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(11)

EP 1 524 311 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
20.04.2005 Bulletin 2005/16

(51) Int Cl.7: **C10L 1/16, C10L 10/00**

(21) Application number: **04255348.7**

(22) Date of filing: **03.09.2004**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PL PT RO SE SI SK TR**
Designated Extension States:
AL HR LT LV MK

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(30) Priority: **15.10.2003 EP 03256488**

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(54) Jet fuel compositions comprising a comb polymer

(57) A method for reducing the level of deposits in a jet engine, the method comprising supplying to the jet engine a jet fuel composition comprising a jet fuel and at least one hydrocarbyl comb polymer; wherein the at least one hydrocarbyl comb polymer has a number av-

erage molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 5,500, preferably less than 5,000.

The low temperature properties of the jet fuel are also improved.

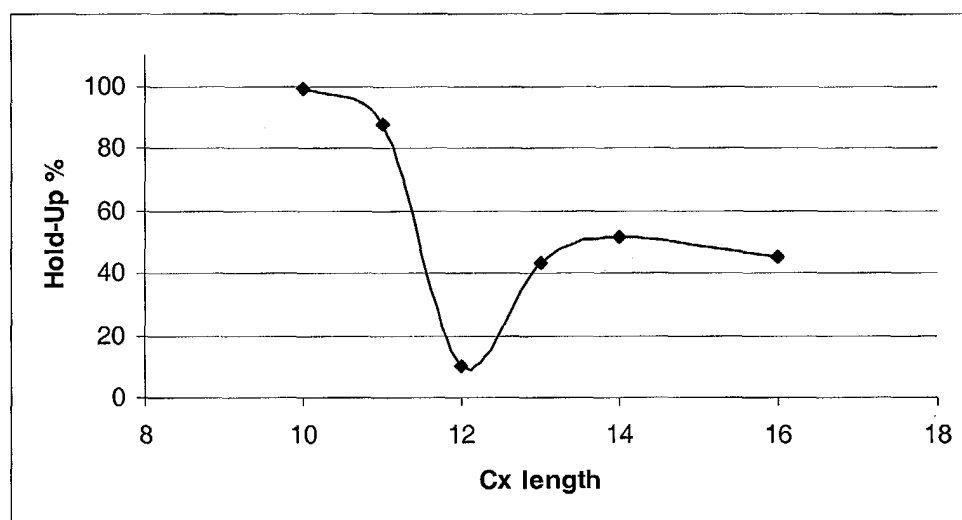


Figure 1

EP 1 524 311 A1

Description

[0001] This invention concerns a method for reducing deposit formation in a jet engine and jet fuel compositions. In particular, jet fuel compositions that are suitable for use at low temperatures, such as, for example, below -40°C or -50°C.

[0002] The most commonly used jet fuels are Jet A and Jet A-1, which have specification maximum freezing points of -40°C and -47°C respectively. At temperatures below the freezing point of jet fuel, hydrocarbon molecules crystallize and precipitate out. Normal paraffins in jet fuel have the highest crystallization temperatures and are therefore the first to come out of solution as wax crystals. As the hydrocarbon molecules crystallize, the viscosity of the fuel increases, which reduces the flow of the fuel. In Boeing® aircraft the fuel temperature must remain at least 3°C above the specification freezing point and in Airbus® aircraft the fuel temperature must remain at least 4°C above the specification freezing point. If the fuel temperature starts to approach the specification freezing point, action must be taken to avoid any further cooling. This action usually involves flying around cold areas, lowering the aircraft to warmer temperatures or increasing the speed of the aircraft to increase aerodynamic warming. In extreme cases it may be necessary to increase the speed and to lower the aircraft. One drawback of this action is that it usually increases fuel consumption. Studies have been carried out to consider the use of heated tanks; however, this would increase the weight of the aircraft and also increase the fuel consumption.

[0003] Currently freezing points of jet fuel are controlled in refineries during distillation. Lowering the freezing point can be achieved by reducing the heavy fractions, which include the waxy fractions, to whatever level is required; however, reducing the heavy fractions has a major negative effect on availability. It has been suggested that switching from Jet A to Jet A-1 could reduce the available volume by 8%.

[0004] Jet A-1 is the standard specified jet fuel in Europe and is usually required for winter conditions and routes such as trans-arctic. Jet A is usually used on flights within the USA.

[0005] Alternatively or additionally, freezing points of jet fuel are controlled by the use of additives. However, certain additives are known to cause the build-up of undesirable combustion deposits on the surfaces of jet engines. These deposits have a detrimental effect on the performance of the engine.

[0006] Temperatures below 0°C also cause water present in the fuel to freeze, which can cause plugging of filters and other small orifices, and occasionally engine flameout. Ground-based water-separators are used to control the amount of water present in a fuel and it is important that additives added to jet fuel do not block or disarm the filters in these separators. ASTM D 3948-93 is a test method that can be used to determine the ability of filter-separators to separate free water from fuel.

[0007] US 5,807,949 describes the use of copolymers of two alpha olefins to improve the low temperature properties of lubricating and fuel oils. Preferred are copolymers of an n-octyl olefin with either an n-tetradecyl olefin or an n-hexadecyl olefin.

[0008] EP 1 357 169 A2 describes jet fuel compositions having good low temperature properties. These compositions may include comb polymers which are preferably formed from a C₄-C₆ 1-alkene and a C₁₀-C₁₄ 1-alkene.

[0009] An aim of this invention is to provide jet fuel compositions that produce a reduced level of deposits in a jet engine.

[0010] A further aim of this invention is to provide jet fuel compositions that are suitable for use at low temperatures such as, for example, below -40°C, preferably below -50°C. In particular, an aim of this invention is to provide jet fuel compositions that are suitable for use at temperatures below their specification freezing points.

[0011] A further aim of this invention is to provide additives that are effective at reducing the low temperature operability of jet fuels.

[0012] In accordance with a first aspect of the present invention, there is provided a method for reducing the level of deposits in a jet engine, the method comprising supplying to the jet engine a jet fuel composition comprising a jet fuel and at least one hydrocarbyl comb polymer; wherein the at least one hydrocarbyl comb polymer has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 5,500, preferably less than 5,000.

[0013] A comb polymer is a polymer having a backbone and pendant side chains.

[0014] Preferably, the hydrocarbyl comb polymer has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 4,800, preferably less than 4,500. More preferably, the hydrocarbyl comb polymer has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 4,300, preferably less than 4,000. Even more preferably, the hydrocarbyl comb polymer has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 3,800, preferably less than 3,500. Most preferably, the hydrocarbyl comb polymer has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 3,000, preferably less than 2,800.

[0015] Preferably, the hydrocarbyl comb polymer is a hydrocarbon polymer or copolymer of a C₃-C₉ 1-alkene and a

C₁₀-C₁₄ 1-alkene, preferably a C₄-C₈ 1-alkene, more preferably a C₆-C₈ 1-alkene and a C₁₀-C₁₄ 1-alkene. Even more preferably the comb polymer is a hydrocarbon polymer or copolymer of a C₆-C₈ 1-alkene and a C₁₂ 1-alkene. Most preferably, the hydrocarbonyl comb polymer is a hydrocarbon polymer or copolymer of a C₈ 1-alkene and a C₁₂ 1-alkene.

[0016] The hydrocarbon comb polymer or copolymer should be added to the jet fuel in an amount ranging from 10 to 20,000 ppm, preferably 100 to 10,000 ppm, and most preferably from 500 to 5,000 ppm (parts additive per million parts fuel).

[0017] The jet fuel may be selected from Jet A, Jet A-1, Jet B, MIL JP 5, MIL JP 7, MIL JP 8 and MIL JP 4. Jet A, Jet A-1 and MIL JP 8 are preferred.

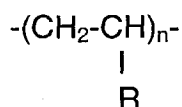
[0018] The inventors have surprisingly found that method defined above leads to low deposit formation in a jet engine, whilst the fuel composition used in the method also exhibits good low temperature operability, that is, the pour point of the jet fuel is reduced.

