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(54) **IMPROVEMENTS IN FUELS**

VERBESSERUNGEN IN BRENNSTOFFEN.
AMÉLIORATIONS DANS LES CARBURANTS.

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WO-A1-96/22344 WO-A2-2007/076163
WO-A2-2007/147753 US-A- 4 211 534
US-A- 5 743 923 US-A1- 2008 016 754

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Description

[0001] The present invention relates to improvements in fuels derived wholly or in part from animal or vegetable oil sources. Such fuels are called herein Bx fuels. Bx fuels may be derived entirely from animal or vegetable oil sources (B100 fuels) or they may comprise a proportion of fuels derived from animal or vegetable oil sources, admixed with fuels from other sources (for example mineral sources, or synthetic sources, e.g. Fischer-Tropsch sources). For example B20 herein is a fuel in which 20 wt% of the fuel is from animal or vegetable oil sources and 80 wt% of the fuel is from other sources. The proportion may be lower still, as in the case of, for example, a B5 fuel.

[0002] A problem has become apparent in Bx fuels,; blocking of filters in distribution systems and vehicles by precipitates in such fuels, typically at temperatures above the cloud point (CP) of the fuels, The problems have been seen in a wide range of Bx fuels, from B100 down to B5.

[0003] WO 2007/076163 describes such problems, and suggests that the problem of filter blocking arises as a result of the precipitation of crystals of steryl glycosides in fuels derived from biological sources. Steryl glycosides are found in plants and it is suggested that they are carried over into Bx fuels.

[0004] WO 2007/076163 proposed a solution to the filter blocking problem; namely the removal of the steryl glycosides, for example using an adsorbent as an additive in conjunction with a process of filtration or centrifugation, or both. In one example soy biodiesel was filtered through a bed of diatomaceous earth.

[0005] The proposals of WO 2007/076163 have the disadvantage that a separation step is needed, in addition to the treatment of the Bx fuel with the additive.

[0006] We are not bound by the explanation for the problem given in WO 2007/076163. We believe it might be more complex, for example also relating to the total glycerides content, including monoglycerides, diglycerides and triglycerides, saturated or unsaturated. We are certainly of the view that such problems now seen in Bx fuels are connected with the Bx fuel component which is derived from vegetable or animal sources, and are quite different from precipitation problems which have arisen in the past predominantly in mineral fuels. The present invention seeks to solve this new problem notwithstanding that an agreed scientific explanation of its nature or cause may follow.

[0007] By mineral fuels herein we mean fuels derived wholly from mineral (i.e. petroleum) sources. By mineral fuel component herein we mean the mineral-derived component in a Bx fuel.

[0008] Filter blocking problems can occur at temperatures below the cloud point in mineral and other fuels. Such problems have been closely analysed over many years. Additives have been developed that allow fuels to be used at lower temperatures than would otherwise be possible.

[0009] The source of the problem of precipitation below the cloud point is the presence of components such as so-called "waxes" (for example n-alkanes and methyl n-alkanoates that crystallise at low temperatures). This may cause the fuels to block filters and to become non-pourable.

[0010] Standardised tests have been devised to measure the temperature at which the fuel hazes (the cloud point - CP), the lowest temperature at which a fuel can flow (the pour point - PP) and the cold filter plugging point - CFPP); and the changes thereto caused by additives (ΔCP , ΔPP , $\Delta CFPP$). The standardised tests for measuring PP and, especially, CP and CFPP are among the common working tools for persons skilled in the art. CP and CFPP may be further described as follows:

Cloud Point (CP)

[0011] The cloud point of a fuel is the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under conditions prescribed in the test method as defined in ASTM D 2500.

[0012] Until recently, it was considered that problems arising from the formation of precipitates would not occur at temperatures above the cloud point.

Cold Filter Plugging Point (CFPP)

[0013] At temperatures below the cloud point but above the pour point, the wax crystals can reach a size and shape capable of plugging fuel lines, screens, and filters even though the fuel will physically flow. These problems are well recognized in the art and have a number of recognised test methods such as the CFPP value (cold filter plugging point, determined in accordance with DIN EN 116).

[0014] Tests such as these were introduced to give an indication of low temperature operability as the cloud point test was considered to be too pessimistic.

[0015] US 5743923 describes the improvement of the low temperature properties of a blend of biofuel and petroleum based fuel oil by addition of an ethylene-unsaturated ester copolymer, a comb polymer, a polar N compound or a a compound having at least one linear alkyl group connected to a non-polymeric organic residue.

[0016] WO2007/147753 describes a paraffin dispersant for fuels, especially having a biodiesel content comprising

polar oil-soluble nitrogen compounds and acid amides.

[0017] WO96/22344 describes chemical markers as additives in fuel oil compositions to improve filterability at temperatures above its cloud point.

[0018] US2008/0016754 describes additive mixtures as cold flow additives for middle distillate fuels comprising a terpolymer of ethylene, propene and at least one ethylenically unsaturated ester and a further additive selected from copolymers of ethylene and ethylenically unsaturated compounds, comb polymers and mixtures thereof.

[0019] The cold flow improvers (CFIs) and wax anti-settling additives (WASAs) which have been devised considerably ameliorate the problems of precipitation below the cloud point in fuels, and their effect can be studied by the test methods described above, comparing the results between unadditised fuels and additised fuels.

[0020] Some such additives may assist in keeping the so-called "waxes" in solution in the mineral fuel; others may alter their crystal morphology or size, so that filterability and pourability are maintained in spite of precipitation.

[0021] The additives devised to deal with the problems arising from precipitation below the cloud point have been very successful, to the extent that such fuels, suitably additised with, for example, CFIs (with or without WASAs), can be used even in severe low temperature conditions. In many fuels the CFPP value may be lowered by 10-20°C, compared with corresponding fuels without additives.

