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(54) **METHOD**

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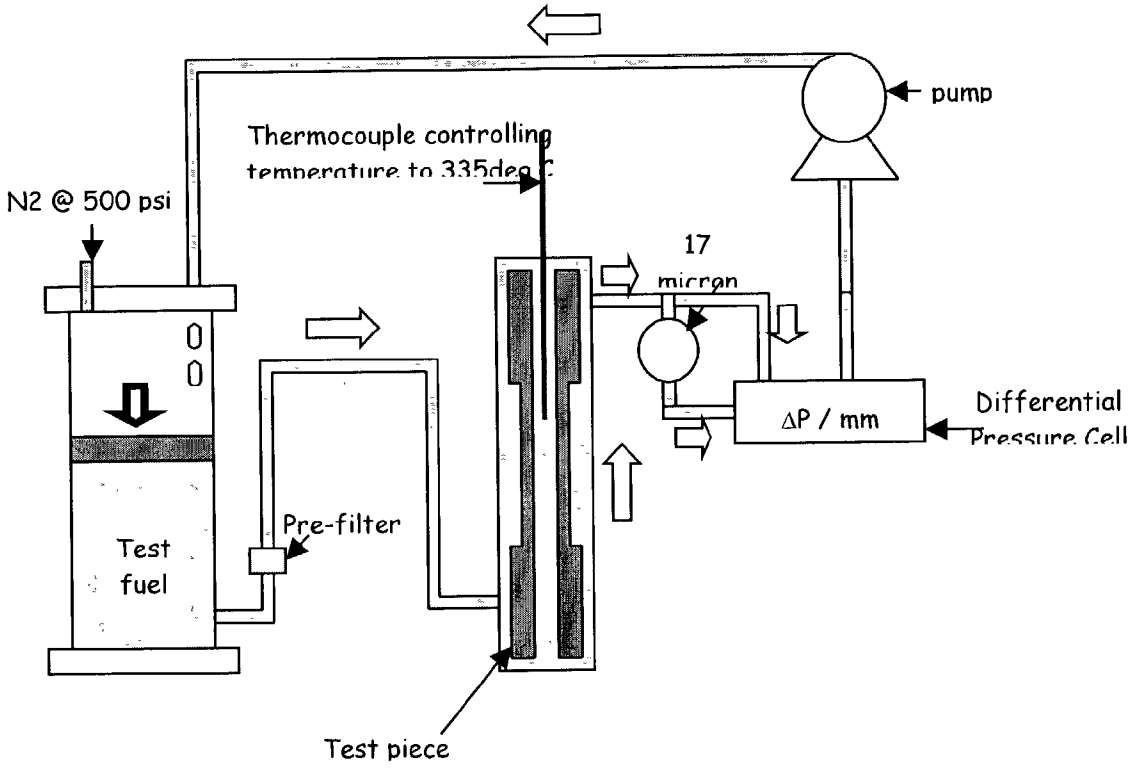
(57) **ABSTRACT**

The present invention provides a method for inhibiting deposit formation in a fuel at a temperature of from 100 to 335° C., the method comprising combining with the fuel a composition comprising: (i) high temperature antioxidant; and (ii) a deposit inhibiting compound.



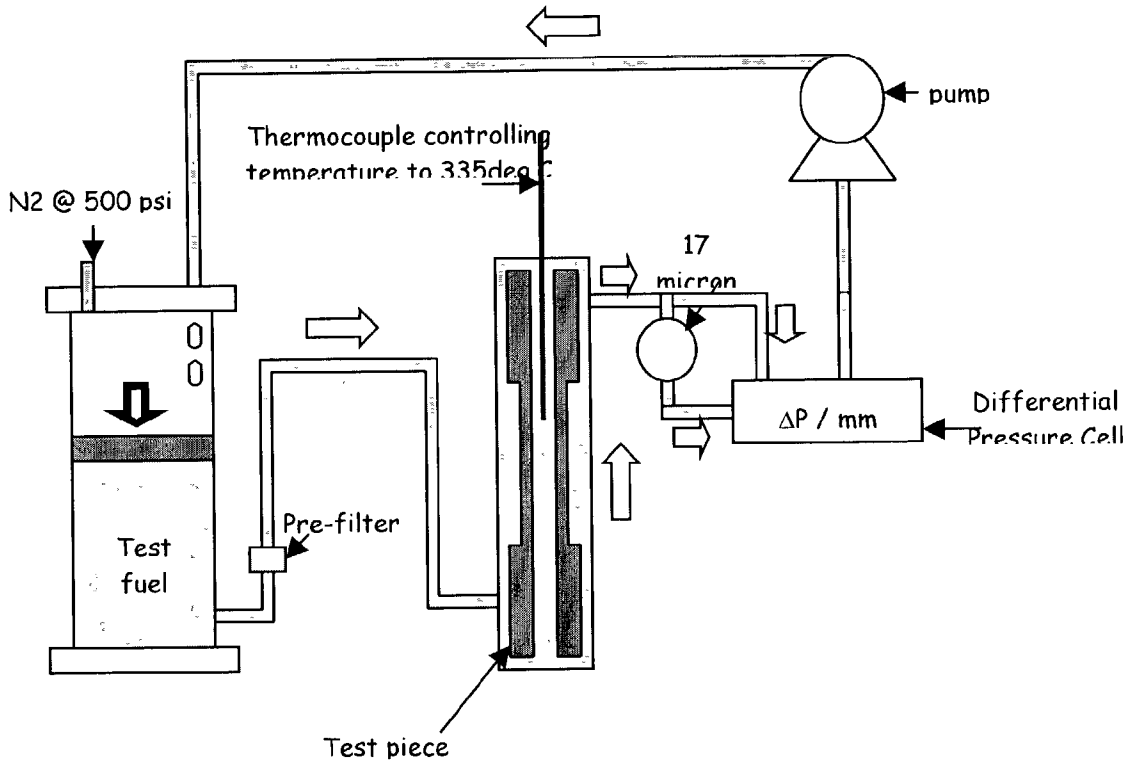

pump
Thermocouple controlling
temperature to 335deg C
N2 @ 500 psi
17
micron
ΔP / mm
Differential
Pressure Cell
Pre-filter
Test
fuel
Test piece

Figure 1

METHOD

[0001] The present invention relates to a composition comprising a high temperature antioxidant and a deposit inhibiting compound.

[0002] As discussed in U.S. Pat. No. 5,621,154, turbine combustion fuel oils i.e. jet fuels, such as JP-4, JP-5, JP-7, JP-8, Jet A, Jet A-1 and Jet B are ordinarily middle boiling distillates, such as kerosene or combinations of naphtha and kerosene. Military grade JP-4, for instance, is used in military aircraft and is a blend of naphtha and kerosene. Military grades JP-7 and JP-8 are primarily highly refined kerosenes, as are Jet A and Jet A-1, which are used for commercial aircraft. Civil grades of jet fuel are defined in ASTM D1655, DefStan 91-91, and other similar specifications. Such jet fuel are produced from a variety of sources including crude oil, oil sands, oil shales, Fischer Tropsch processes and gas to liquid processes. Refinery processing includes fuels produced by straight distillation, sometimes processed by chemical sweetening, or hydrogen processing including hydrocracking operations, and may contain <1 to 3000 ppm sulphur.

[0003] As discussed in U.S. Pat. No. 5,468,262, the thermal stability of jet fuel has been recognised as a problem for some years. High-speed flight necessitates that the heat generated be dissipated through the fuel i.e. the fuel is purposely preheated prior to combustion. As aircraft have become more sophisticated with more electronic components, the heat load has increased and the fuel must be preheated to a higher temperature to absorb the energy. This makes the thermal stability of the fuel even more critical.

[0004] These hydrocarbon jet fuels are known to be subject to deterioration when in contact with oxygen, either on standing in air or during pre-combustion heating. Such deterioration is thought to be due to the presence in the fuel of constituents which undergo oxidative changes resulting in the formation of non-volatile resinous substances. In addition, the high temperatures and oxygen-rich atmospheres in aircraft and engine fuel system components encourage the degradation of the fuel resulting in particulate and deposit formation.

