



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
06.02.2008 Bulletin 2008/06

(21) Application number: **07111665.1**

(22) Date of filing: **03.07.2007**

(51) Int Cl.:
C10L 1/182 ^(2006.01) **C10L 1/185** ^(2006.01)
C10L 1/198 ^(2006.01) **C10L 1/18** ^(2006.01)
C10L 1/19 ^(2006.01) **C10L 10/04** ^(2006.01)
C10L 10/06 ^(2006.01)

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

(30) Priority: **04.08.2006 EP 06118493**

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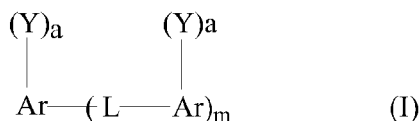
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(54) **Improvements in Diesel fuel compositions**

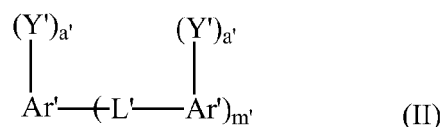
(57) A diesel fuel composition comprising a major amount of a diesel fuel, a minor amount of at least one metallic species and a minor amount of a detergent additive; wherein the detergent additive comprises at least one compound of formula (I) and/or formula (II):



wherein each Ar independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, aryloxy, aryloxyalkyl, hydroxy, hydroxyalkyl, halo and combinations thereof;

each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group;
each Y is independently -OR^{1''} or a moiety of the formula H(O(CR^{1'}₂)_n)_yX⁻, wherein X is selected from the group consisting of (CR^{1'}₂)_z, O and S; R¹ and R^{1'} are each independently selected from H, C₁ to C₆ alkyl and aryl; R^{1''} is selected from C₁ to C₁₀₀ alkyl and aryl; z is 1 to 10; n is 0 to 10 when X is (CR^{1'}₂)_z, and 2 to 10 when X is O or S; and y is 1 to 30;

each a is independently 0 to 3, with the proviso that at least one Ar moiety bears at least one group Y; and m is 1 to 100;



wherein:

each Ar' independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, hydroxy, hydroxyalkyl, acyloxy, acyloxyalkyl, acyloxyalkoxy, aryloxy, aryloxyalkyl, aryloxyalkoxy, halo and combinations thereof; each L' is independently a linking moiety comprising a carbon-carbon single bond or a linking group;
each Y' is independently a moiety of the formula ZO- or Z(O(CR^{2'}₂)_{n'})_{y'}X⁻, wherein X' is selected from the group consisting of (CR^{2'}₂)_{z'}, O and S; R² and R^{2'} are each independently selected from H, C₁ to C₆ alkyl and aryl; z' is 1 to 10; n' is 0 to 10 when X' is (CR^{2'}₂)_{z'}, and 2 to 10 when X' is O or S; y' is 1 to 30; Z is H, an acyl group, a polyacyl group, a lactone ester group, an acid ester group, an alkyl group or an aryl group; each a' is inde-

pendently 0 to 3, with the proviso that at least one Ar' m' is 1 to 100.
moiety bears at least one group Y' in which Z is not H; and

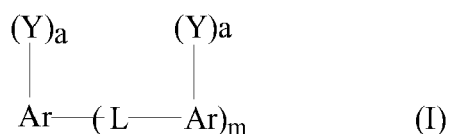
Description

[0001] This invention relates to diesel fuel compositions containing detergent additives and to their use to remove or prevent fuel injector deposits in modern diesel engines. Methods for the removal or prevention of fuel injector deposits are described.

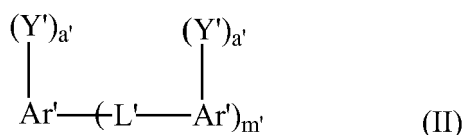
[0002] There is continued legislative pressure to reduce emissions from diesel engines. In Europe by 2008, all new diesel engines must comply with the Euro V specification. This has resulted in the development of advanced fuel injection equipment characterised by fuel injectors which have complex spray-hole geometries, multiple and narrow spray-holes and which operate with high temperatures and pressures at the injector tips. As a consequence of this increasing severity in operating conditions, the injectors of modern common-rail diesel engines are prone to the formation of deposits. These deposits, which are found both inside and outside the spray-holes of the injector nozzles, contribute directly to loss in engine power and increase in smoke production.

[0003] The formation of deposits on diesel fuel injectors is not a new phenomenon and historically any problem has been adequately addressed by the use of conventional diesel detergent additives. It has been observed however, that the types of deposits formed under the more severe operating conditions of engines which are being developed to be Euro V compliant are not adequately removed or prevented by conventional diesel detergent additives. Although not wishing to be bound by any theory, it is presently thought that the formation of injector deposits in modern engines is exacerbated by the presence of minor amounts of metal-containing species in the fuel. Indeed, the Applicant's studies have indicated that the use of fuels with negligible amounts of metal-containing contamination do not result in any significant problems with deposits. However, normal diesel fuels will often contain low but measurable amounts of metal-containing contamination, for example, zinc, copper, iron and lead and metal-containing species may also be deliberately added to perform other functions. Analysis of the deposits formed in modern diesel engines indicates that, in addition to the expected carbonaceous materials, metals such as zinc and copper can be detected. The present invention specifically addresses the removal and prevention of these new types of injector deposits.

[0004] In accordance with a first aspect, the present invention provides a diesel fuel composition comprising a major amount of a diesel fuel, a minor amount of at least one metallic species and a minor amount of a detergent additive; wherein the detergent additive comprises at least one compound of formulae (I) and/or (II):



wherein each Ar independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, aryloxy, aryloxyalkyl, hydroxy, hydroxyalkyl, halo and combinations thereof; each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group; each Y is independently -OR^{1''} or a moiety of the formula H(O(CR^{1'}₂)_n)_yX-, wherein X is selected from the group consisting of (CR^{1'}₂)_z, O and S; R¹ and R^{1'} are each independently selected from H, C₁ to C₆ alkyl and aryl; R^{1''} is selected from C₁ to C₁₀₀ alkyl and aryl; z is 1 to 10; n is 0 to 10 when X is (CR^{1'}₂)_z, and 2 to 10 when X is O or S; and y is 1 to 30; each a is independently 0 to 3, with the proviso that at least one Ar moiety bears at least one group Y; and m is 1 to 100;



wherein each Ar' independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, hydroxy, hydroxyalkyl, acyloxy, acyloxyalkyl, acyloxyalkoxy, aryloxy, aryloxyalkyl, aryloxyalkoxy, halo and combinations thereof; each L' is independently a linking moiety comprising a carbon-carbon single bond or a linking group; each Y' is independently a moiety of the formula ZO- or Z(O(CR^{2'}₂)_{n'})_{y'}X-, wherein X' is selected from the group consisting of (CR^{2'}₂)_{z'}, O and S; R² and R^{2'} are each independently selected from H, C₁ to C₆ alkyl and aryl; z' is 1 to 10; n' is 0 to 10 when X' is (CR^{2'}₂)_{z'}, and 2 to 10 when X' is O or S; y' is 1 to 30; Z is H, an acyl group, a polyacyl group, a lactone ester group, an acid ester group, an alkyl group or an aryl group; each a' is independently

0 to 3, with the proviso that at least one Ar' moiety bears at least one group Y' in which Z is not H; and m' is 1 to 100.