[0022] Additives are also known which improve the CFPP of Bx grades, including B100 grade, and thus it would be expected that fuels treated in this way should have no operating problems even at temperatures significantly below the CP of the fuels.

[0023] However, as noted above, the problems which have emerged in Bx fuels are very different from those which can arise in mineral fuels. In particular the precipitates cause filter blocking with Bx fuels at temperatures above the cloud point, whereas precipitation problems in mineral fuels occur below the cloud point, and generally at much lower temperatures; and the chemical nature of the precipitates is believed to be entirely different. As noted above the origin of the precipitation, though not fully understood, is believed to be entirely different - specific compounds found in animal or vegetable sources, and not found in mineral sources. The testing regimes described above are inappropriate for testing these precipitation issues in Bx fuels because they fail to predict adequately the temperature at which filters are likely to block in real life situations such as in storage, distribution and use in vehicles and heating systems.

[0024] One of the reasons for this failure is believed to be that the precipitation occurs during a period of "cold soaking" over several hours or longer and therefore is not detected by tests such as Cloud Point or CFPP.

[0025] Critically, the precipitate does not redissolve when the temperature is raised again. This is very different to conventional wax precipitation where at temperatures above the cloud point, wax can readily redissolve, particularly if kept dispersed in the fuel through use of WASAs.

[0026] Without wishing to be bound by theory, we believe that the precipitates causing the problem of filter blocking at temperatures above the cloud point are present as minor constituents within the B100 and are more soluble in the B100 than in mineral fuels and hence in Bx blends. Furthermore, it is thought that as the polarity of the mineral fuel is decreased for example removal of sulphur, the solubility of these constituents will be even less and the problem will be exacerbated.

[0027] In the light of differences, in the nature of these precipitation phenomena below and above the cloud point, additives developed to solve a problem arising from precipitation below the cloud point, predominantly in mineral fuels, are not promising starting points to solve a problem arising from precipitation in a Bx fuel, arising from the fuel component derived from an animal or vegetable oil. Indeed, it must be borne in mind that Bx fuels have already contained additives of the type used to improve flow properties below the cloud point; and yet the new problems of higher temperature filter blocking have still arisen.

[0028] However, we have now found that, unexpectedly, there is one class of additive which is particularly effective at improving the flow properties, and hence the filterability, of Bx fuels above the cloud point. This class was already known to improve the flow properties of fuels below the cloud point. The finding of one class of additive which:

- (a) improves the flow properties of fuels having an animal or vegetable origin above the cloud point, and
- (b) improves the flow properties of fuels, including mineral fuels, below the cloud point;

notwithstanding the different nature of the fuels and, in particular, the different nature of the respective problems and precipitates, is serendipitous.

[0029] In accordance with a first aspect of the present invention there is provided the use of a reaction product of (i) a compound containing the segment -NR¹R² where R¹ represents a group containing from 4 to 44 carbon atoms and R² represents a hydrogen atom or a group R¹, and (ii) carboxylic acid having from 1 to 4 carboxylic acid groups or an acid anhydride or acid halide thereof, in order to improve the filterability of a Bx fuel above the cloud point of the Bx fuel; wherein the Bx fuel comprises fuel derived from animal or vegetable oil sources admixed with fuel derived from mineral or synthetic sources;

wherein the Bx fuel has a sulphur content less than 200ppm;

wherein the Bx fuel contains at least 4 wt% of fuel derived from animal or vegetable sources;
and wherein the additive is present in the Bx fuel in an amount (as active material) of from 10 mg/kg up to 200 mg/kg.

[0030] Preferably R¹ is a hydrocarbyl group or a polyethoxylate or polypropoxylate group.

[0031] Preferably the group R¹ is a hydrocarbyl group. Preferably the group R¹ is predominantly a straight chain group.

[0032] The term "hydrocarbyl" as used herein denotes a group having a carbon atom directly attached to the remainder of the molecule and having a predominantly aliphatic hydrocarbon character. Suitable hydrocarbyl based groups may contain non-hydrocarbon moieties. For example they may contain up to one non-hydrocarbyl group for every ten carbon atoms provided this non-hydrocarbyl group does not significantly alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of such groups, which include for example hydroxyl, halo (especially chloro and fluoro), alkoxyl, alkyl mercapto, alkyl sulfoxy, etc. Preferably the group R¹ is an-organic group entirely predominantly containing carbon and hydrogen atoms.

[0033] A hydrocarbyl group R¹ is preferably predominantly saturated, that is, it contain no more than one carbon-to-carbon unsaturated bond for every few (for example six to ten) carbon-to-carbon single bonds present. In the case of a hydrocarbyl group R¹ having from 4 to 10 carbon atom it may contain one unsaturated bond. In the case of a hydrocarbyl group R¹ having from 11 up to 20 carbon atom it may contain up to two unsaturated bonds. In the case of a hydrocarbyl group R¹ having from 21 up to 30 carbon atom it may contain up to three unsaturated bonds. In the case of a hydrocarbyl group R¹ having from 31 up to 40 carbon atom it may contain up to four unsaturated bonds. In the case of a hydrocarbyl group R¹ having from 41 up to 44 carbon atom it may contain up to five unsaturated bonds. Preferably, however, a hydrocarbyl group R¹ is preferably a fully saturated alkyl group, preferably a fully saturated n-alkyl group.

[0034] Preferably a group R¹ comprises from 6 to 36 carbon atoms, preferably 8 to 32, preferably 10 to 24, preferably 12 to 22, most preferably 14 to 20.

[0035] It will be appreciated that the group R¹ will typically include moieties with a range of carbon atoms. The definitions C₄₋₄₄... C₁₄₋₂₂ are not intended to denote that all R¹ groups must fall within the stated range.