[0019] In accordance with a second aspect of the present invention, there is provided the use of at least one hydrocarbonyl comb polymer having a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 5,500, preferably less than 5,000, as an additive for a jet fuel, in order to reduce the level of deposits in a jet engine supplied with such a jet fuel.

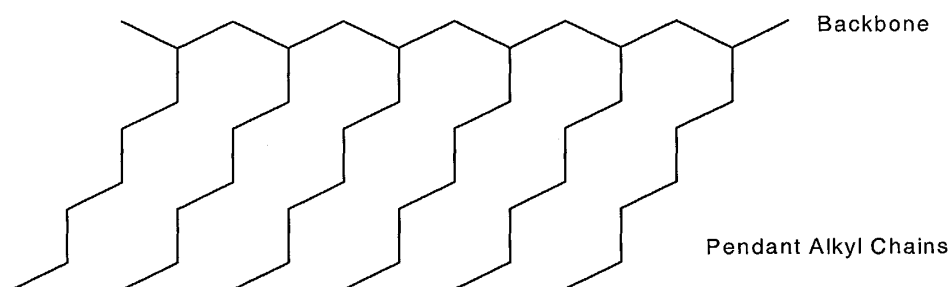
[0020] Comb polymers are discussed in "Comb-Like Polymers. Structure and Properties", N.A. Platé and V.P. Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

[0021] Generally, comb polymers consist of molecules in which long chain branches such as hydrocarbonyl branches, optionally interrupted with one or more oxygen atoms and/or carbonyl groups, having from 6 to 30 such as 8 to 20, carbon atoms, are pendant from a polymer backbone, said branches being bonded directly to the backbone. Generally, comb polymers are distinguished by having a minimum molar proportion of units containing such long chain branches.

[0022] In applications such as in jet fuel, polymers containing polar heteroatoms such as oxygen have an attraction for water and they may make it difficult for the separation of water from jet fuel during the fuelling of aircraft. In order to avoid such an attraction for water, the comb polymers in this invention are hydrocarbonyl only, i.e. they only include carbon and hydrogen atoms. The comb polymers are polymers and copolymers of long chain 1-alkenes such as 1-decene, 1-decene, 1-tridecene, 1-tetradecene or 1-hexadecene. Thus, the polymer repeat unit is a 1,2-disubstituted n-alkene:



in which R is generally a n-C₈H₁₇ (from the polymerisation of 1-decene) to n-C₁₄H₂₉ (polymerisation of 1-hexadecene) alkyl group. The idealised structure of such a comb polymer is (showing only the C-C bonds):



[0023] The pendant n-alkyl group lengths are chosen to best interact with the n-alkanes in the waxes that separate from jet fuel at low temperatures. It has been found that these should be mainly C₁₀ to C₁₄ n-alkyls.

[0024] Such polymers may conveniently be made by metallocene (e.g. zirconocene) polymerisation of the 1-alkenes, which enables flexibility of molecular weight. However, such polymers have a high degree of stereo regularity so have high melting points (relative to less regular structures) and limited low temperature solubility in hydrocarbon. Low temperature solubility in jet fuel (down to -50 to -60°C) is essential in this application, so low molar proportions, preferably less than 40 mole%, more preferably less than 30 mole%, most preferably 10 to 30 mole %, of a short chain 1-alkene

(or mixture thereof) is copolymerised with the longer chain 1-alkene. This has the effect of increasing the comb polymer solubility in liquid hydrocarbon at low temperatures, whilst retaining the matching of the pendant long chain n-alkyl with the n-alkane wax separating from jet fuel.

[0025] In this application, it has been found that the long chain 1-alkene preferably includes greater than 8 carbon atoms and at most 20 carbon atoms. The long chain 1-alkene is preferable a C₁₀-C₁₅ 1-alkene, including 1-decene, 1-dodecene and 1-tetradecene (see, example, WO 93/19106). The comb polymer is preferable a copolymer of at least one long chain 1-alkene, e.g. 1-dodecene, and at least one short chain 1-alkene, e.g. 1-butene, in the ratio of 60-90 mole % long chain 1-alkene to 40-10 mole % short chain 1-alkene, preferably in the ratio of 70-85 mole % long chain 1-alkene to 30-15 mole % short chain 1-alkene. It has been found that the shorter 1-alkene may be C₃ to C₉, e.g. 1-butene, 1-hexene or 1-octene.

[0026] In accordance with a third aspect, there is provided a jet fuel composition comprising a jet fuel and at least one hydrocarbyl comb polymer; wherein the at least one hydrocarbyl comb polymer is a hydrocarbon polymer or copolymer of a C₈ 1-alkene and a C₁₂ 1-alkene, and has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 5,500, preferably less than 5,000.

[0027] The jet fuel composition defined above is capable of reducing the size and modifying the shape of wax crystals formed on cooling of jet fuel so that they do not gel and cause unwanted viscosity increases. The standard pour point test method ASTM D97 can be used to determine the point at which a fuel gels. Other relevant tests are freeze point, cloud point, temperature variable viscometer and DSC, details of which can be found in 'Properties of Jet Fuels at Low Temperature and the Effects of Additives' by S. Zabarnick and M. Vangsness, Petroleum Chemistry Division preprints 2002, 47(1); Waxy Jet Fuel Hold-up test, as described by J. S. Manka in 'Jet Fuel Low Temperature Operability', SAE technical paper 2002-01-1650; and C. Obringer's 'Overview of JP8+100 Low Temperature Program', 2001 Co-ordinating Research Council, Aviation Meeting, Low Temperature Performance Group, May 2001.

[0028] It is a surprising feature of the present invention that the jet fuel composition of the third aspect exhibits unexpectedly good low temperature performance. The Applicants have found that the specific comb polymer formed from a C₈ 1-alkene and a C₁₂ 1-alkene outperforms even closely related polymer species. For example, neither the polymer of a C₈ 1-alkene and a C₁₀ 1-alkene, nor the polymer of a C₈ 1-alkene and a C₁₄ 1-alkene exhibit such good low temperature performance. This is in addition to the beneficial deposit reducing properties which the polymers used in the third aspect share with those used in the first and second aspects.

[0029] In accordance with a fourth aspect, there is also provided a process for reducing the pour point of jet fuels, the process including the following steps:

- a) providing a jet fuel; and
- b) adding to the jet fuel a polymer as defined in relation to the third aspect.

[0030] In accordance with a fifth aspect, there is provided the use of a polymer as defined in relation to the third aspect to reduce the low temperature operability of a jet fuel.

[0031] Jet fuel cold flow testing by means of temperature variable viscometry or waxy jet fuel holdup testing support the use of 1-dodecene copolymerised with 20 to 30 mole % of 1-octene to give a cold flow improvement (i.e. usable flow to lower temperature than does the untreated fuel) over a wide range of molecular weights (e.g. polymers of number average molecular weights, Mn, up to 20,000 as measured by gpc relative to polystyrene standards, have been tested). However, higher molecular weight polymers (Mn of at least 5,500) have been found to leave unwanted deposits in a jet engine during idle cycles. Reduction of the copolymer molecular weight to less than 5,500 has been found to alleviate this deposit formulation problem. In addition, the polymer low viscosity at low temperatures enables the lower molecular weight polymer to be easily pumped at 100% polymer, thus minimising the need for predilution and the shipping of volumes of solvent along with the polymer.

[0032] A further advantage of the present invention is that the jet fuel compositions do not block or disarm filters in water-separators.

[0033] The jet fuel composition may also include at least one of the following additional additives:

- (i) a copolymer of ethylene and at least one unsaturated ester;
- (ii) a copolymer of ethylene and alkene;
- (iii) a nucleator;
- (iv) a wax;
- (v) a substantially branched alkyl phenol formaldehyde condensate (known as 'APFC');
- (vi) a comb polymer selected from a polymer or copolymer of an unsaturated ester or an olefin maleic anhydride copolymer; and
- (vii) a polar nitrogen compound.

[0034] The jet fuel composition preferably also includes at least one copolymer selected from (i) or (ii) and at least one polar nitrogen compound (vi), and optionally at least one nucleator (iii).

