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(54) Title: TURBINE FUEL COMPOSITION EXHIBITING IMPROVED COLD PROPERTIES

(54) Bezeichnung: TURBINENKRAFTSTOFFZUSAMMENSETZUNGEN MIT VERBESSERTEN KÄLTEEIGENSCHAFTEN

(57) Abstract: The invention relates to using polymers containing an α -olefin, an unsaturated α,β carboxylic acid ester and optionally a carboxylic acid alkenyl ester which are incorporated by polymerisation in the form of turbine fuel additives, in particular for improving the cold properties thereof. Turbine fuels containing said polymers and additive packets containing polymers such type polymers are also disclosed.

(57) Zusammenfassung: Die Erfindung betrifft die Verwendung von Polymeren, die ein α -Olefin, einen Ester einer α,β -ungesättigten Carbonsäure und gegebenenfalls einen Alkenylester einer Carbonsäure einpolymerisiert enthalten, als Additiv für Turbinenkraftstoffe und insbesondere als Kaltfließverbesserer für Turbinenkraftstoffe; die mit diesen Polymeren additvierten Turbinenkraftstoffe; sowie Additivpakete, enthaltend derartige Copolymere.

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Turbine fuel composition exhibiting improved cold properties

The invention relates to the use of polymers which comprise, in copolymerized form, an α -olefin, an ester of an α,β -unsaturated carboxylic acid and, if appropriate, an alkenyl ester of a carboxylic acid as an additive for turbine fuels and in particular as a cold flow improver for turbine fuels, to the turbine fuels additized with these polymers, and to additive packages comprising such copolymers.

State of the art

Turbine fuels, which are also known as aviation turbine fuels, jet fuels, aviation fuels or turbo fuels, have to satisfy high demands on their cold properties owing to their use in aviation and the associated temperature conditions. For instance, the freezing point of the turbine fuel has to be sufficiently low that the fuel flow is not impaired under the temperature conditions prevailing at great heights and also passes through fuel filters without difficulty. In the case of turbine fuels, the freezing point refers to that temperature at which precipitated hydrocarbon crystals which have formed by cooling beforehand dissolve again fully. Depending on the field of use, the freezing point in civil and military aviation must not exceed -40°C or about -50°C . When the temperature goes below the freezing point, relatively long-chain paraffins crystallize out and form large, platelet-shaped wax crystals. These wax crystals have a spongelike structure and lead to inclusion of other fuel constituents in the crystal structure. The occurrence of these crystals leads to the fuel being able to pass only slowly through small orifices and filters. Moreover, the viscosity of the fuel increases, as a result of which the fuel flow is worsened. At temperatures below the pour point (PP), the fuel finally no longer flows.

At present, the freezing point of turbine fuels is adjusted in particular by distillative measures in the refineries, for example by the reduction of the proportion of high boiler fractions which also comprise wax fractions. However, a disadvantage in this context is the resulting increasing cost of the turbine fuel.

Chemical measures for freezing point depression are also known. For instance, EP-A-1357168 describes a turbine fuel composition which, in addition to a turbine fuel, comprises one of the following additives: copolymers of ethylene with at least one unsaturated ester which is selected from vinyl esters having at least 5 carbon atoms, alkyl (meth)acrylates, dialkyl fumarates and dialkyl maleates; ethylene/alkene copolymers; ethylene/vinyl acetate copolymers comprising less than 15 mol% of vinyl acetate; nucleators; waxes; alkylphenol/formaldehyde condensates; comb polymers; and organic nitrogen compounds. These additives are intended to keep turbine fuels

additized therewith free-flowing even below the freezing point specified in their specification.

WO 01/62874 describes a composition which, in addition to a turbine fuel, comprises additives which are selected from the reaction products of alkanolamines with long-chain-substituted acylating agents; phenol/aldehyde condensates; specific aromatic systems; and ethylene/vinyl acetate copolymers. These additives are intended to lower the freezing point of the turbine fuel additized therewith.

DE 1250188 describes copolymers of ethylene and an acrylic ester with at least 7 carbon atoms in the ester molecule, which is said to lower the pour point of heating oils, diesel fuels and jet fuels. In the examples, however, no jet fuels are used.

There is therefore still a need for additives which further improve the cold properties of turbine fuels.

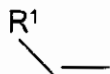
Brief description of the invention

It was accordingly an object of the present invention to provide novel additives of this type.

Surprisingly, this object is achieved by virtue of the unexpected observation that polymers which comprise, in copolymerized form, an α -olefin, an ester of an α,β -unsaturated carboxylic acid and, if appropriate, an alkenyl carboxylate improve the cold properties, in particular the cold flow properties, of turbine fuels and also have better performance than the ethylene/vinyl acetate copolymers described in the prior art.

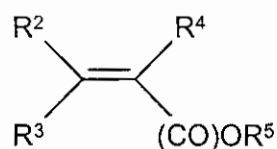
The invention accordingly relates firstly to the use of a polymer which comprises, in copolymerized form, an α -olefin, an ester of an α,β -unsaturated carboxylic acid and, if appropriate, an alkenyl ester of a carboxylic acid as an additive for turbine fuels. In particular, the polymers used comprise, in copolymerized form, the ester of the α,β -unsaturated carboxylic acid and the alkenyl ester present if appropriate, in random distribution. The polymer is preferably a binary polymer which is composed substantially of the α -olefin and the ester of an α,β -unsaturated carboxylic acid, or is alternatively preferably a terpolymer which is composed substantially of the three aforementioned monomers.

Preference is given to using polymers which are composed of monomers comprising the monomers M1, M2 and, if appropriate, M3, where M1, M2 and M3 have the following general formulae

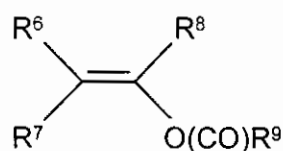


M1

3



M2



M3

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in which

10 R^1 is H or $\text{C}_1\text{-C}_{40}$ -hydrocarbyl;

R^2 , R^3 and R^4 are each independently H or $\text{C}_1\text{-C}_4$ -alkyl;

R^5 is $\text{C}_1\text{-C}_{20}$ -hydrocarbyl;

15

R^6 , R^7 and R^8 are each independently H or $\text{C}_1\text{-C}_4$ -alkyl; and

R^9 is $\text{C}_1\text{-C}_{19}$ -hydrocarbyl.

20 Detailed description of the invention

Unless stated otherwise, the following general definitions apply in the context of the present invention:

25 $\text{C}_1\text{-C}_{40}$ -Hydrocarbyl is a hydrocarbon radical having 1 to 40 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular $\text{C}_1\text{-C}_{40}$ -hydrocarbyl is $\text{C}_1\text{-C}_{40}$ -alkyl. $\text{C}_1\text{-C}_{40}$ -alkyl is a linear or branched alkyl radical having 1 to 40 carbon atoms. Examples of this are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, heptyl, octyl, 2-ethylhexyl, neooctyl, nonyl, neononyl, decyl, 2-propylheptyl, neodecyl, undecyl, neoundecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, hencosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, squalyl, their constitutional isomers, higher homologs and the accompanying constitutional isomers.

35

The same applies to C_1 - C_{20} -hydrocarbyl radicals, i.e. they are a hydrocarbon radical having from 1 to 20 carbon atoms. They are preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C_1 - C_{20} -hydrocarbyl is C_1 - C_{20} -alkyl. C_1 - C_{20} -alkyl is a linear or branched alkyl radical having 1 to 20 carbon atoms.

- 5 Examples of this are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, heptyl, octyl, 2-ethylhexyl, neooctyl, nonyl, neononyl, decyl, 2-propylheptyl, neodecyl, undecyl, neoundecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl and their constitutional isomers.

10

C_1 - C_{19} -Hydrocarbyl is a hydrocarbon radical having from 1 to 19 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C_1 - C_{19} -hydrocarbyl is C_1 - C_{19} -alkyl. C_1 - C_{19} -alkyl is a linear or branched alkyl radical having 1 to 19 carbon atoms. Examples of this are methyl, ethyl, n-propyl,

15 isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, heptyl, octyl, 2-ethylhexyl, neooctyl, nonyl, neononyl, decyl, 2-propylheptyl, neodecyl, undecyl, neoundecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and their constitutional isomers.