[0036] The group R², when present, preferably conforms to the same definitions as are given for R¹. R¹ and R² need not be the same. Preferably, however, R¹ and R² are the same.

[0037] Preferably the species (ii) is a carboxylic acid or an acid anhydride thereof.

[0038] However if an acid halide is used it is preferably an acid chloride.

[0039] Suitable compounds (i) include primary, secondary, tertiary and quaternary amines. Tertiary and quaternary amines only form amine salts.

[0040] Secondary amines, of formula HNR¹R², are an especially preferred class of compounds (i). Examples of especially preferred secondary amines include di-octadecylamine, di-cocoamine, di-hydrogenated tallow amine and methylbehenyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine is a secondary hydrogenated tallow amine, the alkyl groups of which are derived from hydrogenated tallow fat composed of approximately 3-5%wt C₁₄, 30-32%wt C₁₆, and 58-60%wt C₁₈.

[0041] Quaternary amines, of formula [NR¹-R²R³R⁴ -An], are an especially preferred class of compounds (i). R¹ and R² are as defined above (but R² is not hydrogen). R³ and R⁴ independently represent a C(1-4) alkyl group, preferably propyl, ethyl or, most preferably, methyl. +NR¹R²(CH₃)₂ represents a preferred cation. -An represents the anion. The anion may be any suitable species but is preferably a halide, especially a chloride. Where (i) comprises a quaternary amine, the reaction conditions maybe adjusted to assist the reaction between (i) and (ii). Preferably the reaction conditions are adjusted by the introduction of an auxiliary base. The auxiliary base is preferably an inorganic base, such as sodium methoxide, sodium ethoxide, or sodium hydroxide. Preferably the inorganic base is a metal alkoxide or metal hydroxide. Alternatively, the quaternary amine salt may be preformed as the corresponding basic salt, for example, a quaternary ammonium hydroxide or alkoxide.

[0042] Also preferred are mixtures of primary and secondary amines, as species (i).

[0043] Also preferred are mixtures of secondary and quaternary amines, as species (ii).

[0044] Preferred carboxylic acids include carboxylic acids containing two, three or four carboxylic acid groups, and acid anhydrides and acid halides thereof.

[0045] Examples of suitable carboxylic acids and their anhydrides induce aminoalkylenepolycarboxylic acids, for example nitrilotriacetic acid, propylene diamine tetraacetic acid, ethylenediamine tetraacetic acid, and carboxylic acids based on cyclic skeletons, e.g., pyromellitic acid, cyclohexahe-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid and naphthalene dicarboxylic acid, 1,4-dicarboxylic acids, and dialkyl spirobislac-tones. Generally, these acids have about 5 to 13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are optionally substituted benzene dicarboxylic acids, e.g. phthalic acid, isophthalic acid, and terephthalic acid, and their acid anhydrides or acid chlorides. Optional substituents include 1-5 substituents, preferably 1-3 substituents, independently selected from C(1-4)alkyl, C(1-4)alkoxy, halogen, C(1-4)haloalkyl, C(1-4)haloalkoxy, nitrile, -COOH, -CO-OC(1-4)alkyl, and -CONR³R⁴ where R³ and R⁴ are independently selected from hydrogen and C(1-4)alkyl. Preferred halogen atoms are fluorine, chlorine and bromine. However unsubstituted benzene carboxylic acids are preferred. Phthalic acid and its acid anhydride are particularly preferred.

[0046] Preferably the molar ratio of compound (i) to acid, acid anhydride or acid halide (ii) is such that at least 50% of the acid groups (preferably at least 75%, preferably at least 90%, and most preferably 100%) are reacted in the reaction between the compounds (i) and (ii), for example to form the amide and/or the amine salt.

[0047] Where compound (ii) comprises one or more free carboxylic acid groups, reaction conditions may be adjusted to allow reaction between compounds (i) and (ii), for example to form the respective amide or amine salt. The reaction conditions may be adjusted by raising reaction temperatures. The reaction conditions may be adjusted by including a dehydrating agent within the reaction mixture. The one or more carboxylic acid groups may be activated *in situ* ready for coupling (i) and (ii), for example, by the use of such as carbodiimides (eg. EDCI). However, where activated forms of (ii) are employed, the activated forms of (ii) are preferably preformed, for example, as acid halides or acid anhydrides. Acid anhydrides are most preferred.

[0048] In the case of a preferred reaction, between a compound (i) and a dicarboxylic acid, or acid anhydride or acid halide thereof, preferably the molar ratio of compound (i) (or mixtures of compounds (i), in that situation) to acid, acid anhydride or acid halide (ii) (or mixed compounds (ii), in that situation) is at least 0.7:1, preferably 1:1, preferably at least 1.5:1. Preferably it is up to 3:1, preferably up to 2.5:1. Most preferably it is in the range 1.8:1 to 2.2:1. A molar ratio of 2:1, (i) to (ii) is especially preferred. Also preferred is a molar ratio of 1:1.

[0049] It will be understood by those skilled in the art that compound (ii) is defined as the original starting material. However, preferred products may be obtained by step-wise reactions involving reacting compound (i) with an adduct of compound (ii), particularly where (ii) has already reacted in with a compound (i) to form an intermediate. Such an intermediate may be fully isolated or partially isolated so as to allow step-wise reactions. Such an intermediate may comprise a mono-amide/mono-carboxylic acid adduct, for instance, where in a first step a first equivalent of (i) is reacted with a dicarboxylic acid, acid anhydride, or acid halide. Partial isolation may therefore be mere isolation of the reaction mixture resulting from the first step of a reaction to form the mono-amide/mono-carboxylic acid. In such circumstances, a subsequent reaction of compound (i) (optionally a different compound (i) than that used in the first step) with the mono-amide/mono-carboxylic acid adduct may yield further derivatives, for instance, a diamide or a mono-amide/ammonium carboxylate salt. Such a step-wise process provides for greater selectivity of either or both of an amide group and/or an ammonium salt, especially where the amines of said amide group and said ammonium group are different, such as when (i) essentially comprises more than one amine.