[0005] In accordance with a second aspect, the present invention provides a method of substantially removing, or reducing the occurrence of, injector deposits in a diesel engine operated using a diesel fuel containing a minor amount of a metal-containing species, the method comprising adding to the diesel fuel a detergent additive comprising at least one compound of formula (I) and/or a compound of formula (II) as defined in relation to the first aspect, wherein the diesel engine is equipped with fuel injectors having a plurality of spray-holes, each spray-hole having an inlet and an outlet, and wherein the fuel injectors have one or more of the following characteristics:

- (i) spray-holes which are tapered such that the inlet diameter of the spray-holes is greater than the outlet diameter;
- (ii) spray-holes having an outlet diameter of 0.10 mm or less;
- (iii) spray-holes where an inner edge of the inlet is rounded;
- (iv) 6 or more spray-holes;
- (v) an operating tip temperature in excess of 250°C.

[0006] In accordance with a third aspect, the present invention provides the use of a detergent additive comprising a compound of formula (I) and/or a compound of formula (II) as defined in relation to the first aspect to substantially remove, or reduce the occurrence of, injector deposits in a diesel engine operated using a diesel fuel containing a minor amount of a metallic species; wherein the diesel engine is equipped with fuel injectors having a plurality of spray-holes, each spray-hole having an inlet and an outlet, and wherein the fuel injectors have one or more of the following characteristics:

- (i) spray-holes which are tapered such that the inlet diameter of the spray-holes is greater than the outlet diameter;
- (ii) spray-holes having an outlet diameter of 0.10 mm or less;
- (iii) spray-holes where an inner edge of the inlet is rounded;
- (iv) 6 or more spray-holes;
- (v) an operating tip temperature in excess of 250°C.

[0007] It has been found that the detergents of the present invention are particularly effective at reducing the incidence of deposits in modern diesel engine fuel injectors, and more effective than the widely used PIBSA-PAM detergents under similar conditions. It was surprising to note however that in older type diesel engines, such as those used in the industry standard XUD-9 detergency test, the reaction products of use in the present invention were outperformed by conventional PIBSA-PAM detergents.

[0008] As discussed above, the incidence of injector deposits appears to be connected to the presence of metal-containing species in the fuel. Some diesel fuels will contain no measurable metal content, in which case the incidence of injector deposits will be reduced. However, the presence or absence of metal-containing species in diesel fuels is generally not apparent to the user and will vary with fuel production, even with fuels from the same supplier. The present invention is thus useful in those instances where metal-containing species are present and also as a preventative measure to lessen the impact of injector deposits when re-fuelling with a fuel of unknown metal content.

[0009] In the context of the second and third aspects of the present invention, substantial removal of injector deposits should be taken to mean that deposits which may be present on the inside or outside of the spray-holes of the injector nozzles are removed to the extent that the proper functioning of the injector is not significantly impaired. This may be determined for example by measuring increases in exhaust smoke or loss in engine torque. It is not required that all traces of injector deposit are removed. Similarly, a reduction in the occurrence of injector deposits does not require that no deposits whatsoever are formed, only again that the amount of any deposit which may form is not sufficient to significantly impair the proper functioning of the injector.

[0010] It is presently thought that the characteristics (i) to (v) of the fuel injectors all contribute to the formation of injector deposits. It has been observed that diesel engines employing fuel injectors which have a plurality of these characteristics are more prone to deposit formation. Thus in embodiments of the invention, the fuel injectors have two, preferably three, more preferably four, most preferably all five of characteristics (i) to (v).

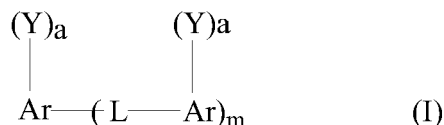
[0011] In a preferred embodiment, the fuel injectors have at least characteristics (i) and (ii). In a more preferred embodiment, the fuel injectors have at least characteristics (i), (ii) and (iii). In an even more preferred embodiment, the fuel injectors have at least characteristics (i), (ii), (iii) and (iv).

[0012] The various features of the invention, which are applicable to all aspects will now be described in more detail.

(a) The detergent additive

[0013] The detergent additive comprises at least one compound of formula (I) and/or a compound of formula (II). Compounds of Formulae (I) and (II) are described in co-pending U.S. Patent Application Serial No. 11/061,800, filed February 18, 2005 (US 2006/0189492 A2, published August 24, 2006), the subject matter of which is incorporated herein

by reference. Compounds of Formula (I) are represented by the following formula:



wherein each Ar independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, aryloxy, aryloxyalkyl, hydroxy, hydroxyalkyl, halo and combinations thereof; each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group; each Y is independently -OR^{1''} or a moiety of the formula H(O(CR^{1'}₂)_n)_yX-, wherein X is selected from the group consisting of (CR^{1'}₂)_z, O and S; R¹ and R^{1'} are each independently selected from H, C₁ to C₆ alkyl and aryl; R^{1''} is selected from C₁ to C₁₀₀ alkyl and aryl; z is 1 to 10; n is 0 to 10 when X is (CR^{1'}₂)_z, and 2 to 10 when X is O or S; and y is 1 to 30; each a is independently 0 to 3, with the proviso that at least one Ar moiety bears at least one group Y; and m is 1 to 100.