20

C_1 - C_{10} -Hydrocarbyl is a hydrocarbon radical having from 1 to 10 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C_1 - C_{10} -hydrocarbyl is C_1 - C_{10} -alkyl. C_1 - C_{10} -alkyl is a linear or branched alkyl radical having 1 to 10 carbon atoms. Examples of this are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl,

25 heptyl, octyl, 2-ethylhexyl, neooctyl, nonyl, neononyl, decyl, 2-propylheptyl, neodecyl and their constitutional isomers.

30

C_1 - C_9 -Hydrocarbyl is a hydrocarbon radical having from 1 to 9 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C_1 - C_9 -hydrocarbyl is C_1 - C_9 -alkyl. C_1 - C_9 -Alkyl is a linear or branched alkyl radical having from 1 to 9 carbon atoms. Examples of this are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, heptyl, octyl, 2-ethylhexyl, neooctyl, nonyl, neononyl and their constitutional isomers.

35

C_5 - C_{16} -Hydrocarbyl is a hydrocarbon radical having from 5 to 16 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C_5 - C_{16} -hydrocarbyl is C_5 - C_{16} -alkyl. C_5 - C_{16} -Alkyl is a linear or branched alkyl radical having from 5 to 16 carbon atoms. Examples of this are pentyl, neopentyl, isopentyl, hexyl, isohexyl, heptyl, octyl, 2-ethylhexyl, neooctyl, nonyl, neononyl,

40 isononyl, decyl, 2-propylheptyl, neodecyl, undecyl, neoundecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl and their constitutional isomers.

C₈-C₁₂-Hydrocarbyl is a hydrocarbon radical having from 8 to 12 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₈-C₁₂-hydrocarbyl is C₈-C₁₂-alkyl. C₈-C₁₂-Alkyl is a linear or branched alkyl radical having from 8 to 12 carbon atoms. Examples of this are octyl, 2-ethylhexyl, 5 neo-octyl, nonyl, neononyl, isononyl, decyl, 2-propylheptyl, neodecyl, undecyl, neoundecyl, dodecyl and their constitutional isomers.

C₈-C₁₄-Hydrocarbyl is a hydrocarbon radical having from 8 to 14 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. 10 In particular, C₈-C₁₄-hydrocarbyl is C₈-C₁₄-alkyl. C₈-C₁₄-Alkyl is a linear or branched alkyl radical having from 8 to 14 carbon atoms. In addition to the alkyl radicals mentioned above for C₈-C₁₂-alkyl, examples are tridecyl und tetradecyl and their constitutional isomers.

C₈-C₁₆-Hydrocarbyl is a hydrocarbon radical having from 8 to 16 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₈-C₁₆-hydrocarbyl is C₈-C₁₆-alkyl. C₈-C₁₆-Alkyl is a linear or branched alkyl radical having from 8 to 16 carbon atoms. In addition to the alkyl radicals 20 mentioned above for C₈-C₁₄-alkyl, examples are pentadecyl und hexadecyl and their constitutional isomers.

C₈-C₂₀-Hydrocarbyl is a hydrocarbon radical having from 8 to 20 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₈-C₂₀-hydrocarbyl is C₈-C₂₀-alkyl. C₈-C₂₀-Alkyl is a linear or branched 25 alkyl radical having from 8 to 20 carbon atoms. In addition to the alkyl radicals mentioned above for C₈-C₁₆-alkyl, examples are heptadecyl, octadecyl, nonadecyl und eicosanyl and their constitutional isomers.

C₆-C₁₄-Hydrocarbyl is a hydrocarbon radical having from 6 to 14 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. 30 In particular, C₆-C₁₄-hydrocarbyl is C₆-C₁₄-alkyl. C₆-C₁₄-Alkyl is a linear or branched alkyl radical having from 6 to 14 carbon atoms. In addition to the alkyl radicals mentioned above for C₈-C₁₄-alkyl, examples are hexyl und heptyl and their constitutional isomers.

C₆-C₁₆-Hydrocarbyl is a hydrocarbon radical having from 6 to 16 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₆-C₁₆-hydrocarbyl is C₆-C₁₆-alkyl. C₆-C₁₆-Alkyl is a linear or branched 35 alkyl radical having from 6 to 16 carbon atoms. In addition to the alkyl radicals mentioned above for C₈-C₁₆-alkyl, examples are hexyl und heptyl and their constitutional isomers. 40

- C₆-C₂₀-Hydrocarbyl is a hydrocarbon radical having from 6 to 20 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₆-C₂₀-hydrocarbyl is C₆-C₂₀-alkyl. C₆-C₂₀-Alkyl is a linear or branched alkyl radical having from 6 to 20 carbon atoms. In addition to the alkyl radicals mentioned above for C₆-C₂₀-alkyl, examples are hexyl und heptyl and their constitutional isomers.
- C₅-C₂₀-Hydrocarbyl is a hydrocarbon radical having from 5 to 20 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₅-C₂₀-hydrocarbyl is C₅-C₂₀-alkyl. C₅-C₂₀-Alkyl is a linear or branched alkyl radical having from 5 to 20 carbon atoms. In addition to the alkyl radicals mentioned above for C₆-C₂₀-alkyl, examples are pentyl and its constitutional isomers.
- C₄-C₁₄-Hydrocarbyl is a hydrocarbon radical having from 4 to 14 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₄-C₁₄-hydrocarbyl is C₄-C₁₄-alkyl. C₄-C₁₄-Alkyl is a linear or branched alkyl radical having from 4 to 14 carbon atoms. In addition to the alkyl radicals mentioned above for C₆-C₁₄-alkyl, examples are pentyl and its constitutional isomers, and also n-butyl, sec-butyl, isobutyl und tert-butyl.
- C₄-C₁₆-Hydrocarbyl is a hydrocarbon radical having from 4 to 16 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₄-C₁₆-hydrocarbyl is C₄-C₁₆-alkyl. C₄-C₁₆-Alkyl is a linear or branched alkyl radical having from 4 to 16 carbon atoms. In addition to the alkyl radicals mentioned above for C₆-C₁₆-alkyl, examples are pentyl and its constitutional isomers, and also n-butyl, sec-butyl, isobutyl und tert-butyl.
- C₄-C₂₀-Hydrocarbyl is a hydrocarbon radical having from 4 to 20 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₄-C₂₀-hydrocarbyl is C₄-C₂₀-alkyl. C₄-C₂₀-Alkyl is a linear or branched alkyl radical having from 4 to 20 carbon atoms. In addition to the alkyl radicals mentioned above for C₅-C₂₀-alkyl, examples are n-butyl, sec-butyl, isobutyl und tert-butyl.
- C₁-C₄-Hydrocarbyl is a hydrocarbon radical having from 1 to 4 carbon atoms. It is preferably an aliphatic hydrocarbon radical such as alkyl, alkenyl, alkadienyl or alkynyl. In particular, C₁-C₄-hydrocarbyl is C₁-C₄-alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl and tert-butyl.

The hydrocarbonyl radicals, for example the alkyl radicals, may be unsubstituted or mono- or polysubstituted. Suitable substituents are, for example, OH, C₁-C₄-alkoxy, NR¹¹R¹² (R¹¹ and R¹² are each independently H or C₁-C₄-alkyl) or carbonyl (COR¹¹). However, they are preferably unsubstituted.

5

C₁-C₄-Alkoxy is a C₁-C₄-alkyl radical bonded via an oxygen atom. Examples thereof are methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, 2-butoxy, isobutoxy and tert-butoxy.

10

C₁-C₄-Alkanol is a C₁-C₄-alkyl radical which is substituted by from 1 to 3 hydroxyl groups on different carbon atoms. C₁-C₁₀-Alkanol is a C₁-C₁₀-alkyl radical which is substituted by from 1 to 6 hydroxyl groups on different carbon atoms. C₁-C₂₀-Alkanol is a C₁-C₂₀-alkyl radical which is substituted by from 1 to 6 hydroxyl groups on different carbon atoms. C₁-C₄₀-Alkanol is a C₁-C₄₀-alkyl radical which is substituted by from 1 to 6 hydroxyl groups on different carbon atoms. Examples of C₁-C₄-alkanols are

15

methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, ethylene glycol, propylene glycol and glycerol.

