

**Motor fuel compositions comprising renewable raw
materials**

5 The present invention relates to fuel compositions which comprise renewable raw materials, to the use of ester-comprising polymers in fuel compositions, and to the processes for operating diesel engines with fuel compositions of the present invention.

10 Fuels are nowadays generally obtained from fossil sources. However, these resources are limited, so that replacements are being sought. Therefore, interest is rising in renewable raw materials which can be used to produce fuels. A very interesting replacement is in
15 particular biodiesel fuels.

The term biodiesel is in many cases understood to mean a mixture of fatty acid esters, usually fatty acid methyl esters (FAMES), with chain lengths of the fatty
20 acid fraction of 14 to 24 carbon atoms with 0 to 3 double bonds. The higher the carbon number and the fewer double bonds are present, the higher is the melting point of the FAME. Typical raw materials are vegetable oils (i.e. glycerides) such as rapeseed oils,
25 sunflower oils, soya oils, palm oils, coconut oils and, in isolated cases, even used vegetable oils. These are converted to the corresponding FAMES by transesterification, usually with methanol under basic catalysis.

30 In contrast to rapeseed oil methyl ester (RME), which is frequently used in Europe and typically contains approx. 5% C16:0+C18:0-FAME, palm oil methyl ester (PME) contains approx. 50% C16:0+C18:0-FAME. A similar
35 high C16:0+C18:0 FAME content is also possessed by the analogous derivatives of animal tallows, for example beef tallow. Such a high wax content can barely be influenced by polymeric flow improvers, which are

typically added with an addition rate of up to 2%. In comparison to rapeseed oil, palm oil can be obtained with more than three times as high a crop yield per hectare. This gives rise to immense economic advantages. However, a disadvantage is the high pour point of PME, which is about +12°C.

The use of pure biodiesel is an important aim from an ecological point of view. However, these fuel oils differ from conventional diesel fuel in important properties. For instance, it is found that many seal materials are attacked by biodiesel. Failure of the seal materials leads inevitably to engine damage. Moreover, in the case of direct-injection diesel engines, fuel can get into the motor oil, which, owing to the low chemical stability of vegetable oil esters, can lead to deposits in the engine. Moreover, biodiesel fuels exhibit different combustion owing to viscosity differences compared to mineral diesel fuels, which lead to different atomization behaviour. In the case of modern diesel engines whose engine electronics are adjusted specifically to fossil diesel fuel, problems can therefore occur as a result of altered combustion characteristics. In particular, the development of economical and high-performance diesel engines which are optimized for the use of fossil fuels has thus to date been a hindrance for the use of pure biodiesel fuel.

In addition to the utilization of 100% biodiesel (usually RME) in Europe, mixtures of fossil diesel, i.e. the middle distillate of crude oil distillation, and biodiesel are therefore also of interest owing to improved low-temperature properties and the better combustion properties. Even as a blend, tax advantages for the renewable raw material can be passed through to the end user. In addition to these economic advantages, the advantageous ecological balance for the renewable

raw material biodiesel should of course also be mentioned. For instance, 5% blends of biodiesel (usually RME) with fossil diesel are being discussed in Europe, and in Asia (South Korea, India, Indonesia, Malaysia, Thailand, Philippines) and Australia even 20% or higher blends (usually PME). In the case of the 20% PME blend, moreover, significantly more wax-like chains are present with approx. 10% C16:0+C18:0-FAME in the fuel mixture than in the RME (approx. 5%). There is also a comprehensive review on this subject in H. Vogel, A. Bertola: *Palmölmethylester - eine neue vorteilhafte Biokomponente für Dieselkraftstoffe* [Palm Oil Methyl Ester - A New Advantageous Biological Component for Diesel Fuels] *Mineralöltechnik* 50 (2005), 1.

Polyalkyl (meth)acrylates PA(M)As as pour point improvers for mineral oils, both without M(M)A (for example US 3 869 396 to Shell Oil Company) and with M(M)A (for example US 5 312 884 to Rohm & Haas Company), or else as pour point improvers for vegetable oils (US 5 696 066 to Rohm & Haas Company), have been established and described for some time. Use of these polymers in fuel compositions which comprise at least one diesel fuel of mineral origin and at least one biodiesel fuel is, however, not described.

Moreover, the publication WO 01/40334 (RohMax Additives GmbH) describes polyalkyl (meth)acrylates which can be used in biodiesel fuels. This publication relates to the particular preparation which imparts exceptional properties to these polymers. However, there is a lack of examples herein which relate to biodiesel fuels. In addition, the advantageousness of polymers which have a high content of certain ester-comprising repeat units is not detailed. Furthermore, the low-temperature properties achievable in lubricant oil by adding additives are not necessarily applicable to mineral

diesel fuels, since their boiling behaviour, their viscosity and hence their composition of hydrocarbons is different. Mixtures which comprise mineral diesel fuel and biodiesel are not described in WO 01/40334.

5 Furthermore, hydroxy-functional PAMAs are known as flow improvers for biodiesel in the literature (EP 1 032 620 to RohMax Additives GmbH). In the general part of the publication EP 1 032 620, mixtures of fossil fuels with biodiesel fuels are described, but no examples which
10 use such a mixture are adduced. In this context, it can be taken from the document that a biodiesel fuel, especially based on RME, which has particularly good low-temperature properties should be provided. In the case of use of mixtures with a high content of diesel
15 fuels of mineral origin, it is found that the effectiveness of the polymers detailed in general terms in EP 1 032 620 can be improved.

Flow improvers based on oil-soluble polymers for
20 mixtures of fossil diesel and biodiesel are also known (WO 94/10267, Exxon Chemical Patents Inc.). However, in the examples, only ethylene-vinyl acetate copolymers (EVA) and copolymers which contain C₁₂/C₁₄-alkyl fumarate and vinyl acetate units are described. There
25 is no comprehensive and unambiguous description of particular ester-comprising polymers in WO 94/10267.

In addition, a series of optimized EVA copolymers for diesel-biodiesel mixtures have also become known (EP
30 1 541 662 to 664). For instance, EP 1 541 663 details mixtures comprising 75% by volume of diesel fuel of mineral origin and 25% by volume of biodiesel, which comprise 150 ppm of poly(dodecyl methacrylate) and from 100 to 200 ppm of ethylene-vinyl acetate copolymer
35 (EVA). However, the use of EVA is described herein as obligatory. EVA is, however, quite an expensive additive. Accordingly, alternatives in which the use of EVA can be dispensed with are desirable. There is no

indication in EP 1 541 663 to the advantageousness of particular ester-comprising polymers.

5 In view of the prior art, it is thus an object of the present invention to provide fuel compositions which, with a property profile which corresponds essentially to that of mineral diesel fuel, comprise a maximum proportion of renewable raw materials. At the same time, the fuel should in particular have very good low-
10 temperature properties. In addition, the combustion behaviour, especially the behaviour of the fuel in relation to the engine control characteristics, should as far as possible correspond to the behaviour of mineral diesel fuel. Furthermore, it was an object of
15 the present invention to provide a fuel which has a high stability towards oxidation. In addition, the fuel should have a maximum cetane number. At the same time, the novel fuels should be simple and inexpensive to produce. Furthermore, it was an object of the present
20 invention to provide the processes for operating diesel engines which have high environmental compatibility.