[0014] Aromatic moieties Ar of Formula (I) can be a mononuclear carbocyclic moiety (phenyl) or a polynuclear carbocyclic moiety. Polynuclear carbocyclic moieties may comprise two or more fused rings, each ring having 4 to 10 carbon atoms (e.g., naphthalene) or may be linked mononuclear aromatic moieties, such as biphenyl, or may comprise linked, fused rings (e.g., binaphthyl). Examples of suitable polynuclear carbocyclic aromatic moieties include naphthalene, anthracene, phenanthrene, cyclopentenophenanthrene, benzanthracene, dibenzanthracene, chrysene, pyrene, benzpyrene and coronene and dimer, trimer and higher polymers thereof. Ar can also represent a mono- or polynuclear heterocyclic moiety. Heterocyclic moieties Ar include those comprising one or more rings each containing 4 to 10 atoms, including one or more hetero atoms selected from N, O and S. Examples of suitable monocyclic heterocyclic aromatic moieties include pyrrole, furan, thiophene, imidazole, oxazole, thiazole, pyrazole, pyridine, pyrimidine and purine. Suitable polynuclear heterocyclic moieties Ar include, for example, quinoline, isoquinoline, carbazole, dipyrindyl, cinnoline, phthalazine, quinazoline, quinoxaline and phenanthroline. Each aromatic moiety (Ar) may be independently selected such that all moieties Ar are the same or different. Polycyclic carbocyclic aromatic moieties are preferred. Most preferred are compounds of Formula I wherein each Ar is naphthalene. Each aromatic moiety Ar may independently be unsubstituted or substituted with 1 to 3 substituents selected from alkyl, alkoxy alkoxyalkyl, hydroxyl, hydroxyalkyl, halo, and combinations thereof. Preferably, each Ar is unsubstituted (except for group(s) Y and terminal groups).

[0015] Each linking group (L) may be the same or different, and can be a carbon to carbon single bond between the carbon atoms of adjacent moieties Ar, or a linking group. Suitable linking groups include alkylene linkages, ether linkages, diacyl linkages, ether-acyl linkages, amino linkages, amido linkages, carbamido linkages, urethane linkages, and sulfur linkage. Preferred linking groups are alkylene linkages such as -CH₂CH(CH₃)₂-, or C(CH₃)₂-; diacyl linkages such as -COCO- or -CO(CH₂)₄CO-; and sulfur linkages, such as -S₁- or -S_x-. More preferred linking groups are alkylene linkages, most preferably -CH₂-.

[0016] Preferably, Ar of Formula (I) represents naphthalene, and more preferably, Ar is derived from 2-(2-naphthyl-oxy)-ethanol. Preferably, each Ar is derived from 2-(2-naphthyl-oxy)-ethanol, and m is 2 to 25. Preferably, Y of Formula (I) is the group H(O(CR₂)₂)_yO-, wherein y is 1 to 6. More preferably, Ar is naphthalene, Y is HOCH₂CH₂O- and L is -CH₂-.

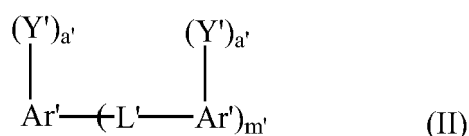
[0017] Methods for forming compounds of Formula (I) should be apparent to those skilled in the art. A hydroxyl aromatic compound, such as naphthol can be reacted with an alkylene carbonate (e.g., ethylene carbonate) to provide a compound of the formula AR-(Y)_a. Preferably, the hydroxyl aromatic compound and alkylene carbonate are reacted in the presence of a base catalyst, such as aqueous sodium hydroxide, and at a temperature of from about 25 to about 300°C, preferably at a temperature of from about 50 to about 200°C. During the reaction, water may be removed from the reaction mixture by azeotropic distillation or other conventional means. If separation of the resulting intermediate product is desired, upon completion of the reaction (indicated by the cessation of CO₂ evolution), the reaction product can be collected, and cooled to solidify. Alternatively, a hydroxyl aromatic compound, such as naphthol, can be reacted with an epoxide, such as ethylene oxide, propylene oxide, butylenes oxide or styrene oxide, under similar conditions to incorporate one or more oxy-alkylene groups.

[0018] To form a compound of Formula (I), the resulting intermediate compound Ar-(Y)_a may be further reacted with a polyhalogenated (preferably dihalogenated) hydrocarbon (e.g., 1,4-dichlorobutane, 2,2-dichloropropane, etc.), or a di- or poly-olefin (e.g., butadiene, isoprene, divinylbenzene, 1,4-hexadiene, 1,5-hexadiene, etc.) to yield a compound of Formula (I) having an alkylene linking groups. Reaction of moieties Ar-(Y)_a and a ketone or aldehyde (e.g., formaldehyde, acetone, benzophenone, acetophenone, etc.) provides an alkylene linked compound. An acyl-linked compound can be formed by reacting moieties Ar-(Y)_a with a diacid or anhydride (e.g., oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, succinic anhydride, etc.). Sulfide, polysulfide, sulfinyl and sulfonyl linkages may be provided by reaction of the moieties Ar-(Y)_a with a suitable difunctional sulfurizing agent (e.g., sulfur monochloride, sulfur dichloride, thionyl

chloride (SOCl_2), sulfuryl chloride (SO_2Cl_2), etc.). To provide a compound of Formula (I) with an alkylene ether linkage, moieties $\text{Ar}(\text{Y})_a$ can be reacted with a divinylether. Compounds of Formula (I), wherein L is a direct carbon to carbon link, may be formed via oxidative coupling polymerization using a mixture of aluminum chloride and cuprous chloride, as described, for example, by P. Kovacic, et al., J. Polymer Science: Polymer Chem. Ed., 21, 457 (1983). Alternatively, such compounds may be formed by reacting moieties $\text{Ar}(\text{Y})_a$ and an alkali metal as described, for example, in "Catalytic Benzene Coupling on Caesium/Nanoporous Carbon Catalysts", M.G. Stevens, K.M. Sellers, S. Subramoney and H.C. Foley, Chemical Communications, 2679-2680 (1988).

[0019] To form the preferred compounds of Formula (I), having an alkylene linking group, more preferably a methylene linking group, base remaining in the Ar-(Y)_a reaction mixture can be neutralized with acid, preferably with an excess of acid (e.g., a sulfonic acid) and reacted with an aldehyde, preferably formaldehyde, and preferably in the presence of residual acid, to provide an alkylene, preferably methylene bridged compound of Formula (I). The degree of polymerization of the compounds of Formula I range from 2 to about 101 (corresponding to a value of m of from 1 to about 100), preferably from about 2 to about 50, most preferably from about 2 to about 25.

[0020] The compounds of Formula (II) can be formed by reacting a compound of Formula (I) with at least one of an acylating agent, an alkylating agent and an arylating agent, and are represented by the formula:



wherein each Ar' independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, hydroxy, hydroxyalkyl, acyloxy, acyloxyalkyl, acyloxyalkoxy, aryloxy, aryloxyalkyl, aryloxyalkoxy, halo and combinations thereof; each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group; each Y' is independently a moiety of the formula ZO- or Z(O(CR²₂)_n)_yX⁻, wherein X' is selected from the group consisting of (CR²₂)_{z'}, O and S; R² and R^{2'} are each independently selected from H, C₁ to C₆ alkyl and aryl; z' is 1 to 10; n' is 0 to 10 when X' is (CR²₂)_{z'}, and 2 to 10 when X' is O or S; y' is 1 to 30; Z is H, an acyl group, a polyacyl group, a lactone ester group, an acid ester group, an alkyl group or an aryl group; each a is independently 0 to 3, with the proviso that at least one Ar' moiety bears at least one group Y' in which Z is not H; and m is 1 to 100.