[0005] The resinous substances and other deposits plug up the components leading to operational problems including reduced thrust and performance anomalies in the augmentor, poor spray patterns and premature failure of mainburner combustors and problems with fuel controls. Further, the engine exhaust becomes smoky and sooty and engine noise increases, both of which are undesirable characteristics for jet engines.

[0006] The problems of deposition from fuels at elevated temperatures is not limited to the use of fuels in the extreme environments encountered in aviation. As discussed in WO-A-99/25793 in some oil fired devices, such as boilers and slow heating cookers, e.g. of the Aga™ type, kerosene oil fuel is passed down a narrow metal feed pipe to the combustion chamber where it is burnt. Parts of the pipe are sufficiently near the hot chamber for them to be heated to significant temperatures, resulting in the risk of thermal degradation of the fuel in the pipe, especially with slow feed rates and high residence times in the pipe. This degradation can form solid deposits which reduce the flow and ultimately stop it, causing the combustion to stop. To overcome this manufacturers of such devices have for many years recommended to their users that at least once each six months such pipe parts are cleaned of solid deposits of coke or other materials.

[0007] GB 2261441 teaches a fuel composition in the gasoline boiling range containing a polyoxyalkylene compound and the reaction product of a polyamine and a hydrocarbyl succinic acylating agent.

[0008] U.S. Pat. No. 5,601,624 discloses a fuel composition comprising a fuel and a minor amount of a multifunctional additive such as a dispersant, corrosion inhibitor or antioxidant. The additive is the reaction product of an oxygenated amine with a dicarbonyl compound and a hydrocarbyl or hydrocarbylene amine. e.g. a polyetheramine, glyoxal and a succinimide.

[0009] U.S. Pat. No. 5,990,056 relates to a lubricant composition comprising an organo substituted benzophenone and at least one co-additive such as a lubricant antioxidant, a lubricant dispersant, or an antiwear additive. The compound is thought to act as a lubricant base or blend stock, a solubility enhancer or a deposit reducing agent.

[0010] GB 923190 teaches a synergistic antioxidant mix for use in organic material. The mix comprises a phosphite ester and a methylene bis phenol. The use in jet fuel, kerosene, and fuel oil is disclosed.

[0011] GB 791526 discloses dimethyl-(phenyl)-phosphates (e.g. dimethyl-(tolyl)-phosphate).

[0012] Use of the compounds in hydrocarbons in the gasoline boiling range is taught.

[0013] In order to alleviate some of the problems outlined above and meet certain performance and storage requirements, fuels including jet fuels often contain additives such as antioxidants, deposit inhibiting compounds, metal deactivators, corrosion inhibitors and lubricity improvers. It would be apparent to one skilled in the art that synergistic combinations of any of these additives would be desirable.

[0014] Antioxidant additives are used not only in fuel but also in a range of other substances such as lubricants, plastics and food products.

[0015] The present invention alleviates the problems of the prior art.

[0016] The present invention relates to the provision of combinations, in particular synergistic combinations, of antioxidants and deposit inhibiting compounds.

[0017] Aspects of the invention are defined in the appended claims.

[0018] In one aspect the present invention provides a method for inhibiting deposit formation in a fuel at a temperature of from 100 to 335° C., the method comprising combining with the fuel a composition comprising: (i) high temperature antioxidant; and (ii) a deposit inhibiting compound.

[0019] By the term "high temperature antioxidant" it is meant an antioxidant which may prevent oxidation in a fuel at high temperature. In particular it is meant an antioxidant which provides improved antioxidant performance when measured in accordance with the High Temperature Antioxidant Protocol below.

[0020] In one aspect the present invention provides a composition comprising (i) a phosphorus-containing anti-oxidant; and (ii) a deposit inhibiting compound

[0021] In one aspect the present invention provides a fuel composition comprising (a) a fuel (b) a composition as defined herein.

[0022] In one aspect the present invention provides a use of a composition as defined herein for

[0023] (i) the inhibition of oxidation of a fuel composition comprising the composition and a fuel; and/or

[0024] (ii) the inhibition of deposit formation in a fuel composition comprising the composition and a fuel; and/or

[0025] (iii) the inhibition of particle formation from the oxidation product(s) of a fuel; and/or

[0026] (iv) the solubilisation of deposits and/or deposit precursors.

[0027] In one aspect the present invention provides a composition comprising (i) a phosphorus-containing anti-oxidant; and (ii) a deposit inhibiting compound, in an amount or a ratio to produce an antioxidant and/or deposit inhibitory synergistic effect.

[0028] We have found that the combination of a phosphorus-containing antioxidant, such as di-dodecyl hydrogen phosphonate, and a deposit inhibiting compound, such as 2300 ButA Mannich, act in fuels to inhibit oxidation and/or deposition of material from fuels at elevated temperatures. The oxidation products or deposited material may block filters and reduce the efficiency of an engine in which the fuel is combusted. We have surprisingly found that the combination of products which form the present composition act in a synergistic manner to prevent or inhibit oxidation and/or deposition of material.

[0029] We have found that by the provision of the compositions of the present invention an anti-oxidant and/or deposit inhibitory effect may be observed, for example by study using Hot Liquid Process Simulator (HLPS). The anti-oxidant and/or deposit inhibitory effect is greater than one would expect from the anti-oxidant and/or deposit inhibitory effect of each of the composition components, i.e. the combination of components provides a synergistic effect.

[0030] Preferred Aspects

[0031] Antioxidant

[0032] As discussed above in one aspect the present invention provides a method for inhibiting deposit formation in a fuel at a temperature of from 100 to 335° C., the method comprising combining with the fuel a composition comprising: (i) high temperature antioxidant; and (ii) a deposit inhibiting compound.

[0033] Preferably the high temperature antioxidant of the present invention is a phosphorus-containing antioxidant.

[0034] Preferably the phosphorus-containing antioxidant is an organophosphorus-containing antioxidant.

[0035] By the term "organophosphorus-containing anti-oxidant" it is meant a compound comprising at least P and C and may optionally comprise one or more other suitable atoms. Examples of such atoms may include hydrogen, sulphur and oxygen.

[0036] By the term "organophosphorus-containing anti-oxidant" it is meant a compound containing a C—P bond and/or a C—O—P bond and/or a C—S—P bond.

[0037] Preferably the phosphorus-containing antioxidant is or is derived from an organophosphorus acid. Preferably the organophosphorus acid is selected from phosphorus acid, phosphonous acid, phosphinous acid, phosphoric acid, phosphonic acid or phosphinic acid.

[0038] In one preferred aspect the phosphorus-containing antioxidant is or is derived from an ester of an organophosphorus acid. Preferably the organophosphorus acid is selected from phosphorus acid, phosphonous acid, phosphinous acid, phosphoric acid, phosphonic acid or phosphinic acid.

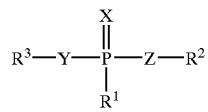
[0039] In a preferred aspect the phosphorus-containing antioxidant is an ester of an organophosphorus acid. More preferably the phosphorus-containing antioxidant is an ester of an organophosphorus acid selected from phosphorus acid, phosphonous acid, phosphinous acid, phosphoric acid, phosphonic acid or phosphinic acid.

[0040] In a highly preferred aspect the phosphorus-containing antioxidant is or is an ester of a phosphonic acid.

[0041] In a highly preferred aspect the phosphorus-containing antioxidant is an ester of a phosphonic acid.

[0042] Preferably the phosphorus-containing antioxidant contains a trivalent or pentavalent phosphorus.

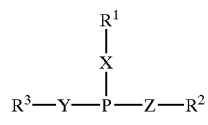
[0043] Preferably the phosphorus-containing antioxidant is a compound of Formula I:



I

[0044] wherein R^1, R^2 and R^3 are independently selected from H and hydrocarbyl; and X, Y, and Z are independently selected from O and S.

[0045] Preferably the phosphorus-containing antioxidant is a compound of Formula II:



II

[0046] wherein R^1, R^2 and R^3 are independently selected from H and hydrocarbyl; and X, Y, and Z are independently selected from O and S.