[0035] The jet fuel composition preferably also includes at least one copolymer selected from (i) or (ii) and at least one comb polymer (vi), and optionally at least one nucleator (iii).

[0036] The jet fuel composition preferably also includes at least one polar nitrogen compound (vii) and at least one comb polymer (vi).

[0037] The jet fuel composition preferably also includes at least one polar nitrogen compound (vii) and at least one substantially branched alkyl phenol formaldehyde condensate (v).

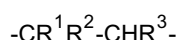
[0038] The jet fuel composition preferably also includes at least one polar nitrogen compound (vii) and at least one nucleator (iii).

[0039] The additional additives will now be discussed in more detail below:

(i) Copolymers of ethylene and at least one unsaturated ester:

[0040] The unsaturated ester may be a vinyl ester, an alkyl (meth) acrylate, a di-alkyl fumarate and a di-alkyl maleate.

[0041] The vinyl ester preferably has the formula:

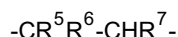


wherein R^2 represents hydrogen or a methyl group; R^1 represents a $-OOCR^4$ group wherein R^4 represents a C_1 to C_{28} , more preferably a C_1 to C_{16} , more preferably a C_1 to C_9 , straight or branched chain alkyl group; R^3 represents hydrogen or alkyl.

[0042] The vinyl ester is preferably selected from: vinyl propionate, vinyl butyrate, vinyl hexanoate, vinyl 2-ethylhexanoate, vinyl octanoate and vinyl benzoate. Neo acid vinyl esters are also useful, such as vinyl neononanoate and vinyl pivalate.

[0043] Preferably the unsaturated ester is less than 15 mol% of vinyl acetate, preferably less than 14 mol%, more preferably less than 12 mol% of vinyl acetate. The copolymer preferably has a number average molecular weight, as measured by gel permeation chromatography (GPC), of 1,000 to 10,000, more preferably 2,000 to 5,000.

[0044] The alkyl (meth)acrylate preferably has the formula:

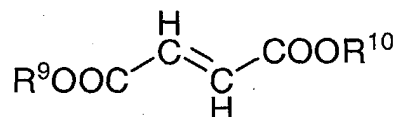


wherein R^6 represents hydrogen or a methyl group; R^5 represents a $-COOR^8$ group wherein R^8 represents a C_1 to C_{28} , more preferably a C_1 to C_{16} , more preferably a C_1 to C_9 , straight or branched chain alkyl group; and R^7 represents hydrogen or alkyl.

[0045] The term '(meth)acrylate' is used to include both acrylate and methacrylate.

[0046] The alkyl (meth)acrylate is preferably selected from: 2-ethylhexyl(meth)acrylate, ethyl (meth)acrylate, n, iso or t-butyl (meth)acrylate, hexyl (meth)acrylate, isopropyl (meth)acrylate and lauryl (meth)acrylate.

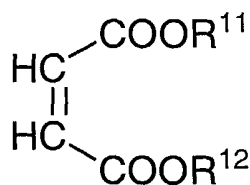
[0047] The di-alkyl fumarate preferably has the formula:



wherein R^9 and R^{10} are independently selected from alkyl groups having from 1 to 9 carbon atoms, preferably from 1 to 8 carbon atoms.

[0048] The di-alkyl fumarate is preferably selected from: di-ethyl fumarate, di-butyl fumarate and di(2-ethyl-hexyl) fumarate.

[0049] The di-alkyl maleate preferably has the formula:



wherein R¹¹ and R¹² are independently selected from alkyl groups having from 1 to 9 carbon atoms, preferably from 1 to 8 carbon atoms.

[0050] The di-alkyl maleate is preferably selected from: di-ethyl maleate and di-butyl-maleate.

[0051] Preferably the copolymer has a number average molecular weight, as measured by Gel Permeation Chromatography using polystyrene standards, of 1,000 to 20,000, more preferably 1,000 to 10,000, more preferably 2,000 to 5,000.

[0052] If desired, the copolymers may be derived from additional comonomers, e.g. they may be terpolymers or tetrapolymers or higher polymers, for example where the additional comonomer is 1-butene, propene, or diisobutene or another unsaturated ester giving rise to different units of the above formula.

[0053] Also, the copolymers may additionally include small proportions of chain transfer agents and/or molecular weight modifiers (e.g. acetaldehyde or propionaldehyde) that may be used in the polymerisation process to make the copolymer.

[0054] The copolymers may be made by direct polymerisation of comonomers. Such copolymers may also be made by transesterification, or by hydrolysis and reesterification, of an ethylene unsaturated ester copolymer to give a different ethylene unsaturated ester copolymer. For example, ethylene-vinyl hexanoate and ethylene-vinyl octanoate copolymers may be made in this way, e.g. from an ethylene vinyl acetate copolymer.

[0055] The copolymers may, for example, have 15 or fewer, preferably 10 or fewer, more preferably 6 or fewer, most preferably 2 to 5, methyl terminating side branches per 100 polymer backbone methylene groups, as measured by nuclear magnetic resonance spectroscopy, other than methyl groups on a comonomer ester and other than terminal methyl groups.

[0056] The copolymers may have a polydispersity of 1 to 6, preferably 1.5 to 4; polydispersity being the ratio of weight average molecular weight to number average molecular weight both as measured by Gel Permeation Chromatography using polystyrene standards.

[0057] The copolymer preferably has a molar ethylene content of between 50 and 95 mol%. Preferably the ethylene content is from 55 to 90 mol%, more preferably 60 to 90 mol%, and most preferably 70 to 90 mol%.

(ii) Copolymers of ethylene and alkene:

[0058] The alkene preferably includes at most 20 carbon atoms. The alkene is preferably a 1-alkene having at most 20 carbon atoms. The 1-alkene is preferably selected from: propylene, 1-butene, 1-hexene, 1-octene, methyl-1-pentene, 1-decene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-octadecene, 1-eicosene and vinyl-cyclohexane, and mixtures thereof.

[0059] The copolymer may also include small amounts e.g. up to 10% by weight of other copolymerizable monomers.

[0060] The copolymer may have a molecular weight of 1,000 to 50,000, preferably from 1,000 to 20,000, and most preferably from 1,000 to 10,000, as measured by gel permeation chromatography (GPC) relative to polystyrene standards.

[0061] The copolymer preferably has a molar ethylene content of between 50 and 90 mol%. Preferably the ethylene content is from 55 to 85 mol%, more preferably 60 to 85 mol%, and most preferably 70 to 85 mol%.

[0062] The copolymers may be prepared by any of the methods known in the art, for example, using catalysts selected from: Ziegler-Natta type catalysts and metallocene catalysts.

(iii) Nucleators:

[0063] The nucleator is preferably a polyoxyalkylene compound. Examples include polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two, C₁₀ to C₃₀ linear alkyl groups and one or more polyoxyalkylene glycol group of molecular weight up to 5,000, preferably 200 to 5,000, the alkylene group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms, as described in EP-A-61 895 and in U.S. Patent No. 4,491,455.

[0064] Preferred glycols are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having

a molecular weight of about 100 to 5,000, preferably about 200 to 1,500. Esters are also preferred and fatty acids containing from 10 to 30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use C₁₂ to C₁₈ fatty acid, especially myristic, palmitic and stearic acids. The esters may also be prepared by esterifying polyethoxylated fatty acids, polyethoxylated alcohols or polyols.

[0065] Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. In particular, myristic, palmitic or stearic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

[0066] Examples of other compounds in this general category are those described in Japanese Patent Publication Nos. 2-51477 and 3-34790, and EP-A-117,108 and EP-A-326,356, and cyclic esterified ethoxylates such as described EP-A-356,256.

[0067] Other suitable esters are those obtainable by the reaction of:

(i) an aliphatic monocarboxylic acid having 10 to 30 carbon atoms, and

(ii) an alkoxyated aliphatic monohydric alcohol, in which the alcohol has greater than 12 carbon atoms prior to alkoxylation and in which the degree of alkoxylation is 3 to 25 moles of alkylene oxide per mole of alcohol.