This object and further objects which are not stated explicitly but are immediately derivable or discernible
25 from the connections discussed herein by way of introduction, are achieved by a fuel composition having all features of Claim 1. Appropriate modifications of the inventive fuel composition are protected in subclaims. With regard to the process for operating a
30 diesel engine and to the use of ester-comprising polymers as flow improvers, Claims 24 and 25 constitute a solution to the problem.

By virtue of a fuel composition containing 20% by
35 weight of diesel fuel of mineral origin and from 0.05 to 5% by weight of at least one ester-comprising polymer which comprises repeat units which are derived from ester monomers having 16 to 40 carbon atoms in the

alcohol radical, and repeat units which are derived from ester monomers having 7 to 15 carbon atoms in the alcohol radical, it is surprisingly possible to provide a fuel composition which comprises at least one diesel
5 fuel of mineral origin and at least one biodiesel fuel, which, with a property profile which is very similar to that of mineral diesel fuel, comprises a very high proportion of renewable raw materials.

10 At the same time, the inventive fuel compositions can achieve a series of further advantages. These include:

The inventive fuel compositions can be used in conventional diesel engines without the seal materials
15 used customarily being attacked.

Furthermore, modern diesel engines can be operated with the fuel of the present invention without the engine control having to be altered.

20 Preferred fuel compositions of the present invention have a particularly high cetane number which can be improved in particular by the use of biodiesel fuels having a high proportion of long-chain saturated fatty
25 acids.

In addition, the present invention is aimed at the use of very oxidation-stable biodiesel fuels. This allows reduction of the formation of deposits in the engine,
30 which can lead to a low overall performance of the engine.

Moreover, very high fractions of palm oil alkyl esters can be used in the fuels. For ecological and economic
35 reasons, palm oil is preferred over the customarily used rapeseed oil. For instance, the crop yield in the production of palm oil is significantly higher than that of rapeseed oil. Moreover, to obtain rape, very

large amounts of ecologically controversial chemicals, especially fertilizers and crop protection compositions, are used. At the same time, rape is not self-compatible in production and has to be cultivated
5 in a crop rotation system, in which case cultivation of rape in the same field is possible only every 3 to 5 years. For this reason, a further increase in rape production is difficult.

10 However, palm oil alkyl esters have a significantly higher cloud point (approx. +13°C in the case of the methyl ester) in comparison to rapeseed oil alkyl esters; the cloud point of rapeseed oil alkyl ester is significantly lower (approx. -7°C in the case of the
15 methyl ester). In a particular aspect, the present invention thus enables the use of particularly high proportions of palm oil alkyl esters for producing fuel compositions without the low-temperature properties assuming impermissible values.

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The fuel composition of the present invention comprises diesel fuel of mineral origin, i.e. diesel, gas oil or diesel oil. Mineral diesel fuel is widely known per se and is commercially available. This is understood to
25 mean a mixture of different hydrocarbons which is suitable as a fuel for a diesel engine. Diesel can be obtained as a middle distillate, in particular by distillation of crude oil. The main constituents of the diesel fuel preferably include alkanes, cycloalkanes
30 and aromatic hydrocarbons having about 10 to 22 carbon atoms per molecule.

Preferred diesel fuels of mineral origin boil in the range of 120 to 450°C, more preferably 170 and 390°C.
35 Preference is given to using those middle distillates which contain 0.05% by weight of sulphur and less, more preferably less than 350 ppm of sulphur, in particular less than 200 ppm of sulphur and in special cases less

than 50 ppm of sulphur, for example less than 10 ppm of sulphur. They are preferably those middle distillates which have been subjected to refining under hydrogenating conditions, and which therefore contain only small proportions of polyaromatic and polar compounds. They are preferably those middle distillates which have 95% distillation points below 370°C, in particular below 350°C and in special cases below 330°C. Synthetic fuels, as obtainable, for example, by the Fischer-Tropsch process, are also suitable as diesel fuels of mineral origin.

The kinematic viscosity of diesel fuels of mineral origin to be used with preference is in the range of 0.5 to 8 mm²/s, more preferably 1 to 5 mm²/s and especially preferably 1.5 to 3 mm²/s, measured at 40°C to ASTM D 445.

The fuel compositions of the present invention comprise at least 20% by weight, in particular at least 30% by weight, preferably at least 50% by weight, more preferably at least 70% by weight and most preferably at least 80% by weight of diesel fuels of mineral origin.

In addition, the present fuel composition comprises at least one biodiesel fuel component. Biodiesel fuel is a substance, especially an oil, which is obtained from vegetable or animal material or both, or a derivative thereof which can be used in principle as a replacement for mineral diesel fuel.

In a preferred embodiment, the biodiesel fuel, which is frequently also referred to as "biodiesel" or "biofuel" comprises fatty acid alkyl esters formed from fatty acids having preferably 6 to 30, more preferably 12 to 24 carbon atoms, and monohydric alcohols having 1 to 4 carbon atoms. In many cases, some of the fatty acids

may contain one, two or three double bonds. The monohydric alcohols include in particular methanol, ethanol, propanol and butanol, methanol being preferred.

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Examples of oils which derive from animal or vegetable material and which can be used in accordance with the invention are palm oil, rapeseed oil, coriander oil, soya oil, cottonseed oil, sunflower oil, castor oil,
10 olive oil, groundnut oil, corn oil, almond oil, palm kernel oil, coconut oil, mustardseed oil, oils which are derived from animal tallow, especially beef tallow, bone oil, fish oils and used cooking oils. Further examples include oils which derive from cereal, wheat,
15 jute, sesame, rice husks, jatropha, arachis oil and linseed oil. The fatty acid alkyl esters to be used with preference may be obtained from these oils by processes known in the prior art.

20 Preference is given in accordance with the invention to highly C16:0/C18:0-glyceride-containing oils, such as palm oils and oils which are derived from animal tallow, and also derivatives thereof, especially the palm oil alkyl esters which are derived from monohydric
25 alcohols. Palm oil (also: palm fat) is obtained from the fruit flesh of the palm fruits. The fruits are sterilized and pressed. Owing to their high carotene content, fruits and oils have an orange-red colour which is removed in the refining. The oil may contain
30 up to 80% C18:0-glyceride.

Particularly suitable biodiesel fuels are lower alkyl esters of fatty acids. Useful examples here are commercial mixtures of the ethyl, propyl, butyl and
35 especially methyl esters of fatty acids having 6 to 30, preferably 12 to 24, more preferably 14 to 22 carbon atoms, for example of caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, margaric

acid, stearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid or erucic acid.

In a particular aspect of the present invention, a biodiesel fuel is used which comprises preferably at least 30% by weight, more preferably at least 35% by weight and most preferably at least 40% by weight of saturated fatty acid esters which have at least 16 carbon atoms in the fatty acid radical. These include in particular the esters of palmitic acid and stearic acid.

For reasons of cost, these fatty acid esters are generally used as a mixture. Biodiesel fuels usable in accordance with the invention preferably have an iodine number of at most 150, in particular at most 125, more preferably at most 70 and most preferably at most 60. The iodine number is a measure known per se for the content in a fat or oil of unsaturated compounds, which can be determined to DIN 53241-1. As a result of this, the fuel compositions of the present invention form a particularly low level of deposits in the diesel engines. Moreover, these fuel compositions have particularly high cetane numbers.