[0047] In the present specification by the term "hydrocarbyl group" it is meant a group comprising at least C and H and may optionally comprise one or more other suitable

substituents. Examples of such substituents may include halo-, alkoxy-, nitro-, a hydrocarbon group, an N-acyl group, a cyclic group etc. In addition to the possibility of the substituents being a cyclic group, a combination of substituents may form a cyclic group. If the hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked via a suitable element or group. Thus, the hydrocarbyl group may contain hetero atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for instance, sulphur, nitrogen and oxygen.

[0048] In one preferred embodiment of the present invention, the hydrocarbyl group is a hydrocarbon group.

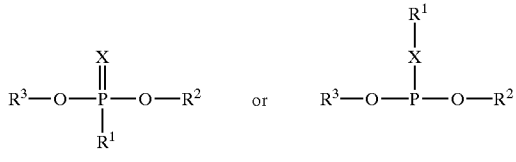
[0049] Here the term "hydrocarbon" means any one of an alkyl group, an alkenyl group, an alkynyl group, an acyl group, which groups may be linear, branched or cyclic, or an aryl group. The term hydrocarbon also includes those groups but wherein they have been optionally substituted. If the hydrocarbon is a branched structure having substituent(s) thereon, then the substitution may be on either the hydrocarbon backbone or on the branch; alternatively the substitutions may be on the hydrocarbon backbone and on the branch.

[0050] X, Y and Z

[0051] Preferably at least one of X, Y or Z is O.

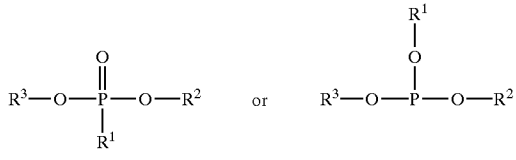
[0052] Preferably at least one of Y and Z is O.

[0053] Preferably X is S or O, Y is O and Z is O. Thus in a highly preferred aspect the antioxidant of the present invention is of the formula



[0054] wherein X, R^1, R^2 and R^3 are as defined above.

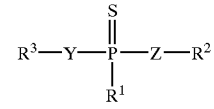
[0055] Preferably each of X, Y and Z is O. Thus in a highly preferred aspect the antioxidant of the present invention is of the formula



[0056] wherein R^1, R^2 and R^3 are as defined above.

[0057] In one aspect at least one of X, Y or Z is O and wherein at least one of X, Y or Z is S.

[0058] In one aspect, preferably when the antioxidant is of formula I X is S. Thus in this aspect the antioxidant of the present invention is of the formula



[0059] wherein Y, Z, R^1, R^2 and R^3 are as defined above.

[0060] R^1, R^2 and R^3

[0061] As disclosed above R^1, R^2 and R^3 are independently selected from H and hydrocarbyl.

[0062] Preferably R^1 is selected from H and hydrocarbon.

[0063] Preferably R^1 is selected from H and C_{1-30} hydrocarbyl, such as C_{1-20} hydrocarbyl, C_{1-15} hydrocarbyl, C_{1-10} hydrocarbyl, C_1, C_2, C_3, or C_4 hydrocarbyl.

[0064] Preferably R^1 is selected from H and C_{1-30} hydrocarbon, such as C_{1-20} hydrocarbon, C_{1-15} hydrocarbon, C_{1-10} hydrocarbon, C_1, C_2, C_3, or C_4 hydrocarbon.

[0065] Preferably R^1 is selected from H and C_{1-30} alkyl, such as C_{1-20} alkyl, C_{1-15} alkyl, C_{1-10} alkyl, C_1, C_2, C_3, or C_4 alkyl.

[0066] Preferably R^1 is selected from H and C_{1-10} alkyl, for example C_1, C_2, C_3, or C_4 alkyl.

[0067] In a highly preferred aspect R^1 is H.

[0068] In some aspects, for example when the compound is formula II, R^1 is selected from

[0069] H and C_{1-100} hydrocarbyl, such as C_{1-50} hydrocarbyl, C_{1-30} hydrocarbyl, C_{1-25} hydrocarbyl, C_{1-20} hydrocarbyl, C_{1-15} hydrocarbyl, C_{1-12} hydrocarbyl, C_{5-25} hydrocarbyl, C_{8-20} hydrocarbyl, C_{10-15} hydrocarbyl, C_{10}, C_{11}, C_{12}, C_{13}, or C_{14} hydrocarbyl.

[0070] H and C_{1-100} hydrocarbon, such as C_{1-50} hydrocarbon, C_{1-30} hydrocarbon, C_{1-25} hydrocarbon, C_{1-20} hydrocarbon, C_{1-15} hydrocarbon, C_{1-12} hydrocarbon, C_{5-25} hydrocarbon, C_{8-20} hydrocarbon, C_{10-15} hydrocarbon, C_{10}, C_{11}, C_{12}, C_{13}, or C_{14} hydrocarbon.

[0071] H and C_{1-100} alkyl, such as C_{1-50} alkyl, C_{1-30} alkyl, C_{1-25} alkyl, C_{1-20} alkyl, C_{1-15} alkyl, C_{1-12} alkyl, C_{5-25} alkyl, C_{8-20} alkyl, C_{10-15} alkyl, C_{10}, C_{11}, C_{12}, C_{13}, or C_{14} alkyl.

[0072] H and C_{1-100} straight chain alkyl, such as C_{1-50} alkyl, C_{1-30} alkyl, C_{1-25} alkyl, C_{1-20} alkyl, C_{1-15} alkyl, C_{1-12} alkyl, C_{5-25} alkyl, C_{8-20} alkyl, C_{10-15} alkyl, C_{10}, C_{11}, C_{12}, C_{13}, or C_{14} alkyl.

[0073] In a preferred aspect R^2 and R^3 are independently selected from H and hydrocarbon groups.

[0074] Preferably R^2 and R^3 are independently selected from H and C_{1-100} hydrocarbyl, such as C_{1-50} hydrocarbyl, C_{1-30} hydrocarbyl, C_{1-25} hydrocarbyl, C_{1-20} hydrocarbyl, C_{1-15} hydrocarbyl, C_{1-12} hydrocarbyl, C_{5-25} hydrocarbyl, C_{8-20} hydrocarbyl, C_{10-15} hydrocarbyl, C_{10}, C_{11}, C_{12}, C_{13}, or C_{14} hydrocarbyl.

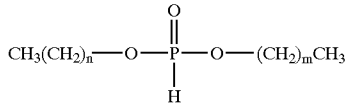
[0075] Preferably R^2 and R^3 are independently selected from H and C_{1-100} hydrocarbon, such as C_{1-50} hydrocarbon,

C_{1-30} hydrocarbon, C_{1-25} hydrocarbon, C_{1-20} hydrocarbon, C_{1-15} hydrocarbon, C_{1-12} hydrocarbon, C_{5-25} hydrocarbon, C_{8-20} hydrocarbon, C_{10-15} hydrocarbon, C_{10}, C_{11}, C_{12}, C_{13}, or C_{14} hydrocarbon.

[0076] Preferably R^2 and R^3 are independently selected from H and C_{1-100} alkyl, such as C_{1-50} alkyl, C_{1-30} alkyl, C_{1-25} alkyl, C_{1-20} alkyl, C_{1-15} alkyl, C_{1-12} alkyl, C_{5-25} alkyl, C_{8-20} alkyl, C_{10-15} alkyl, C_{10}, C_{11}, C_{12}, C_{13}, or C_{14} alkyl.

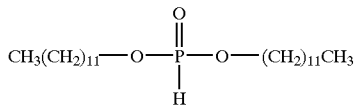
[0077] Preferably R^2 and R^3 are independently selected from H and C_{1-100} straight chain alkyl, such as C_{1-50} alkyl, C_{1-30} alkyl, C_{1-25} alkyl, C_{1-20} alkyl, C_{1-15} alkyl, C_{1-12} alkyl, C_{5-25} alkyl, C_{8-20} alkyl, C_{10-15} alkyl, C_{10}, C_{11}, C_{12}, C_{13}, or C_{14} alkyl.