[0021] Preferred compounds for Formula (II) include compounds in which at least one Ar' moiety bears at least one group $Z(O(CR^2_2)_{n'})_vX'$ in which Z is not H.

[0022] Suitable acylating agents include hydrocarbyl carbonic acid, hydrocarbyl carbonic acid halides, hydrocarbyl sulfonic acid and hydrocarbyl sulfonic acid halides, hydrocarbyl phosphoric acid and hydrocarbyl phosphoric halides, hydrocarbyl isocyanates and hydrocarbyl succinic acylating agents. Preferred acylating agents are C₈ and higher hydrocarbyl isocyanates, such as dodecyl isocyanate and hexadodecyl isocyanate and C₈ or higher hydrocarbyl acylating agents, more preferably polybutenyl succinic acylating agents such as polybutenyl, or polyisobutenyl succinic anhydride (PIBSA). Preferably the hydrocarbyl succinic acylating agent will have a number average molecular weight ($\overline{M}_n$) of from 100 to 5000, preferably from 200 to 3000, more preferably from 450 to 2500. Preferred hydrocarbyl isocyanate acylating agent will have a number average molecular weight ($\overline{M}_n$) of from 100 to 5000, preferably from 200 to 3000, more preferably from 200 to 2000. Those skilled in the art will recognise that the number average molecular weight ($\overline{M}_n$) is a value which cannot often be defined with absolute precision. The numerical limits given above should be understood and construed in this light.

[0023] Acylating agents can be prepared by conventional methods known to those skilled in the art, such as chlorine-assisted, thermal and radical grafting methods. The acylating agents can be mono- or polyfunctional. Preferably, the acylating agents have a functionality of less than 1.3, where functionality (F) is determined according to the following formula:

$$F = (\text{SAP} \times \overline{M}_n) / ((112,200 \times \text{A.I.}) - (\text{SAP} \times \text{MW}))$$

wherein SAP is the saponification number (i.e., the number of milligrams of KOH consumed in the complete neutralization of the acid groups in one gram of the acyl group-containing reaction product, as determined according to ASTM D94); $\overline{M}_n$ is the number average molecular weight of the starting polyalkene; A.I. is the percent active ingredient of the acyl

group-containing reaction product (the remainder being unreacted polyalkene, saturates, acylating agent and diluent); and MW is the molecular weight of the acyl group (e.g., 98 for succinic anhydride). Acylating agents are used in the manufacture of dispersants, and a more detailed description of methods for forming acylating agents is described in the description of suitable dispersants, presented *infra*.

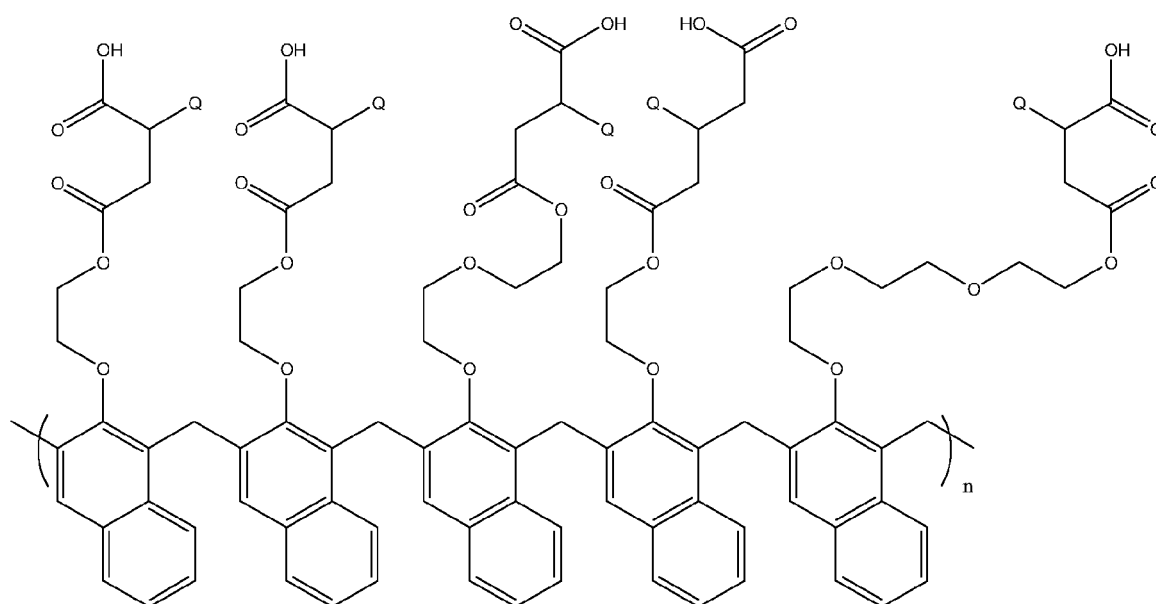
[0024] Suitable alkylating agents include C₈ to C₃₀ alkane alcohols, preferably C₈ to C₁₈ alkane alcohols. Suitable arylating agents include C₈ to C₃₀, preferably C₈ to C₁ alkane-substituted aryl mono- or polyhydroxide.

[0025] Compounds of Formula (II) can be derived from the compounds of Formula (I) by reacting the compounds of Formula (I) with the acylating agent, preferably in the presence of a liquid acid catalyst, such as sulfonic acid, e.g., dodecyl benzene sulfonic acid, paratoluene sulfonic acid or polyphosphoric acid or a solid acid catalyst such as Amberlyst-15, Amberlyst-36, zeolites, mineral acid clay or tungsten polyphosphoric acid; at a temperature of from about 0 to about 300°C, preferably from about 50 to about 250°C. Under the above conditions, the preferred polybutenyl succinic acylating agents can form diesters, acid esters or lactone esters with the compound of Formula (I).

[0026] Compounds of Formula (II) can be derived from the compounds of Formula (I) by reacting the compounds of Formula (I) with the alkylating agent or arylating agent, preferably in the presence of triphenylphosphine and diethyl azodicarboxylate (DEAD), a liquid acid catalyst, such as sulfonic acid, e.g., dodecyl benzene sulfonic acid, paratoluene sulfonic acid or polyphosphoric acid or a solid acid catalyst such as Amberlyst-15, Amberlyst-36, zeolites, mineral acid clay or tungsten polyphosphoric acid; at a temperature of from about 0 to about 300°C, preferably from about 50 to about 250°C.