In general, the fuel compositions of the present invention may comprise at least 0.5% by weight, in particular at least 3% by weight, preferably at least 5% by weight and more preferably at least 15% by weight of biodiesel fuel.

In addition, the fuel composition of the present invention comprises 0.05 to 5% by weight, preferably

0.08 to 3% by weight and more preferably 0.1 to 1.0% by weight of at least one ester-comprising polymer.

In the present context, ester-comprising polymers are understood to mean polymers which are obtainable by polymerizing monomer compositions which comprise ethylenically unsaturated compounds having at least one ester group, which are referred to hereinafter as ester monomers. Accordingly, these polymers contain ester groups as part of the side chain. These polymers include in particular polyalkyl (meth)acrylates (PAMAs), polyalkyl fumarates and/or polyalkyl maleates.

Ester monomers are known per se. These include in particular (meth)acrylates, maleates and fumarates which may have different alcohol radicals. The term (meth)acrylates encompasses methacrylates and acrylates, and also mixtures of the two. These monomers are widely known. In this context the alkyl radical may be linear, cyclic or branched. Moreover, the alkyl radical may have known substituents.

The ester-comprising polymers contain repeat units which are derived from ester monomers having 16 to 40 carbon atoms in the alcohol radical, and repeat units which are derived from ester monomers having 7 to 15 carbon atoms in the alcohol radical.

The term "repeat unit" is widely known in the technical field. The present ester-comprising polymers may preferably be obtained via free-radical polymerization of monomers, the ATRP, RAFT and NMP processes which will be detailed later being included in the free-radical processes in the context of the invention, without any intention that this should impose a restriction. In the polymerization, double bonds are opened up to form covalent bonds. Accordingly, the repeat unit is formed from the monomers used.

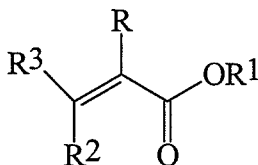
The ester-comprising polymer may contain 5 to 99.9% by weight, in particular 20 to 98% by weight, preferably 30 to 95% by weight and most preferably 70 to 92% by weight of repeat units which are derived from ester monomers having 7 to 15 carbon atoms in the alcohol radical.

In a particular aspect, the ester-comprising polymer may contain 0.1 to 80% by weight, preferably 0.5 to 60% by weight, more preferably 2 to 50% by weight and most preferably 5 to 20% by weight of repeat units which are derived from ester monomers having 16 to 40 carbon atoms in the alcohol radical.

In addition, the ester-comprising polymer may contain 0.1 to 30% by weight, preferably 0.5 to 20% by weight, of repeat units which are derived from ester monomers having 1 to 6 carbon atoms in the alcohol radical.

The ester-comprising polymer comprises preferably at least 40% by weight, more preferably at least 60% by weight, especially preferably at least 80% by weight and most preferably at least 95% by weight of repeat units which are derived from ester monomers.

Mixtures from which the inventive ester-comprising polymers are obtainable may contain 0 to 40% by weight, preferably 0.1 to 30% by weight, in particular 0.5 to 20% by weight, of one or more ethylenically unsaturated ester compounds of the formula (I)



(I)

in which R is hydrogen or methyl, R¹ is a linear or

branched alkyl radical having 1 to 6 carbon atoms, R^2 and R^3 are each independently hydrogen or a group of the formula $-COOR'$ in which R' is hydrogen or an alkyl group having 1 to 6 carbon atoms.

- 5 Examples of component (I) include
- (meth)acrylates, fumarates and maleates which derive from saturated alcohols, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, tert-butyl (meth)acrylate and pentyl (meth)acrylate, hexyl (meth)acrylate;
- cycloalkyl (meth)acrylates such as cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate;
- (meth)acrylates which derive from unsaturated alcohols, 15 such as 2-propynyl (meth)acrylate, allyl (meth)acrylate and vinyl (meth)acrylate.

The compositions to be polymerized preferably contain 10 to 98% by weight, in particular 20 to 95% by weight, of one or more ethylenically unsaturated ester 20 compounds of the formula (II)



in which R is hydrogen or methyl, R^4 is a linear or branched alkyl radical having 7 to 15 carbon atoms, R^5 and R^6 are each independently hydrogen or a group of the formula $-COOR''$ in which R'' is hydrogen or an alkyl 25 group having 7 to 15 carbon atoms.

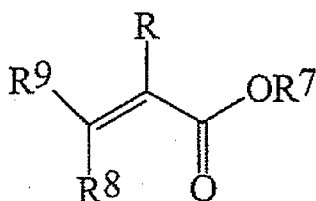
Examples of component (II) include:

(meth)acrylates, fumarates and maleates which derive from saturated alcohols, such as 2-ethylhexyl (meth)acrylate, heptyl (meth)acrylate, 2-tert-butylheptyl(meth)acrylate, octyl (meth)acrylate, 3-isopropylheptyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate;

(meth)acrylates which derive from unsaturated alcohols, for example oleyl (meth)acrylate;

cycloalkyl (meth)acrylates such as 3-vinylcyclohexyl (meth)acrylate, bornyl (meth)acrylate; and the corresponding fumarates and maleates.

In addition, preferred monomer compositions contain 0.1 to 80% by weight, preferably 0.5 to 60% by weight, more preferably 2 to 50% by weight and most preferably 5 to 20% by weight of one or more ethylenically unsaturated ester compounds of the formula (III)



(III),

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in which R is hydrogen or methyl, R⁷ is a linear or branched alkyl radical having 16 to 40, preferably 16 to 30, carbon atoms, R⁸ and R⁹ are each independently hydrogen or a group of the formula -COOR''' in which

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R''' is hydrogen or an alkyl group having 16 to 40, preferably 16 to 30, carbon atoms.

Examples of component (III) include (meth)acrylates
5 which derive from saturated alcohols, such as hexadecyl
(meth)acrylate, 2-methylhexadecyl (meth)acrylate,
heptadecyl (meth)acrylate, 5-isopropylheptadecyl
(meth)acrylate, 4-tert-butyl octadecyl (meth)acrylate,
5-ethyloctadecyl (meth)acrylate, 3-isopropyloctadecyl
10 (meth)acrylate, octadecyl (meth)acrylate, nonadecyl
(meth)acrylate, eicosyl (meth)acrylate, cetyleicosyl
(meth)acrylate, stearyleicosyl (meth)acrylate, docosyl
(meth)acrylate and/or eicosyltetratriacontyl (meth)-
acrylate;
15 cycloalkyl (meth)acrylates such as 2,4,5-tri-t-butyl-
3-vinylcyclohexyl (meth)acrylate, 2,3,4,5-tetra-
t-butylcyclohexyl (meth)acrylate;
and the corresponding fumarates and maleates.