[0068] The ester may be formed from a single acid reactant (i) and single alcohol reactant (ii), or from mixtures of acids (i) or alcohols (ii) or both. In the latter cases, a mixture of ester products will be formed which may be used without separation if desired, or separated to give discrete products before use.

[0069] These materials may also be prepared by alkoxylation of a fatty acid ester of a polyol (e.g. ethoxylated sorbitan tristearate having the trade name TWEEN 65, which is available from Uniqema, owned by ICI).

[0070] The degree of alkoxylation of the aliphatic monohydric alcohol is preferably 3 to 25 moles of alkylene oxide per mole of alcohol, more preferably 3 to 10 moles. The alkoxylation is preferably ethoxylation, although propoxylation or butoxylation can also be used successfully. Mixed alkoxylation, for example a mixture of ethylene and propylene oxide units, may also be used.

[0071] The acid reactant (i) preferably has 12 to 30 carbon atoms, more preferably 12 to 18 carbon atoms such as 14 or 16 carbon atoms. The acid is preferably a saturated aliphatic acid, more preferably an alkanoic acid. Alkanoic acids of 12 to 30 carbon atoms are particularly useful. n-Alkanoic acids are preferred. Such acids include myristic acid, palmitic acid and stearic acid, with myristic and palmitic acids being preferred. Where mixtures of acids are used, it is preferred that the average number of carbon atoms in the acid mixture lies in the above-specified ranges and preferably the individual acids within the mixture will not differ by more than 8 (and more preferably 4) carbon numbers.

[0072] The alcohol reactant (ii) is preferably derived from an aliphatic monohydric alcohol having no more than 28 carbon atoms, and more preferably no more than 18 (or better, 16) carbon atoms, prior to alkoxylation. The range of 12 to 18 is particularly advantageous for obtaining good wax crystal modification. The aliphatic alcohol is preferably a saturated aliphatic alcohol, especially an alkanol (i.e. alkyl alcohol).

[0073] Where the alcohol reactant (ii) is a mixture of alcohols, this mixture may comprise a single aliphatic alcohol alkoxyated to varying degrees, or a mixture of aliphatic alcohols alkoxyated to either the same or varying degrees. Where a mixture of aliphatic alcohols is used, the average carbon number prior to alkoxylation should be above 12 and preferably within the preferred ranges recited above. Preferably, the individual alcohols in the mixture should not differ by more than 4 carbon atoms.

[0074] The esterification can be conducted by normal techniques known in the art.

[0075] The alkoxylation of the aliphatic alcohol is also conducted by well-known techniques.

[0076] The nucleator may also be a block copolymer comprising a single crystallizable block and a single non-crystallizable block (a 'di-block' polymer) and those comprising a single non-crystallizable block having at each end a single crystallizable block (a 'tri-block' polymer). Other tri- and tetra-block copolymers are also available. In preferred embodiments, in which the copolymer is derived from butadiene and isoprene, these di- and tri-block polymers are referred to as PE-PEP and PE-PEP-PE respectively.

[0077] The crystallizable blocks will be the hydrogenation product of the unit resulting from predominantly 1,4- or end-to-end polymerization of butadiene, while the non-crystallizable blocks will be the hydrogenation product of the unit resulting from 1,2-polymerization of butadiene (PE-PEB) or from 1,4-polymerization of an alkyl-substituted butadiene, for example isoprene (PE-PEP).

(iv) Waxes:

[0078] The waxes may include both normal and non-normal paraffin hydrocarbons.

[0079] The normal paraffin hydrocarbons preferably range from C₈H₁₈ to C₃₅H₇₂. Preferably the number average

molecular weight of the paraffin hydrocarbon is in the range of about 150 to 300. While it is possible to use individual paraffin hydrocarbons, better results are usually obtained with a paraffin hydrocarbon comprising a mixture of hydrocarbons. Preferably the normal hydrocarbons range from C₈ to C₃₀, preferably C₁₀ to C₂₅.

[0080] The paraffin hydrocarbon may be selected from crude waxes such as slack wax and slop wax. The paraffin hydrocarbon may be obtained by conventional dewaxing of various paraffinic petroleum refinery streams boiling within the range of about 200°C to about 500°C. Particularly suitable waxes are slack waxes obtained from solvent dewaxing of oils having a boiling range of from about 200°C to 400°C.

[0081] The non-normal paraffin hydrocarbons preferably include amorphous solid materials having melting points within the range of 10 to 60°C, preferably 20 to 40°C, and having number average molecular weights within the range of 150 to 500.

[0082] A suitable amorphous hydrocarbon fraction can be obtained by 'de-oiling' or 'sweating' of waxes in the wax refining process. Non-normal alkane waxes are also known as foots oils and filtrates.

(v) Substantially branched alkyl phenol formaldehyde condensates ('APFC's):

[0083] Alkyl phenol formaldehyde condensates are disclosed in EP 0 311 452 and EP 0 851 776.

[0084] The alkyl phenol formaldehyde condensate may be obtainable by the condensation reaction between:

(i) at least one aldehyde or ketone or reactive equivalent thereof, and

(ii) at least one compound comprising one or more aromatic moieties bearing at least one substituent of the formula -XR¹³ and at least one further substituent -R¹⁴, wherein:

X represents oxygen or sulphur,

R¹³ represents hydrogen or a moiety bearing at least one hydrocarbyl group, and

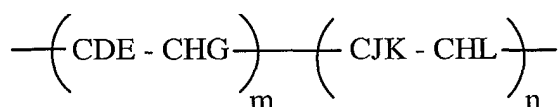
R¹⁴ represents a substantially branched hydrocarbyl group, preferably containing from 4 to 40 carbon atoms, more preferably containing from 8 to 30 carbon atoms and most preferably containing from 8 to 18 carbon atoms.

[0085] Suitable substantially branched alkyl phenol formaldehyde condensates include isononyl phenol formaldehyde condensates and iso-dodecyl phenol formaldehyde condensates.

(vi) Comb polymers:

[0086] The additional comb polymer is selected from a polymer or copolymer of an unsaturated ester or an olefin maleic anhydride copolymer.

[0087] The comb polymer may be a polymer or copolymer including units of the general formula



where

D represents R¹⁶, COOR¹⁵, OCOR¹⁵, R¹⁶COOR¹⁵ or OR¹⁵;

E represents H or D;

G represents H or D;

J represents H, R¹⁶, R¹⁶COOR¹⁵, or a substituted or unsubstituted aryl or heterocyclic group;

K represents H, COOR¹⁶, OCOR¹⁶, OR¹⁶ or COOH;

L represents H, R¹⁶, COOR¹⁶, OCOR¹⁶ or substituted or unsubstituted aryl;

R¹⁵ representing a hydrocarbyl group having 10 or more carbon atoms, and

R¹⁶ representing a hydrocarbylene (divalent) group in the R¹⁶COOR¹⁵ moiety and otherwise a hydrocarbyl (monovalent) group,

and m and n represent mole ratios, their sum being 1 and m being finite and being up to and including 1 and n being from zero to less than 1, preferably m being within the range of from 1.0 to 0.4 and n being in the range of from 0 to

0.6. R¹⁵ advantageously represents a hydrocarbyl group with from 10 to 30 carbon atoms, preferably 10 to 24, more preferably 10 to 18. Preferably, R¹⁵ is a linear or slightly branched alkyl group and R¹⁶ advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms when monovalent, preferably with 6 or greater, more preferably 10 or greater, preferably up to 24, more preferably up to 18 carbon atoms. Preferably, R¹⁶, when monovalent, is a linear or slightly branched alkyl group. When R¹⁶ is divalent, it is preferably a methylene or ethylene group. By "slightly branched" is meant having a single methyl branch.

[0088] The comb polymer may contain units derived from other monomers if desired or required, examples being CO, vinyl acetate and ethylene.

[0089] The comb polymer may also be a copolymer of maleic anhydride acid and another ethylenically unsaturated monomer, e.g. an α -olefin or an unsaturated ester, for example, vinyl acetate as described in EP-A-214,786. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g. maleic anhydride, include 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and styrene. Other examples of comb polymers include polyalkyl(meth)acrylates.