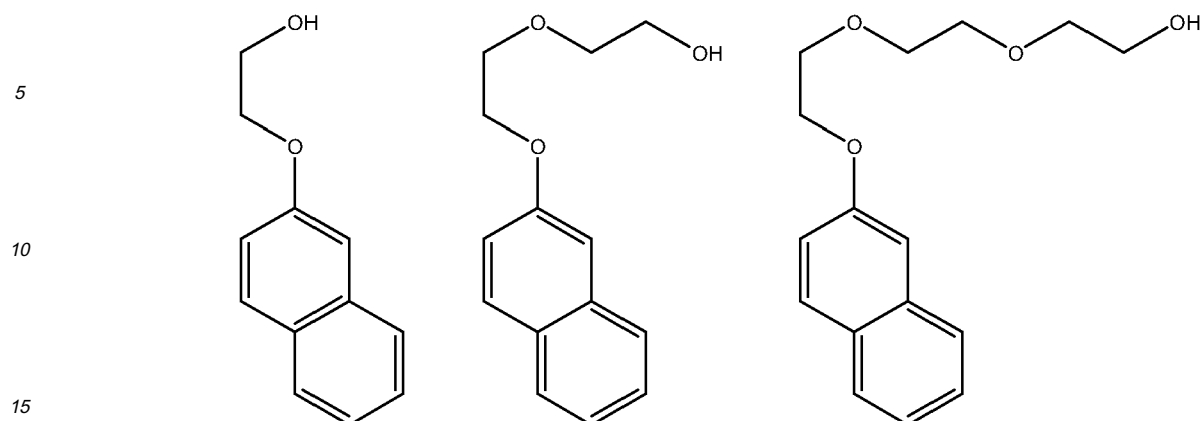
[0027] Molar amounts of the compound of Formula (I) and the acylating, alkylating and/or arylating agent can be adjusted such that all, or only a portion, such as 25% or more, 50% or more or 75% or more of groups Y are converted to groups Y'. In the case where the compound of Formula (I) has hydroxy and/or alkyl hydroxy substituents, and such compounds are reacted with an acylating group, it is possible that all or a portion of such hydroxy and/or alkylhydroxy substituents will be converted to acyloxy or acyloxy alkyl groups. In the case where the compound of Formula (I) has hydroxy and/or alkyl hydroxy substituents, and such compounds are reacted with an arylating group, it is possible that all or a portion of such hydroxy and/or alkylhydroxy substituents will be converted to aryloxy or aryloxy alkyl groups. Therefore, compounds of Formula (II) substituted with acyloxy, acyloxy alkyl, aryloxy and/or aryloxy alkyl groups are considered within the scope of the present invention. A salt form of compounds of Formula (II) in which Z is an acylating group, which salts result from neutralization with base (as may occur, for example, due to interaction with a metal detergent, either in an additive package or a formulated lubricant), is also considered to be within the scope of the invention.

[0028] In one preferred embodiment, the detergent comprises a compound of the structure:



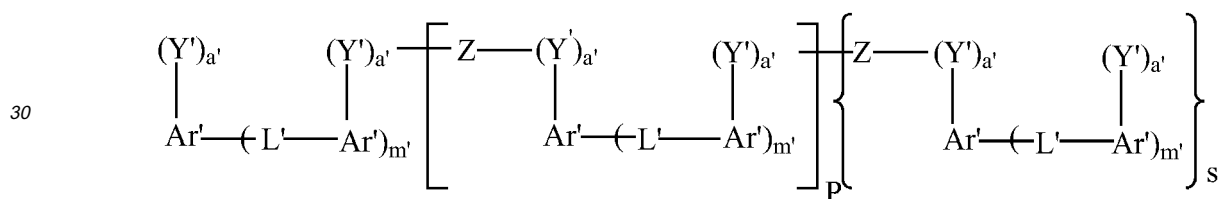
where Q is e.g. an alkyl group.

[0029] Such a molecule can, for example, be prepared from a monomer mixture containing the following species



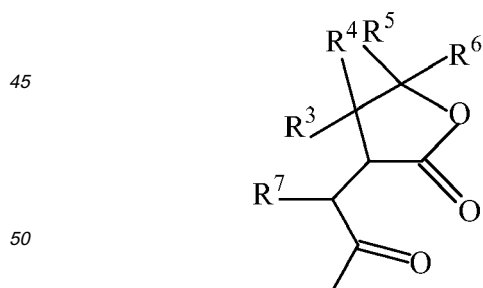
20 which mixture is oligomerised with para-formaldehyde. This is followed by post-reaction of the oligomer with an acylating agent, e.g. an alkyl-substituted succinic anhydride (where the group Q is the alkyl substituent of the anhydride). It will be appreciated by those skilled in the art that other monomer mixtures, or single monomers, may equally be employed and also that post reaction with an acylating agent is an optional step. It will also be evident to those skilled in the art that by altering the reaction conditions, e.g. by extending reaction times, residual acid functionality may be converted to lactone functionality.

25 **[0030]** A particularly preferred class of compounds of Formula (II) includes compounds of Formula (III):

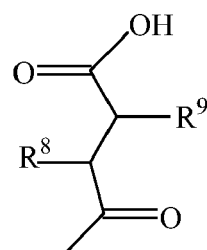


(III)

40 wherein one or more Y' are groups $Z(O(CR^2_2)_n)_yX'$ in which Z is derived from lactone ester of formula IV, acid ester of formula V, or a combination thereof;

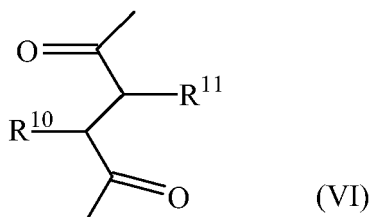


(IV)



(V)

55 wherein R^3, R^4, R^5, R^6, R^7 and R^8 are independently selected from H, alkyl and polyalkyl and polyalkenyl containing up to 200 C; and Z is bisacyl of formula VI;



wherein R^9 and R^{10} are independently selected from H, alkyl and polyalkyl and polyalkenyl containing up to 300 C; m is 0 to 100; and p and s are each independently about 0 to about 25, with the proviso that $p \leq m'$; $s \leq m'$; and $p + s \geq 1$.

[0031] Preferred compounds of Formula (III) are those wherein from about 2% to about 98% of the Y' units are $Z(O(CR^2_2)_2)_yO-$, wherein Z is an acyl group and y' is 1 to 6, and from about 98% to 2% of Y' units are $-OR^{2'}$, such as compounds of Formula (III) wherein Ar is naphthalene; from about 2% to about 98% of Y' units are $ZOCH_2CH_2O-$ from about 98% to 2% of Y' units are $-OCH_3$; and L' is CH_2 . Particularly preferred are compounds of Formula (III) wherein Ar' is naphthalene; from about 40% to about 60% of Y' units are $ZOCH_2CH_2O-$, and from about 60% to 40% of Y' units are $-OCH_3$; m' is from about 2 to about 25; p is from 1 to about 10; and s is from about 1 to about 10. Preferably, group Z of Formula (III) is derived from a polyalkyl or polyalkenyl succinic acylating agent, which is derived from polyalkene having $\overline{M}_n$ of from about 100 to about 5000, or a hydrocarbyl isocyanate.