20

C₁-C₁₀-Alkanol is additionally, for example, pentanol, hexanol, heptanol, octanol, 2-ethylhexanol, nonanol, decanol, their constitutional isomers, and also erythritol, pentaerythritol and sorbitol.

25

C₁-C₂₀-Alkanol is additionally, for example, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, nonadecanol and eicosanol and their constitutional isomers.

a) Polymers used in accordance with the invention

30

The remarks made below on the preferred embodiments of the polymers used in accordance with the invention and of the monomers from which they are formed apply both alone and in combination.

The polymers used in accordance with the invention may comprise the monomers M1, M2 and M3 in the following molar fractions ($M_x/(M1+M2+M3)$) in the polymer:

35

M1: preferably from 0.60 to 0.99;
M2: preferably from 0.01 to 0.40;
M3: preferably from 0 to 0.20.

40

In the case that the polymers used in accordance with the invention do not comprise the monomer M3 in copolymerized form:

M1: preferably from 0.60 to 0.99, more preferably from 0.7 to 0.95, in particular from 0.75 to 0.85;

M2: preferably from 0.01 to 0.6, more preferably from 0.05 to 0.3, in particular from 0.05 to 0.25.

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In the case that the polymers used in accordance with the invention comprise the monomer M3 in copolymerized form:

10 M1: preferably from 0.60 to 0.98, more preferably from 0.7 to 0.95, in particular from 0.75 to 0.9;

M2: preferably from 0.01 to 0.20, more preferably from 0.01 to 0.17, in particular from 0.015 to 0.16;

M3: preferably from 0.01 to 0.20, more preferably from 0.02 to 0.15, in particular from 0.03 to 0.12, especially from 0.03 to 0.11.

15

The monomers M1 are preferably monoalkenes with a terminal double bond, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, their constitutional isomers and also the higher monounsaturated homologs having up to 40 carbon atoms.

20

In the monomers M1, R^1 is preferably H or C_1 - C_{20} -hydrocarbyl, more preferably H or C_1 - C_{10} -hydrocarbyl, and even more preferably H or C_1 - C_4 -hydrocarbyl. Hydrocarbyl is preferably alkyl. In particular, R^1 is H, methyl or ethyl. Accordingly, the monomer M1 is in particular ethylene, propylene or 1-butene. R^1 is especially H, i.e. M1 is especially
25 ethylene.

25

In the monomer M2, the R^2 , R^3 and R^4 radicals are preferably each H or methyl. More preferably, two of the R^2 , R^3 and R^4 radicals are each H and the other radical is H or methyl. In particular, all three R^2 , R^3 and R^4 are H.

30

Accordingly, the monomer M2 is preferably the esters of α,β -unsaturated carboxylic acids which are selected from acrylic acid, methacrylic acid, crotonic acid and isocrotonic acid, more preferably from acrylic acid and methacrylic acid, and in particular acrylic acid.

35

Examples of such preferred α,β -unsaturated carboxylic acids M2 include: acrylic esters of C_1 - C_{20} -alkanols, such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, n-pentyl acrylate, neopentyl acrylate, isopentyl acrylate, hexyl acrylate, isohexyl acrylate, heptyl acrylate, octyl acrylate, neooctyl acrylate, 2-ethylhexyl acrylate, nonyl acrylate, neononyl
40 acrylate, decyl acrylate, neodecyl acrylate, 2-propylheptyl acrylate, lauryl acrylate,

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palmityl acrylate and stearyl acrylate; and also the corresponding methacrylic, crotonic and isocrotonic esters, preference being given to the acrylates (acrylic esters).

R^5 is C_1 - C_{20} -hydrocarbyl, preferably C_1 - C_{20} -alkyl.

5

In the case that the polymer used in accordance with the invention comprises no alkenyl ester and especially no monomer M3, R^5 in a preferred embodiment of the invention is a hydrocarbyl radical having at least 5 carbon atoms, for example C_5 - C_{20} -hydrocarbyl. R^5 is more preferably a hydrocarbyl radical having at least 6 carbon atoms, for example C_6 - C_{20} -hydrocarbyl, preferably C_6 - C_{16} -hydrocarbyl or more preferably C_6 - C_{14} -hydrocarbyl. In particular, R^5 is a hydrocarbyl radical having at least 8 carbon atoms, for example C_8 - C_{20} -hydrocarbyl, preferably C_8 - C_{16} -hydrocarbyl and more preferably C_8 - C_{14} -hydrocarbyl. R^5 is especially C_8 - C_{12} -hydrocarbyl. Hydrocarbyl is preferably alkyl. Accordingly, R^5 in this case is preferably an alkyl radical having at least 5 carbon atoms, for example C_5 - C_{20} -alkyl. R^5 is more preferably an alkyl radical having at least 6 carbon atoms, for example C_6 - C_{20} -alkyl, preferably C_6 - C_{16} -alkyl or more preferably C_6 - C_{14} -alkyl. In particular, R^5 is an alkyl radical having at least 8 carbon atoms, for example C_8 - C_{20} -alkyl, preferably C_8 - C_{16} -alkyl and more preferably C_8 - C_{14} -alkyl. R^5 is especially C_8 - C_{12} -alkyl.

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In the case that the polymer used in accordance with the invention comprises, in copolymerized form, an alkenyl ester and especially the monomer M3, R^5 in a preferred embodiment of the invention is C_4 - C_{20} -hydrocarbyl, for example C_4 - C_{18} -hydrocarbyl or C_4 - C_{16} -hydrocarbyl or C_4 - C_{14} -hydrocarbyl or C_4 - C_{12} -hydrocarbyl, more preferably C_5 - C_{20} -hydrocarbyl, for example C_5 - C_{18} -hydrocarbyl or C_5 - C_{16} -hydrocarbyl or C_5 - C_{14} -hydrocarbyl or C_5 - C_{12} -hydrocarbyl, even more preferably C_6 - C_{20} -hydrocarbyl, for example C_6 - C_{18} -hydrocarbyl or C_6 - C_{16} -hydrocarbyl or C_6 - C_{14} -hydrocarbyl or C_6 - C_{12} -hydrocarbyl, and in particular C_8 - C_{20} -hydrocarbyl, for example C_8 - C_{18} -hydrocarbyl or C_8 - C_{16} -hydrocarbyl or C_8 - C_{14} -hydrocarbyl or C_8 - C_{12} -hydrocarbyl. R^5 is especially C_8 - C_{12} -hydrocarbyl. Hydrocarbyl is preferably alkyl. Accordingly, R^5 in this case is preferably C_4 - C_{20} -alkyl, for example C_4 - C_{18} -alkyl or C_4 - C_{16} -alkyl or C_4 - C_{14} -alkyl or C_4 - C_{12} -alkyl, more preferably C_5 - C_{20} -alkyl, for example C_5 - C_{18} -alkyl or C_5 - C_{16} -alkyl or C_5 - C_{14} -alkyl or C_5 - C_{12} -alkyl, even more preferably C_6 - C_{20} -alkyl, for example C_6 - C_{18} -alkyl or C_6 - C_{16} -alkyl or C_6 - C_{14} -alkyl or C_6 - C_{12} -alkyl, and in particular C_8 - C_{20} -alkyl, for example C_8 - C_{18} -alkyl or C_8 - C_{16} -alkyl or C_8 - C_{14} -alkyl or C_8 - C_{12} -alkyl. R^5 is especially C_8 - C_{12} -alkyl.