The ester compounds having a long-chain alcohol
20 radical, especially the components (II) and (III), can
be obtained, for example, by reacting (meth)acrylates,
fumarates, maleates and/or the corresponding acids with
long-chain fatty alcohols, which generally gives a
mixture of esters, for example (meth)acrylates with
25 various long-chain alcohol radicals. These fatty
alcohols include Oxo Alcohol® 7911 and Oxo Alcohol®
7900, Oxo Alcohol® 1100; Alfol® 610, Alfol® 810, Lial®
125 and Nafol® types (Sasol); Alphanol® 79 (ICI);
Epal® 610 and Epal® 810 (Afton); Linevol® 79, Linevol®
30 911 and Neodol® 25E (Shell AG); Dehydad®, Hydrenol®
and Lorol® types (Cognis); Acropol® 35 and Exxal® 10
(Exxon Chemicals); Kalcol 2465 (Kao Chemicals).

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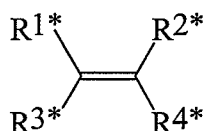
Among the ethylenically unsaturated ester compounds, particular preference is given to the (meth)acrylates over the maleates and fumarates, i.e. R2, R3, R5, R6, R8 and R9 of the formulae (I), (II) and (III) are each
5 hydrogen in particularly preferred embodiments.

The weight ratio of ester monomers of the formula (II) to the ester monomers of the formula (III) may be within a wide range. The ratio of ester compounds of
10 the formula (II) which contain 7 to 15 carbon atoms in the alcohol radical to the ester compounds of the formula (III) which contain 16 to 40 carbon atoms in the alcohol radical is preferably in the range of 50:1 to 1:30, more preferably in the range of 10:1 to 1:3,
15 especially preferably 5:1 to 1:1.

Component (IV) comprises in particular ethylenically unsaturated monomers which can be copolymerized with the ethylenically unsaturated ester compounds of the
20 formulae (I), (II) and/or (III).

However, particularly suitable comonomers for polymerization according to the present invention are those which correspond to the formula:

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(IV)

in which R^{1*} and R^{2*} are each independently selected from the group consisting of hydrogen, halogens, CN, linear or branched alkyl groups having 1 to 20,
30 preferably 1 to 6 and more preferably 1 to 4, carbon

atoms which may be substituted by 1 to (2n+1) halogen atoms, where n is the number of carbon atoms of the alkyl group (for example CF₃), α,β -unsaturated linear or branched alkenyl or alkynyl groups having 2 to 10, preferably 2 to 6 and more preferably 2 to 4, carbon atoms which may be substituted by 1 to (2n-1) halogen atoms, preferably chlorine, where n is the number of carbon atoms of the alkyl group, for example CH₂=CCl-, cycloalkyl groups having 3 to 8 carbon atoms which may be substituted by 1 to (2n-1) halogen atoms, preferably chlorine, where n is the number of carbon atoms of the cycloalkyl group; C(=Y*)R^{5*}, C(=Y*)NR^{6*}R^{7*}, Y*C(=Y*)R^{5*}, SOR^{5*}, SO₂R^{5*}, OSO₂R^{5*}, NR^{8*}SO₂R^{5*}, PR^{5*}₂, P(=Y*)R^{5*}₂, Y*PR^{5*}₂, Y*P(=Y*)R^{5*}₂, NR^{8*}₂ which may be quaternized with an additional R^{8*}, aryl or heterocyclyl group, where Y* may be NR^{8*}, S or O, preferably O; R^{5*} is an alkyl group having from 1 to 20 carbon atoms, an alkylthio having 1 to 20 carbon atoms, OR¹⁵ (R¹⁵ is hydrogen or an alkali metal), alkoxy of 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; R^{6*} and R^{7*} are each independently hydrogen or an alkyl group having 1 to 20 carbon atoms, or R^{6*} and R^{7*} together may form an alkylene group having 2 to 7, preferably 2 to 5 carbon atoms, in which case they form a 3- to 8-membered, preferably 3- to 6-membered, ring, and R^{8*} is hydrogen, linear or branched alkyl or aryl groups having 1 to 20 carbon atoms; R^{3*} and R^{4*} are independently selected from the group consisting of hydrogen, halogen (preferably fluorine or chlorine), alkyl groups having 1 to 6 carbon atoms and COOR^{9*} in which R^{9*} is hydrogen, an alkali metal or an alkyl group having 1 to 40 carbon atoms, or R^{3*} and R^{4*} together may form a group of the formula (CH₂)_{n'} which may be substituted by 1 to 2n' halogen atoms or C₁ to C₄

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alkyl groups, or form the formula $C(=O)-Y^*-C(=O)$ where n' is 2 to 6, preferably 3 or 4, and Y^* is as defined above; and where at least 2 of the R^{1*} , R^{2*} , R^{3*} and R^{4*} radicals are hydrogen or halogen.

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The preferred comonomers (IV) include hydroxyalkyl (meth)acrylates such as 3-hydroxypropyl methacrylate, 3,4-dihydroxybutyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2,5-dimethyl-1,6-hexanediol (meth)acrylate, 1,10-decanediol (meth)acrylate; aminoalkyl (meth)acrylates such as N-(3-dimethylaminopropyl)methacrylamide, 3-diethylaminopentyl methacrylate, 3-dibutylaminohexadecyl (meth)acrylate; nitriles of (meth)acrylic acid and other nitrogen-containing methacrylates, such as N-(methacryloyloxyethyl)diisobutyl ketimine, N-(methacryloyloxyethyl)dihexadecyl ketimine, methacryloylamidoacetonitrile, 2-methacryloyloxyethylmethylcyanamide, cyanomethyl methacrylate; aryl (meth)acrylates such as benzyl methacrylate or phenyl methacrylate in which the aryl radicals may each be unsubstituted or up to tetrasubstituted; carbonyl-containing methacrylates such as 2-carboxyethyl methacrylate, carboxymethyl methacrylate, oxazolidinylethyl methacrylate, N-(methacryloyloxy)-formamide, acetonyl methacrylate, N-methacryloylmorpholine, N-methacryloyl-2-pyrrolidinone, N-(2-methacryloyloxyethyl)-2-pyrrolidinone, N-(3-methacryloyloxypropyl)-2-pyrrolidinone, N-(2-methacryloyloxy-pentadecyl)-2-pyrrolidinone, N-(3-methacryloyloxyheptadecyl)-2-pyrrolidinone; glycol dimethacrylates such as 1,4-butanediol methacrylate, 2-butoxyethyl methacrylate, 2-ethoxyethoxymethyl methacrylate, 2-ethoxyethyl methacrylate; methacrylates