[0078] In a highly preferred aspect the antioxidant is of the formula



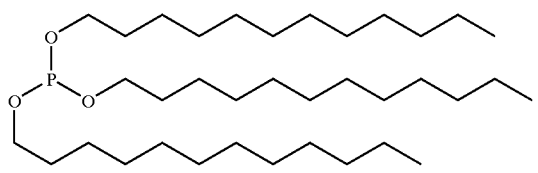
[0079] wherein n and m are independently selected from 1 to 15, preferably 5 to 15, preferably 7 to 13, preferably 8 to 12, preferably 9, 10 or 11.

[0080] In a highly preferred aspect the antioxidant is of the formula



[0081] This compound is commonly known as di-dodecyl hydrogen phosphonate.

[0082] In a highly preferred aspect the antioxidant is of the formula



[0083] This compound is commonly known as tridodecylphosphite.

[0084] Deposit Inhibiting Compound

[0085] Preferably the deposit inhibiting compound is of Formula II

Polymer-Q-R (II)

[0086] wherein Polymer is a polymeric hydrocarbyl group; wherein Q is an optional ring system; and wherein R is a group selected from H and hydrocarbyl.

[0087] R

[0088] In one aspect if R is a hydrocarbyl group it is free of a carboxylic acid group (—COOH).

[0089] In one aspect if R is a hydrocarbyl group it is free of a hydroxyl group (—OH).

[0090] In one aspect R is selected from H and a nitrogenous hydrocarbyl group.

[0091] In one aspect R is a nitrogenous hydrocarbyl group.

[0092] The term "nitrogenous hydrocarbyl group" as used herein means a group comprising at least C, H and N and may optionally comprise one or more other suitable substituents. Examples of such substituents may include halo-, alkoxy-, an alkyl group, a cyclic group etc. In addition to the possibility of the substituents being a cyclic group, a combination of substituents may form a cyclic group. If the nitrogenous hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked via a suitable element or group. Thus, the nitrogenous hydrocarbyl group may contain hetero atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for instance, sulphur.

[0093] In one preferred embodiment of the present invention, the nitrogenous hydrocarbyl group is a nitrogenous hydrocarbon group.

[0094] Here the term "nitrogenous hydrocarbon group" means a group containing only C, H and N (with the proviso of course that Q together with R contains no greater than 2 nitrogen) including primary, secondary and tertiary amines, which group may be linear, branched or cyclic. The term nitrogenous hydrocarbon group also includes groups which have been optionally substituted. If the nitrogenous hydrocarbon group is a branched structure having substituent(s) thereon, then the substitution may be on either the hydrocarbon backbone or on the branch; alternatively the substitutions may be on the hydrocarbon backbone and on the branch.

[0095] Preferably the combined total of nitrogen and carbon atoms in the nitrogenous hydrocarbon group is from 1 to 10, preferably from 2 to 8, preferably 2 to 6, for example 2, 4 or 6. Preferably in this aspect the nitrogenous hydrocarbon group is a straight chain.

[0096] Q

[0097] Q is an optional ring system. In one aspect the optional ring system Q is present.

[0098] In one aspect Q is substituted. Preferably Q is substituted with one or more groups selected from =O and —OH.

[0099] In one preferred aspect Q is an aromatic ring.

[0100] In one preferred aspect Q has 4 to 10 members, preferably 4 to 6 members, preferably 5 or 6 members.

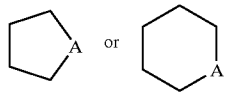
[0101] Q may be heterocyclic ring or may contain only carbon. The ring may be a hydrocarbyl ring. In the present specification by the term "hydrocarbyl ring" it is meant a cyclic group comprising at least C and H and may optionally comprise one or more other suitable ring members. Suitable

ring members will be apparent to those skilled in the art and include, for instance, sulphur, and nitrogen.

[0102] In one preferred aspect Q is a carbon ring or a heterocyclic ring containing carbon and one nitrogen.

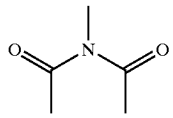
[0103] In one aspect Q is selected from a ring system of the formula

[0104] wherein A is C or N and n is an integer from 1 to 5. In this aspect preferably Q is selected from a ring system of the formula

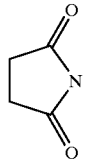


[0105] wherein A is C or N, i.e. n is 1 or 2.

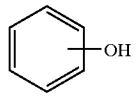
[0106] In one aspect Q contains an imide group, namely a group of the formula



[0107] Preferably Q is a ring system of the formula



[0108] In one aspect Q is a hydrocarbon ring substituted with at least one alcohol group. The hydrocarbon ring may be aromatic and in a preferred aspect is a six membered aromatic ring. Preferably Q is a ring system of the formula



[0109] In one aspect Q together with R is a Mannich group or is derived from or derivable from a Mannich reaction.

[0110] When the ring Q contains a nitrogen, preferably group R is attached to ring Q via the nitrogen. In other words, the nitrogen of group Q may be substituted by group R.

[0111] R & Q

[0112] In one aspect Q together with R contains no greater than 2 nitrogens.

[0113] In one aspect when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring.

[0114] In one aspect Q together with R contains only 2 nitrogens and wherein each of the nitrogens is a member of a heterocyclic ring.

[0115] In one aspect Q together with R contains no greater than 1 nitrogen.

[0116] In one aspect Q together with R contains no greater than 1 basic nitrogen.

[0117] Polymer

[0118] Preferably Polymer is a hydrocarbyl group having from 10 to 200 carbons.

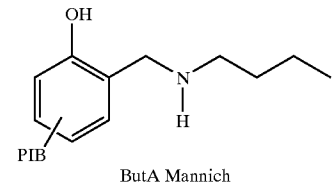
[0119] Preferably Polymer is a branched or straight chain alkyl group, preferably a branched alkyl group.

[0120] Preferably Polymer has a molecular weight of from 700 to 2500, preferably 1000 to 2300, preferably approximately 1000 or approximately 2300.

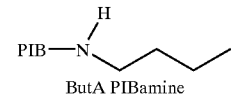
[0121] Preferably Polymer is polyisobutene (PIB). Conventional PIBs and so-called "high-reactivity" PIBs (see for example EP 0565285) are suitable for use in the invention. High reactivity in this context is defined as a PIB wherein at least 50%, preferably 70% or more, of the terminal olefinic double bonds are of the vinylidene type.

[0122] Preferably Polymer is polyisobutene having a molecular weight of from 700 to 2500, preferably 1000 to 2300, preferably approximately 1000 or approximately 2300.

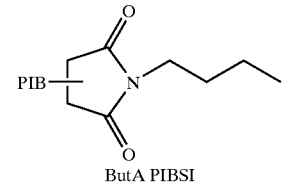
[0123] In a highly preferred aspect the deposit inhibiting compound is selected from compounds of the formulae



ButA Mannich



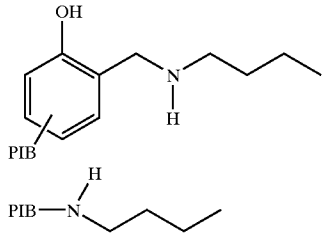
ButA PIBamine



ButA PIBSI

[0124] wherein PIB is polyisobutene.

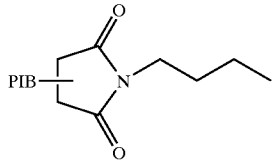
[0125] In a highly preferred aspect the deposit inhibiting compound is selected from compounds of the formulae



[0126] wherein PIB is polyisobutene having a molecular weight of approximately 2300

[0127] wherein PIB is polyisobutene having a molecular weight of approximately 1000

[0128] 1000 ButA PIBamine



2300 ButA Mannich

[0129] wherein PIB is polyisobutene having a molecular weight of approximately 1000

[0130] 1000 ButA PIBSI

[0131] Composition

[0132] In a preferred aspect the deposit inhibiting compound is provided in the composition to provide a fuel treat rate of 1-500 mg/l active concentration, preferably 50-300 mg/l, preferably 50-150 mg/l, preferably 75-125 mg/l, preferably approximately 100 mg/l.

