

5 **ETHYLENE /VINYL ACETATE/UNSATURATED ESTERS TERPOLYMER AS**
 AN ADDITIVE FOR IMPROVING THE RESISTANCE TO COLD OF LIQUID
 HYDROCARBONS SUCH AS MIDDLE DISTILLATES AND FUELS

Technical field.

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

Prior art.

 At a reduced temperature, compositions of hydrocarbons, notably based on middle distillate types containing paraffinic waxes, such as for example diesel fuels and heating oils, exhibit a significant decrease in their flow properties. It is well-known that
15 the crystallization of paraffins is a limiting factor in the use of middle distillates. Also, it is important to prepare diesel fuels adapted to temperatures at which they will be used in motor vehicles, i.e. to the surrounding climate. Generally, cold operability of fuels at -10 °C is sufficient in many hot or temperate countries. But in countries with a cold
20 climate such as the Scandinavian countries, Canada and the countries of North Asia, temperatures of use of the fuels much lower than -20 °C may be attained. The same applies to domestic oils stored outside buildings (houses, apartment blocks,...). This adequacy of cold operability of fuels of the middle distillate type is important, notably for the cold starting of engines. If the paraffins are crystallized at the bottom of the tank,
25 upon starting they may be driven into the fuel circuit and notably block the filters and pre-filters positioned upstream from the injection systems (pump and injectors). Also, when storing domestic oils, paraffins precipitate to the bottom of the tank and may be driven and obstruct the conduits upstream from the pump and from the supply system of the boiler (nozzle and filter). It is obvious that the presence of solids, such as paraffin
30 crystals, prevents normal circulation of the middle distillate.

 In order to improve their flow either in the engine or towards the boilers, several types of additives have been developed.

 In a first phase, the petrol industry was committed to developing so-called cold flow additives (cold flow improvers or CFI) promoting dispersion of paraffin crystals
35 and thereby preventing them from organizing themselves as large size lattices,

responsible for obstructing the filter pores. These additives essentially act on the limiting filterability temperature (LFT) and on the pour point, but do not modify the cloud point.

The prior art has described many CFI additives (see for example US 3,048,479, US 3,627,838, US 3,790,359, US 3,961,961, EP 261 957) which are generally
5 copolymers of ethylene and of an 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 standard CFIs, the prior art also proposes mixtures of conventional CFI additives of the ethylene/unsaturated ester type with
10 lubricants (mono- or poly-carboxylic acid esters of mono- or poly-alcohols (see for example EP 721 492), with anti-sedimentation agents (see for example FR 2 490 669), with ethers (see for example US 3,999,960, EP 187 488)

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

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

US 3,642,459 describes terpolymers comprising 40-89% by weight of ethylene,
20 10-40% by weight of vinyl ester derived from a short chain (C₂-C₄) carboxylic acid, such as vinyl acetate, and unsaturated monoesters having a C₁₀-C₂₂ alkyl chain; these terpolymers are used as additives for lowering the pour point of petroleum distillates and as anti-wax agents and for improving their filterability.

US 4,156,434 describes terpolymers of ethylene, vinyl acetate and of acrylic
25 ester deriving from a C₁₂-C₂₄ alcohol which lower the pour point of the fuels into which they are incorporated but nothing is said on the improvement of cold filterability of these additives.

WO 2005/054314 describes terpolymers of α -olefin, vinyl ester and α,β -unsaturated mono carboxylic acid ester, which may be used. Terpolymers are
30 exemplified, particularly preferred by the applicant, which contain more than 80% by moles of ethylene and less than 9% by moles of vinyl acetate. Now, these terpolymers containing less than 9% by moles of vinyl acetate although having an effect on the decrease in LFT for middle distillates containing more than 18% of n-paraffins, are not satisfactory as regards solubility on the one hand and tendency to blocking (or room
35 temperature filterability) on the other hand: damageable filter cloggings are reported.