[0032] Preferably, the detergent additive is present in an amount such that the fuel contains between 50 and 300 ppm by weight of a compound of formula (I) and/or a compound of formula (II), based on the weight of the fuel.

(b) The diesel fuel

[0033] Preferably, the diesel fuel is a petroleum-based fuel oil, especially a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of from 110°C to 500°C, e.g. 150°C to 400°C. The fuel oil may comprise atmospheric distillate or vacuum distillate, cracked gas oil, or a blend in any proportion of straight run and thermally and/or refinery streams such as catalytically cracked and hydro-cracked distillates.

[0034] Other examples of diesel fuels include Fischer-Tropsch fuels. Fischer-Tropsch fuels, also known as FT fuels, include those described as gas-to-liquid (GTL) fuels, biomass-to-liquid (BTL) fuels and coal conversion fuels. To make such fuels, syngas ($CO + H_2$) is first generated and then converted to normal paraffins by a Fischer-Tropsch process. The normal paraffins may then be modified by processes such as catalytic cracking/reforming or isomerisation, hydro-cracking and hydroisomerisation to yield a variety of hydrocarbons such as iso-paraffins, cyclo-paraffins and aromatic compounds. The resulting FT fuel can be used as such or in combination with other fuel components and fuel types. Also suitable are diesel fuels derived from plant or animal sources such as FAME. These may be used alone or in combination with other types of fuel.

[0035] Preferably, the diesel fuel has a sulphur content of at most 0.05% by weight, more preferably of at most 0.035% by weight, especially of at most 0.015%. Fuels with even lower levels of sulphur are also suitable such as, fuels with less than 50ppm sulphur by weight, preferably less than 20 ppm, for example 10ppm or less.

[0036] As discussed herein, the Applicants have observed that the problems associated with the formation of injector deposits in engines being developed to be Euro V compliant are associated with the presence of metal-containing species in the diesel fuel. Commonly when present, metal-containing species will be present as a contaminant, for example through the oxidation of metal surfaces by acidic species present in the fuel. In use, fuels such as diesel fuels routinely come into contact with metal surfaces for example, in vehicle fuelling systems, fuel tanks, fuel transportation means etc. Typically, metal-containing contamination will comprise metals such as zinc, iron, copper and lead.

[0037] In addition to metal-containing contamination which may present in diesel fuels there are circumstances where metal-containing species may deliberately be added to the fuel. For example, as is known in the art, metal-containing fuel-borne catalyst species may be added to aid with the regeneration of particulate traps. Such catalysts are often based on metals such as iron, cerium and Group II metals e.g., calcium and strontium, either as mixtures or alone. Also used are platinum and manganese. The presence of such catalysts may also give rise to injector deposits when the fuels are used in engines being developed to be Euro V compliant.

[0038] Metal-containing contamination, depending on its source, may be in the form of insoluble particulates or soluble compounds or complexes. Metal-containing fuel-borne catalysts are often soluble compounds or complexes or colloidal species. It will be understood that metal-containing species in the context of the present invention include both species which are metallic and those where the metal constituent is in compounded form.

[0039] In an embodiment, the metal-containing species comprises a fuel-borne catalyst.

[0040] In a preferred embodiment, the metal-containing species comprises zinc.

[0041] Typically, the amount of metal-containing species in the diesel fuel, expressed in terms of the total weight of metal in the species, is between 0.1 and 50 ppm by weight, for example between 0.1 and 10 ppm by weight, based on the weight of the diesel fuel.

(c) Fuel injector characteristics

[0042] Historically, diesel engine fuel injectors have been simple in design. In recent years, the connection between injector design and engine performance has become better understood. For example, the knowledge that a fine distribution of fuel droplets promotes a decrease in emissions has led to a gradual narrowing of fuel injector spray-holes and increased injector pressures. As mentioned hereinabove, the drive to meet the upcoming Euro V emissions specification has led to further advances in fuel injector design.

(i) Tapered spray-holes

[0043] The majority of fuel injectors have spray-holes which are uniform in cross-section. In the present invention, preferably the spray-holes are tapered such that diameter at the point where the fuel enters the spray-hole (the inlet) is greater than the diameter at the point where the fuel exits the spray-hole (the outlet). Most typically, the spray-holes will be conical or frusto-conical in shape.

(ii) Spray-hole diameter

[0044] The spray-holes preferably have an outlet diameter of 0.10mm or less, more preferably 0.08mm or less. This may be compared to injectors of 10 to 15 years ago which had spray-holes of typically 0.25mm.

(iii) Rounded spray-holes

[0045] In the context of the present invention, rounded spray-holes are those where the inner edge of the inlet of the hole has been formed, smoothed or eroded to have a curved or radial profile, rather than an angled profile.

(iv) Multiple spray-holes

[0046] Historically, fuel injectors have had up to four spray-holes. The present invention relates to fuel injectors preferably having 6 or more spray-holes, for example 6, 7, 8, 9, 10 or more. It is anticipated that future designs of fuel injectors will have even more spray-holes.

(v) Operating tip temperature

[0047] The combination of lower fuel flow due to a large number of spray-holes, higher fuel pressures and complex spray-hole geometry leads to increased injector tip temperatures. Typically, the fuel injectors will have an operating tip temperature in excess of 250°C, preferably in excess of 300°C.

