the Fischer Tropsch process,
- 25 - synthetic distillates resulting from the treatment of biomass of vegetable and/or animal origin, such as in particular NExBTL,
- oils and/or esters of vegetable and/or animal oils,
- or also biodiesels of animal and/or vegetable origin.

These novel motor fuel bases can be used alone or in a mixture with standard
30 petroleum middle distillates as a motor fuel base and/or domestic fuel oil base; they

generally comprise long paraffin chains greater than or equal to 10 carbon atoms and preferably C14 to C30.

The copolymers as defined previously, with an Mw comprised between 5,000 and 27,000 and an Mn comprised between 1,500 and 22,000, preferably with an Mw comprised between 5,000 and 25,000 and an Mn comprised between 1,500 and 20,000, are particularly effective when they are incorporated into the light middle distillates and/or distillates with a low sulphur content (typically less than 50 ppm) and/or at a low initial crystallization temperature (which may typically be as low as -20°C). By light middle distillates, is meant distillates in which the content of n-paraffins having 24 carbon atoms or more ranges from 0 to approximately less than 0.7% by weight of the total motor fuel composition; wherein the C18-C23 n-paraffins represent approximately 3 to approximately 5% of the total weight of the motor fuel and wherein the mass ratio of the C18-C23 n-paraffins to the C24+ paraffins generally ranges from 10 to 35.

The copolymers with an Mw comprised between 5,000 and 10,000 and an Mn comprised between 1,500 and 8,000, preferably with an Mw comprised between 5,000 and 8,000 and an Mn comprised between 1,500 and 5,000 are particularly effective when they are incorporated into heavy middle distillates and/or at a rather high initial crystallization temperature (typically being able to range from 0 to 15°C). By heavy middle distillates is meant distillates in which the content of n-paraffins having 24 carbon atoms or more ranges from approximately 0.7 to approximately 2% by weight of the total motor fuel composition; wherein the C18-C23 n-paraffins represent approximately 1 to approximately 10% of the total weight of the motor fuel and wherein the mass ratio of the C18-C23 n-paraffins to the C24+ paraffins generally ranges from 1 to 10.

The copolymers can be added to the hydrocarbon compositions as such or preferably in the form of concentrated solutions, in particular solutions containing 50 to 80%, preferably 60 to 70% by weight of copolymer(s) in a solvent, such as the aliphatic or aromatic hydrocarbons, alone or in a mixture (naphtha, kerosene, hydrocarbon fractions such as Solvesso solvent, paraffinic hydrocarbons, such as pentane, hexane.)

According to a preferred embodiment of the invention, the hydrocarbon compositions comprise 10 to 5,000 ppm by weight of at least one copolymer described above optionally, preferably 100 to 1000 ppm, and advantageously 150 to 500 ppm.

Apart from the CFI additives or cold resistance additives described above, the hydrocarbon compositions can also contain one or more other additives different from the copolymers according to the invention, chosen from detergents, anti-corrosive agents, dispersants, demulsifiers, anti-foam agents, biocides, reodorants, procetane additives, friction modifiers, lubricity additives or anti-friction additives, combustion-promoting agents (catalytic combustion and soot promoters), cloud point, pour point, cold filter plugging point improvers, anti-sedimentation agents, anti-wear agents and/or conductivity modifying agents.

Among these additives, there can particularly be mentioned:

a) procetane additives, in particular (but not limitatively) chosen from alkyl nitrates, preferably 2-ethyl hexyl nitrate, aroyl peroxides, preferably benzyl peroxide, and alkyl peroxides, preferably ter-butyl peroxide;

b) anti-foam additives, in particular (but not limitatively) chosen from polysiloxanes, oxyalkylated polysiloxanes, and fatty acid amides from vegetable or animal oils. Examples of such additives are given in EP 861182, EP 663000, EP 736590;

c) detergent and/or anti-corrosion additives, in particular (but not limitatively) chosen from the group constituted by amines, succinimides, alkenylsuccinimides, polyalkylamines, polyalkyl polyamines and polyetheramines. Examples of such additives are given in EP 938535.

d) lubricity additive or anti-wear agent, in particular (but not limitatively) chosen from the group constituted by fatty acids and their ester or amide derivatives, in particular glycerol monooleate, and mono- and polycyclic carboxylic acid derivatives. Examples of such additives are given in the following documents: EP 680506, EP 860494, WO 98/04656, EP 915944, FR 2772783, FR 2772784.

e) cloud point additives, in particular (but not limitatively) chosen from the group constituted by long-chain olefin/(meth)acrylic ester/maleimide terpolymers, and fumaric/maleic acid ester polymers. Examples of such additives are given in EP 71513,

EP 100248, FR 2528051, FR 2528051, FR 2528423, EP 112195, EP 172758, EP 271385, EP 291367;

5 f) anti-sedimentation additives and/or paraffin dispersants in particular (but not limitatively) chosen from the group constituted by (meth)acrylic acid / polyamine-amidified alkyl (meth)acrylate copolymers, polyamine alkenylsuccinimides, derivatives of phthalamic acid and of double-chain fatty amine; alkyl phenol resins. Examples of such additives are given in EP 261959, EP 593331, EP 674689, EP 327423, EP 512889, EP 832172; US 2005/0223631; US 5,998,530; WO 93/14178.