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Irrespective of their chain length and irrespective of whether the polymer does or does not comprise an alkenyl ester, especially the monomer M3, in copolymerized form, preferred alkyl radicals R^5 are preferably linear or lightly branched. Lightly branched means that, in the case of n carbon atoms in the longest carbon chain of the alkyl radical, a maximum of $(n-3)$ branches are present. Examples of such lightly branched

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alkyl radicals are isopentyl $-(\text{CH}_2)_2\text{-CH}(\text{CH}_3)_2$, isohexyl $-(\text{CH}_2)_3\text{-CH}(\text{CH}_3)_2$, 2-ethylhexyl, isononyl (3,5,5-dimethylhexyl), 2-propylheptyl and the like. The alkyl radical R^5 is more preferably linear or comprises at most 2 branches. In particular, it is linear or comprises one branch.

5

Irrespective of whether the polymer comprises, in copolymerized form, an alkenyl ester and especially the monomer M3, R^5 is in particular n-octyl, 2-ethylhexyl, n-nonyl, isononyl, n-decyl, 2-propylheptyl, n-undecyl, lauryl (= n-dodecyl) or n-tridecyl, and especially 2-ethylhexyl or lauryl.

10

More preferably, the monomer M2 is selected from octyl acrylate, 2-ethylhexyl acrylate, n-nonyl acrylate, isononyl acrylate, n-decyl acrylate, 2-propylheptyl acrylate, n-undecyl acrylate, lauryl acrylate, and n-tridecyl acrylate. In particular, the monomer M2 is selected from 2-ethylhexyl acrylate and lauryl acrylate. It is especially 2-ethylhexyl acrylate.

15

The monomer M3 is the alkenyl ester, for example a vinyl or propenyl ester, of an aliphatic carboxylic acid, which may be unsaturated or preferably saturated.

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Examples of the alkenyl esters, in particular of the vinyl or propenyl esters, of an aliphatic carboxylic acid which may be unsaturated or preferably saturated are the vinyl or propenyl esters of aliphatic $\text{C}_2\text{-C}_{20}$ -carboxylic acids such as acetic acid, propionic acid, butyric acid, valeric acid, isovaleric acid, pivalic acid, neopentanoic acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, 2-ethylhexanoic acid, versatic (VersaticTM acid), in particular neononanoic acid and neodecanoic acid (e.g. VeoVaTM = vinyl ester of versatic acid), capric acid, neoundecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, nonadecanoic acid and arachic acid. Preference is given to the vinyl esters of the carboxylic acids mentioned.

30

In the monomer M3, R^6 , R^7 and R^8 are each independently preferably H or methyl, and more preferably H.

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R^9 is preferably $\text{C}_1\text{-C}_9$ -hydrocarbyl. Hydrocarbyl is preferably alkyl. R^9 is more preferably ethyl or methyl, and in particular methyl.

The monomer M3 is more preferably vinyl acetate.

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In a specific embodiment of the invention, the copolymer used in accordance with the invention comprises the monomer M3 in copolymerized form and is thus formed from monomers comprising the monomers M1, M2 and M3.

The polymers used in accordance with the invention are preferably formed substantially from the above-defined monomers M1, M2 and, if appropriate, M3. As a result of the preparation, small fractions of a compound used as a regulator (chain terminator) may be present if appropriate.

The polymers used in accordance with the invention also have a number-average molecular weight M_n in the range from about 1000 to 20 000, more preferably from 1000 to 10 000, in particular from 1500 to 6000 and especially from 1500 to 5000.

The polymers may also have a weight-average molecular weight M_w of from 1000 to 30 000, in particular from 2000 to 20 000, and/or an M_w/M_n ratio of from 1.5 to 5.0, preferably from 1.8 to 4.0 and in particular from 1.9 to 3.5.

The number-average and weight-average molecular weights M_n and M_w relate to values obtained by means of gel permeation chromatography (GPC).

The viscosity of such polymers (determined to Ubbelohde DIN 51562) is from about 5 to 25 000 mm²/s, preferably from about 10 to 1000 mm²/s, in particular from about 50 to 700 mm²/s, in each case at a temperature of about 120°C.

Polymers used with preference are selected from the copolymers of ethylene and C₅-C₂₀-alkyl acrylates, e.g. C₅-C₁₈-alkyl acrylates or C₅-C₁₆-alkyl acrylates or C₅-C₁₄-alkyl acrylates, and the copolymers of ethylene, vinyl acetate and C₅-C₂₀-alkyl acrylates, e.g. C₅-C₁₈-alkyl acrylates or C₅-C₁₆-alkyl acrylates or C₅-C₁₄-alkyl acrylates. Polymers used with particular preference are selected from the copolymers of ethylene and C₆-C₂₀-alkyl acrylates, e.g. C₆-C₁₈-alkyl acrylates or C₆-C₁₆-alkyl acrylates or C₆-C₁₄-alkyl acrylates, and the copolymers of ethylene, vinyl acetate and C₆-C₂₀-alkyl acrylates, e.g. C₆-C₁₈-alkyl acrylates or C₆-C₁₆-alkyl acrylates or C₆-C₁₄-alkyl acrylates. Polymers used with even greater preference are selected from the copolymers of ethylene and C₈-C₂₀-alkyl acrylates, e.g. C₈-C₁₈-alkyl acrylates or C₈-C₁₆-alkyl acrylates or C₈-C₁₄-alkyl acrylates or C₈-C₁₂-alkyl acrylates, and the copolymers of ethylene, vinyl acetate and C₈-C₂₀-alkyl acrylates, e.g. C₈-C₁₈-alkyl acrylates or C₈-C₁₆-alkyl acrylates or C₈-C₁₄-alkyl acrylates or C₈-C₁₂-alkyl acrylates.

In particular, the polymers used are selected from ethylene / 2-ethylhexyl acrylate polymers, ethylene / 2-ethylhexyl acrylate / vinyl acetate polymers and ethylene / lauryl acrylate / vinyl acetate polymers.

Based on a polymer composed of ethylene, 2-ethylhexyl acrylate (EHA) and vinyl acetate (VAC), the proportion by weight of the monomers is:

EHA: 4 – 80% by weight, preferably from 5 to 62% by weight, in particular from 7 to 47% by weight

VAC: 1 – 42% by weight, preferably from 1 to 30% by weight, in particular from about 1 to 25% by weight, especially from 1 to 20% by weight

The difference to 100% by weight corresponds to the fraction of ethylene.

Preference is given to using the polymers as cold flow improvers. Particular preference is given to using them to lower the pour point (PP) of the turbine fuel additized therewith.

The above-described polymers are used alone or in combination with other such polymers in amounts which are sufficient to exhibit an effect on the cold properties, in particular on the cold flow performance of the turbine fuel additized therewith.

The polymers used in accordance with the invention may also be used in combination with further conventional cold flow improvers and/or further turbine fuel additives.

b) Preparation of the polymers

The polymers used in accordance with the invention are prepared by processes known per se. Preference is given to preparing them by free-radical polymerization, in particular high-pressure polymerization, of the monomers M1, M2 and, if appropriate, M3. Such processes for direct free-radical high-pressure copolymerization of unsaturated compounds are known from the prior art (cf., for example, *Ullmann's Encyclopedia of Industrial Chemistry* 5th edition, "Waxes", Vol. A 28, p. 146 ff., VCH Weinheim, Basle, Cambridge, New York, Tokyo, 1996; and also US 3,627,838; DE-A 2515805; DE-A 3141507; EP-A 0007590).

The copolymers which are to be used in accordance with the invention and are obtainable by the polymerization process are preferably formed substantially from the above-defined monomers M1, M2 and, if appropriate, M3. As a result of the preparation, small proportions of a compound used as a regulator (chain terminator) may be present if appropriate.

The copolymers are preferably prepared in stirred high-pressure autoclaves or in high-pressure stirred reactors or combinations of the two. In this apparatus, the length/diameter ratio varies predominantly within ranges of from 5:1 to 30:1, preferably 10:1 to 20:1.

Suitable pressure conditions for the polymerization are from 1000 to 3000 bar, preferably from 1500 to 2000 bar. The reaction temperatures are, for example, in the range from 160 to 320°C, preferably in the range from 200 to 280°C.

- 5 The regulator used to control the molecular weight of the copolymers is, for example, an aliphatic aldehyde or an aliphatic ketone of the general formula I



or mixtures thereof.