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of ether alcohols, such as tetrahydrofurfuryl methacrylate, vinyloxyethoxyethyl methacrylate, methoxyethoxyethyl methacrylate, 1-butoxypropyl methacrylate, 1-methyl-(2-vinyloxy)ethyl methacrylate, 5 cyclohexyloxymethyl methacrylate, methoxymethoxyethyl methacrylate, benzyloxymethyl methacrylate, furfuryl methacrylate, 2-butoxyethyl methacrylate, 2-ethoxyethoxymethyl methacrylate, 2-ethoxyethyl methacrylate, allyloxymethyl methacrylate, 1-ethoxybutyl methacrylate, methoxymethyl methacrylate, 10 1-ethoxyethyl methacrylate, ethoxymethyl methacrylate; methacrylates of halogenated alcohols, such as 2,3-dibromopropyl methacrylate, 4-bromophenyl methacrylate, 1,3-dichloro-2-propyl methacrylate, 2-bromoethyl 15 methacrylate, 2-iodoethyl methacrylate, chloromethyl methacrylate; oxiranyl methacrylates such as 2,3-epoxybutyl methacrylate, 3,4-epoxybutyl methacrylate, 10,11-epoxyundecyl methacrylate, 10,11-epoxyhexadecyl methacrylate, 2,3-epoxycyclohexyl 20 methacrylate; glycidyl methacrylate; phosphorus-, boron- and/or silicon-containing methacrylates such as 2-(dimethylphosphato)propyl methacrylate, 2-(ethylenephosphito)propyl methacrylate, 25 dimethylphosphinomethyl methacrylate, dimethylphosphonoethyl methacrylate, diethylmethacryloyl phosphonate, dipropylmethacryloyl phosphate, 2-(dibutylphosphono)-ethyl methacrylate, 30 2,3-butylenemethacryloylethyl borate, methyldiethoxymethacryloylethoxysilane,

diethylphosphatoethyl methacrylate;

vinyl halides, for example vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride;

heterocyclic (meth)acrylates, such as 2-(1-
5 imidazolyl)ethyl (meth)acrylate, 2-(4-morpholinyl)ethyl (meth)acrylate and 1-(2-methacryloxyethyl)-2-pyrrolidinone;

vinyl esters such as vinyl acetate;

styrene, substituted styrenes having an alkyl
10 substituent in the side chain, for example α -methylstyrene and α -ethylstyrene, substituted styrenes having an alkyl substituent on the ring, such as vinyltoluene and p-methylstyrene, halogenated styrenes, for example monochlorostyrenes, dichlorostyrenes, tribromostyrenes
15 and tetrabromostyrenes;

heterocyclic vinyl compounds such as 2-vinylpyridine, 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinyl-
20 carbazole, 4-vinylcarbazole, 1-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinylloxolane, vinylfuran, vinylthiophene, vinylthiolane, vinyl-
25 thiazoles and hydrogenated vinylthiazoles, vinyl-oxazoles and hydrogenated vinylloxazoles;

vinyl and isoprenyl ethers;

maleic acid and maleic acid derivatives different from those mentioned under (I), (II) and (III), for example
30 maleic anhydride, methylmaleic anhydride, maleimide, methylmaleimide;

fumaric acid and fumaric acid derivatives different

from those mentioned under (I), (II) and (III).

The proportion of comonomers (IV) can be varied depending on the use and property profile of the polymer. In general, this proportion may be in the
5 range from 0 to 60% by weight, preferably from 0.01 to 20% by weight and more preferably from 0.1 to 10% by weight. Owing to the combustion properties and for ecological reasons, the proportion of the monomers
10 which comprise aromatic groups, heteroaromatic groups, nitrogen-containing groups, phosphorus-containing groups and sulphur-containing groups should be minimized. The proportion of these monomers can therefore be restricted to 1% by weight, in particular
15 0.5% by weight and preferably 0.01% by weight.

The comonomers (IV) and the ester monomers of the formulae (I), (II) and (III) can each be used individually or as mixtures.

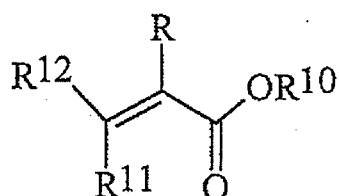
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Surprisingly, ester-comprising polymers have a better activity in mixtures of mineral diesel fuel and biodiesel fuel which comprise merely a small proportion, if any, of units which are derived from
25 hydroxyl-containing monomers. This is especially true of biodiesel fuels which have a high proportion of saturated fatty acids which have at least 16 carbon atoms in the acid radical. Accordingly, ester-comprising polymers to be used with preference in the
30 inventive fuel mixtures preferably contain at most 5% by weight, preferably at most 3% by weight, more preferably at most 1% by weight and most preferably at most 0.1% by weight of units which are derived from hydroxyl-containing monomers. These include

hydroxyalkyl (meth)acrylates and vinyl alcohols. These monomers have been detailed above.

Similarly, ester-comprising polymers have a better activity in mixtures of mineral diesel fuel and biodiesel fuel which comprise only a small proportion, if any, of repeat units which derive from monomers having oxygen-containing alcohol radicals of the formula

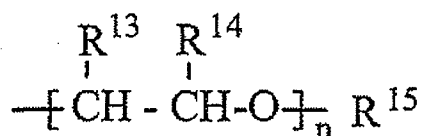
(IV')



(IV'),

where

R is hydrogen or methyl, R¹⁰ is an alkyl radical which is substituted by an OH group and has 2 to 20 carbon atoms, or an alkoxyated radical of the formula (V)



(V),

in which R¹³ and R¹⁴ are each independently hydrogen or methyl, R¹⁵ is hydrogen or an alkyl radical having 1 to 20 carbon atoms, and n is an integer of 1 to 30, R¹¹ and R¹² are each independently hydrogen or a group of the formula -COOR'''' in which R'''' is hydrogen or an alkyl radical which is substituted by an OH group and has 2 to 20 carbon atoms, or an alkoxyated radical

of the formula (V)



- 5 in which R^{13} and R^{14} are each independently hydrogen or methyl, R^{15} is hydrogen or an alkyl radical having 1 to 20 carbon atoms, and n is an integer of 1 to 30.

10 Ester-comprising polymers to be used with preference have a thickening efficiency TE100 in the range of 4.0 to 50 mm^2/s , preferably 7.5 to 29 mm^2/s . The thickening efficiency (TE100) is determined at 100°C in a 150N reference oil (KV100 = 5.42 mm^2/s , KV40 = 31.68 mm^2/s and VI = 103), using 5% by weight of polymer. The
15 designations KV100 and KV40 describe the kinematic viscosity of the oil at 100°C and 40°C respectively to ASTM D445, the abbreviation VI the viscosity index determined to ASTM D 2270.

20 The ester-comprising polymers to be used in accordance with the invention may generally have a molecular weight in the range of 1000 to 1 000 000 g/mol, preferably in the range of 25 000 to 700 000 g/mol and more preferably in the range of 40 000 to 600 000 g/mol
25 and most preferably in the range of 60 000 to 300 000 g/mol, without any intention that this should impose a restriction. These values are based on the weight-average molecular weight M_w of the polydisperse polymers in the composition. This parameter can be
30 determined by GPC.

The preferred copolymers which can be obtained by polymerizing unsaturated ester compounds preferably have a polydispersity M_w/M_n in the range of 1 to 10, more preferably 1.05 to 6.0 and most preferably 1.2 to 5.0. This parameter can be determined by GPC.

The architecture of the ester-comprising polymers is not critical for many applications and properties. Accordingly, the ester-comprising polymers may be random copolymers, gradient copolymers, block copolymers and/or graft copolymers.

Block copolymers and gradient copolymers can be obtained, for example, by altering the monomer composition discontinuously during the chain growth. The blocks derived from ester compounds of the formulae (I), (II) and/or (III) preferably have at least 30 monomer units.

The preparation of the polyalkyl esters from the above-described compositions is known per se. Thus, these polymers can be obtained in particular by free-radical polymerization and related processes, for example ATRP (= Atom Transfer Radical Polymerization) or RAFT (= Reversible Addition Fragmentation Chain Transfer).