10 g) cold operability multi-functional additives chosen from the group constituted by the polymers based on olefin and alkenyl nitrate as described in EP 573 490.;

h) other CFI additives improving resistance to cold and filterability, such as EVA and/or EVP copolymers

These other additives are generally added in a quantity ranging from 100 to 1,000 ppm (each).

15 The improved cold-resistance additives according to the invention can be added to the hydrocarbon compositions within the refinery, and/or be incorporated downstream of the refinery, optionally in a mixture with other additives, in the form of a package of additives.

Examples

20 Terpolymers of ethylene, vinyl acetate and ethyl-2,hexyl acrylate were synthesized in a tubular reactor by radical polymerization under high pressure (1,400 to 2,500 bars (140 to 250 MPa)) and at a polymerization temperature of 200 to 280°C. The synthesis was carried out using an aliphatic aldehyde (propanal) to control the molecular weights and using peroxides as polymerization initiators. Table 1 below shows the Mn and Mw
25 of the synthesized terpolymers as well as their percentages of monomers.

Table 1: Characteristics of the polymers synthesized

Copolymer	[vinyl acetate]		[ethyl-2 hexyl acrylate]		Mn	Mw
	wt. %	mol. %	wt. %	mol. %		
1	28.4	13.1	9.2	2.1	2 550	7 190
2	32.1	15.5	9.7	2.2	2 440	6 870
3	24.5	11	9.8	2.1	2 480	6 990
4	27	12.1	9	1.9	12 687	14 775
5	28.8	13.1	9.1	1.9	13 195	15 185
6 (comparative)	13.3	6.6	22.1	5.1	12 627	14 610
7 (comparative)	13.1	6.5	22.4	5.2	8 842	10 460
8 (comparative)	17.9	8.9	16.8	3.9	12 875	15 675
9 (comparative)	17.8	8.8	16.7	3.9	8 384	9 885
10 (comparative)	28.7	14.3	19	4.4	11585	14210
11 (comparative)	28.9	14.4	17.5	4.1	12250	14852
12 (comparative)	27.6	13.7	20.7	4.8	11180	13255
13 (comparative)	28.4	14.1	20.4	4.7	12100	14372
14	33.6	16.7	10	2.3	9712	11876
15	31.5	15.7	13.3	3.1	11420	13667
16 (comparative)	19.3	9.6	21.5	5	4 498	8 443

The ability to improve the resistance to cold of these terpolymers was evaluated by incorporating them into 6 engine gas oil type distillates known as GOM 1 to GOM 6, the characteristics of which are compiled in Table 2 below.

Table 2: Characteristics of the motor fuels

	GOM 1	GOM 2	GOM 3	GOM 4	GOM 5	GOM 6
Distillation ASTM D86						
T90-T20 (°C)	112.7	100.4	96.9	112.2	100.5	112
MP-T90 (°C)	18.6	24.9	26.1	26.2	17	23
T95-°C.	353.9	362.4	351.1	350.5	350	356
Cloud point (°C)						
NF EN 23015	-4	-4	-5	-5	-9	-7
CFPP (°C)						
EN 116	-5	-7	-6	-5	-9	-6
Pour point (°C)						
NF T 60105	-12	-10	-12	-12	-15	-9
Paraffins content (% by mass)						
Chromatography	19.27	14.68	17.5	18.95	16.1	15.64
ICT (°C)						
IP 389	-6	-6.3	-6.2	-6.3	-12.6	-9.5
Sulphur content (ppm)						
EN ISO 20846	39.8	38	9	9.5	9.2	48

400 ppm by weight of each copolymer 1 to 16 below was incorporated into the engine gas oil type distillate called GOM 1, then the FBT (Filter Blocking Tendency) index was measured according to the standard IP 387. The GOM 1 without additives has an FBT index of 1.01.

It is noted that the terpolymers according to the invention make it possible not to degrade the filter blocking tendency of GOM 1 i.e. that GOM 1 with 400 ppm of terpolymer added has an FBT of less than 1.41. The results are shown in Table 3 below.

Table 3 Filter blocking tendency (IP387) of the GOM 1 with 400 ppm of the
5 different terpolymers added.