In the formula, the R^a and R^b radicals are the same or different and are selected from

- 15 - hydrogen;
 - C_1 - C_6 -alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl; more preferably C_1 - C_4 -alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl;
 20 - C_3 - C_{12} -cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl and cyclododecyl; preference is given to cyclopentyl, cyclohexyl and cycloheptyl.

The R^a and R^b radicals may also be covalently bonded to one another to form a 4- to
 25 13-membered ring. For example, R^a and R^b together may form the following alkylene groups: $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$, $-(CH_2)_7-$, $-CH(CH_3)-CH_2-CH_2-CH(CH_3)-$ or $-CH(CH_3)-CH_2-CH_2-CH_2-CH(CH_3)-$.

Very particular preference is given to the use of propionaldehyde or ethyl methyl
 30 ketone as a regulator.

Further very suitable regulators are unbranched aliphatic hydrocarbons, for example propane, or branched aliphatic hydrocarbons having tertiary hydrogen atoms, for example isobutane, isopentane, isooctane or isododecane (2,2,4,6,6-
 35 pentamethylheptane). Further additional regulators which can be used are higher olefins, for example propylene.

Preference is likewise given to mixtures of the above regulators with hydrogen or hydrogen alone.

The amount of regulator used corresponds to the amounts customary for the high-pressure polymerization process.

Useful initiators for the free-radical polymerization are the customary free-radical initiators, for example organic peroxides, oxygen or azo compounds. Also suitable are mixtures of a plurality of free-radical initiators. Useful free-radical initiators include, for example, one or more peroxides selected from the following commercially obtainable substances:

- didecanoyl peroxide, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane, tert-amyl peroxy-2-ethylhexanoate, dibenzoyl peroxide, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethyl acetate, tert-butyl peroxydiethyl isobutyrate, 1,4-di(tert-butylperoxycarbo)cyclohexane as an isomer mixture, tert-butyl perisononanoate, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(tert-butylperoxy)cyclohexane, methyl isobutyl ketone peroxide, tert-butyl peroxyisopropyl carbonate, 2,2-di-tert-butylperoxy)butane or tert-butyl peroxyacetate;
- tert-butyl peroxybenzoate, di-tert-amyl peroxide, dicumyl peroxide, the isomeric di(tert-butylperoxyisopropyl)benzenes, 2,5-dimethyl-2,5-di-tert-butylperoxyhexane, tert-butyl cumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hex-3-yne, di-tert-butyl peroxide, 1,3-diisopropyl monohydroperoxide, cumene hydroperoxide or tert-butyl hydroperoxide; or
- dimeric or trimeric ketone peroxides, as disclosed, for example, by EP-A-0 813 550.

Particularly suitable peroxides are di-tert-butyl peroxide, tert-butyl peroxy-pivalate, tert-butyl peroxyisononanoate or dibenzoyl peroxide or mixtures thereof. An example of an azo compound is azobisisobutyronitrile (AIBN). The free-radical initiators are used in amounts customary for polymerizations.

In a preferred method, the polymers to be used in accordance with the invention are prepared in such a way that a mixture of the monomers M1, M2 and, if appropriate, M3 is passed in the presence of the regulator at a temperature within the range from about 20 to 50°C, for example of 30°C, preferably continuously, through a stirred autoclave which is maintained at a pressure in the range from about 1500 to 2000 bar, for example of about 1700 bar. The preferably continuous addition of initiator which is generally dissolved in a suitable solvent, for example isododecane, keeps the temperature in the reactor at the desired reaction temperature, for example at from 200 to 250°C. The polymer obtained after decompression of the reaction mixture is then isolated in a customary manner.

Modifications to this method are of course possible and can be undertaken by those skilled in the art without unreasonable effort. For example, the comonomers and the

regulator can be separately metered into the reaction mixture, or the reaction temperature can be varied during the process, to name only a few examples.

c) Turbine fuel compositions

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The invention further relates to turbine fuel compositions comprising a major proportion by weight of a turbine fuel and a minor proportion by weight of at least one polymer used in accordance with the invention, as defined above.

- 10 In the context of the present invention, the polymers used in accordance with the invention may be used in combination with further conventional cold flow improvers and/or further turbine fuel additives.

- 15 The turbine fuel composition comprises a majority of a liquid turbine fuel, which may be a turbine fuel customary in civil or military aviation. These include, for example, fuels of the designations Jet A, Jet A-1, Jet B, JP-4, JP-5, JP-7, JP-8 and JP-8+100. Jet A and Jet A-1 are commercially obtainable turbine fuel specifications based on kerosine. The accompanying standards are ASTM D 1655 and DEF STAN 91-91. According to their particular specification, Jet A and Jet A-1 have maximum freezing points of,
20 respectively, -40°C and -47°C. Jet B is a fuel which has been further fractionated and is based on naphtha and kerosine fractions. JP-4 is equivalent to Jet B. JP 4, JP-5, JP-7, JP-8 and JP-8+100 are military turbine fuels, as used, for example, by the marines and air force. Some of these standards designate formulations which already comprise further additives such as corrosion inhibitors, icing inhibitors, static dissipators, etc.
25 Preferred turbine fuels are Jet A, Jet A-1 and JP 8.

- The polymer used in accordance with the invention is preferably used in a proportion, based on the total amount of the turbine fuel composition, which in itself has a substantially sufficient influence on the cold flow properties of the turbine fuel
30 composition. Preference is given to using the polymer in an amount of from 10 to 10 000 mg/l, more preferably from 50 to 7000 mg/l, in particular from 100 to 5000 mg/l, based on 1 l of the turbine fuel composition.

d) Coadditives

35

The polymers used in accordance with the invention may be added to the turbine fuel compositions individually or as a mixture of such polymers and, if appropriate, in combination with further additives known per se.

- 40 Suitable additives which may be present in the inventive turbine fuel compositions comprise further additives which improve the cold properties of the fuel (cold flow

improvers), detergents, corrosion inhibitors, antioxidants such as sterically hindered tert-butylphenols or N-butylphenylenediamines, metal deactivators such as N,N'-disalicylidene-1,2-diaminopropane, solubilizers, antistats such as Stadis 450, biocides, antiicing agents such as diethylene glycol methyl ether, and mixtures thereof.

5

Conventional cold flow improvers include in particular:

- 10 (a) copolymers of ethylene with at least one further ethylenically unsaturated monomer which are different from the polymers used in accordance with the invention;
- (b) comb polymers;
- (c) nucleators;
- (d) polar nitrogen compounds;
- (e) sulfo carboxylic acids or sulfonic acids or their derivatives;
- 15 (f) poly(meth)acrylic esters;
- (g) reaction products of alkanolamines with acylating agents;
- (h) condensation products of hydroxyaromatics with aldehydes; and
- (i) waxes.

- 20 In the copolymers of ethylene with at least one further ethylenically unsaturated monomer (a), the monomer is preferably selected from alkenylcarboxylic esters, (meth)acrylic esters, fumaric esters, maleic esters and olefins.

25 Suitable olefins are, for example, those having from 3 to 20 carbon atoms and having from 1 to 3, preferably having 1 or 2, carbon-carbon double bonds, in particular having one carbon-carbon double bond. In the latter case, the carbon-carbon double bond may either be terminal (α -olefins) or internal. However, preference is given to α -olefins, particular preference to α -olefins having from 3 to 20, more preferably from 3 to 10 and in particular from 3 to 6 carbon atoms, such as propene, 1-butene, 1-pentene and 1-hexene.

30 Suitable (meth)acrylic esters are, for example, esters of (meth)acrylic acid with C₁-C₁₀-alkanols, in particular with methanol, ethanol, propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, pentanol, hexanol, heptanol, octanol, 2-ethylhexanol, nonanol and decanol. The notation "(meth)acrylic acid" is intended to express that both acrylic acid and methacrylic acid are comprised.