[0133] In a preferred aspect the antioxidant is provided in the composition to provide a fuel treat rate of 1-100 mg/l active concentration, preferably 5-80 mg/l, preferably 5-50 mg/l preferably 5-20 mg/l , preferably 7-15 mg/l, preferably 10-13 mg/l.

[0134] In a preferred aspect the composition further comprises a metal deactivator. Preferably the metal deactivator is N,N'-disalicylidene 1,2-propanediamine or N,N'-disalicylidene 1,2-cyclohexyldiamine.

[0135] In a preferred aspect the metal deactivator is provided in the composition to provide a fuel treat rate of 1-50 mg/l active concentration, preferably 1-30 mg/l, preferably 1-20 mg/l, preferably 1-10 mg/l, preferably 1-5 mg/l, preferably approximately 2 mg/l.

[0136] In a preferred aspect the composition further comprises a further antioxidant. A possible further antioxidant is BHT (2,6-di-t-butyl-4-methyl phenol) or other aviation approved hindered phenol antioxidants. The additional antioxidants may be added in order to protect fuel from the build up peroxides on storage. In a preferred aspect the further antioxidant is provided in the composition to provide a fuel treat rate 0-100 mg/l, preferably 5-80 mg/l, preferably 10-50 mg/l, preferably 10-30 mg/l, preferably approximately 25 mg/l.

[0137] Fuel Composition

[0138] In one aspect the present invention provides a fuel composition comprising (a) a fuel (b) a composition comprising (i) a phosphorus-containing antioxidant; and (ii) a deposit inhibiting compound

[0139] Preferably the fuel is an aviation turbine fuel.

[0140] Preferably the fuel is JP-8 aviation fuel.

[0141] The deposit inhibiting compound may be present in the composition in amount of at least 1 mg/l or at least 5 mg/l, such as 1 to 1000, 5 to 1000 for example 5 to 500, 5 to 200 or 10 to 100 mg/l active ingredient based on the weight of the composition e.g. the fuel composition. The additive may be mixed with the jet or other fuel composition in the form of a concentrate in solution, e.g. in an aliphatic aromatic hydrocarbon in 20-80% w/w solution, or it may be added as such to give a solution in the fuel.

[0142] The composition can comprise jet fuel. The composition can comprise kerosene, in particular in jet fuel. The main component of the jet fuel itself is usually a middle boiling distillate boiling point in the range 150-300° C. at atmospheric pressure and the fuel is usually kerosene which may be mixed with gasoline (naphtha) and optionally light petroleum distillate as in mixtures of gasoline and kerosene. The jet fuel may comprise mixtures of gasoline and light petroleum distillate, e.g. in weight amounts of 20-80:80-20 such as 50-75:50-25 which weight amounts may also be used for mixtures of gasoline and kerosene. The jet fuels for military use are designated JP-4 to 8 e.g. JP-4 as 65% gasoline/35% light petroleum distillate (according to US Mil. Spec. (MIL 5624G)), JP-5, similar to JP-4 but of higher flash point, JP-7, a high flash point special kerosene for advanced supersonic aircraft and JP-8, a kerosene similar to Jet AI (according to MIL 83133C). Jet fuel for civilian use is usually a kerosene type fuel and designated Jet A or Jet AI. The jet fuel may have a boiling point of 66-343° C. or 66-316° C. (150-650° F. e.g. 150-600° F.), initial boiling point of 149-221° C., e.g. 204 C. (300-430° F., e.g. 400° F.), a 50% boiling point of 221-316° C. (430-600° F.) and a 90% boiling point of 260-343° C. (500-650° F.) and API Gravity of 30-40. Jet fuel for turbojet use may boil at 93-260° C. (200-500° F.) (ASTM D1655-006). Further details on aviation fuels may be obtained from "Handbook of Aviation Fuel Properties", Co-ordinating Research Council Inc., CRC Report No. 530 (Society of Automotive Engineers Inc., Warrendale, Pa., USA, 1983) and on US military fuels, from "Military Specification for Aviation Turbine Fuels", MIL-T-5624P.

[0143] The jet fuel may be the straight run kerosene optionally with added gasoline (naphtha), but frequently has been purified to reduce its content of components contributing to or encouraging formation of coloured products and/or precipitates.

[0144] Among such components are aromatics, olefins, mercaptans, phenols and various nitrogen compounds. Thus the fuels may be purified to reduce their mercaptan content

e.g. Merox fuels and copper sweetened fuels or to reduce their sulphur content e.g. hydrogen treated fuels or Merifined fuels. Merox fuels are made by oxidation of the mercaptans and have a low mercaptan S content (e.g. less than 0.005% wt S) such as 0.0001-0.005% but a higher disulphide S content (e.g. at most 0.4% or at most 0.3% wt S such as 0.05-0.25 e.g. 0.1-2%); their aromatic (e.g. phenolics) and olefins content are hardly changed. Hydrogen processed jet fuels are ones in which the original fuel has been hydrogenated to remove at least some of sulphur compounds e.g. thiols and under severe conditions to saturate the aromatics and olefins; hydrofined jet fuels have very low sulphur contents (e.g. less than 0.01% S by weight). Merifined fuels are fuels that have been extracted with an organic extractant to reduce or remove their contents of sulphur compounds and/or phenols. The jet fuel may also contain metals, either following contact with metal pipes or carried over from the crude oil, oil sands, shale oil or sources; examples of such metals are copper, nickel, iron and chromium usually in amounts of less than 1 ppm e.g. each in 10-150 ppb amounts. Merox, straight run and hydrogen processed are preferred and may be used in JP- 4-8 jet fuels.

[0145] The fuel comprising kerosene may also be a fuel for combustion especially for non motive purposes, e.g. power generation, steam generation, and heating, especially for use in buildings and for cooking, e.g. as described above. The fuel is particularly suitable for the devices e.g. boilers and slow cookers as described above in which there is localised preheating of the fuel before it is combusted.

[0146] Such fuels are known as burning kerosene and may have the same physical properties as the kerosene based jet fuels described above, e.g. straight run kerosene, or kerosene modified to reduce its content of at least one of aromatics, olefins and sulphur compounds, as described above. The fuel may also contain metals as described above.

[0147] The fuel compositions of the invention contains the deposit inhibiting compound and may also contain at least one conventional additive e.g. for jet fuels or burning fuels such as an antioxidant, corrosion inhibitor, lubricity improvers, metal deactivators (MDA), leak detection additives, "special purpose" additives such as drag reducing agents, anti-icing additives and static dissipaters such as Stadis®, especially in amounts each of 1-2000 ppm.

[0148] The use or method of the present invention is typically performed when the fuel or fuel composition is at a temperature of no greater than 1100° F. The fuel or fuel composition is typically at a temperature of 325 to 425° F. during use. In a one aspect the use or method of the present invention is preferably performed when the fuel or fuel composition is at a temperature of from 100 to 335° C.

[0149] The present invention will now be described in further detail by way of example only with reference to the accompanying figures in which:—

[0150] **FIG. 1** shows HLPS apparatus.

[0151] The present invention will now be described in further detail in the following examples.

EXAMPLES

[0152] The additives discussed below were tested for HLPS data. The Protocol for this test is given below.

HLPS Protocol

[0153] Scope—HLPS is a self-contained testing apparatus designed to test the thermal properties of base and additised jet fuels. The test involves the flow of the test fuel over a heated test surface (@335° C.) under high pressure (500 psi).

[0154] Summary—The HLPS is run in accordance with ASTM D-3241. The conditions for testing are set to those used by the USAF in extensive thermal stability programmes.

[0155] The basic principles of the HLPS are shown in **FIG. 1**. As shown in **FIG. 1,** 1 litre of test fuel is pressurised in a stainless steel reservoir to 500 psi. The fuel is then pumped via a pre-filter over a heated test section (@335° C.). As deposition occurs on both the tube and in the fuel bulk the bulk deposit is measured as a filter drop change across a 17 micron filter. A pressure transducer cell measures the rate of pressure drop (in mmHg min-1). Finally the spent fuel is returned to the top of the reservoir, separated by an appropriate seal.