[0050] In the case of a preferred reaction, between a secondary amine as the only compound (i) and a dicarboxylic acid, or acid anhydride or acid halide thereof, preferably the molar ratio of-amine (i) to acid, acid anhydride or acid halide (ii) is at least 1:1, preferably at least 1.5:1. Most preferably it is in the range 1.8:1, to 2.2:1. A molar ratio of 2:1, (i) to (ii) is especially preferred.

[0051] In the case of another preferred reaction, between a quaternary ammonium salt as the only compound (i) and a dicarboxylic acid, or acid anhydride or acid halide thereof, preferably the molar ratio of quaternary ammonium salt (i) to acid, acid anhydride or acid halide (ii) is at least 1:1, preferably at least 1.5:1. Most preferably it is in the range 1.8:1 to 2.2:1. A molar ratio of 2:1, (i) to (ii) is especially preferred.

[0052] Preferred reaction products for use in this invention contain at least the mono-amide adduct and quaternary ammonium salt and this may be achieved by using a mixture of compounds as compound (i), preferably both a secondary amine and a quaternary ammonium-compound.

[0053] Another preferred reaction employs both a secondary amine and a quaternary ammonium salt as compounds (i). Preferably the ratio of the secondary amine to the quaternary ammonium salt in the reaction mixture is 30-70% to 70-30% molar/molar, preferably 40-60% to 60-40%, and most preferably they are present in equimolar amounts. Consistent with what is stated above, 11 therefore, this reaction employs in its most preferred embodiment equimolar amounts of the secondary amine, the quaternary ammonium salt and the acid, acid anhydride or acid halide (ii).

[0054] Preferably the reaction between the compound (i) and the carboxylic acid, acid anhydride or acid halide forms one or more amide, imide or ammonium salts, combinations of these within the same compound, and mixtures of these compounds.

[0055] Thus, in one preferred embodiment a dicarboxylic acid, acid anhydride or acid halide is reacted with a secondary amine in a mole ratio of 1:2 such that one mole of the amines form an amide and one mole forms an ammonium salt.

[0056] An especially preferred additive is a N,N-dialkylammonium salt of 2-N',N'-dialkylamide benzoic acid, which suitably is the reaction product of di(hydrogenated) tallow amine (i) and phthalic acid or its acid anhydride (ii); preferably at a molar ratio of 2:1.

[0057] An especially preferred additive is the reaction product of di(hydrogenated) tallow amine (i) and phthalic acid or its acid anhydride (ii); preferably at a molar ratio of 1:1.

[0058] Other preferred additives are the reaction products (hydrogenated) tallow amine with EDTA reaction in a molar ratio of 4:1 with removal of four moles of water or two moles of water to form respectively the tetraamide derivative or the diamide diammonium salt derivative.

[0059] Another preferred additive is the reaction product of one mole of alkylspirobis lactone, for example dodecenylspirobis lactone with one mole of mono-tallow amine and one mole of di-tallow amine.

[0060] The fuel composition of the present invention contains at least 4 wt% of fuel derived from animal or vegetable sources, 12

preferably at least 5 wt%, at least 6 wt%, at least 8 wt%, or at least 10 wt%, of fuel derived from animal or vegetable sources. Some embodiments may contain at least 15 wt%, or at least 20 wt%, of fuel derived from animal or vegetable sources. The fuel composition may contain up to 99 wt% of fuel derived from animal or vegetable sources, for example up to 95 wt%, up to 90 wt%, up to 85 wt%, up to 80 wt%, up to 75 wt%, up to 70 wt%, up to 60 wt%, up to 50 wt%, up to 40 wt%, up to 30 wt%, up to 25 wt%, up to 20 wt%, up to 15 wt%, or up to 12 wt%, of fuel derived from animal or vegetable sources.

[0061] A fuel which comprises 100% fuel produced from an animal or vegetable source is denoted as B100, a fuel which comprises 90% mineral diesel and 10% biodiesel is known as B10; fuel comprising 50% mineral diesel and 50% biodiesel is known as B50; and so on.

[0062] Fuel of animal or vegetable origin may include ethyl or methyl esters of fatty acids of biological origin. Starting materials for the production of such fuel include, but are not limited to, materials containing fatty acids. These materials include, without limitation, triacylglycerols, diacylglycerols, monoacylglycerols, phospholipids, esters, free fatty acids, or any combinations thereof. The diesel is produced by incubating the material including the fatty acids with a short chain alcohol in the presence of heat, pressure, a catalyst, or combinations of any thereof to produce fatty acid esters of the short chain alcohols.

[0063] The fatty acids used to produce the fuel may originate from a wide variety of natural sources including, but not limited to, vegetable oil, canola oil, safflower oil, sunflower oil, nasturtium seed oil, mustard seed oil, olive oil, sesame oil, soybean oil, corn oil, peanut oil, cottonseed oil, rice bran oil, babassu nut oil, castor oil, palm oil, palm oil, rapeseed oil, low erucic acid rapeseed oil, palm kernel oil, lupin oil, jatropha oil, coconut oil, flaxseed oil, evening primrose oil, jojoba oil, camelina oil, tallow, beef tallow, butter, chicken fat, lard, dairy butterfat, shea butter, used frying oil, oil miscella, used cooking oil, yellow trap grease, hydrogenated oils, derivatives of the oils, fractions of the oils, conjugated derivatives of the oils, and mixtures of any thereof. grease, hydrogenated oils, derivatives of the oils, fractions of the oils, conjugated derivatives of the oils, and mixtures of any thereof.