Customary free-radical polymerization is described, inter alia, in Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition. In general, a polymerization initiator and a chain transferrer are used for this purpose. The usable initiators include the azo initiators widely known in the technical field, such as AIBN and 1,1-azobiscyclohexanecarbonitrile, and also

- 25 -

peroxy compounds such as methyl ethyl ketone peroxide, acetylacetone peroxide, dilauryl peroxide, tert-butyl per-2-ethylhexanoate, ketone peroxide, tert-butyl peroctoate, methyl isobutyl ketone peroxide,

5 cyclohexanone peroxide, dibenzoyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropylcarbonate, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy-3,5,5-trimethylhexanoate, dicumyl peroxide, 1,1-

10 bis(tert-butylperoxy)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, cumyl hydroperoxide, tert-butyl hydroperoxide, bis(4-tert-butylcyclohexyl) peroxydicarbonate, mixtures of two or more of the aforementioned compounds with one another,

15 and mixtures of the aforementioned compounds with compounds which have not been mentioned but can likewise form free radicals. Suitable chain transferrers are in particular oil-soluble mercaptans, for example dodecyl mercaptan or 2-mercaptoethanol, or

20 else chain transferrers from the class of the terpenes, for example terpineols.

The ATRP process is known per se. It is assumed that it is a "living" free-radical polymerization, without any intention that this should restrict the description of

25 the mechanism. In these processes, a transition metal compound is reacted with a compound which has a transferable atom group. This transfers the transferable atom group to the transition metal compound, which oxidizes the metal. This reaction forms

30 a radical which adds onto ethylenic groups. However, the transfer of the atom group to the transition metal compound is reversible, so that the atom group is transferred back to the growing polymer chain, which

forms a controlled polymerization system. The structure of the polymer, the molecular weight and the molecular weight distribution can be controlled correspondingly. This reaction is described, for example, by J S. Wang, 5 et al., J. Am. Chem. Soc., vol. 117, p. 5614-5615 (1995), by Matyjaszewski, Macromolecules, vol. 28, p. 7901-7910 (1995). In addition, the patent applications WO 96/30421, WO 97/47661, WO 97/18247, WO 98/40415 and WO 99/10387 disclose variants of the ATRP explained 10 above.

In addition, the inventive polymers may be obtained, for example, also via RAFT methods. This process is presented in detail, for example, in WO 98/01478 and WO 15 2004/083169, to which reference is made explicitly for the purposes of disclosure.

In addition, the inventive polymers are also obtainable by NMP processes (nitroxide-mediated polymerization), 20 which is described, inter alia, in US 4581429.

These methods are described comprehensively, in particular with further references, inter alia, in K. Matyjaszewski, T.P. Davis, Handbook of Radical 25 Polymerization, Wiley Interscience, Hoboken 2002, to which reference is made explicitly for the purposes of disclosure.

The polymerization may be carried out at standard 30 pressure, reduced pressure or elevated pressure. The polymerization temperature too is uncritical. However, it is generally in the range of -20° - 200°C, preferably 0° - 130°C and more preferably 60° - 120°C.

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The polymerization may be carried out with or without solvent. The term solvent is to be understood here in a broad sense.

5 The polymerization is preferably carried out in a nonpolar solvent. These include hydrocarbon solvents, for example aromatic solvents such as toluene, benzene and xylene, saturated hydrocarbons, for example cyclohexane, heptane, octane, nonane, decane, dodecane,
10 which may also be present in branched form. These solvents may be used individually and as a mixture. Particularly preferred solvents are mineral oils, diesel fuels of mineral origin, natural vegetable and animal oils, biodiesel fuels and synthetic oils (e.g.
15 ester oils such as dinonyl adipate), and also mixtures thereof. Among these, very particular preference is given to mineral oils and mineral diesel fuels.

The inventive fuel composition may comprise further
20 additives in order to achieve specific solutions to problems. These additives include dispersants, for example wax dispersants and dispersants for polar substances, demulsifiers, defoamers, lubricity additives, antioxidants, cetane number improvers,
25 detergents, dyes, corrosion inhibitors and/or odourants.

For example, the inventive fuel composition may comprise ethylene copolymers which are described, for
30 example, in EP-A-1 541 663. These ethylene copolymers may contain 8 to 21 mol% of one or more vinyl and/or (meth)acrylic esters and 79 to 92% by weight of ethylene. Particular preference is given to ethylene copolymers containing 10 to 18 mol% and especially 12

to 16 mol% of at least one vinyl ester. Suitable vinyl esters derive from fatty acids having linear or branched alkyl groups having 1 to 30 carbon atoms. Examples include vinyl acetate, vinyl propionate, vinyl butyrate, vinyl hexanoate, vinyl heptanoate, vinyl octanoate, vinyl laurate and vinyl stearate, and also esters of vinyl alcohol based on branched fatty acids, such as vinyl isobutyrate, vinyl pivalate, vinyl 2-ethylhexanoate, vinyl isononanoate, vinyl neononanoate, vinyl neodecanoate and vinyl neoundecanoate. Comonomers which are likewise suitable are esters of acrylic acid and methacrylic acid having 1 to 20 carbon atoms in the alkyl radical, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n- and isobutyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, tetradecyl (meth)acrylate, hexadecyl (meth)acrylate, octadecyl (meth)acrylate, and also mixtures of two, three or four or else more of these comonomers.

Particularly preferred terpolymers of vinyl 2-ethylhexanoate, of vinyl neononanoate and of vinyl neodecanoate contain, apart from ethylene, preferably 3.5 to 20 mol%, in particular 8 to 15 mol%, of vinyl acetate and 0.1 to 12 mol%, in particular 0.2 to 5 mol%, of the particular long-chain vinyl ester, the total comonomer content being between 8 and 21 mol%, preferably between 12 and 18 mol%. Further preferred copolymers contain, in addition to ethylene and 8 to 18 mol% of vinyl esters, also 0.5 to 10 mol% of olefins such as propene, butene, isobutylene, hexene, 4-methylpentene, octene, diisobutylene and/or norbornene.

The ethylene copolymers preferably have molecular weights which correspond to melt viscosities at 140°C of from 20 to 10 000 mPas, in particular 30 to 5000 mPas and especially 50 to 1000 mPas. The degrees
5 of branching determined by means of ¹H NMR spectroscopy are preferably between 1 and 9 CH₃/100 CH₂ groups, in particular between 2 and 6 CH₃/100 CH₂ groups, for example 2.5 to 5 CH₃/100 CH₂ groups, which do not stem from the comonomers.

10

Such ethylene copolymers are described in detail, inter alia, in DE-A-34 43 475, EP-B-0 203 554, EP-B-0 254 284, EP-B-0 405 270, EP-B-0 463 518, EP-B-0 493 769, EP-0 778 875, DE-A-196 20 118, DE-A-196 20 119 and EP-
15 A-0 926 168.

Preference is given in this context to ethylene-vinyl acetate copolymers and terpolymers which, in addition to ethylene and vinyl acetate repeat units, also have
20 repeat (meth)acrylic ester units. These polymers may be structured, for example, as random copolymers, as block copolymers or as graft copolymers.

In a preferred embodiment, the inventive fuel
25 composition may comprise 0.0005 to 2% by weight, preferably 0.01 to 0.5% by weight, of ethylene copolymers.