40 Suitable alkenylcarboxylic esters are, for example, the vinyl and propenyl esters of carboxylic acids having from 2 to 20 carbon atoms, whose hydrocarbon radical may be linear or branched. Among these, preference is given to the vinyl esters. Among the carboxylic acids having branched hydrocarbon radicals, preference is given to those

whose branch is disposed in the α -position to the carboxyl group, and particular preference is given to the α -carbon atom being tertiary, i.e. to the carboxylic acid being a neocarboxylic acid.

- 5 Examples of suitable alkenylcarboxylic esters are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl neopentanoate, vinyl hexanoate, vinyl octanoate, vinyl 2-ethylhexanoate, vinyl neononanoate, vinyl neodecanoate and the corresponding propenyl esters, preference being given to the vinyl esters. A particularly preferred alkenylcarboxylic ester is vinyl acetate.

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Particular preference is given to selecting the ethylenically unsaturated monomer from alkenylcarboxylic esters.

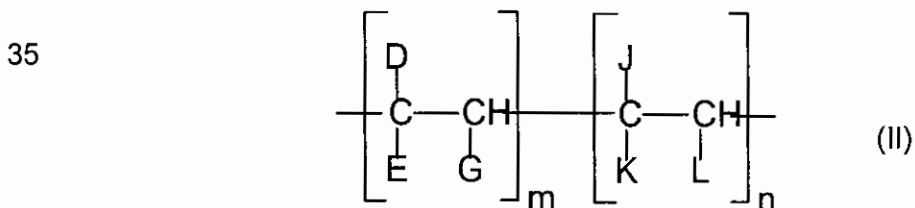
- Also suitable are copolymers which comprise, in copolymerized form, two or more different alkenylcarboxylic esters which differ in the alkenyl function and/or in the carboxylic acid group. Likewise suitable are copolymers which, in addition to the alkenylcarboxylic ester(s), comprise at least one copolymerized olefin and/or at least one copolymerized (meth)acrylic ester.

- 20 The ethylenically unsaturated monomer is copolymerized in the copolymer in an amount of preferably from 1 to 50 mol%, more preferably from 10 to 50 mol% and in particular from 5 to 20 mol%, based on the overall copolymer.

- The copolymer (a) preferably has a number-average molecular weight M_n of from 1000 to 20 000, more preferably from 1000 to 10 000 and in particular from 1000 to 6000.

- Such ethylene copolymers (a) are described, for example, in WO 01/62874 or EP-A 1357168, which are hereby fully incorporated by reference.

- 30 Comb polymers (b) are, for example, those described in "Comb-Like Polymers, Structure and Properties", N. A. Platé and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs. 8, pages 117 to 253 (1974). Among those described there, suitable comb polymers are, for example, those of the formula II



in which

- 40 D is R^{17} , COOR^{17} , OCOR^{17} , R^{18} , OCOR^{18} or OR^{17} ,
E is H, CH_3 , D or R^{18} ,

G is H or D,

J is H, R^{18} , $R^{18}COOR^{17}$, aryl or heterocyclyl,

K is H, $COOR^{18}$, $OCOR^{18}$, OR^{18} or $COOH$,

L is H, R^{18} , $COOR^{18}$, $OCOR^{18}$, $COOH$ or aryl,

5 where

R^{17} is a hydrocarbon radical having at least 10 carbon atoms, preferably having from 10 to 30 carbon atoms,

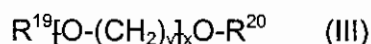
R^{18} is a hydrocarbon radical having at least one carbon atom, preferably having from 1 to 30 carbon atoms,

10 m is a molar fraction in the range from 1.0 to 0.4 and

n is a molar fraction in the range from 0 to 0.6.

Preferred comb polymers are obtainable, for example, by copolymerization of maleic anhydride or fumaric acid with another ethylenically unsaturated monomer, for example
 15 with an α -olefin or an unsaturated ester, such as vinyl acetate, and subsequent esterification of the anhydride or acid function with an alcohol having at least 10 carbon atoms. Further preferred comb polymers are copolymers of α -olefins and esterified comonomers, for example esterified copolymers of styrene and maleic anhydride or esterified copolymers of styrene and fumaric acid. Also suitable are mixtures of comb
 20 polymers. Comb polymers may also be polyfumarates or polymaleates. Homo- and copolymers of vinyl ethers are also suitable comb polymers.

Suitable nucleators (c) are in particular polyoxyalkylenes, for example polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof. The polyoxyalkylene compounds
 25 preferably comprise at least one, more preferably at least two, linear alkyl group(s) having from 10 to 30 carbon atoms and a polyoxyalkylene group having a molecular weight of up to 5000. The alkyl group of the polyoxyalkylene radical preferably comprises from 1 to 4 carbon atoms. Such polyoxyalkylene compounds are described, for example, in EP-A-0 061 895, in EP-A 1357168 and in US 4,491,455, which are
 30 hereby fully incorporated by reference. Preferred polyoxyalkylene esters, ethers and ester/ethers have the general formula III



35 in which

R^{19} and R^{20} are each independently R^{21} , $R^{21}-CO-$, $R^{21}-O-CO(CH_2)_z-$ or $R^{21}-O-CO(CH_2)_z-CO-$, where R^{21} is linear C_1-C_{30} -alkyl,

y is from 1 to 4,

x is from 2 to 200, and

40 z is from 1 to 4.

Preferred polyoxyalkylene compounds of the formula III in which both R^{19} and R^{20} are R^{21} are polyethylene glycols and polypropylene glycols having a number-average molecular weight of from 100 to 5000. Preferred polyoxyalkylenes of the formula III in which one of the R^{19} radicals is R^{21} and the other is R^{21} -CO- are polyoxyalkylene esters of fatty acids having from 10 to 30 carbon atoms, such as stearic acid or behenic acid. Preferred polyoxyalkylene compounds in which both R^{19} and R^{20} are an R^{21} -CO- radical are diesters of fatty acids having from 10 to 30 carbon atoms, preferably of stearic acid or behenic acid.

Further suitable nucleators (c) are block copolymers as described in EP-A-1357168, whose contents are hereby fully incorporated by reference. Suitable block copolymers comprise at least one crystallizable block and at least one noncrystallizable block. The copolymers may be diblock, triblock or higher block copolymers. Preferred triblock copolymers have a crystallizable block at both polymer ends.

Such block copolymers are preferably formed from butadiene and isoprene units.

The polar nitrogen compounds (d) are also referred to as wax antisetling additives (WASA). They are advantageously oil-soluble, may be either ionic or nonionic and preferably have at least one, more preferably at least 2, substituent(s) of the formula $>NR^{22}$ in which R^{22} is a C_8 - C_{40} -hydrocarbon radical. The nitrogen substituents may also be quaternized, i.e. be in cationic form. One example of such nitrogen compounds is that of ammonium salts and/or amides which are obtainable by the reaction of at least one amine substituted with at least one hydrocarbon radical with a carboxylic acid having from 1 to 4 carboxyl groups or with a suitable derivative thereof. The amines preferably comprise at least one linear C_8 - C_{40} -alkyl radical. Suitable primary amines are, for example, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tetradecylamine and the higher linear homologs. Suitable secondary amines are, for example, dioctadecylamine and methylbehénylamine. Also suitable are amine mixtures, in particular amine mixtures obtainable on the industrial scale, such as fatty amines or hydrogenated tallamines, as described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 6th Edition, 2000 electronic release, "Amines, aliphatic" chapter. Acids suitable for the reaction are, for example, cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid, naphthalenedicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid and succinic acids substituted with long-chain hydrocarbon radicals.

A further example of polar nitrogen compounds is that of ring systems which bear at least two substituents of the formula $-A-NR^{23}R^{24}$ in which A is a linear or branched aliphatic hydrocarbon group which is optionally interrupted by one or more groups selected from O, S, NR^{35} and CO, and R^{23} and R^{24} are each a C_9 - C_{40} -hydrocarbon

radical which is optionally interrupted by one or more groups selected from O, S, NR^{35} and CO, and/or substituted by one or more substituents selected from OH, SH and $\text{NR}^{35}\text{R}^{36}$ where R^{35} is $\text{C}_1\text{-C}_{40}$ -alkyl which is optionally substituted by one or more moieties selected from CO, NR^{35} , O and S, and/or substituted by one or more radicals selected from $\text{NR}^{37}\text{R}^{38}$, OR^{37} , SR^{37} , COR^{37} , COOR^{37} , $\text{CONR}^{37}\text{R}^{38}$, aryl or heterocyclyl, where R^{37} and R^{38} are each independently selected from H or $\text{C}_1\text{-C}_4$ -alkyl; and R^{36} is H or R^{35} .