[0090] The copolymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols that may be used include n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 2-methylpentadecan-1-ol, 2-methyltridecan-1-ol as described in EP-A-213,879. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than alcohol mixtures such as may be commercially available; if mixtures are used, the number of carbon atoms in the alkyl group is taken to be the average number of carbon atoms in the alkyl groups of the alcohol mixture; if alcohols that contain a branch at the 1 or 2 positions are used, the number of carbon atoms in the alkyl group is taken to be the number in the straight chain backbone segment of the alkyl group of the alcohol.

[0091] The copolymer may also be reacted with a primary and/or secondary amine, for example, a mono- or di-hydrogenated tallow amine.

[0092] The comb polymers may especially be fumarate or itaconate polymers and copolymers such as for example those described in European Patent Applications 153 176, 153 177, 156 577 and 225 688, and WO 91/16407. The comb polymers are preferably C₈ to C₁₂ dialkylfumarate-vinyl acetate copolymers.

[0093] Other suitable comb polymers are the polymers and copolymers of α -olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid as described in EP-A-282,342; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above, such use may be advantageous.

(vii) Polar nitrogen compounds:

[0094] Polar nitrogen compounds are also known as Wax Anti-Settling Additives ('WASA').

[0095] Polar nitrogen compounds include an oil-soluble polar nitrogen compound carrying one or more, preferably two or more, hydrocarbyl substituted amino or imino substituents, the hydrocarbyl group being monovalent and containing 8 to 40 carbon atoms, and the substituents optionally being in the form of a cation derived therefrom. The oil-soluble polar nitrogen compound is either ionic or non-ionic and is capable of acting as a wax crystal growth modifier in fuel oils. Preferably, the hydrocarbyl group is linear or slightly linear, i.e. it may have one short length (1-4 carbon atoms) hydrocarbyl branch. When the substituent is amino, it may carry more than one said hydrocarbyl group, which may be the same or different.

[0096] The term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred.

[0097] Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ke-topropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

[0098] More especially, the or each amino or imino substituent is bonded to a moiety via an intermediate linking group such as -CO-, -CO₂⁽⁻⁾, -SO₃⁽⁻⁾ or hydrocarbylene. Where the linking group is anionic, the substituent is part of a cationic group, as in an amine salt group. If the linking group is a carbonyl, the substituent part is either an imide or amide group.

[0099] When the polar nitrogen compound carries more than one amino or imino substituent, the linking groups for each substituent may be the same or different.

[0100] Suitable amino substituents are long chain C_{12} - C_{24} , preferably C_{12} - C_{18} , alkyl primary, secondary, tertiary or quaternary amino substituents.

[0101] Preferably, the amino substituent is a dialkylamino substituent, which, as indicated above, may be in the form of an amine salt thereof, an amide thereof, or both; tertiary and quaternary amines can form only amine salts. Said alkyl groups may be the same or different.

[0102] Preferably the amino substituents include dodecylamino, tetradecylamino, cocoamino, and hydrogenated tallow amino. Examples of secondary amino substituents include dioctadecylamino and methylbehenylamino. Mixtures of amino substituents may be present such as those derived from naturally occurring amines. A preferred amino substituent is the secondary hydrogenated tallow amino or dicocoamine substituent, the alkyl groups of which are derived from hydrogenated tallow fat and are typically composed of approximately 4% C_{14} , 31 % C_{16} and 59% C_{18} n-alkyl groups by weight.

[0103] Suitable imino substituents are long chain C_{12} - C_{40} , preferably C_{12} - C_{24} , alkyl substituents.

[0104] The moiety may be monomeric (cyclic or non-cyclic) or polymeric. When non-cyclic, it may be obtained from a cyclic precursor such as an anhydride or a spirobis lactone.

[0105] The cyclic ring system may include homocyclic, heterocyclic, or fused polycyclic assemblies, or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic assemblies may be the same or different. Where there are two or more such cyclic assemblies, the substituents may be on the same or different assemblies, preferably on the same assembly. Preferably, the or each cyclic assembly is aromatic, more preferably a benzene ring. Most preferably, the cyclic ring system is a single benzene ring when it is preferred that the substituents are in the ortho or meta positions, which benzene ring may be optionally further substituted.

[0106] The ring atoms in the cyclic assembly or assemblies are preferably carbon atoms but may for example include one or more ring N, S or O atom, in which case or cases the compound is a heterocyclic compound.

[0107] Examples of such polycyclic assemblies include polycyclic aromatics, rings joined "end-on" such as diphenyl, heterocyclics or alicyclics.

[0108] Examples of polar nitrogen compounds are described below:

[0109] (i) an amine salt and/or amide of a mono- or poly-carboxylic acid, e.g. having 1 to 4 carboxylic acid groups. It may be made, for example, by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of the acid or its anhydride.

[0110] When an amide is formed, the linking group is $-CO-$, and when an amine salt is formed, the linking group is $-CO_2^{(-)}$.

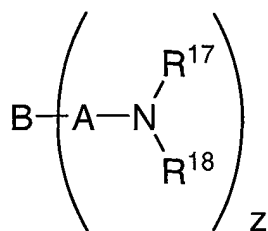
[0111] The moiety may be cyclic or non-cyclic. Examples of cyclic moieties are those where the acid is cyclohexane 1,2-dicarboxylic acid; cyclohexene 1,2-dicarboxylic acid; cyclopentane 1,2-dicarboxylic acid; and naphthalene dicarboxylic acid. Generally, such acids have 5 to 13 carbon atoms in the cyclic moiety. Preferred such cyclic acids are benzene dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid, and benzene tetracarboxylic acids such as pyromellitic acid, phthalic acid being particularly preferred. US-A-4,211,534 and EP-A-272,889 describes polar nitrogen compounds containing such moieties.

[0112] Examples of non-cyclic moieties are those when the acid is a long chain alkyl or alkylene substituted dicarboxylic acid such as a succinic acid, as described in US-A-4,147,520 for example.

[0113] Other examples of non-cyclic moieties are those where the acid is a nitrogen-containing acid such as ethylene diamine tetracetic acid and nitrilotriacetic acid.

[0114] Further examples are the moieties obtained where a dialkyl spirobis lactone is reacted with an amine as described in DE-A-392699.

[0115] (ii) A compound having the formula I, or a salt thereof:



wherein B represents an aromatic system, A represents a hydrocarbyl group, R^{17} and R^{18} are the same or are different

and each independently is an aliphatic hydrocarbyl group containing 12-24 carbon atoms, z is at least 1 and wherein the aromatic system carries at least one substituent group which is an activating group for the ring system or a derivative of an activating group.

[0116] By the term hydrocarbyl in this specification is meant an organic moiety that is composed of hydrogen and carbon, which is bonded to the rest of the molecule by a carbon atom or atoms and which, unless the context states otherwise, may be aliphatic, including alicyclic, aromatic or a combination thereof. It may be substituted or unsubstituted, alkyl, aryl or alkaryl and may optionally contain unsaturation or heteroatoms such as O, N or S, provided that such heteroatoms are insufficient to alter the essentially hydrocarbyl nature of the group. It is preferred that A is an aliphatic hydrocarbyl group and more preferably that A is a methylene group.

[0117] The term aromatic system is meant to include aromatic homocyclic, heterocyclic or fused polycyclic assemblies, or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic assemblies may be the same or different. Where there are two or more cyclic assemblies and z is 2 or more the $-(A-NR^{17}R^{18})$ groups present may be in the same or different assemblies. It is preferred that the aromatic system is a ring system based on benzene rings.

[0118] The ring atoms in the aromatic system are preferably carbon atoms but may, for example, include one or more heteroatoms such as N, S, or O in the system in which case the compound is a heterocyclic compound.

[0119] Examples of such polycyclic assemblies include

(a) condensed benzene structures such as naphthalene;

(b) condensed ring structures where none of or not all of the rings are benzene such as indene;

(c) rings joined "end-on" such as diphenyl;

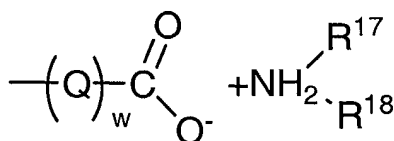
(d) heterocyclic compounds such as quinoline; and

(e) bisaromatic systems wherein the rings are linked by one or more divalent groups such as for example bisphenol A.