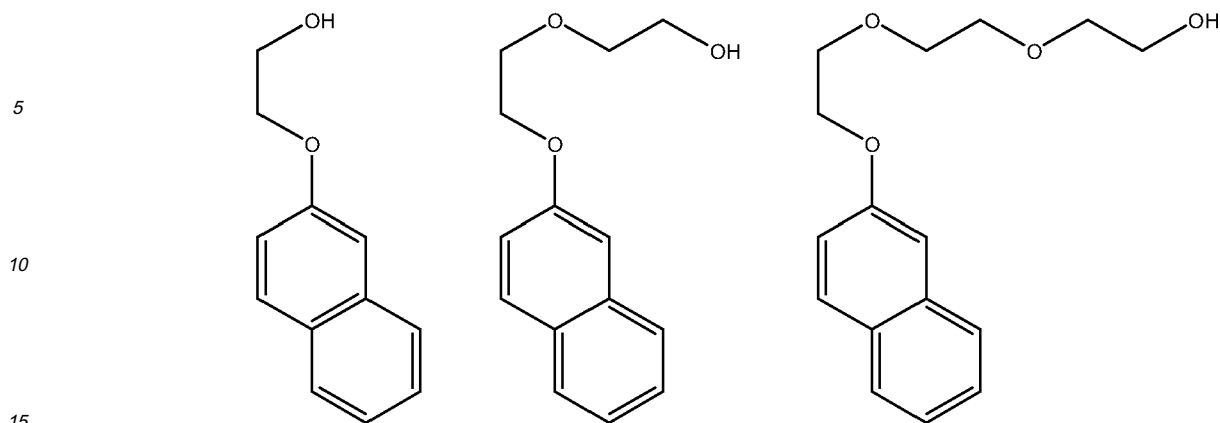
[0048] Characteristics (i) to (iv) result in a less turbulent fuel flow through the injector. Whilst this is generally advantageous, it lessens the possibility for the fuel to physically erode any deposits which may be present. The increase in operating tip temperature is also thought to contribute to the formation of deposits.

[0049] The invention will now be described by way of example only.

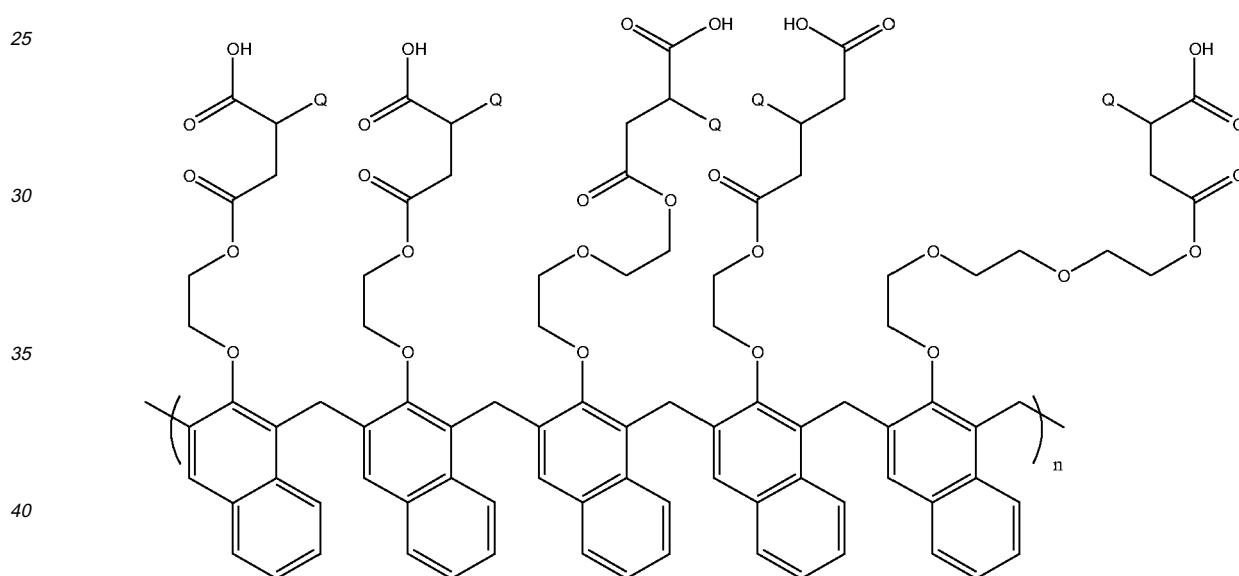
Preparative routes

Example 1

[0050] A mixture of monomers was used containing the following species:



20 **[0051]** The mono-ethoxylated species (2-(2-naphthoxy)-ethanol) comprised around 60% of the mixture with the remainder being made up of the di- and tri-ethoxylated species. Oligomerisation of the monomer mixture with para-formaldehyde was carried out in toluene in the presence of an oil soluble acid catalyst. After removal of the solvent, the oligomer was reacted with iso-octadecylsuccinic anhydride to produce the following species:



45 where Q = iso-octadecyl.

Example 2

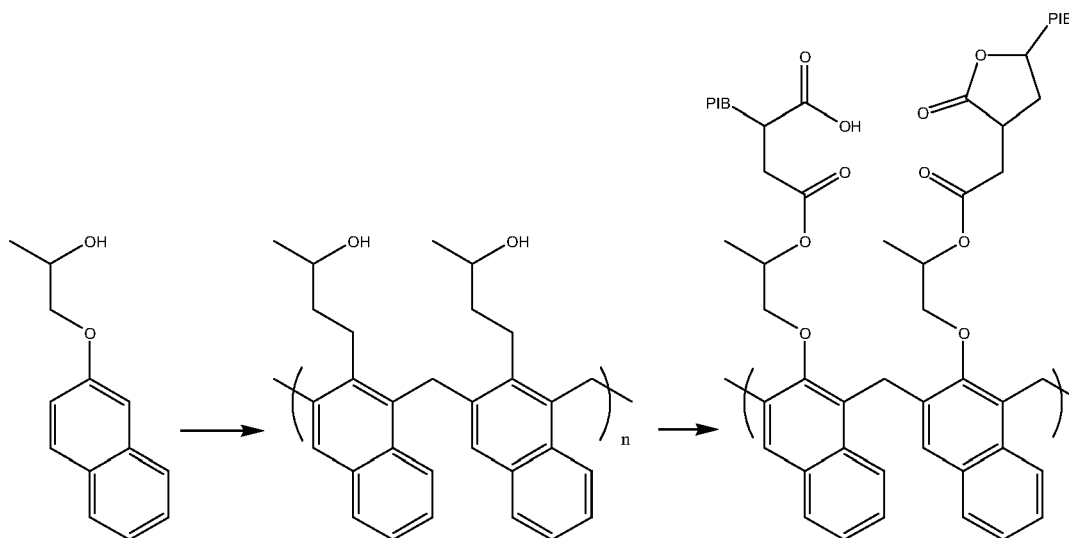
50 **[0052]** Example 1 was repeated except that polyisobutylene succinic anhydride (molecular weight of PIB ~ 450) was used in place of iso-octadecyl succinic anhydride. Also, around half of the residual acid functionality of the oligomer was converted to lactone functionality by extending the reaction time.

Example 3

55 **[0053]** Example 2 was repeated except that the majority of the residual acid functionality of the oligomer was converted to lactone functionality by extending the reaction time.

Example 4

[0054] The following reaction scheme was employed. This example used a single monomer species containing a methyl branch in the ethoxy group (as shown below). After oligomerisation, the material was post-reacted with the same polyisobutylene succinic anhydride used in Example 2. Also, common with Example 2, half of the residual acid functionality was converted to lactone functionality.