[0064] Preferably the precipitates which form above the cloud point and which the present invention seeks to combat are not revealed by cloud point test ASTM D 2500.

[0065] Preferably the precipitates which form above the cloud point and which the present invention seeks to combat are not revealed immediately merely by cooling the fuel to a given temperature. Preferably they form following an incubation period, by holding the fuel at a temperature above the cloud point for a incubation period. Preferably the incubation period is at least 4 hours, preferably at least 12 hours, preferably at least 16 hours, preferably at least 48 hours, preferably at least 96 hours.

[0066] Preferably the precipitates which form above the cloud point and which the present invention seeks to combat are not removed merely by raising the temperature of the fuel above the temperature at which they formed.

[0067] Preferably the Bx fuel is a middle distillate fuel, generally boiling within the range of from 110 to 500, e.g. 150 to 400° C. Preferably it is a Bx fuel for use in diesel engines or heating fuel oil.

[0068] In one embodiment the fuel is B100. Preferably however the fuel is a blend of fuel derived from animal or vegetable sources and fuel derived from mineral sources and/or synthetic sources j(e.g. FT fuels, derived from the Fischer-Tropsch process).

[0069] Preferably the fuel is a blend of a fuel derived from vegetable sources and a fuel derived from non-vegetable sources; preferably from mineral sources.

[0070] 14

[0071] The Bx fuel may contain other flow-improving additives to provide the usual benefits, in reducing the CP and CFPP. Such compounds may include CFIs and WASAs.

[0072] Examples of such additives and their use in petroleum-based oils are described in US 3048479; GB 1263152; US 3961916; US 4211534; EP 153176A; and EP 153177A.

[0073] US 3048479 describes ethylene-vinyl ester pour depressants for middle distillates. GB 1263152 describes distillate petroleum oil compositions containing ethylene ester copolymers. The preferred copolymers are of ethylene and vinyl acetate. US 3961916 describes middle distillate compositions with improved filterability containing mixtures of two different EVA copolymers. US 4211534 describes combinations of ethylene polymer, polymer having alkyl side chains, and nitrogen containing compound to improve cold flow properties of distillate fuel oils. EP 153176A and EP 153177A describe polymers or copolymers containing an n-alkyl ester of a mono-ethylenically unsaturated C4 to C8 mono- or dicarboxylic acid.

[0074] Use of an ethylene vinyl acetate copolymer as a CFI in conjunction with an adduct of compounds (i) and (ii) as defined herein, is especially preferred.

[0075] The Bx fuel is a low sulphur content fuel, having a sulphur content less than 200 ppm, preferably less than 100 ppm, preferably less than 50 ppm, preferably less than 20 ppm, preferably less than 15 ppm, preferably less than 10 ppm.

[0076] The additive is present in the fuel in an amount (as active material) from 10 mg/kg fuel, preferably from 20

mg/kg fuel, preferably from 30 mg/kg fuel.

[0077] The additive is present in the fuel in an amount (as active material) up to 200 mg/kg fuel, preferably up to 100 mg/kg

fuel, preferably up to 80 mg/kg fuel, preferably up to 60 mg/kg fuel, preferably up to 45 mg/kg fuel.

[0078] The additive may be added to Bx fuel which is known to exhibit a filtration problem above the cloud point, to reduce the problem or, preferably, to obviate the problem by preventing precipitation above the cloud point.

[0079] Reducing or solving the problem may be achieved by reducing the size or quantity of the precipitates which may appear in the Bx fuel above the cloud point, or by controlling the morphology of the precipitates in the Bx fuel above the cloud point.

[0080] Preferably, however, the additive is added to Bx fuel in order to prevent the emergence of precipitates above the cloud point. By preventing the emergence of precipitates above the cloud point we mean that detectable precipitates do not appear in the Bx fuel under normal storage or use conditions.

[0081] In accordance with some embodiments of the present invention there is provided the use of an additive which is the reaction product of (i) a compound containing the segment -NR¹R² where R¹ represents a group containing from 4 to 44 carbon atoms and R² represents a hydrogen atom or a group R¹, and (ii) a carboxylic acid having from 1 to 4 carboxylic acid groups or an acid anhydride or acid halide thereof in order to prevent the emergence of precipitates in the Bx fuel above the cloud point of the Bx fuel.

[0082] The invention will now be further described, by way of example, with reference to the following test descriptions.

[0083] The invention will now be further described, by way of example, with reference to the following test descriptions.

Example Set A

[0084] The tests involved using a modified version of the IP387 (Determination of filter blocking tendency of gas oils and distillate diesel fuels) method.

[0085] In the IP 387 method, a sample of the fuel to be tested is passed at a constant rate of flow through a glass fibre filter medium. The pressure drop across the filter is monitored, and the volume of fuel passing the filter medium within a prescribed pressure drop is measured.

[0086] The filter blocking tendency (FBT) can be described in one of the following ways:

- The pressure drop (P) across a GF/A (glass fibre) filter medium for 300 ml of fuel to pass at a rate of 20 ml/min is recorded.
- The volume of fuel (v) passed when a pressure of 105kPa is reached. This method of report is used when less than 300 ml passes at that pressure drop.

[0087] The FBT may be expressed on a single scale by combining these using the following formulae

$$FBT = \sqrt{1 + \left(\frac{P}{105}\right)^2} \quad \text{and} \quad FBT = \sqrt{1 + \left(\frac{300}{v}\right)^2}$$

[0088] Thus when exactly 300ml passes through the filter at a pressure of 105 kPa, the FBT is 1.41. Values of FBT >1.41 indicate that less than 300 ml pass through the filter before a pressure of 105 kPa is reached. Values Of FBT <1.41 indicate that 300ml pass through the filter at a pressure of less than 105kPa

[0089] An FBT <1.4 is considered to be a good result.