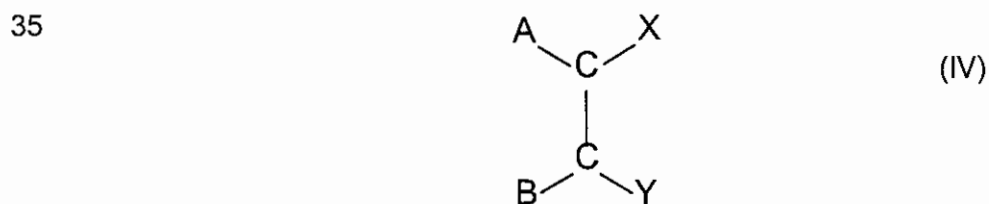
A is preferably a methylene or polymethylene group having from 2 to 20 methylene units. Examples of suitable R^{23} and R^{24} radicals are 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl and propoxypropyl. The cyclic system may be homocyclic, heterocyclic, fused polycyclic or nonfused polycyclic systems. The ring system is preferably carbo- or heteroaromatic, in particular carboaromatic. Examples of such polycyclic ring systems are fused benzoid structures such as naphthalene, anthracene, phenanthrene and pyrene, fused nonbenzoid structures such as azulene, indene, hydrindene and fluorene, nonfused polycycles such as diphenyl, heterocycles such as quinoline, indole, dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophene, carbazole, diphenylene oxide and diphenylene sulfide, nonaromatic or partly saturated ring systems such as decalin, and three-dimensional structures such as α -pinene, camphene, bornylene, norbornane, norbornene, bicyclooctane and bicyclooctene.

A further example of suitable polar nitrogen compounds is that of condensates of long-chain primary or secondary amines with carboxyl group-comprising polymers.

The polar nitrogen compounds mentioned here are described in WO 00/44857 and also in the references cited therein, which are hereby fully incorporated by reference.

Suitable polar nitrogen compounds are also described, for example, in DE-A-198 48 621 and DE-A-196 22 052, EP-A-1357168 or EP-B 398 101, which are hereby incorporated by reference.

Suitable sulfo carboxylic acids/sulfonic acids or their derivatives (e) are, for example, those of the general formula IV



in which

Y is $\text{SO}_3^-(\text{NR}^{25}_3\text{R}^{26})^+$, $\text{SO}_3^-(\text{NHR}^{25}_2\text{R}^{26})^+$, $\text{SO}_3^-(\text{NH}_2\text{R}^{25}\text{R}^{26})$, $\text{SO}_3^-(\text{NH}_3\text{R}^{26})$ or $\text{SO}_2\text{NR}^{25}\text{R}^{26}$,
 X is Y, $\text{CONR}^{25}\text{R}^{27}$, $\text{CO}_2^-(\text{NR}^{25}_3\text{R}^{27})^+$, $\text{CO}_2^-(\text{NHR}^{25}_2\text{R}^{27})^+$, $\text{R}^{28}\text{-COOR}^{27}$, $\text{NR}^{25}\text{COR}^{27}$,
 $\text{R}^{28}\text{OR}^{27}$, $\text{R}^{28}\text{OCOR}^{27}$, $\text{R}^{28}\text{R}^{27}$, $\text{N}(\text{COR}^{25})\text{R}^{27}$ or $\text{Z}^-(\text{NR}^{25}_3\text{R}^{27})$,

where

- 5 R^{25} is a hydrocarbon radical,
 R^{26} and R^{27} are each alkyl, alkoxyalkyl or polyalkoxyalkyl having at least 10 carbon atoms in the main chain,
 R^{28} is C_2 - C_5 -alkylene,
 Z^- is one anion equivalent and
- 10 A and B are each alkyl, alkenyl or two substituted hydrocarbon radicals or, together with the carbon atoms to which they are bonded, form an aromatic or cycloaliphatic ring system.

Such sulfo carboxylic acids and sulfonic acids and their derivatives are described in

- 15 EP-A-0 261 957, which is hereby fully incorporated by reference.

Suitable poly(meth)acrylic esters (f) are either homo- or copolymers of acrylic and methacrylic esters. Preference is given to acrylic ester homopolymers which derive from C_1 - C_{40} -alcohols. Preference is given to copolymers of at least two different
 20 (meth)acrylic esters which differ in the esterified alcohol. If appropriate, the copolymer comprises a further, different copolymerized olefinically unsaturated monomer. The weight-average molecular weight of the polymer is preferably from 50 000 to 500 000. A particularly preferred polymer is a copolymer of methacrylic acid and methacrylic esters of saturated C_{14} - and C_{15} -alcohols, in which the acid groups have been
 25 neutralized with hydrogenated tallamine. Suitable poly(meth)acrylic esters are described, for example, in WO 00/44857, which is fully incorporated herein by way of reference.

- 30 To prepare suitable reaction products of alkanolamines with acrylating agents (g), the acylating agents used are preferably those which comprise a hydrocarbon radical having from 8 to 50 carbon atoms. Examples thereof are succinic acids or succinic acid derivatives substituted by C_8 - C_{50} -alkyl or alkenyl radical, preferably C_{12} - C_{35} -alkyl or alkenyl radical. The alkanolamines are, for example, diethanolamine, dipropanolamine, dibutanolamine, N-methylethanolamine or N-ethylethanolamine. Such compounds are
 35 described, for example, in WO 01/62874, which is hereby incorporated by reference.

- 40 The hydroxyaromatics used to prepare the condensation products of hydroxyaromatics with aldehydes (h) are those which are substituted by a linear or branched hydrocarbon radical. The hydroxyaromatic may either be a substituted phenol or any other hydroxy-containing aromatic such as naphthol. The aldehyde component used may either be the aldehydes themselves or suitable aldehyde sources. Examples of suitable

aldehydes are formaldehyde (which may be used, for example, as paraldehyde or trioxane), acetaldehyde, propanol, butanal, isobutyraldehyde, heptanal, 2-ethylhexanal and glyoxalic acid. Suitable condensation products are described, for example, in WO 01/62874 or in EP-A-1357168, which are hereby incorporated by reference.

5

Suitable waxes (I) are both linear and nonlinear paraffins. The n-paraffins are preferably C₈-C₃₅-alkanes, more preferably C₈-C₃₀-alkanes and in particular C₈-C₂₅-alkanes. The nonlinear paraffins comprise preferably amorphous solids having a melting point of from 10 to 60°C and a molecular weight of from 150 to 500. Such

10 waxes are described, for example, in EP-A-1357168, which is hereby incorporated by reference.

e) Additive packages

15 The invention lastly also relates to additive packages comprising at least one polymer used in accordance with the invention, as defined above, and at least one further conventional turbine fuel additive, and also, if appropriate, at least one diluent.

Suitable conventional turbine fuel additives are the above-described coadditives.

20 Preferred coadditives are antiicing additives; and also the conventional cold flow improvers mentioned, preference being given to those of group (a); corrosion inhibitors; detergents; antioxidants; antistats and metal deactivators. In particular, the additive package comprises, in addition to at least one of the above-described polymers, at least one antiicing agent and, if appropriate, at least one of the following coadditives:

25 conventional cold flow improvers, preference being given to those of group (a); corrosion inhibitors; detergents; antioxidants; antistats and metal deactivators.

In the additive packages, the polymer used in accordance with the invention is present in an amount of preferably from 0.1 to 99% by weight, more preferably from 1 to 95%
30 by weight and in particular from 5 to 90% by weight.

The additive package may also, if appropriate, comprise at least one diluent. Suitable diluents are, for example, fractions obtained during oil processing, such as kerosine, naphtha or brightstock. Additionally suitable are aromatic hydrocarbons such as
35 Solvent Naphtha heavy, Solvesso® or Shellisol®, and aliphatic hydrocarbons.