For reasons of cost, however, a proportion of the
30 above-described ethylene copolymers can be dispensed with in a further embodiment, in which case these fuel compositions without a significant proportion of ethylene copolymers have outstanding properties. In this specific embodiment, the proportion of ethylene

- 30 -

copolymers may preferably be at most 0.05% by weight, more preferably at most 0.001% by weight and most preferably at most 0.0001% by weight.

- 5 Preferred fuel compositions consist of
20.0 to 97.95% by weight, in particular 70 to 94.95% by weight, of mineral diesel fuel,
2.0 to 79.95% by weight, in particular 5.0 to 29.95% by weight, of biodiesel fuel,
10 0.05 to 5% by weight, in particular 0.1 to 1% by weight, of ester-comprising polymer
and
0 to 60% by weight, in particular 0.1 to 10% by weight, of additives.

- 15 The inventive fuel compositions preferably have an iodine number of at most 30, more preferably at most 20 and most preferably at most 10.

- 20 In addition, the inventive fuel compositions have outstanding low-temperature properties. In particular, the pour point (PP) to ASTM D97 preferably has values of less than or equal to 0°C, preferably less than or equal to -5°C and more preferably less than or equal to
25 -10°C. The limit of filterability (cold filter plugging point, CFPP) measured to DIN EN 116 is preferably at most 0°C, more preferably at most -5°C and more preferably at most -10°C. Moreover, the cloud point (CP) to ASTM D2500 of preferred fuel compositions may
30 assume values of less than or equal to 0°C, preferably less than or equal to -5°C and more preferably less than or equal to -10°C.

- The cetane number to DIN 51773 of inventive fuel
35 compositions is preferably at least 50, more preferably

at least 53, in particular at least 55 and most preferably at least 58.

The viscosity of the present fuel compositions may be within a wide range, and this can be adjusted to the intended use. This adjustment can be effected, for example, by selecting the biodiesel fuels or the mineral diesel fuels. In addition, the viscosity can be varied by the amount and the molecular weight of the ester-comprising polymers used. The kinematic viscosity of preferred fuel compositions of the present invention is in the range of 1 to 10 mm²/s, more preferably 2 to 5 mm²/s and especially preferably 2.5 to 4 mm²/s, measured at 40°C to ASTM D445.

15

The use of ester-comprising polymers which comprise repeat units derived from unsaturated esters having 7 to 15 carbon atoms in the alcohol radical and repeat units derived from unsaturated esters having 16 to 40 carbon atoms in the alcohol radical in a concentration of 0.05 to 5% by weight as a flow improver in fuel compositions which comprise at least one diesel fuel of mineral origin and at least one biodiesel fuel accordingly provides fuel compositions with exceptional properties, as a result of which known diesel engines can be operated in a simple and inexpensive manner.

The invention will be illustrated in detail hereinafter with reference to examples and a comparative example, without any intention that this should impose a restriction.

Examples and Comparative Examples

35 *General method for the preparation of the polymers*

600 g of monomer composition according to the composition detailed in each case in Table 1 and n-dodecyl mercaptan (20 g to 2 g depending on the desired

molecular weight) are mixed. 44.4 g of this monomer/regulator mixture are charged together with 400 g of carrier oil (e.g. 100N mineral oil, synthetic dinonyl adipate or vegetable oil) into the 2 l reaction flask of an apparatus with sabre stirrer, condenser, thermometer, feed pump and N₂ feed line. The apparatus is inertized and heated to 100°C with the aid of an oil bath. The remaining amount of 555.6 g of monomer/regulator mixture is admixed with 1.4 g of tert-butyl peroctoate. When the mixture in the reaction flask has attained a temperature of 100°C, 0.25 g of tert-butyl peroctoate is added, and the feed of the monomer/regulator/initiator mixture by means of a pump is started simultaneously. The addition is effected uniformly over a period of 210 min at 100°C. 2 h after the end of feeding, another 1.2 g of tert-butyl peroctoate are added and the mixture is stirred at 100°C for a further 2 h. A 60% clear concentrate is obtained.

The mass-average molecular weight M_w and the polydispersity index PDI of the polymers were determined by GPC. The measurements were effected in tetrahydrofuran at 35°C against a polymethyl methacrylate calibration curve composed of a set of ≥25 standards (Polymer Standards Service or Polymer Laboratories), whose M_{peak} was distributed in a logarithmically uniform manner over the range of 5×10^6 to 2×10^2 g/mol. A combination of six columns (Polymer Standards SDV 100Å / 2xSDV LXL / 2xSDV 100Å / Shodex KF-800D) was used. To record the signal, an RI detector (Agilent 1100 Series) was used.

Table 1: Properties of the polymers used

Polymer	Monomer composition (weight ratio)	Mw [g/mol]	PDI (Mw/Mn)	TE 100
Example 1	DPMA-SMA-MMA 75.4-14.6-10	130 000	2.3	10.8
Example 2	DPMA-SMA 70-30	490 000	3.5	24.6
Example 3	DPMA-SMA-MMA	60 000	2.2	8.65
Comparative Example 1	DPMA-MMA 99-1	60 000	2.2	8.54

DPMA: alkyl methacrylate which has 12 to 15 carbon atoms in the alkyl radical

5 SMA: alkyl methacrylate which has 16 to 18 carbon atoms in the alkyl radical

MMA: methyl methacrylate

Subsequently, the polymers thus obtained were
 10 investigated in an 80/20 mixture of mineral diesel/
 biodiesel. The amount of polymer used is shown in Table
 2. The mineral diesel used was a summer diesel of
 Australian origin with a pour point of -9°C. A palm oil
 methyl ester (PME) (source of palm oil raw material:
 15 Malaysia) having a pour point of +12°C was used as the
 biodiesel. An 80/20 mixture of mineral diesel/biodiesel
 exhibited a pour point of 0°C.

To investigate the low-temperature properties, the pour
 20 point (PP) to ASTM D97 of the mixtures and of the
 mineral diesel fuel was determined. The results
 obtained are shown in Table 2.

Table 2: Properties of mineral diesel fuels and of the
 25 mixtures comprising approx. 80% by weight of mineral
 diesel and approx. 20% by weight of biodiesel, each of
 which contain ester-comprising polymers.

Polymer used	Proportion of the polymer in the mixture [% by wt.]	Pour point to ASTM D97 of the 80/20 mixture [°C]	Pour point to ASTM D97 of the mineral diesel [°C]
unadditized	-	-	-9
Example 1	0.280	-6	
Example 1	0.350	-12	-12
Example 1	0.420	-9	
Example 1	0.490	-9	
Example 1	0.700	-9	-12
Example 1	1.400	-6	-12
Example 2	0.350	-6	-9
Example 3	0.350	-6	-9
Comparative Example 1	0.350	-3	-9

The examples detailed above show that ester-comprising polymers containing repeat units which are derived from ester monomers having 16 to 40 carbon atoms in the alcohol radical lead to significantly better low-temperature properties of mixtures which comprise biodiesel, especially palm oil esters, and mineral diesel.

10 Particularly surprisingly, preferred mixtures which comprise certain ester-comprising polymers have an improved pour point compared to the pure mineral diesel fuel without additive, this improved pour point also being retained in the case of addition of biodiesel.