[0120] By the term activating group is meant any group, other than a substituent aliphatic hydrocarbyl group which activates the aromatic system to substitution reactions such as electrophilic substitution, nucleophilic substitution or to the Mannich reaction. The activating group may be a non-substituent group such as functionality that is within the aromatic system as in, for example, heterocyclic compounds such as indole. The activating group is located at least within or on each of the rings of the aromatic system which are substituted with an $-(A-NR^{17}R^{18})$ group. It is preferred that the activating group is a group that is on the ring system as opposed to being within the aromatic system. Desirably the activating group or groups activate the aromatic system to electrophilic substitution or to the Mannich reaction, most preferably to the Mannich reaction. It is preferred that the activating group activates the aromatic system in the ortho or para position relative to itself. The preferred activating group is a hydroxyl group. The preferred activated aromatic system is a hydroxy aromatic system. By the term derivative of an activating group is meant any group that can be produced by the reaction of the activating group. For example, when the activating group is a hydroxyl group one derivative would be an $-O-C(O)-CH_3$ group produced by reaction of the hydroxyl group with, for example, acetic anhydride. There may be more than one activating group or a derivative of an activating group on or in the aromatic system; they may be in or on the same or different rings. There may also be other substituents present that are in or on the aromatic system and are not activating groups or derivatives of activating groups.

[0121] Each aliphatic hydrocarbyl group constituting R^{17} and R^{18} in the invention may, for example, be an alkyl or alkylene group or a mono or polyalkoxyalkyl group or aliphatic hydrocarbyl group that contains heteroatoms such as O, N or S. Preferably each aliphatic hydrocarbyl group is a straight chain alkyl group. The number of carbon atoms in each aliphatic hydrocarbyl group is preferably 12-24, most preferably 12 to 18.

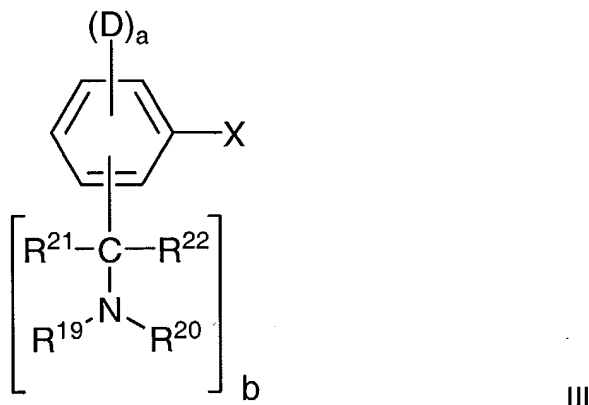
[0122] Preferably, such as when $z = 1$, the aromatic system also carries a substituent of general formula II



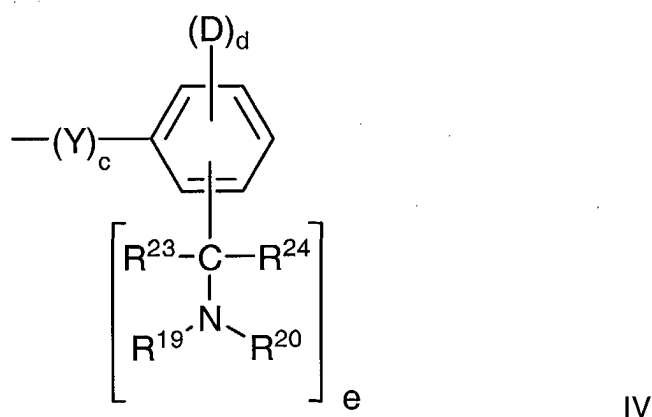
II

wherein $w = 0$ or 1 ; Q represents A ; and R^{17} and R^{18} have the meaning as given above. It is preferred that $w = 0$ and that there is only one additional substituent of the above general formula II. The additional substituent of general formula II may also be present in the aromatic system when z is 2 or more. When there is no additional substituent of general formula II present in the ring system it is preferred that z is 2 or more.

[0123] The most preferred compounds of general formula I are those which may be represented by general formula III



wherein X represents hydrogen, or a hydrocarbyl group, or a non-hydrocarbyl group, or a group of general formula IV:



wherein Y is a divalent group and wherein $a = 1, 2, 3$ or 4 , $b = 1, 2, 3$ or 4 , $c = 0, 1$ or 2 , $d = 0, 1, 2, 3$ or 4 and $e = 0, 1, 2, 3$ or 4 and wherein R^{21} , R^{22} , R^{23} and R^{24} are hydrogen or hydrocarbyl, and wherein R^{19} and R^{20} are independently C_8 - C_{30} aliphatic hydrocarbyl groups. D represents a hydroxyl group or a derivative of a hydroxyl group. When D is a derivative of a hydroxyl group it is preferably a $-O-C(O)-CH_3$ group. The C_{10} - C_{40} aliphatic hydrocarbyl groups may be linear or branched chains. It is preferred that the chains are linear.

[0124] When X is a group other than a group of formula IV preferably $a = 1$ or 2 and $b = 1, 2, 3$ or 4 , most preferably $a = 1$ or 2 and $b = 1, 2$ or 3 .

[0125] When X is a group of formula IV and $c = 0$, preferably $a = 1, 2$ or 3 , $b = 1, 2$ or 3 , $d = 0, 1, 2$ or 3 , and $e = 0, 1, 2$ or 3 , most preferably $a = 1$, $b = 1$, $d = 1$ and $e = 1$.

[0126] When X is a group of formula IV and $c = 1$, preferably $a = 1, 2$ or 3 , $b = 1, 2$ or 3 , $d = 0, 1, 2$ or 3 and $e = 0, 1, 2$ or 3 , most preferably $a = 1$ or 2 , $b = 1$ or 2 , $d = 0, 1$ or 2 and $e = 0, 1$ or 2 .

[0127] In both formulas III and IV the benzene ring may be part of a larger ring system such as a fused polycyclic ring system or may be a heterocyclic ring or an aromatic ring other than benzene.

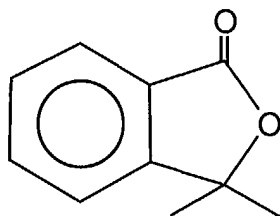
[0128] When $c = 1$ groups III and IV may also be joined directly, as in when $c = 0$, in addition to being joined by the divalent group Y . When $c = 2$ the divalent groups Y may be the same or different.

[0129] Preferably R^{21} , R^{22} , R^{23} and R^{24} are hydrogen. The aliphatic hydrocarbyl groups R^{19} and R^{20} may be the same or different and are preferably independently C_{10} - C_{40} alkyl groups. Desirably the alkyl groups are independently C_{12} - C_{24} alkyl groups and most preferably C_{12} - C_{18} alkyl groups. When there is more than one R^{19} or R^{20} group present they may be the same or different aliphatic hydrocarbyl groups. Preferred combinations of alkyl groups are those

wherein R^{19}/R^{20} are either C_{16}/C_{18} , C_{12}/C_{14} , C_{18}/C_{18} or C_{12}/C_{12} .

[0130] The aliphatic hydrocarbyl groups may also contain hetero atoms such as O, N or S. It is preferred that no hetero atoms are present in the aliphatic hydrocarbyl groups and that the groups are linear or those which have low levels of branching.

[0131] The divalent group Y may be a substituted or unsubstituted aliphatic group such as for example methylene, $-C(CH_3)_2-$, $-CH(Ph)-$, a group of formula V or similar groups,



V

or groups such as $-C(O)-$, $S(O)-$, $S(O)_2-$, $-O-$, $-S-$, $-C(O)-O-$ and $-C(O)-O-R^{15}-O-C(O)-$ wherein R^{15} is a hydrocarbyl group as hereinbefore defined. When there are two divalent groups present i.e. when $c = 2$ they may be the same or different e.g. the combination of the group of formula V and $-O-$ as in fluorescein. The divalent group Y may also be an aromatic group. The divalent group Y may also contain activated cyclic rings which have the substituent group $-(A-NR^{17}R^{18})$ present in the cyclic ring.