Additive added	FBT index (IP 387)
1	1.01
2	1
3	1.3
4	1.14
5	1.06
6 (comparative)	6.08
7 (comparative)	6.08
8 (comparative)	1.53
9 (comparative)	1.8
10 (comparative)	1.02
11 (comparative)	2.69
12 (comparative)	1.01
13 (comparative)	1.03
14	1.01
15	1.01
16 (comparative)	5.1

The cold resistance effectiveness CFPP of the terpolymers incorporated into GOM 2 to GOM 6 was measured at a concentration of 140, 210 or 280 ppm; the results are compiled in Table 4.

5 Table 4: CFPP effectiveness tests on different gas oils with a low sulphur content.

Additive added	CFPP (°C) measurements EN 116					
	GOM 2	GOM 3	GOM 3	GOM 4	GOM 5	GOM 6
	210 ppm	210 ppm	280 ppm	210 ppm	210 ppm	140 ppm
1	-21	-13	-14	-14		
2	-16	-15	-14	-14	-16	-14
4	-21	-16	-18	-17		
5	-19	-15		-15	-12	-10
6					-12	-9
7	-16	-15		-15	-12	-9
8					-12	-9
9					-12	-9
10	-12	-13		-13	-13	-10
11	-17	-13		-13	-13	-10
12	-4	-5		-4		-9
13	-5	-4		-3		-9
14	-12	-11		-5	-17	-10
16	-17	-16		-14	-12	-9

10 It is noted that the terpolymers 1; 2; 3; 4 according to the invention are the most effective in the different gas oils GOM 2 to GOM 6. Moreover, from the results in Table 3, it is noted that these terpolymers 1; 2; 3 and 4 added at a level of 400 ppm to the GOM 1 do not degrade the filter blocking tendency. This is not the case with the comparative terpolymers 6; 7; 8; 9; 11 and 16 according to WO 2005/054314, which greatly degrade the filter blocking tendency measured according to IP 387 and are also

not as effective as regards CFPP as the additives of the invention such as for example the additives 1; 2; 4 and 5.

CLAIMS

1. Use as an additive improving the resistance to cold and filterability of motor fuels, of at least one copolymer comprising

- 5
- 78 to 87% in moles of at least one alpha-olefin, preferably at least ethylene,
 - 12 to 18% in moles of at least one vinyl ester, preferably at least vinyl acetate,
 - 1 to 4% in moles of at least one alpha-beta unsaturated mono carboxylic acid ester, preferably at least ethyl-2,hexyl acrylate.

10

2. Use according to claim 1 of at least one terpolymer comprising

- 78 to 87% in moles of ethylene,
- 12 to 18% in moles of vinyl acetate,
- 1 to 4% in moles of ethyl-2,hexyl acrylate.

15

3. Use according to claim 1 or 2 of at least one copolymer with a numerical molecular weight (Mw) measured by GPC comprised between 3,000 and 30,000, preferably 3,000 to 20,000 and an average numerical molecular weight (Mn) measured by GPC generally comprised between 1,000 and 20,000, preferably ranging from 1,500 to 15,000.

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4. Use according to claim 1 to 3 of at least one copolymer as an additive improving the resistance to cold and filterability without degrading the filter blocking tendency of middle distillates, such as diesel fuels, domestic fuel oils for heating installations (DF), kerosene, aviation fuels, heavy fuel oils.

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5. Use according to any one of claims 1 to 4 of at least one copolymer as an additive improving the resistance to cold and filterability of motor fuels the sulphur content of which is less than 5,000 ppm, preferably less than 500 ppm, more preferably less than 50 ppm, or even less than 10 ppm and advantageously sulphur-free.

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6. Composition of hydrocarbons comprising a major quantity of a middle distillate with a boiling temperature ranging from 100 to 500°C and a minority quantity of at least one copolymer as defined in any one of claims 1 to 5.

5 7. Composition according to claim 6, characterized in that it contains 0 to 100% by weight of biodiesel of animal and/or vegetable origin.

 8. Composition according to claim 6 or 7, characterized in that it is chosen from diesel fuels, domestic fuel oils for heating installations (DF), kerosene, aviation
10 fuels, heavy fuel oils.

 9. Composition according to any one of claims 6 to 8, characterized in that it comprises 10 to 5,000 ppm by weight of at least one copolymer as defined in claims 1 to 5, preferably 100 to 1,000 ppm, and advantageously 150 to 500 ppm.

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 10. Composition according to any one of claims 6 to 9, characterized in that it comprises one or more other additives different from the copolymers according to the invention, chosen from detergents, anti-corrosive agents, dispersants, demulsifiers, anti-foam agents, biocides, reodorants, procetane additives, friction modifiers, lubricity
20 additives or anti-friction additives, combustion-promoting agents (catalytic combustion and soot promoters), agents improving the cloud point, pour point, cold filter plugging point, anti-sedimentation agents, anti-wear agents and/or conductivity modifying agents.