[0090] The modification to the IP 387 method relates to thermal conditioning and cold soak of a sample being tested.

1. the sample is heated to a temperature of 60°C for 3 hours, and then allowed to cool to 20°C.
2. The sample is then cooled to 5°C for 16 hours and then allowed to warm to room temperature.

Following this conditioning, the Filter Blocking Tendency is determined using IP 387.

[0091] The base fuel used in these tests was a B5 fuel which met the requirements of DIN EN 590 and contained a commercially available cold flow additive believed to comprise EVA copolymers in an amount effective to achieve a CFPP of < -15°C. The fuel had the following properties:

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Method	Method Number	Result
Density at 15°C	IP 365	0.8417g/ml
CFPP	IP 309	-17°C
Cloud Point	ASTM D5772	-5.8°C
Distillation	JP 123	
IBP		175.5°C
5%		195.9°C
10%		206.4°C
20%		226.0°C
30%		244.0°C
40%		260.5°C
50%		275.0°C
60%		288.7°C
70%		302.3°C
80%		317.2°C
90%		335.3°C 348,6%
95%		348.6°C
FBP		359.5°C

[0092] Testing was carried out using

- a) this base fuel,
- b) this base fuel additised with 37.5 mg/kg of Compound A, and
- c) this base fuel additised with a commercial WASA (believed to be a nitrogen-containing polymeric WASA) long used with success to improve the flow properties of mineral diesel fuels below the cloud point.

[0093] To prepare Compound A phthalic anhydride (7.4g) was mixed with di (hydrogenated tallow) amine (Commercially available as Armeen 2HT) (50.02g) at a molar ratio of 1:2 in Shellsol AB solvent (57.5g). The reaction mixture was heated at 65°C for approximately 6hours.

The results are as follows:

Sample	(a) base fuel	(b) base fuel + 37.5 mg/kg Compound A	(c) base fuel + 150 mg/kg WASA
Filter Blocking Tendency	1.8	1.23	1.87
Initial pressure (kPa)	10	10	10
Final pressure (kPa)	105	75	105
Volume filtered (ml)	200	300	190
Test temperature (°C)	23	23	23

[0094] Using Compound A allowed tall 300 ml of the fuel to pass through the filter without the pressure reaching 105 kPa. The improvement over the performance of the base fuel is very marked. In contrast it is observed that the commercial WASA, at a higher treat rate, causes no discernable improvement in the flow properties of the base fuel.

Example Set B

[0095] In Example Set B the testing was the same as in Example Set-A but the base fuel ("Basefuel 2") also met the requirements of DIN EN90 and was a B10 fuel prepared from a standard diesel meeting the specifications of CEC Fuel Specification RF-06-03, blended with rapeseed methyl ester (RME) and a commercially available cold flow additive believed to comprise EVA copolymers in an amount effective to achieve a CFPP of $< -15^{\circ}\text{C}$.

[0096] The FBT of Basefuel 2 was 2.52.

[0097] The FBT of Basefuel 2 additised with 37.5 mg/kg of Compound A was 1.03.

[0098] The FBT of Basefuel 2 additised with 150 mg/kg of WASA (believed to be a nitrogen-containing polymeric WASA) was 2.03.

Claims

1. Use of a reaction product of (i) a compound containing the segment $\text{-NH}^1\text{R}^2$ where R^1 represents a group containing from 4 to 44 carbon atoms and R^2 represents a hydrogen atom or a group R^1 , and (ii) carboxylic acid having from 1 to 4 carboxylic acid groups or an acid anhydride or acid halide thereof, in order to improve the filterability of a Bx fuel above the cloud point of the Bx fuel; wherein the Bx fuel comprises fuel derived from animal or vegetable oil sources admixed with fuel derived from mineral or synthetic sources; wherein the Bx fuel has a sulphur content less than 200ppm; wherein the Bx fuel contains at least 4 wt% of fuel derived from animal or vegetable sources; and wherein the additive is present in the Bx fuel in an amount (as active material) of from 10 mg/kg up to 200 mg/kg.
2. Use as claimed in claim 1, wherein the group R^1 is a predominantly straight chain, substantially saturated group comprising from 10 to 24 carbon atoms.
3. Use as claimed in claim 1 or 2, in which the group R^2 is a group which conforms to the same definitions as are given in any preceding claim for R^1 .
4. Use as claimed in claim 3, in which the compound (i) is a secondary amine of formula HNR^1R^2 where R^1 and R^2 are as defined in claim 3; or is an ammonium salt having the cation $+\text{NR}^1\text{H}^2\text{R}^3\text{R}^4$ where R^1 and R^2 are as defined in claim 3 and R^3 and R^4 independently represent a C(1-4) alkyl group.
5. Use as claimed in any preceding claim, in which the carboxylic acid is selected from aminoalkylenepolycarboxylic acids, for example nitrilotriacetic acid, propylene diamine tetraacetic acid, ethylenediamine tetraacetic acid, dialkyl spirobis lactones, and carboxylic acids based on cyclic skeletons, having 5 to 13 carbon atoms in the cyclic moiety (and their acid anhydrides and acid halides), in which the carboxylic acids based on cyclic skeletons are preferably selected from pyromellitic acid, cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid, naphthalene dicarboxylic acid, 1,4-dicarboxylic acids and benzene dicarboxylic acids.
6. Use as claimed in claim 5, in which the benzene dicarboxylic acids are selected from isophthalic acid, terephthalic acid and, especially, phthalic acid (and their acid anhydrides or acid halides).
7. Use as claimed in any preceding claim, in which the molar ratio of compound (i) to acid anhydride or acid halide (ii) is such that at least 50% of the acid groups (preferably at least 75%, preferably at least 90%, and most preferably 100%) are reacted in the reaction between the compounds (i) and (ii).
8. Use as claimed in any preceding claim, in which compound (i) is a secondary amine and/or quaternary ammonium salt and compound (ii) is a dicarboxylic acid, or an acid anhydride or acid halide thereof, wherein the molar ratio of compound(s) (i) to acid, acid anhydride or acid halide (ii) is at least 1:1, preferably at least 1.5:1, preferably 2:1.
9. Use as claimed in any preceding claim, wherein the said additive is present in the Bx fuel in an amount of from 5 mg/kg fuel to 500 mg/kg fuel, preferably from 10 mg/kg fuel to 80 mg/kg fuel, preferably from 20 mg/kg fuel to 60 mg/kg fuel, preferably from 30 mg/kg fuel to 45 mg/kg fuel.
10. Use as claimed in any preceding claim, in which the Bx fuel is a blended fuel comprising a fuel component derived from an animal or, preferably, a vegetable oil source and a fuel component derived from a mineral source.