[0156] Apparatus—Alcor HLPS—is a modular version of the equipment set up as defined in ASTM D-3241. The test section must be of stainless steel 316 and free from grease. The filter to be used must be of 17 micron mesh as supplied by Alcor.

[0157] Materials

[0158] Base fuels—are fuels free of additives

[0159] Main Test Procedure

[0160] Sample Preparation

[0161] 1. Filter 1 litre of base test fuel through a 0.7 micron filter.

[0162] 2. If fuel is to be additised transfer the known weight of additive(s) to a 1 litre volumetric flask using base test fuel.

[0163] 3. Transfer the test fuel to a 2 litre beaker. Aerate using the glass bubbler attachment for a minimum of 6 minutes. Test run must be initiated within 1 hour of aeration.

[0164] 4. Transfer the test fuel to the stainless steel reservoir.

[0165] 5. Check the piston seal for degradation. If OK place the piston head on the surface of the fuel and push down using the supplied handle until fuel begins to seep up from the reservoir.

[0166] 6. Place the large 'O' ring seal in the reservoir top and secure to the top of the reservoir using a socket wrench.

[0167] 7. Connect the connector tube from the filter unit to the test cell using new 'O' ring.

[0168] 8. Connect all remaining pipe-work using new 'O' rings.

[0169] Main Test Run Procedure.

[0170] 1. Close BLEED valve on front of HLPS and open PRESSURISE valve. Ensure that system is pressurised to 500 psi.

[0171] 2. Ensure that lower knob on delta P cell is turned to BYPASS and upper knob is VENT CLOSED.

[0172] 3. Switch on PUMP. Red indicator light will come on. Ensure that FUEL FLOW CONTROL is set to 230. This equates to a flow rate of 3 mls/min.

[0173] 4. Allow fuel to pump round system until a steady drop rate is seen through the Perspex window on top of the fuel reservoir. When steady count the time taken for 20 drops. If the time is 9 seconds±1 seconds this is acceptable for 3 mls/min.

[0174] 5. Ensure that HEATER TUBE TEMP. CONTROL is set to 335 deg. C. Switch on HEATER. Red indicator light will come on. Needle will then rise to the vertical. Heater power is controlled by using the POWER CONTROL dial. A typical setting for this procedure is 82±10 volts.

[0175] 6. Switch on the differential pressure module (DPM) by depressing the POWER button.

[0176] 7. When needle reads correct temperature switch the delta P lower knob to RUN. This will divert the fuel flow through the differential pressure cell.

[0177] 8. Allow the pressure read out on the differential pressure module to equilibrate and press RECORD. The differential pressure will be recorded every 5 minutes on the in-built printer.

[0178] 9. Allow the test to run whilst monitoring the differential pressure change. The DPM has an alarm setting that will cause multi-point printing at 125 mmHg. If the differential pressure rises above 300 mmHg turn the lower DPM knob to bypass and note the time.

[0179] 10. In all cases allow the test run to complete a 5 hour test sequence. The HLPS will shut down automatically after 5 hours.

[0180] Analysis—Analysis is carried out on the Leco Carbon Analyser RC412.

[0181] Results—Are quoted for 2 readings.

[0182] Filter blockage—Record the change in differential pressure during the run. Results are quoted in mmHg min-1, e.g. 300/45, 0/300. The first figure is the change in differential pressure in mmHg the latter the time in minutes

[0183] Carbon deposit weight—Record the value in μgcm^{-2}

High Temperature Antioxidant Protocol

[0184] A high temperature antioxidant candidate is formulated in a composition comprising the high temperature antioxidant candidate, 2300 ButA Mannich (a deposit inhibiting compound) and N,N'-disalicylidene 1,2-propanediamine (an MDA). The composition is dosed into at least three test fuels at a treat rate for each fuel of

[0185] (i) 100 mg 2300 ButA Mannich per litre of fuel;

[0186] (ii) 0.032 mmoles high temperature antioxidant candidate per litre of fuel; and

[0187] (iii) 2 mg N,N'-disalicylidene 1,2-propanediamine per litre of fuel

[0188] Each dosed fuel is subjected to HPLS testing in accordance with the above Protocol.

[0189] The currently approved stabiliser package SpecAid 8Q462 (available from Shell Aviation as AeroShell Performance Additive 101) is dosed into the same base fuels at a treat rate 256 mg/l for each fuel. Each dosed fuel is subjected to HPLS testing in accordance with the above Protocol.

[0190] The pressure drop of each fuel containing the candidate and the pressure drop of each fuel containing SpecAid 8Q462 is recorded.

[0191] The pressure drop recorded for the candidate composition in a given fuel is compared to pressure drop recorded for SpecAid 8Q462 in the same fuel. A candidate is considered to "pass" if for each fuel the pressure drop recorded for the candidate composition is no greater than 2 mmHg more than the pressure drop recorded for SpecAid 8Q462.

[0192] The carbon deposit weight of each fuel containing the candidate composition and the carbon deposit weight of each fuel containing SpecAid 8Q462 is recorded. The carbon deposit weight for the candidate composition is averaged across the number of fuels tested. The carbon deposit weight for SpecAid 8Q462 is averaged across the number of fuels tested. A candidate is considered to "pass" if the average carbon deposit weight for the candidate composition is less than, equal to or no greater than 10 mg more than the average carbon deposit weight for the SpecAid 8Q462.

[0193] A candidate which "passes" in respect of both pressure drop and carbon deposit weight constitutes a "high temperature antioxidant" within the scope of the present invention.

[0194] The at least three test fuels may be selected from Shell HT, POSF 3684 (USAF B), Phillips HT, Sunoco, Shell Merox, USAF A, BP Air Merox, Marathon HT, and Phillips Merox. In one aspect of this protocol the candidate composition is dosed into POSF 3684 (USAF B), Phillips HT, Sunoco, Shell Merox, USAF A, BP Air Merox, and Phillips Merox. In one aspect of this protocol the candidate composition is dosed into Shell HT, POSF 3684 (USAF B), Phillips HT, Sunoco, Shell Merox, USAF A, BP Air Merox, Marathon HT, and Phillips Merox.

[0195] Syntheses

[0196] PIBSIs

[0197] 1000/Butylamine PIBSI

[0198] 1000 mwt high reactive PIB derived PIBSA (467.6 g) was stirred with Shellsol AB (311.8 g) in a 1 l oil jacketed reactor equipped with an overhead stirrer, thermometer and Dean & Stark trap. Whilst still at room temperature butylamine (31.5 g) was added in one aliquot with continued stirring. An immediate exotherm was noted. The reaction mix was heated to ~150° C. for three hours whilst removing water. 720 g of product was isolated.

[0199] Analysis of the product showed it to contain 40% m/m solvent, 0.81% m/m nitrogen.

[0200] 1000 ButA PlBamine

[0201] PIB chloride (153 g, chlorine content 4.89% m/m) was placed in a stirred reactor with butylamine (61.6 g) and Shellsol (50 ml. The reactor contents were heated to reflux for 19.5 hours. Crystalline solid could be seen in the solution as the reaction proceeded. The reaction was allowed to cool and an excess of aqueous sodium carbonate was mixed with the reactor contents. After separation the organics were washed with water and dried over sodium sulphate. The unreacted butylamine was removed under reduced pressure leaving the 190 g product plus solvent.

[0202] Analysis of the product showed it to contain 23% m/m solvent, 0.95% m/m nitrogen, 1% m/m residual chlorine.

[0203] Mannich Compounds

[0204] The Mannichs for use in the present invention may be synthesised in accordance with the teaching of EP 0831141.

[0205] Results

[0206] The following data were obtained.

[0207] HLPS testing was performed and data collected. Results given are surface carbon deposit weight (μgcm^{-2}) and filter blockage, ΔP, (mmHg/min). A result of 0/300 means that no blockage has occurred over the 300 minutes of the test, a result of 300/101 means that the filter has completely blocked in 101 minutes.