EP 1 391 498 describes additives improving low temperature fluidity of middle distillates, which are vinyl polymers (A), preferably ethylene-vinyl ester copolymers, for which the amount of hexane-insoluble materials exceeds 60 % by weight at -20 °C and is less than 30% by weight at 10°C; the examples of EP 1 391 498 clearly show that the filterability temperature (cold filter plug point (CFPP)) is lowered for copolymers and terpolymers, for which the amount of hexane-insoluble material exceeds 60% by weight at -20 °C and is less than 30% by weight at 10°C as compared with copolymers and terpolymers having the same recurrent units present in the same proportions, but for which the amount of hexane-insoluble materials is out of the claimed range; the exemplified copolymers are EVA copolymers and ethylene-(vinyl acetate)-(vinyl neodecanoate or 2-ethylhexanoate) terpolymers.

There is an unsolved need for additives in order to improve cold resistance of fuels (LFT and pour point) while reducing or even eliminating the risk of clogging, so as to avoid blocking of the filters of supply systems for engines or boilers (injection system and tanks).

Description of the invention

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

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

- from 81 to 87 % by moles of at least one α -olefin, preferably at least ethylene,
- from 10.5 to less than 12% by moles of at least one vinyl ester, preferably at least vinyl acetate,
- from 1 to 8.5 % by moles of at least one α,β -unsaturated mono-carboxylic acid ester, preferably at least ethyl-2-hexyl acrylate.

Preferably, the copolymers which may be used as CFI additives are inscribed in a quadrilateral ABCD in which A, B, C and D represent the apices of said quadrilateral and correspond to the molar percentages of at least the vinyl ester and of at least the α,β -unsaturated mono-carboxylic acid ester:

A: 12; 1

B: 12; 6

C: 10.5; 4

D: 10.5; 8.5.

Advantageously, the copolymers which may be used as CFI additives are inscribed in a quadrilateral A_1BC_1D wherein A_1 , B, C_1 and D represent the apices of said quadrilateral and correspond to the molar percentages of at least the vinyl ester and of at least the α,β -unsaturated mono-carboxylic acid ester:

A_1 : 12; 2

B: 12; 6

C_1 : 10.5; 5

D: 10.5; 8.5.

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

These copolymers may be prepared in a known way by any polymerization method, (see for example, Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, "Waxes", Vol. A 28, p.146; US 3,627,838; EP 7 590) notably by radical polymerization, preferably under high pressure, typically of the order of 1,000 to 3,000 bars (100 to 300 MPa), preferably from 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 selected from organic peroxides and/or oxygen- or nitrogen-containing compounds, and of a molecular weight regulator (aliphatic ketone or aldehyde,...). The copolymers may for example be prepared in a tubular reactor according to the method described in US 6,509,424.

The compositions based on hydrocarbons into which the copolymers according to the invention are incorporated, are selected from all types of oils or fuels, such as diesel fuels, domestics oils for heating installations (DOF), kerosene, aviation fuels, heavy fuels, etc ...

Generally, the sulfur content of the hydrocarbon compositions is less than 5,000 ppm, preferably less than 500 ppm, and more preferentially less than 50 ppm, or even less than 10 ppm and advantageously without any sulfur.

The compositions based on hydrocarbons comprise middle distillates with a boiling temperature comprised between 100 and 500°C; their initial crystallization temperature T_{cc} is often greater than or equal to -20°C, generally comprised between -15°C and +10°C. These distillates may for example be selected from distillates obtained

by direct distillation of crude hydrocarbons, distillates *in vacuo*, hydrotreated distillates, distillates from catalytic cracking and/or from hydrocracking of distillates *in vacuo*, distillates resulting from ARDS (atmospheric residue desulfurization) type conversion processes and/or viscoreduction processes, distillates from upgrading of Fischer Tropsch cuts, distillates resulting from BTL (biomass to liquid) conversion of plant and/or animal biomass, taken alone or as a combination, and/or esters of plant and animal oils or mixtures thereof.

The compositions of hydrocarbons may also contain distillates from more complex refining operations than those from direct distillation of hydrocarbons which may for example stem from cracking, hydrocracking and/or catalytic cracking processes and viscoreduction processes.