[0132] The compounds of general formula III may also be substituted with one or more groups of general formula II. It is preferred that when X is a group other than that of formula IV and when $b = 1$ that at least one group of general formula II is present in the compound of formula III. The compounds of general formula III may also be substituted with non-hydrocarbyl groups such as for example NO_2 or CN groups.

[0133] In the compound of formula I as defined above the activating group is preferably a hydroxyl group. The hydroxyl-aromatic system is hereinafter referred to as an activated compound. The compound is prepared by reacting under Mannich condensation conditions a formaldehyde or an aldehyde and a secondary amine which comprises independently C_8-C_{30} aliphatic hydrocarbyl groups.

[0134] The reactants may be used in equimolar or substantially equimolar proportions. The mole ratio of the activated compound to secondary amine may be less than equimolar for example 1:2, 1:3 or 1:4 or more. It is preferred that the mole ratio of activated compound to secondary amine is 1:2 or substantially 1:2 and that there is sufficient formaldehyde present to enable this mole ratio to be achieved in the final product.

[0135] The reaction may be carried out in a solvent for example toluene or without a solvent and at a temperature in the range of $80^\circ C$ to $120^\circ C$.

[0136] The aldehyde may be any aldehyde that reacts with an activated compound and a C_8-C_{30} aliphatic hydrocarbyl secondary amine under Mannich condensation conditions. It is preferred that formaldehyde is used in the method. The formaldehyde may be employed in any of its conventional forms; it may be used in the form of an aqueous solution such as formalin, as paraformaldehyde or as trioxane.

[0137] Suitable hydroxyaromatic compounds include for example: substituted phenols such as 2-, 3-, or 4-hydroxybenzophenone, 2-, 3-, or 4-hydroxybenzoic acid and 1 or 2-naphthol; dihydroxy compounds such as resorcinol, catechol, hydroquinone, 2,2'-biphenol, 4,4'-biphenol, fluorescein, 2,2-bis(p-hydroxy phenyl)propane, dihydroxybenzophenones, 4,4'-thiodiphenol, or dihydroxy benzoic acids such as 2,4-, or 3,5-dihydroxybenzoic acid; or trisphenolic compounds such as 1,1,1-tris-(4-hydroxy phenyl)ethane. The hydroxy aromatic compounds may be substituted, for example, with one or more of the following substituents: no-hydrocarbyl groups such as $-NO_2$ or CN; or hydrocarbyl groups such as $-CHO$, $-COOR$, $-COR$, $-COOR$; or aliphatic hydrocarbyl groups such as alkyl groups. The substituent or substituents may be in the ortho, para or meta or any combination of these positions in relation to the hydroxyl group or groups. When the hydroxyaromatic compound is a substituted phenol it is preferred that the substitution is in the ortho or para position. Phenols which have certain para substituents have been found to produce bisdialkylaminomethyl Mannich reaction products, derived from secondary amines with aliphatic hydrocarbyl groups of C_8 to C_{30} , under milder reaction conditions and with greater ease than when using unsubstituted phenol. In some cases substitution in the ortho position also allows easier reaction under milder conditions, though some such substituents are not beneficial, such as those substituents which are able to hydrogen bond with the hydroxyl group. A suitable ortho substituent is a cyano group. It will be understood that with dihydroxy compounds such as catechol where two or more hydroxy groups are present in the same ring, that any one substituent may be ortho with respect to one of these hydroxy groups and meta in relation to the other.

[0138] The amine may be any secondary amine that contains linear and/or branched chain aliphatic hydrocarbyl groups of C₈-C₃₀, and preferably C₁₀-C₂₂ and most preferably C₁₂-C₁₈. Preferred secondary amines are linear or those that have low levels of branching.

[0139] Examples of suitable secondary amines include the simple secondary amines such as N,N-dodecylamine, N,N-dihexadecylamine, N,N-di-octadecylamine, N,N-di-eicosylamine, N,N-di-docosylamine, N,N-di hydrogenated tallow amine and secondary amines in which the two alkyl groups are the same or different and selected from the following functionality: dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl, cetyl, stearyl, arachidyl, behenyl or hydrogenated tallow or that derived from the fatty acids of coconut oil.

[0140] Additional substituents of general formula II may be formed on the aromatic system during the above reaction by reacting activated compounds which have a carboxylic acid group present, with the corresponding amount of amine to take part in the above reaction and also to neutralise the carboxylic acid groups present. Alternatively the carboxylic acid groups may be neutralised after the reaction by adding the required amount of amine, which may be the same or a different amine to that used in the reaction, to neutralise the carboxylic acid groups.

[0141] There may be an additional reaction stage to convert the activating group into a derivative of the activating group such as, for example, the conversion of a hydroxyl group to its acetate ester by reaction for example with acetic anhydride.

[0142] (iii) A condensate of a long chain primary or secondary amine with a carboxylic acid-containing polymer.

[0143] Specific examples include polymers such as described in GB-A-2,121,807, FR-A-2,592,387 and DE-A-3,941,561; and also esters of telomer acid and alkanoloamines such as described in US-A-4,639,256; and the reaction product of an amine containing a branched carboxylic acid ester, an epoxide and a mono-carboxylic acid polyester such as described in US-A-4,631,071.

[0144] EP 0,283,292 describes amide containing polymers and EP 0,343,981 describes amine-salt containing polymers.

[0145] It should be noted that the polar nitrogen compounds may contain other functionality such as ester functionality.

[0146] The jet fuel composition may also include at least one of the following additives: antioxidant, metal deactivator, static dissipater to provide a conductivity of 50 to 450 pS/m, anti-freeze additive such as ethylene glycol monomethyl ether (EGME), corrosion inhibitor, biocide, anti-foamant, lubricity additive and detergent.

[0147] The invention will now be described by way of example only with reference to the drawing where;

[0148] Figure 1 is a plot of the results of the (L)CAST test at -58°C for a series of copolymers formed from a C₈ 1-alkene and a C_x 1-alkene.

Examples

Deposit reduction

[0149] Two jet fuel compositions were prepared including jet fuel MIL JP 8 and a hydrocarbon comb polymer of a C₆ 1-alkene and a C₁₂ 1-alkene. The first jet fuel composition (A) included a hydrocarbon comb polymer having a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of 2,500, and the second comparative jet fuel composition (B) included a hydrocarbon comb polymer having a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of 5,500.

[0150] The jet fuel compositions were tested a single burner jet engine including a combustor. The jet engine was run at idle (100°C air inlet temperature) for two runs of 20 minutes duration and one run of 40 minutes duration. The total duration of the test was thus 80 minutes. The air flow was 350 g/s and the fuel mass flow was 3.4 g/s.

[0151] The test results are shown in Table 1.

Table 1

Fuel composition	20 min	20 min	40 min	Total 80 min	Deposit
(B) comparative	1.05g	1.12g	2.08g	4.25g	100%
(A)	0.79g	1.00g	1.70g	3.49g	82%

[0152] The results show that there was an 18% decrease in the amount of deposit recovered from the jet engine when it was run using fuel composition (A) compared to the amount recovered when the high molecular weight polymer was used in fuel composition (B).

Cold flow performance

[0153] Cold flow performance was measured using the (L)CAST Cold-Flow additive screening test. The purpose of this test is to establish the low temperature properties of a jet fuel and the effect that fuel additives have on these properties.

[0154] In the (L)CAST test, a formulation of fuel and additive is cooled to a specified temperature. The test specimen is then filtered through a 417 μ m (35 mesh) screen until suction is lost or 60 seconds elapses.