Claims

1. Fuel composition comprising at least one diesel fuel of mineral origin and at least one biodiesel fuel, characterized in that the fuel composition contains at least 20% by weight of diesel fuel of mineral origin and from 0.05 to 5% by weight of at least one ester-comprising polymer which comprises repeat units which are derived from ester monomers having 16 to 40 carbon atoms in the alcohol radical, and repeat units which are derived from ester monomers having 7 to 15 carbon atoms in the alcohol radical.
2. Fuel composition according to Claim 1, characterized in that the ester-comprising polymer is selected from polyalkyl (meth)acrylates (PAMAs), polyalkyl fumarates and/or polyalkyl maleates.
3. Fuel composition according to Claim 1 or 2, characterized in that the ester-comprising polymer contains 0.5 to 60% by weight of units which are derived from ester monomers having 16 to 40 carbon atoms in the alcohol radical.
4. Fuel composition according to at least one of the preceding claims, characterized in that the ester-comprising polymer contains 0.1 to 30% by weight of units which are derived from ester monomers having 1 to 6 carbon atoms in the alcohol radical.
5. Fuel composition according to at least one of the preceding claims, characterized in that the ester-comprising polymer is obtainable by polymerizing a monomer mixture which comprises 0 to 40% by weight of one or more ethylenically unsaturated ester compounds of the formula (I)

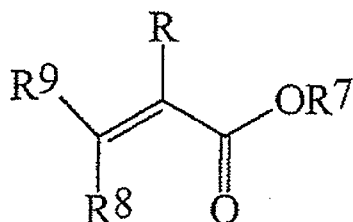


5 in which R is hydrogen or methyl, R¹ is a linear or branched alkyl radical having 1 to 6 carbon atoms, R² and R³ are each independently hydrogen or a group of the formula -COOR' in which R' is hydrogen or an alkyl group having 1 to 6 carbon atoms,
10 10 to 98% by weight of one or more ethylenically unsaturated ester compounds of the formula (II)



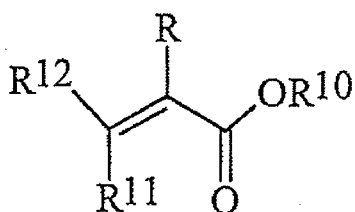
15 in which R is hydrogen or methyl, R⁴ is a linear or branched alkyl radical having 7 to 15 carbon atoms, R⁵ and R⁶ are each independently hydrogen or a group of the formula -COOR" in which R" is hydrogen or an alkyl group having 7 to 15 carbon atoms, and
20 0.1 to 80% by weight of one or more ethylenically unsaturated ester compounds of the formula (III)

25



(III),

- 5 in which R is hydrogen or methyl, R⁷ is a linear or branched alkyl radical having 16 to 40 carbon atoms, R⁸ and R⁹ are each independently hydrogen or a group of the formula -COOR''' in which R''' is hydrogen or an alkyl group having 16 to 40 carbon atoms.
- 10 6. Fuel composition according to at least one of the preceding claims, characterized in that the ester-comprising polymer comprises at most 3% by weight of units which are derived from hydroxyl-containing monomers.
- 15 7. Fuel composition according to at least one of the preceding claims, characterized in that the ester-comprising polymer comprises at most 3% by weight of repeat units which are derived from ester-comprising monomers with acid-containing alcohol radicals of the formula (IV')
- 20



(IV'),

- 25 in which R is hydrogen or methyl, R¹⁰ is an alkyl radical which is substituted by an OH group and has 2 to 20 carbon atoms, or an alkoxyated radical of the formula (V)



in which R^{13} and R^{14} are each independently hydrogen or methyl, R^{15} is hydrogen or an alkyl radical having 1 to 20 carbon atoms, and n is an integer from 1 to 30, R^{11} and R^{12} are each independently hydrogen or a group of the formula $-\text{COOR}''''$ in which R'''' is hydrogen or an alkyl radical which is substituted by an OH group and has 2 to 20 carbon atoms, or an alkoxyated radical of the formula (V) shown above.

8. Fuel composition according to at least one of the preceding claims, characterized in that the ester-comprising polymer has a molecular weight in the range of 40 000 to 600 000 g/mol.
9. Fuel composition according to at least one of the preceding claims, characterized in that the ester-comprising polymer has a polydispersity index in the range of 1.0 to 10.0.
10. Fuel composition according to at least one of the preceding claims, characterized in that the ester-comprising polymer has a thickening efficiency TE100 measured at 100°C in the range of 7.5 to 29 mm²/s.
11. Fuel composition according to at least one of the preceding claims, characterized in that the diesel fuel of mineral origin has a boiling point in the range of 120°C to 450°C.
12. Fuel composition according to at least one of the preceding claims, characterized in that the diesel

fuel of mineral origin has a kinematic viscosity measured at 40°C to ASTM D445 in the range of 1 to 5 mm²/s.

- 5 13. Fuel composition according to at least one of the preceding claims, characterized in that the biodiesel fuel comprises fatty acid esters which are derived from monohydric alcohols having 1 to 4 carbon atoms.
- 10 14. Fuel composition according to Claim 13, characterized in that the monoester is a methyl ester.
- 15 15. Fuel composition according to at least one of the preceding claims, characterized in that the biodiesel fuel comprises at least 35% by weight of saturated fatty acid esters which have at least 16 carbon atoms in the fatty acid radical.
- 20 16. Fuel composition according to at least one of the preceding claims, characterized in that the biodiesel fuel is derived from palm oil or an animal tallow.
- 25 17. Fuel composition according to at least one of the preceding claims, characterized in that the fuel composition comprises at least one additive.
- 30 18. Fuel composition according to Claim 17, characterized in that at least one additive is selected from the group of the dispersants, demulsifiers, defoamers, lubricity additives, antioxidants, cetane number improvers, detergents, 35 dyes, corrosion inhibitors and/or odourants.
19. Fuel composition according to at least one of the preceding claims, characterized in that the fuel

composition comprises at least 80% by weight of diesel fuel of mineral origin.

20. Fuel composition according to at least one of the preceding claims, characterized in that the fuel composition contains 0.1 to 1% by weight of at least one ester-comprising polymer.
21. Fuel composition according to at least one of the preceding claims, characterized in that the fuel composition consists of
20.0 to 97.95% by weight of diesel fuel of mineral origin,
20 to 79.95% by weight of biodiesel fuel,
0.05 to 5% by weight of ester-comprising polymer and
0 to 60% by weight of additives.
22. Fuel composition according to at least one of the preceding claims, characterized in that the fuel composition comprises 0.01 to 0.5% by weight of ethylene copolymer.
23. Fuel composition according to at least one of the preceding claims, characterized in that the fuel composition comprises at most 0.05% by weight of ethylene copolymer.
24. Use of ester-comprising polymers which comprise repeat units derived from unsaturated esters having 7 to 15 carbon atoms in the alcohol radical, and repeat units derived from unsaturated esters having 16 to 40 carbon atoms in the alcohol radical, in a concentration of 0.05 to 5% by weight as flow improvers in fuel compositions which comprise at least one diesel fuel of mineral origin and at least one biodiesel fuel.

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25. Process for operating a diesel engine, characterized in that a fuel composition according to at least one of Claims 1 to 23 is used.