They may also contain novel sources of distillates, among which mention may notably be made of:

- the heaviest cuts from cracking and viscoreduction processes, concentrated in heavy paraffins, comprising more than 18 carbon atoms,
- synthetic distillates from the transformation of gas such as those from the Fischer Tropsch process,
- synthetic distillates resulting from the treatment of biomass of plant and/or animal origin, such as notably NexBTL,
- and oils and/or esters of plant and/or animal oils,
- or further biodiesel fuels of animal and/or plant origin.

These novel fuel bases may be used alone or as a mixture with standard petroleum middle distillates as a fuel base or as a domestic oil base; they generally comprise long paraffinic chains of 10 carbon atoms or more and preferentially from C₁₄ to C₃₀.

The copolymers as defined earlier with Mw comprised between 5,000 and 27,000 and Mn comprised between 1,500 and 22,000, preferably with Mw comprised between 5,000 and 25,000 and Mn comprised between 1,500 and 20,000 are particularly effective when they are incorporated into light middle distillates and/or with low sulfur content (typically less than 50 ppm) and/or with low initial crystallization temperature (which may typically range down to -20°C). By light middle distillates are meant distillates for which the content in n-paraffins having 24 carbon atoms or more ranges from 0 to less than about 0.7% by weight of the total fuel composition; the C₁₈-C₂₃ n-paraffins of which account for about 3 to about 5% of the total weight of the fuel and for which the mass ratio of C₁₈-C₂₃ n-paraffins over the C₂₄ and higher paraffins generally ranges from 10 to 35.

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

The copolymers may be added as such in the compositions of hydrocarbons or preferentially as concentrated solutions, in particular solutions containing from 50 to 80%, preferably from 60 to 70% by weight of copolymer(s) in a solvent, such as aliphatic or aromatic hydrocarbons, either alone or as 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 compositions of hydrocarbons comprise from 10 to 50,000 ppm by weight of at least one copolymer described above, optionally, preferably from 100 to 1,000 ppm and advantageously from 150 to 500 ppm.

In addition to the CFI additives or cold resistance additives described above, the compositions of hydrocarbons may also contain one or more other additives different from the copolymers according to the invention, selected from detergents, anti-corrosion agents, dispersants, de-emulsifiers, antifoaming agents, biocides, reodorants, procetane additives, friction modifiers, lubricity additives or unctuousness additives, combustion aids (combustion and soot catalytic promoters), agents improving the cloud point, the pour point, the limiting filterability temperature, antisedimentation agents, antiwear agents and/or agents modifying conductivity.

Among these additives, mention may particularly be made of:

- a) procetane additives, notably (but not as a limitation) selected from alkyl nitrates, preferably 2-ethyl hexyl nitrate, aroyl peroxides, preferably benzyl peroxide and alkyl peroxides, preferably tert-butyl peroxide;
- b) antifoaming additives, notably (but not as a limitation) selected from polysiloxanes, oxyalkylated polysiloxanes, and fatty acid amides from plant or animal oils. Examples of such additives are given in EP 861 882, EP 663 000, EP 736 590;

- c) detergent and/or anticorrosion additives, notably (but not as a limitation) selected from the group formed by amines, succinimides, alkenyl succinimides, polyalkylamines, polyalkyl polyamines and polyetheramines. Examples of such additives are given in EP 938 535;
- 5 d) lubricity additive or antiwear agent, notably (but not as a limitation) selected from the group formed by fatty acids and their ester or amide derivatives, notably glycerol monooleate, and mono- and poly-cyclic carboxylic acid derivatives. Examples of such additives are given in the following documents: EP 680 506, EP 860 494, WO 98/04656, EP 915 944, FR 2 772 783, FR 2 772 784.
- 10 e) cloud point additives, notably (but not as a limitation) selected from the group formed by long chain olefin/(meth)acrylic ester/maleimide terpolymers, and maleic/fumaric acid ester polymers. Examples of such additives are given in EP 71 513, EP 100 248, FR 2 528 051, FR 2 528 051, FR 2 528 423, EP 1 12 195, EP 1 727 58, EP 271 385, EP 291 367;
- 15 f) antisedimentation additives and/or paraffin dispersants notably (but not as a limitation) selected from the group formed by (meth)acrylic acid/polyamine-amidified alkyl (meth)acrylate copolymers, polyamine alkenyl succinimides, derivatives of phthalamic acid and dual-chain fatty amine derivatives; alkyl phenol resins. Examples of such additives are given in EP 261 959, EP 593 331, EP 674 689, EP 327 423, EP 512 889, EP 832 172; US 2005/0223631; US 5,998,530; WO 93/14178.
- 20 g) cold operability polyfunctional additives selected from the group formed by polymers based on olefin and alkenyl nitrates as described in EP 573 490;
- 25 h) other CFI additives improving cold resistance and filterability, such as EVA and/or EVP copolymers.