When the package comprises a diluent, the polymer used in accordance with the invention is present in the concentrates preferably in an amount of from 0.1 to 90% by weight, more preferably from 1 to 80% by weight and in particular from 10 to 70% by
40 weight, based on the total weight of the concentrate.

The inventive use of the polymers described improves the cold flow properties of the turbine fuels additized therewith. In particular, the freezing point, the cloud point (CP) and in particular the pour point (PP) are lowered.

- 5 The invention will now be illustrated in detail with reference to the nonlimiting examples which follow.

Experimental section:

- 10 1. Preparative examples 1 to 28

A total of 28 different polymers to be used in accordance with the invention were prepared by high-pressure polymerization of ethylene and 2-ethylhexyl acrylate (EHA) or of ethylene, 2-ethylhexyl acrylate (EHA) or lauryl acrylate (LA) and vinyl acetate (VAC).

15

Table 1 compares the properties of the polymers used in the test examples which follow.

20

The content of ethylene, EHA or LA and VAC in the resulting polymers was determined by NMR spectroscopy. The viscosities were determined at 120°C to Ubbelohde DIN 51562.

Table 1

Polymer No.	E [mol%]	VAC [mol%]	Acrylate [mol%]	Viscosity [mm ² /s]	M _n	M _w	M _w /M _n
1	79.9	-	20.1 ¹	150	3197	8499	2.66
2	88.0	4.2	7.8 ¹	60	2088	4189	2.01
3	88.0	4.4	7.6 ¹	150	2959	6666	2.25
4	88.1	4.4	7.5 ¹	605	4635	12 811	2.76
5	86.6	3.9	9.5 ¹	60	2124	4285	2.02
6	86.4	4.3	9.3 ¹	150	3022	6754	2.23
7	86.4	4.1	9.5 ¹	595	4797	13 238	2.76
8	83.8	4.1	12.1 ¹	60	2064	4280	2.07
9	83.2	4.4	12.4 ¹	150	2994	7203	2.41
10	83.1	4.4	12.5 ¹	600	4744	14 503	3.06
11	80.2	4.5	15.3 ¹	150	3038	7279	2.40
12	80.4	4.1	15.5 ¹	600	4681	15 697	3.35
13	89.6	8.0	2.4 ¹	60	1977	3910	1.98
14	89.8	7.9	2.3 ¹	150	2831	6212	2.19
15	89.2	8.2	2.6 ¹	605	3862	11 098	2.87
16	89.8	8.4	4.8 ¹	60	1928	3902	2.02
17	86.5	8.4	5.1 ¹	150	2926	6337	2.17
18	86.3	8.5	5.2 ¹	620	4613	12 019	2.61
19	84.2	8.1	7.7 ¹	60	2003	4025	2.01
20	83.1	8.7	8.2 ¹	150	2855	6382	2.24
21	84.3	8.0	7.7 ¹	615	4858	13 061	2.69
22	81.1	7.9	11.0 ¹	60	2100	4276	2.04
23	80.8	8.0	11.2 ¹	150	2878	6634	2.31
24	81.1	7.6	11.3 ¹	630	4774	14 263	2.99
25	77.6	8.7	13.7 ¹	150	3134	7195	2.30
26	86.8	4.8	8.4 ¹	60	1928	3902	2.02
27	86.3	5.2	8.5 ¹	620	4613	12019	2.61
28	87.9	10.5	1.6 ²	153	3100	7301	2.36

- 5 E: ethylene
 VAC: vinyl acetate
¹ 2-ethylhexyl acrylate
² lauryl acrylate

2. Test examples

The polymers 1 to 28 prepared above were used to carry out the experiments which follow. For comparative purposes, a conventional ethylene/vinyl acetate copolymer was also tested:

A Jet A turbine fuel having a pour point (PP) of -48°C was additized firstly with a conventional ethylene/vinyl acetate copolymer and secondly with the copolymers from examples 1, 17 and 25 to 28 in an amount of in each case 1000 mg/l, and the PP value of the additized turbine fuel was determined in each case to ISO 3016. The PP value of the turbine fuel additized with the conventional ethylene/vinyl acetate copolymer was -48°C , i.e. it had not been possible to reduce it. The PP values of the turbine fuel additized in each case with the copolymers used in accordance with the invention are listed in the table which follows.

Table 2

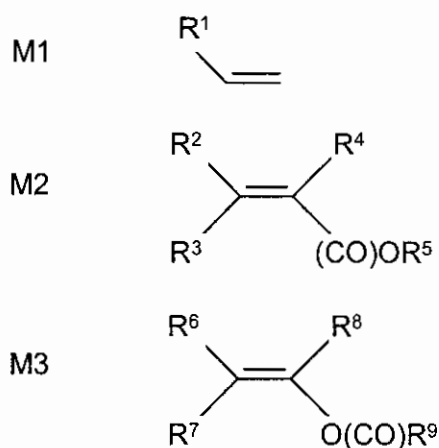
Polymer No.	PP [$^{\circ}\text{C}$]
-	-48
EVA*	-48
1	<-68
17	-63
25	<-70
26	-63
27	-51
28	-51

*EVA = conventional ethylene/vinyl acetate copolymer (comparative example)

As the examples show, the Jet A turbine fuel additized with the copolymers used in accordance with the invention has a distinctly lower pour point than the unadditized fuel, while the conventional ethylene/vinyl acetate copolymer has no effect on the pour point.

What is claimed is:

1. The use of a polymer which comprises, in copolymerized form, an α -olefin, an ester of an α,β -unsaturated carboxylic acid and, if appropriate, an alkenyl ester of a carboxylic acid as an additive for turbine fuels.
2. The use according to claim 1, wherein the polymer comprises, in copolymerized form, the ester of an α,β -unsaturated carboxylic acid and, if appropriate, the alkenyl ester in random distribution.
3. The use according to either of the preceding claims, wherein the polymer is composed of monomers comprising M1, M2 and, if appropriate, M3 and where M1, M2 and M3 have the following general formulae:



in which

R^1 is H or C_1 - C_{40} -hydrocarbyl;

R^2 , R^3 and R^4 are each independently H or C_1 - C_4 -alkyl;

R^5 is C_1 - C_{20} -hydrocarbyl;

R^6 , R^7 and R^8 are each independently H or C_1 - C_4 -alkyl; and

R^9 is C_1 - C_{19} -hydrocarbyl.

4. The use according to claim 3, wherein the monomers M1, M2 and M3 are comprised in the following molar fractions in the polymer:

M1: from 0.60 to 0.99

M2: from 0.01 to 0.40

M3: 0 to 0.20.

5. The use according to either of claims 3 and 4, wherein monomer M1 is ethylene.

6. The use according to any of claims 3 to 5, wherein R^2 , R^3 and R^4 are each H or two of the R^2 , R^3 and R^4 radicals are each H and the other radical is methyl.
7. The use according to any of claims 3 to 6, wherein R^5 is C_5 - C_{16} -hydrocarbyl.
8. The use according to claim 7, wherein R^5 is C_8 - C_{12} -alkyl.
9. The use according to claim 8, wherein R^5 is 2-ethylhexyl or lauryl.
10. The use according to any of claims 3 to 9, wherein M2 is 2-ethylhexyl acrylate or lauryl acrylate.
11. The use according to any of claims 3 to 10, wherein M3 is vinyl acetate.
12. The use according to any of the preceding claims, wherein the polymer is used as a cold flow improver.
13. The use according to claim 12, wherein the polymer decreases the pour point of the turbine fuel additized therewith.
14. A turbine fuel composition comprising a major proportion by weight of a turbine fuel and a minor proportion by weight of at least one polymer as defined in any of claims 1 to 11.
15. The use or composition according to any of the preceding claims, wherein the polymer is used in combination with further turbine fuel additives.
16. An additive package comprising at least one polymer as defined in any of claims 1 to 11 in combination with at least one further turbine fuel additive and, if appropriate, at least one diluent.