[0208] The following antioxidants/antioxidant compositions were used in the Examples

AO1	2,6-di-t-butyl-4-methyl phenol
AO2	Octadecyl-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate
AO3	Methylene bis (dibutylthiocarbamate)
AO4	2,2'thiodiethyl bis-(3,5-di-t-butyl-4-hydroxyphenyl) propionate
AO5	commercially available alkylated phenol

-continued

AO6	3,5-bis-(1,1-dimethyl-ethyl)-4-hydroxybenzenepropanoic ester of C_{14-15} alcohol
AO7	"synergistic blend of an aminic and a phenolic antioxidant"
AO8	di-dodecyl hydrogen phosphonate
AO9	SpecAid 8Q462
AO10	dioleyl hydrogenophosphite
AO11	tridodecylphosphite
AO12	trinonylphenylphosphite
AO13	di-n-octylphosphite
AO14	isodecyl diphenylphosphite
AO15	butylated triphenyl phosphorothioate
AO16	ethyl-3-((bis(1-methylethoxy)phosphinothionyl)thio)propionate
AO17	ascorbyl palmitate
AO18	tocopherol

Example 1

[0209] Assessment of Different Antioxidants in Two Fuels

[0210] A number of different antioxidants/antioxidant compositions were assessed in two basefuels in a package containing a ButA Mannich detergent and a MDA. The results were compared against the fuel, MDA and detergent alone or in various combinations. The HLPS data are given below.

	Shell HT		POSF 3684 (USAF B)	
Composition	Carbon μgcm^{-2}	ΔP	Carbon μgcm^{-2}	ΔP
Basefuel	39	300/230	125	300/45
Basefuel + detergent	38	0/300	90.5	12/300
Basefuel + MDA	62	0/300	24	300/101
Basefuel, detergent + MDA	39	0/300	29.5	5/300
Basefuel, detergent, MDA + AO1 (25 mg/l)	41.5	0/300	27	0/300
Basefuel, detergent, MDA + AO2 (60.3 mg/l)	18	0/300	32	1/300
Basefuel, detergent, MDA + AO3 (50 mg/l)	66	0/300	32	4/300
Basefuel, detergent, MDA + AO4 (45 mg/l)	60	0/300	34	0/300
Basefuel, detergent, MDA + AO5 (25 mg/l)	19	300/270	19	9/300
Basefuel, detergent, MDA + AO6 (60 mg/l)	47	6/300	32	6/300
Basefuel, detergent, MDA + AO7 (50 mg/l)	40.3	4/300	28.4	300/26
Basefuel, detergent, MDA + AO8 (13.7 mg/l)	6	0/300	7	0/300
Basefuel, detergent, MDA + AO8 (5 mg/l)	26	0/300	—	—
Basefuel, detergent, MDA, AO8 (5 mg/l) + AO1 (25 m/l)	15	1/300	—	—
Basefuel, detergent, MDA, AO8 (5 mg/l) + AO2 (60 mg/l)	23	0/300	—	—
Basefuel, detergent, MDA, AO8 (13.7 mg/l) + AO2 (60 mg/l)	13	0/300	—	—
Basefuel + AO9 (256 mg/l)	10	0/300	19	0/300
Basefuel, detergent, MDA + AO10 (21 mg/l)	8	0/300	17	4/300
Basefuel, detergent, MDA + AO11 (18.8 mg/l)	5	0/300	19	1/300
Basefuel, detergent, MDA + AO12 (12 mg/l)	12	0/300	66	13/300
Basefuel, detergent, MDA + AO13 (10 mg/l)	9	0/300	16	13/300
Basefuel, detergent, MDA + AO14 (12 mg/l)	52	0/300	17	2/300
Basefuel, detergent, MDA + AO15 (12 mg/l)	68	0/300	22	0/300
Basefuel, detergent, MDA + AO16 (9 mg/l)	11	0/300	22	3/300
Basefuel, detergent, MDA + AO17 (10 mg/l*)	42	0/300	—	—
Basefuel, detergent, MDA + AO18 (13.8 mg/l)	48	0/300	—	—

*nominally 10 mg/l however solubility in fuel not good
Detergent-2300 ButA Mannich, active concentration of 100 mg/l.
MDA-metal deactivator, active concentration of 2 mg/l.
Concentrations of anti-oxidant linked, where possible, to the number of moles AO1 in 25 mg. Otherwise 50 mg/l used as standard.

[0211] In at least one the fuels and in some instances in both fuels, the addition of a phosphorus containing antioxidant to a package already containing detergent and MDA decreases the amount of carbon depositing on the surface of the HLPS tube and/or decreases filter blockage. The traditional antioxidant (BHT—AO1) tested does not show this effect.

Example 2

[0212] Assessment of Different Detergents in combination with Preferred Antioxidant

[0213] The preferred anti-oxidant of Example 1, namely AO8, was combined with three different detergents. The results were compared against the fuel, MDA, detergent and anti-oxidant alone or in various combinations. The HLPS data are given below.

	Shell HT	
Composition	Carbon μgcm^{-2}	ΔP
Basefuel	39	300/230
Basefuel + detergent A	38	0/300
Basefuel + A08 alone (10 mg/l)	86.5	3/300
Basefuel + MDA	62	0/300
Basefuel, detergent A + AO8	25	0/300
Basefuel, detergent A + MDA	39	0/300
Basefuel, detergent A, MDA + AO8	13	0/300
Basefuel, detergent B, MDA + AO8	23	0/300
Basefuel, detergent C, MDA + AO8	12	0/300

Detergent A-2300 ButA Mannich, active concentration of 100 mg/l
Detergent B-1000/ButA PIBamine, active concentration of 100 mg/l
Detergent C-1000/ButA PIBSI, active concentration of 100 mg/l
MDA-metal deactivator, active concentration of 2 mg/l.

[0214] Each of the full packages gives better performance than each component individually at the treat rate used in the package.

Example 3

[0215] Assessment of Package in Different Fuels

[0216] HLPS results for package based on AO8 in different fuels. For comparison the HPLS results for basefuel and SpecAid 8Q462 at a treat rate 256 mg/l are also given.

Fuel	ΔP Base	ΔP Spec-Aid	ΔP Package	Carbon Base μgcm^{-2}	Carbon SpecAid μgcm^{-2}	Carbon Package μgcm^{-2}
Shell HT	300/230	0/300	0/300	39	10	13
POSF 3684	300/45	0/300	2/300	125	19	17
USAF B						
Phillips HT	1/300	0/300	0/300	31	25	3
Sunoco	0/300	0/300	0/300	51	35	10.6
Shell Merox	300/170	3/300	0.8/300	157	46	24
USAF A	300/148	0/300	0/300	95	31	9
BP Air Merox	3/300	0/300	0/300	44	33	13
Marathon HT	4/300	1/300	0/300	55	9	15
Phillips Merox	300/27	1/300	0/300	26	46	20

Package contains
AO8-active concentration of 10 mg/l.
Detergent-2300 ButA Mannich, active concentration of 100 mg/l.
MDA-metal deactivator, active concentration of 2 mg/l.

[0217] In all the fuels tested there is a large decrease in both bulk and surface carbon deposits when using the above additive package.

[0218] All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims

1. A method for inhibiting deposit formation in a fuel at a temperature of from 100 to 335° C., the method comprising combining with the fuel a composition comprising:

(i) high temperature antioxidant; and

(ii) a deposit inhibiting compound

2. A method according to claim 1 wherein the high temperature antioxidant is a phosphorus-containing antioxidant.

3. A composition comprising:

(i) a phosphorus-containing antioxidant; and

(ii) a deposit inhibiting compound

4. The invention according to claim 2 or **3** wherein the phosphorus-containing antioxidant is an organophosphorus-containing antioxidant.

5. The invention according to claim 2, **3** or **4** wherein the phosphorus-containing antioxidant is or is derived from an organophosphorus acid.

6. The invention according to any one of claims 2 to 5 wherein the phosphorus-containing antioxidant is or is derived from an ester of an organophosphorus acid.