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

30 The improved cold resistance additives according to the invention may be added into the compositions of hydrocarbons inside the refinery, and/or be incorporated downstream from the refinery, optionally as a mixture with other additives, as a package or packet of additives.

Examples

35 In a tubular reactor, terpolymers of ethylene, vinyl acetate and ethyl-2 hexyl acrylate are synthesized by radical polymerization under high pressure (1,400 to

2,500 bars (140 to 250 MPa) and at a polymerization temperature from 200 to 280°C. The synthesis is carried out by using an aliphatic aldehyde (propanal) in order to control the molecular masses and by using peroxides as polymerization initiators. In the Table I below, are indicated the Mn and Mw of the synthesized terpolymers as well as their percentages of monomers.

Table 1: Characteristics of the synthesized polymers

Copolymer	[vinyl acetate]		[ethyl-2 hexyl acrylate]		Mn	Mw
	weight%	mol %	weight%	mol %		
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
12 (comparative)	27.6	13.7	20.7	4.8	11,180	13,255
13 (comparative)	28.4	14.1	20.4	4.7	12,100	14,372
16 (comparative)	19.3	9.6	21.5	5	4,498	8,443
18 (comparative)	36.7	17	3.5	0.8	10,000	11,000
17	19	10.4	30.8	7.9	12,000	15,000
19 (comparative)	28	11	0	0	3,000	8,000
20 (comparative)	30.5	12	0	0	4,000	9,000

The capability of improving the cold resistance of these terpolymers is evaluated by incorporating them in 2 distillates of the motor gasoil type, called GOM 1 and GOM 2, the characteristics of which are grouped in the Table 2 below.

Table 2: Characteristics of the fuels

ASTM D86 distillation			GOM 1	GOM 2
T90-T20	(°C)		129.6	100.4
PF-T90	(°C)		19.5	24.9
T95	(°C)		353.5	362.4
Cloud point	(°C)	NF EN 23015	-6	-4
LFT	(°C)	EN 116	-6	-7
Pour point	(°C)	NF T 60105	-15	-10
Paraffin content (mass %)	Chromatography		14.72	14.68
TCC	(°C)	IP 389	-6.2	-6.3
Sulfur content	(ppm)	EN ISO 20846	18.6	38

400 ppm by weight of each copolymer below are incorporated into the distillate of the motor gasoil type called GOM 1 and then the blocking index FBT (Filter Blocking Tendency) is measured according to the IP 387 standard. GOM 1 without any additive has an FBT blocking index of 1.01. It is seen that with the terpolymer 17 according to the invention, the blocking tendency of GOM 1 cannot be degraded, i.e. GOM 1

additived with 400 ppm of terpolymer has an FBT of less than 1.41. The results are shown in Table 3 below.

Table 3 : Blocking tendency (IP387) of GOM 1 additived with 400 ppm of different terpolymers.

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Added additive	Blocking index FBT (IP 387)
6 (comparative)	6.08
7 (comparative)	6.08
12 (comparative)	1.01
13 (comparative)	1.03
16 (comparative)	5.1
17	1.0
18 (comparative)	1.24
19 (comparative)	5.1
20 (comparative)	1.9

The cold resistance LFT efficiency of the terpolymers incorporated in GOM 1 and GOM 2 is measured at the concentration of 210 ppm; the results are grouped in Table 4.

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Table 4 : LFT efficiency tests on 2 low sulfur content gasoils.