11. Use as claimed in claim 10, wherein the Bx fuel comprises one or more compounds which improve the flow properties of the fuel derived from the mineral source at a temperature below the cloud point of the Bx fuel.

Patentansprüche

1. Verwendung

eines Reaktionsprodukts von (i) einer Verbindung, die das Segment $-NR^1R^2$ enthält, wobei R^1 eine Gruppe darstellt, die von 4 bis 44 Kohlenstoffatome enthält, und R^2 ein Wasserstoffatom oder eine Gruppe R^1 darstellt, und (ii) Carbonsäure mit 1 bis 4 Carbonsäuregruppen oder einem Säureanhydrid oder Säurehalogenid davon zum Verbessern der Filtrierbarkeit eines Bx-Brennstoffs über dem Trübungspunkt des Bx-Brennstoffs; wobei der Bx-Brennstoff Brennstoff abgeleitet aus Tier- oder Pflanzenölquellen gemischt mit Brennstoff abgeleitet aus mineralischen oder synthetischen Quellen umfasst; wobei der Bx-Brennstoff einen Schwefelgehalt von weniger als 200 ppm aufweist; wobei der Bx-Brennstoff wenigstens 4 Gew.-% an Brennstoff abgeleitet aus Tier- oder Pflanzenquellen enthält; und wobei der Zusatzstoff in dem Bx-Brennstoff in einer Menge (als aktives Material) von 10 mg/kg bis 200 mg/kg vorhanden ist.

2. Verwendung gemäß Anspruch 1, wobei die Gruppe R^1 eine vorwiegend geradkettige, im Wesentlichen gesättigte Gruppe ist, die 10 bis 24 Kohlenstoffatome umfasst.

3. Verwendung gemäß Anspruch 1 oder 2, wobei die Gruppe R^2 eine Gruppe ist, die den gleichen Definitionen, die in einem der vorstehenden Ansprüche für R^1 gegeben werden, entspricht.

4. Verwendung gemäß Anspruch 3, wobei die Verbindung (i) ein sekundäres Amin der Formel HNR^1R^2 ist, wobei R^1 und R^2 wie in Anspruch 3 definiert sind; oder ein Ammoniumsalz mit dem Kation $+NR^1R^2R^3R^4$ ist, wobei R^1 und R^2 wie in Anspruch 3 definiert sind und R^3 und R^4 unabhängig eine C(1-4)Alkylgruppe darstellen.

5. Verwendung gemäß einem der vorstehenden Ansprüche, wobei die Carbonsäure ausgewählt ist aus Aminoalkylenpolycarbonsäuren, beispielsweise Nitrilotriessigsäure, Propylendiamintetraessigsäure, Ethylendiamintetraessigsäure, Dialkylspirobis lactonen und Carbonsäuren auf der Grundlage von cyclischen Skeletten mit 5 bis 13 Kohlenstoffatomen in der cyclischen Einheit (und ihren Säureanhydriden und Säurehalogeniden), wobei die Carbonsäuren auf der Grundlage von cyclischen Skeletten vorzugsweise ausgewählt sind aus Pyromellitsäure, Cyclohexan-1,2-dicarbonsäure, Cyclohexen-1,2-dicarbonsäure, Cyclopentan-1,2-dicarbonsäure, Naphthalindicarbonsäure, 1,4-Dicarbonsäuren und Benzoldicarbonsäuren.

6. Verwendung gemäß Anspruch 5, wobei die Benzoldicarbonsäuren ausgewählt sind aus Isophthalsäure, Terephthalsäure und insbesondere Phthalsäure (und ihren Säureanhydriden und Säurehalogeniden).

7. Verwendung gemäß einem der vorstehenden Ansprüche, wobei das Molverhältnis von Verbindung (i) zu Säureanhydrid oder Säurehalogenid (ii) so ist, dass wenigstens 50 % der Säuregruppen (vorzugsweise wenigstens 75 %, vorzugsweise wenigstens 90 % und höchst bevorzugt 100 %) bei der Reaktion zwischen den Verbindungen (i) und (ii) umgesetzt werden.

8. Verwendung gemäß einem der vorstehenden Ansprüche, wobei Verbindung (i) ein sekundäres Amin und/oder quaternäres Ammoniumsalz ist und Verbindung (ii) eine Dicarbonsäure oder ein Säureanhydrid oder Säurehalogenid davon ist, wobei das Molverhältnis von Verbindung(en) (i) zu Säure, Säureanhydrid oder Säurehalogenid (ii) wenigstens 1:1 beträgt, vorzugsweise wenigstens 1,5:1, vorzugsweise 2:1.