7. The invention according to any one of claims 2 to 6 wherein the organophosphorus acid is selected from phosphorus acid, phosphonous acid, phosphinous acid, phosphoric acid, phosphonic acid or phosphinic acid.

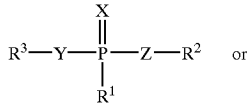
8. The invention according to claim 7 wherein the phosphorus-containing antioxidant is an ester of organophospho-

rus acid selected from phosphorus acid, phosphonous acid, phosphinous acid, phosphoric acid, phosphonic acid or phosphinic acid.

9. The invention according to claim 8 wherein the phosphorus-containing antioxidant is an ester of a phosphonic acid.

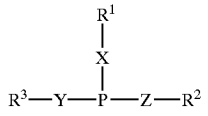
10. The invention according to any one of claims 2 to 9 wherein the phosphorus-containing antioxidant is a compound of Formula I or II:

Formula I



or

Formula II



wherein R^1, R^2 and R^3 are independently selected from H and hydrocarbyl; and X, Y, and Z are independently selected from O and S.

11. The invention according to claim 10 wherein at least one of X, Y or Z is O.

12. The invention according to claim 8 or **9** wherein at least one of Y and Z is O.

13. The invention according to claim 10, **11** or **12** wherein X is S or O, Y is O and Z is O.

14. The invention according to any one of claims 10 to 13 wherein each of X, Y and Z is O.

15. The invention according to claim 10 or **11** wherein at least one of X, Y or Z is O and wherein at least one of X, Y or Z is S.

16. The invention according to any one of claims 10 to 15 wherein R^1 is selected from H and hydrocarbon.

17. The invention according to any one of claims 10 to 16 wherein R^1 is selected from H and C1-15 alkyl.

18. The invention according to any one of claims 10 to 17 wherein R^1 is H.

19. The invention according to any one of claims 10 to 18 wherein R^2 and R^3 are independently selected from H and hydrocarbon groups having from 1 to 50 carbons.

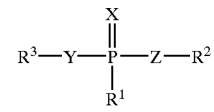
20. The invention according to claim 19 wherein R^2 and R^3 are independently selected from H and hydrocarbon groups having from 1 to 25 carbons.

21. The invention according to claim 19 wherein R^2 and R^3 are independently selected from H and straight chain alkyl groups having from 1 to 25 carbons.

22. The invention according to claim 19 wherein R^2 and R^3 are independently straight chain alkyl groups having from 10 to 15 carbons.

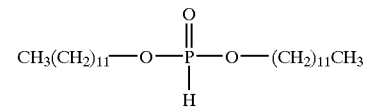
23. The invention according to any one of claims 2 to 22 wherein the phosphorus-containing antioxidant is a compound of Formula l:

Formula I



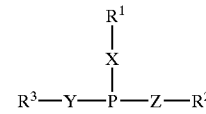
wherein R^1, R^2 and R^3 are independently selected from H and hydrocarbyl; and X, Y, and Z are independently selected from O and S.

23. The invention according to claim 23 wherein the antioxidant is of the formula



24. The invention according to any one of claims 2 to 22 wherein the phosphorus-containing antioxidant is a compound of Formula II:

Formula II



wherein R^1, R^2 and R^3 are independently selected from H and hydrocarbyl; and X, Y, and Z are independently selected from O and S.

25. The invention according to claim 24 wherein the antioxidant is tridodecylphosphite.

26. The invention according to any one of claims 1 to 25 wherein the deposit inhibiting compound is of Formula II

Polymer-Q-R (II)

wherein Polymer is a polymeric hydrocarbyl group; wherein Q is an optional ring system; and wherein R is a group selected from H and hydrocarbyl.

27. The invention according to claim 26 wherein if R is a hydrocarbyl group it is free of a carboxylic acid group (—COOH).

28. The invention according to claim 26 or **27** wherein Q together with R contains no greater than 2 nitrogens.

29. The invention according to claim 26, **27** or **28** wherein when Q together with R contains 2 nitrogens each of the nitrogens is a member of a heterocyclic ring.

30. The invention according to any one of claims 26 to 29 wherein Q together with R contains only 2 nitrogens and wherein each of the nitrogens is a member of a heterocyclic ring.

31. The invention according to claim 26, **27** or **28** wherein Q together with R contains no greater than 1 nitrogen.

32. The invention according to claim 31 wherein Q together with R contains no greater than 1 basic nitrogen.

33. The invention according to any one of claims 26 to 32 wherein if R is a hydrocarbyl group it is free of a hydroxyl group (—OH).

34. The invention according to any one of claims 26 to 33 wherein the optional ring system Q is present.

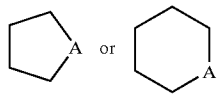
35. The invention according to any one of claims 26 to 34 wherein Q is substituted, preferably Q is substituted with one or more groups selected from =O and —OH.

36. The invention according to any one of claims 26 to 35 wherein Q is an aromatic ring.

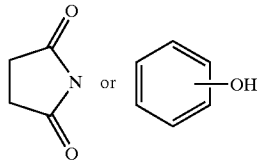
37. The invention according to any one of claims 26 to 36 wherein Q has 4 to 10 members, preferably 4 to 6 members, preferably 5 or 6 members.

38. The invention according to any one of claims 26 to 37 wherein Q is a carbon ring or a heterocyclic ring containing carbon and one nitrogen.

39. The invention according to any one of claims 26 to 38 wherein Q is selected from a ring system of the formula



wherein A is C or N, preferably Q is selected from a ring system of the formula



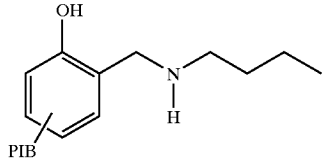
40. The invention according to any one of claims 26 to 39 wherein Polymer is a hydrocarbyl group having from 10 to 200 carbons.

41. The invention according to any one of claims 26 to 40 wherein Polymer is a branched or straight chain alkyl group, preferably a branched alkyl group.

42. The invention according to any one of claims 26 to 41 wherein Polymer is polyisobutene.

43. The invention according to any one of claims 26 to 42 wherein Polymer has a molecular weight of from 700 to 2300, preferably 800 to 1200.

44. The invention according to any one of the preceding claims wherein the deposit inhibiting compound is selected from compounds of the formulae



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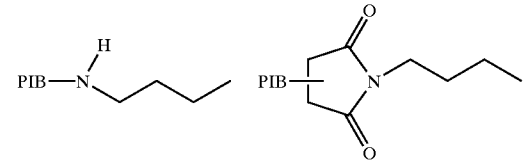

wherein PIB is polyisobutene.

45. The invention according to claim 44 wherein PIB is polyisobutene having a molecular weight of from 1000 to 2300.

46. The invention according to any one of the preceding claims wherein the composition further comprises a metal deactivator.

47. The invention according to claim 46 wherein the metal deactivator is selected from N,N'-disalicylidene 1,2-propanediamine and N,N'-disalicylidene 1,2-cyclohexyldiamine.

48. The invention according to any one of the preceding claims wherein the composition further comprises a further antioxidant.

49. A fuel composition comprising

(a) a fuel

(b) a composition as defined in any one of the preceding claims.

50. A fuel composition according to claim 49 wherein the fuel is an aviation fuel.

51. A fuel composition according to claim 49 or **50** wherein the fuel is JP-8 aviation fuel.

52. Use of a composition as defined in any one of the preceding claims for

(i) the inhibition of oxidation of a fuel composition comprising the composition and a fuel; and/or

(ii) the inhibition of deposit formation in a fuel composition comprising the composition and a fuel; and/or

(iii) the inhibition of particle formation from the oxidation product(s) of a fuel; and/or

(iv) the solubilisation of deposits and/or deposit precursors.

53. A method as substantially herein before described with reference to any one of the Examples.

54. A composition as substantially herein before described with reference to any one of the Examples.

55. A fuel composition as substantially herein before described with reference to any one of the Examples.

56. A use as substantially herein before described with reference to any one of the Examples.

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