Added additive	Measurements of TLF(°C) EN 116	
	GOM 1	GOM 2
	210 ppm	210 ppm
Without any additive	-6	-5
6		-15
7	-16	-15
12	-7	-4
13	-7	-5
17	-19	-
18	-7	-
19	-15	-
20	-16	-

It is seen that the terpolymer 17 according to the invention is the most efficient on the gasoil GOM 1. Moreover, from the results obtained in Table 3, it is seen that the terpolymer 17 added in an amount of 400 ppm in GOM 1 does not degrade the blocking tendency. This is not the case of the comparative terpolymers 6; 7; 16 and 18 according to WO 2005/054314, which strongly degrade the blocking tendency measured according to IP 387 and are not as LFT-efficient as the additive 17 of the invention.

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CLAIMS

1. The use as an additive improving cold resistance and filterability of fuels, of at least one copolymer comprising
 - 5 ▪ from 81 to 87% by moles of at least one α -olefin, preferably at least ethylene,
 - from 10.5 to less than 12% by moles of at least one vinyl ester, preferably at least vinyl acetate,
 - from 1 to 8.5% by moles of at least one α,β -unsaturated mono-carboxylic acid ester, preferably at least ethyl-2-hexyl acrylate.
- 10 2. The use as an additive improving cold resistance and filterability of fuels, of at least one copolymer according to claim 1 inscribed in a quadrilateral ABCD in which A, B, C and D represent the apices of said quadrilateral and correspond to the molar percentages of at least the vinyl ester and of at least the α,β -unsaturated mono-carboxylic acid ester:
 - 15 A: 12; 1
 - B: 12; 6
 - C: 10.5; 4
 - D: 10.5; 8.5.
- 20 3. The use as an additive improving cold resistance and filterability of fuels, of at least one copolymer according to claim 1 or 2 inscribed in a quadrilateral A_1BC_1D in which A_1 , B, C_1 and D represent the apices of said quadrilateral and correspond to the molar percentages of at least the vinyl ester and of at least the α,β -unsaturated mono-carboxylic acid ester:
 - 25 A_1 : 12; 2
 - B: 12; 6
 - C_1 : 10.5; 5
 - D: 10.5; 8.5.
- 30 4. The use according to any of claims 1 to 3 of at least one terpolymer comprising units derived from ethylene, units derived from vinyl acetate and units derived from ethyl-2-hexyl acrylate.
- 35 5. The use according to any of claims 1 to 4 of at least one copolymer of weight average molecular weight (Mw) measured by GPC comprised between 3,000 and 30,000, preferably 3,000 to 20,000 and a number average molecular weight (Mn) measured by GPC generally comprised between 1,000 and 20,000, preferably ranging from 1,500 to 15,000.

6. The use according to any of claims 1 to 5 of at least one copolymer as an additive improving cold resistance and filterability without degrading the blocking tendency of middle distillates such as diesel fuels, domestic oils for heating installations (FOD), kerosene, aviation fuels, heavy fuels.

5 7. The use according to any of claims 1 to 6 of at least one copolymer as an additive improving cold resistance and filterability of fuels, the sulfur content of which is less than 5,000 ppm, preferably less than 500 ppm, more preferentially less than 50 ppm, or even less than 10 ppm, and advantageously without any sulfur.

10 8. A composition of hydrocarbons comprising a majority amount of a middle distillate with a boiling temperature ranging from 100 to 500°C and a minority amount of at least one copolymer as defined in any of claims 1 to 7.

9. The composition according to claim 8, characterized in that it contains from 0 to 100% by weight of biodiesel fuel of animal and/or plant origin.

15 10. The composition according to claim 8 or 9, characterized in that it is selected from diesel fuels, domestic oils for heating installations (FOD), kerosene, aviation fuels, heavy fuels.

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

20 12. The composition according to any of claims 8 to 11, characterized in that it comprises one or several other additives different from the copolymers according to the invention, selected from detergents, anticorrosion agents, dispersants, de-emulsifiers, antifoaming agents, biocides, reodorants, procetane additives, friction modifiers, lubricity additives or unctuousness additives, combustion aids (combustion and soot
25 catalytic promoters), agents improving the cloud point, the pour point, the limiting filterability temperature, antisedimentation agents, antiwear agents and/or agents modifying conductivity.