9. Verwendung gemäß einem der vorstehenden Ansprüche, wobei der Zusatzstoff in dem Bx-Brennstoff in einer Menge von 5 mg/kg Brennstoff bis 500 mg/kg Brennstoff vorhanden ist, vorzugsweise von 10 mg/kg Brennstoff bis 80 mg/kg Brennstoff, vorzugsweise von 20 mg/kg Brennstoff bis 60 mg/kg Brennstoff, vorzugsweise von 30 mg/kg Brennstoff bis 45 mg/kg Brennstoff.

10. Verwendung gemäß einem der vorstehenden Ansprüche, wobei der Bx-Brennstoff ein gemischter Brennstoff ist, der eine Brennstoffkomponente umfasst, die aus einer Tier- oder vorzugsweise einer Pflanzenölquelle abgeleitet ist, und eine Brennstoffkomponente, die aus einer Mineralquelle abgeleitet ist.

11. Verwendung gemäß Anspruch 10, wobei der Bx-Brennstoff eine oder mehrere Verbindungen umfasst, die die Fließeigenschaften des Brennstoffs abgeleitet aus der Mineralquelle bei einer Temperatur unter dem Trübungspunkt des Bx-Brennstoffs verbessern.

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Revendications

1. Utilisation d'un produit de la réaction de (i) un composé contenant le segment $-NR^1R^2$ où R^1 représente un groupe contenant de 4 à 44 atomes de carbone et R^2 représente un atome d'hydrogène ou un groupe R^1 , et (ii) un acide carboxylique ayant de 1 à 4 groupes acide carboxylique ou un anhydride d'acide ou un halogénure d'acide de celui-ci, afin d'améliorer la filtrabilité d'un carburant Bx au-delà du point de trouble du carburant Bx ;
dans laquelle le carburant Bx comprend du carburant dérivé de sources huileuses animales ou végétales mélangées avec du carburant dérivé de sources minérales ou synthétiques ;
dans laquelle le carburant Bx a une teneur en soufre inférieure à 200 ppm ;
dans laquelle le carburant Bx contient au moins 4 % en poids de carburant dérivé de sources animales ou végétales ;
et dans laquelle l'additif est présent dans le carburant Bx en une quantité (sous forme de matériau actif) de 10 mg/kg jusqu'à 200 mg/kg.
2. Utilisation selon la revendication 1, dans laquelle le groupe R^1 est un groupe pratiquement saturé principalement à chaîne droite comprenant de 10 à 24 atomes de carbone.
3. Utilisation selon la revendication 1 ou 2, dans laquelle le groupe R^2 est un groupe qui se conforme aux mêmes définitions que celles indiquées à propos de R^1 dans l'une quelconque des revendications précédentes.
4. Utilisation selon la revendication 3, dans laquelle le composé (i) est une amine secondaire de formule HNR^1R^2 où R^1 et R^2 sont tels que définis dans la revendication 3 ; ou est un sel d'ammonium ayant le cation $+NR^1R^2R^3R^4$ où R^1 et R^2 sont tels que définis dans la revendication 3 et R^3 et R^4 représentent indépendamment un groupe alkyle en C_1 à C_4 .
5. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle l'acide carboxylique est choisi parmi les acides aminoalkylène polycarboxyliques, par exemple l'acide nitrilotriacétique, l'acide propylènediamine-tétraacétique, l'acide éthylènediaminetétraacétique, les dialkylspirobis lactones, et les acides carboxyliques basés sur des charpentes cycliques, ayant 5 à 13 atomes de carbone dans le fragment cyclique (et leurs anhydrides d'acide et halogénures d'acide), et dans laquelle les acides carboxyliques basés sur des charpentes cycliques sont de préférence choisis parmi l'acide pyromellitique, l'acide cyclohexane-1,2-dicarboxylique, l'acide cyclohexène-1,2-dicarboxylique, l'acide cyclopentane-1,2-dicarboxylique, l'acide naphtalènedicarboxylique, les acides 1,4-dicarboxyliques et les acides benzènedicarboxyliques.
6. Utilisation selon la revendication 5, dans laquelle les acides benzènedicarboxyliques sont choisis parmi l'acide isophtalique, l'acide téréphtalique, et en particulier l'acide phtalique (et leurs anhydrides d'acide ou halogénures d'acide).
7. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le rapport molaire du composé (i) à l'anhydride d'acide ou à l'halogénure d'acide (ii) est tel qu'au moins 50 % des groupes acides (de préférence au moins 75 %, de préférence au moins 90 %, et tout spécialement 100 %) réagissent dans la réaction entre les composés (i) et (ii).
8. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le composé (i) est un sel d'amine secondaire et/ou d'ammonium quaternaire et le composé (ii) est un acide dicarboxylique, ou un anhydride d'acide ou halogénure d'acide de celui-ci, et dans laquelle le rapport molaire du ou des composés (i) à l'acide, l'anhydride d'acide ou l'halogénure d'acide (ii) est d'au moins 1/1, de préférence d'au moins 1,5/1, de préférence de 2/1.
9. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle ledit additif est présent dans le carburant Bx en une quantité de 5 mg par kg de carburant à 500 mg par kg de carburant, de préférence de 10 mg par kg de carburant à 80 mg par kg de carburant, de préférence de 20 mg par kg de carburant à 60 mg par kg de carburant, de préférence de 30 mg par kg de carburant à 45 mg par kg de carburant.
10. Utilisation selon l'une quelconque des revendications précédentes, dans laquelle le carburant Bx est un carburant

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mixte comprenant un composant carburant dérivé d'une source huileuse animale ou de préférence végétale et un composant carburant dérivé d'une source minérale.

- 5 **11.** Utilisation selon la revendication 10, dans laquelle le carburant Bx comprend un ou plusieurs composés qui améliorent les propriétés d'écoulement du carburant dérivé de la source minérale à une température inférieure au point de trouble du carburant Bx.

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REFERENCES CITED IN THE DESCRIPTION

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