[0155] The test procedure in detail is as follows:

a) 250 ml of fuel is weighed into a glass or nalgene bottle. This is then doped with the test additive at the test concentration, 4.0 g/l.

b) The sample is poured into a conical test flask of known mass and reweighed. The total mass of fuel plus additive being tested is then recorded as the total weight of the sample. A filter assembly is placed into the fuel after it has been checked visually to ensure that it is intact and free of particulates.

c) The test flask and filter assembly are placed in a cooling box set at the test temperature. The sample is then left overnight and the temperature of both the cooling box and the sample verified as being at the chosen test temperature with the aid of a temperature probe.

d) The sample is stirred with the filter assembly (15 revolutions at 1 rev/s)

e) The appearance of the sample is noted (e.g. clear, cloudy & fluid or gelled).

f) A vacuum pump is switched on to put the receiving vessel and attached tubes under vacuum at a pressure of 20kPa. The test flask is then subjected to the vacuum and the fuel is sucked through the filter assembly into the receiving vessel. A stopwatch is started the moment the valve is opened, and is stopped when suction is lost. If the fuel is still flowing at 60 sec, the valve is closed, stopping any further flow after that time..

g) The test flask and filter assembly are allowed to warm up to ambient temperature. The filter assembly is then removed allowing adhering fuel to drop back into the test flask, and the test flask is reweighed with any remaining fuel that it contains.

h) The percentage of wax hold-up is calculated according to the following equation:

$$\frac{[\text{Mass of test flask plus remaining fuel at test end} - \text{Mass empty test flask}]}{[\text{Mass test flask plus test fuel before cooling} - \text{Mass empty test flask}]} \times 100$$

[0156] A percentage of wax hold-up of greater than 15% is normally considered to be a failure.

[0157] Figure 1 shows the results of the (L)CAST test at -58°C for a number of hydrocarbyl polymers. All polymers tested were copolymers of a C₈ 1-alkene with a second alkene which was either a C₁₀, C₁₁, C₁₂, C₁₃, C₁₄ or C₁₆ 1-alkene. It is clear from Fig. 1, that only the copolymer of a C₈ 1-alkene with a C₁₂ 1-alkene recorded a pass (actual percentage wax hold-up was 10%). All other copolymers failed the (L)CAST test. These results confirm the unexpectedly good cold flow performance of the C₈/C₁₂ copolymers.

Claims

1. A method for reducing the level of deposits in a jet engine, the method comprising supplying to the jet engine a jet fuel composition comprising a jet fuel and at least one hydrocarbyl comb polymer; wherein the at least one hydrocarbyl comb polymer has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 5,500, preferably less than 5,000.

2. A method according to claim 1, wherein the hydrocarbyl comb polymer has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 4,800, preferably less than 4,500, more preferably less than 4,300, even more preferably less than 4,000, and most preferably less

than 3,800.

3. A method according to claim 1 or claim 2, wherein the hydrocarbonyl comb polymer is a hydrocarbon polymer or copolymer of a C₃-C₉ 1-alkene and a C₁₀-C₁₄ 1-alkene.

4. A method according to any preceding claim, wherein the hydrocarbonyl comb polymer is a hydrocarbon polymer or copolymer of a C₆-C₈ 1-alkene and a C₁₂ 1-alkene.

5. A method according to any preceding claim, wherein the hydrocarbonyl comb polymer is a hydrocarbon polymer or copolymer of a C₈ 1-alkene and a C₁₂ 1-alkene.

6. A method according to any preceding claim, wherein the jet fuel composition further comprises at least one of the following:

- (i) a copolymer of ethylene and at least one unsaturated ester;
- (ii) a copolymer of ethylene and alkene;
- (iii) a nucleator;
- (iv) a wax;
- (v) a substantially branched alkyl phenol formaldehyde condensate (known as 'APFC');
- (vi) a comb polymer selected from a polymer or copolymer of an unsaturated ester or an olefin maleic anhydride copolymer; and
- (vii) a polar nitrogen compound.

7. A method according to any preceding claim, wherein the at least one hydrocarbonyl comb polymer is present in the jet fuel composition in an amount ranging from 10 to 20,000 ppm, preferably 100 to 10,000 ppm, and most preferably from 500 to 5,000 ppm (parts additive per million parts jet fuel w/w).

8. A method according to any preceding claim, wherein the pour point of the jet fuel is reduced.

9. Use of at least one hydrocarbonyl comb polymer having a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 5,500, preferably less than 5,000, as an additive for a jet fuel, in order to reduce the level of deposits in a jet engine supplied with such a jet fuel.

10. A jet fuel composition comprising a jet fuel and at least one hydrocarbonyl comb polymer; wherein the at least one hydrocarbonyl comb polymer is a hydrocarbon polymer or copolymer of a C₈ 1-alkene and a C₁₂ 1-alkene, and has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 5,500, preferably less than 5,000.

11. A jet fuel composition according to claim 10, wherein the hydrocarbon polymer or copolymer has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 4,800, preferably less than 4,500, more preferably less than 4,300, even more preferably less than 4,000, and most preferably less than 3,800.

12. A jet fuel composition according to claim 10 or claim 11, further comprising at least one of the following:

- (i) a copolymer of ethylene and at least one unsaturated ester;
- (ii) a copolymer of ethylene and alkene;
- (iii) a nucleator;
- (iv) a wax;
- (v) a substantially branched alkyl phenol formaldehyde condensate (known as APFC');
- (vi) a comb polymer selected from a polymer or copolymer of an unsaturated ester or an olefin maleic anhydride copolymer; and,
- (vii) a polar nitrogen compound.

13. A jet fuel composition according to any of claims 10 to 12, wherein the hydrocarbon polymer or copolymer is present in the jet fuel in an amount ranging from 10 to 20,000 ppm, preferably 100 to 10,000 ppm, and most preferably from 500 to 5,000 ppm (parts additive per million parts jet fuel w/w).

14. A process for reducing the pour point of a jet fuel, the process including the following steps:

a) providing a jet fuel; and,

b) adding to the jet fuel at least one hydrocarbyl comb polymer; wherein the at least one hydrocarbyl comb polymer is a hydrocarbon polymer or copolymer of a C₈ 1-alkene and a C₁₂ 1-alkene, and has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 5,500, preferably less than 5,000.

15. Use of at least one hydrocarbyl comb polymer to reduce the low temperature operability of a jet fuel; wherein the at least one hydrocarbyl comb polymer is a hydrocarbon polymer or copolymer of a C₈ 1-alkene and a C₁₂ 1-alkene, and has a number average molecular weight, as measured by Gel Permeation Chromatography against polystyrene standards, of less than 5,500, preferably less than 5,000..

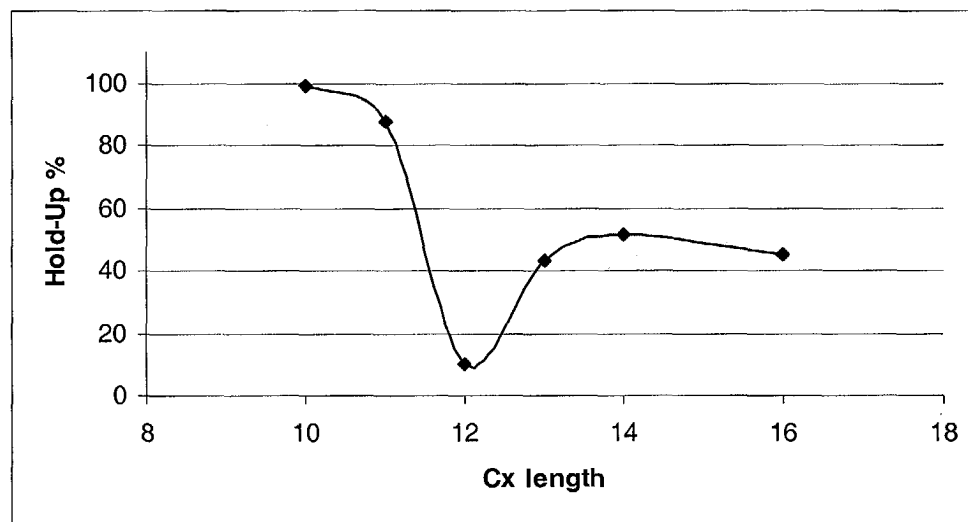


Figure 1



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EUROPEAN SEARCH REPORT

Application Number
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