Test protocol

[0055] The protocol used is described by Graupner et al. "Injector deposit test for modern diesel engines", Technische Akademie Esslingen, 5th International Colloquium, 12-13 Jan 2005, 3.10, p157, Edited by Wilfried J Bartz. Briefly, the protocol aims to replicate the operating conditions in a modern diesel engine with an emphasis on the fuel injector tip. The test is split into five stages:

- a) an iso-speed measurement of engine power output
- b) an 8 hour endurance run
- c) an extended soaking period (3 to 8 hours) during which the engine is stopped and allowed to cool
- d) a second 8 hour endurance run
- e) an iso-speed measurement of engine power output.

[0056] For the data presented herein, the five stages above were used however, stages b), c) and d) can be repeated any number of times to suit the testing programme being undertaken. Also, stages a) and e) may be omitted but are useful to improve understanding of the results. Results are reported as the difference between the average torque at the start of the test during stage a) and the average torque at the end of the test during stage e). Alternatively, if the isospeed procedure is not run, the measured difference between starting torque at full load/full speed and final load/speed can be used. Differences in smoke production are also noted. The formation of injector deposits will have a negative influence on the final power output and will increase the amount of smoke observed. The injectors used had the physical characteristics (i) - (v) described above.

[0057] To replicate the conditions expected in a modern diesel engine, a small amount of metal contamination in the form of zinc neodecanoate was added to the fuel used to run the engine.

[0058] The fuel used was a low-sulphur content diesel fuel with the characteristics shown in Table 1 below.

Table 1

Test description	Value	Units
sulphur content	0.0005	mass %
cetane number	55.4	-

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(continued)

Test description	Value	Units
density @ 15°C	844.9	kgm ⁻³
distillation characteristics		
D5%	204.8	°C
D10%	211.6	°C
D20%	222.2	°C
D30%	232.2	°C
D40%	242.1	°C
D50%	252.3	°C
D60%	262.8	°C
D70%	275.1	°C
D80%	290.5	°C
D90%	315.1	°C
D95%	337.1	°C
FBP	353.6	°C
IBP	179.7	°C
kinematic viscosity @ 20°C	3.935	cSt
kinematic viscosity @ 40°C - D445		
cloud point	-14.0	°C
CFPP	-33.0	°C

[0059] The detergent species were tested using the protocol described above. Results are given in Table 2 below. 3 ppm of Zn in the form of zinc neodecanoate was added to the fuel for all tests (except for the untreated fuel alone).

Table 2

Species	Treat rate wppm (active ingredient)	Torque loss
Untreated fuel	-	4.3%
Untreated fuel + 3 ppm Zn	-	17.2%
PIBSA-PAM	60	13.7%
Example 1	60	6.6%
Example 2	60	8.2%
Example 3	60	12.1%
Example 4	60	7.9%

[0060] The results show that the addition of zinc to the untreated fuel gives rise to a large increase in torque loss. The commercial PIBSA-PAM detergent gave a marginal improvement. All Example species provided a greater improvement than the commercial detergent. Particularly good performance was obtained for the species of Examples 1, 2 and 4.

[0061] For comparative purposes, the species of the invention were tested in the industry standard XUD9 detergency test. A commercial PIBSA-PAM detergent was tested also. The results are given in Table 3 below.

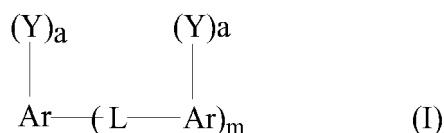
Table 3

Species	Treat rate wppm (active ingredient)	Needle lift in XUD9
Untreated fuel	-	92
PIBSA-PAM	60	64
Example 3	60	91

[0062] These results show that the commercial PIBSA-PAM detergent gave the expected excellent performance in the XUD9 test. Contrastingly, the species of the invention gave no improvement over the untreated fuel.

Claims

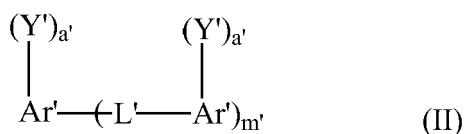
1. A diesel fuel composition comprising a major amount of a diesel fuel, a minor amount of at least one metallic species and a minor amount of a detergent additive; wherein the detergent additive comprises at least one compound of formula (I) and/or formula (II):



wherein each Ar independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, aryloxy, aryloxyalkyl, hydroxy, hydroxyalkyl, halo and combinations thereof; each L is independently a linking moiety comprising a carbon-carbon single bond or a linking group;

each Y is independently -OR^{1''} or a moiety of the formula H(O(CR¹₂)_n)_yX-, wherein X is selected from the group consisting of (CR^{1'}₂)_z, O and S; R¹ and R^{1'} are each independently selected from H, C₁ to C₆ alkyl and aryl; R^{1''} is selected from C₁ to C₁₀₀ alkyl and aryl; z is 1 to 10; n is 0 to 10 when X is (CR^{1'}₂)_z, and 2 to 10 when X is O or S; and y is 1 to 30;

each a is independently 0 to 3, with the proviso that at least one Ar moiety bears at least one group Y; and m is 1 to 100;



wherein:

each Ar' independently represents an aromatic moiety having 0 to 3 substituents selected from the group consisting of alkyl, alkoxy, alkoxyalkyl, hydroxy, hydroxyalkyl, acyloxy, acyloxyalkyl, acyloxyalkoxy, aryloxy, aryloxyalkyl, aryloxyalkoxy, halo and combinations thereof;

each L' is independently a linking moiety comprising a carbon-carbon single bond or a linking group;

each Y' is independently a moiety of the formula ZO- or Z(O(CR²₂)_{n'})_{y'}X'-, wherein X' is selected from the group consisting of (CR^{2'}₂)_{z'}, O and S; R² and R^{2'} are each independently selected from H, C₁ to C₆ alkyl and aryl; z' is 1 to 10; n' is 0 to 10 when X' is (CR^{2'}₂)_{z'}, and 2 to 10 when X' is O or S; y' is 1 to 30; Z is H, an acyl group, a polyacyl group, a lactone ester group, an acid ester group, an alkyl group or an aryl group;

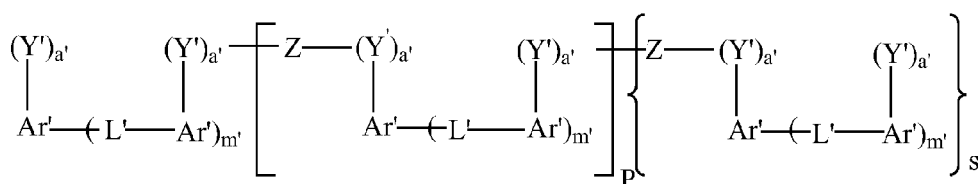
each a' is independently 0 to 3, with the proviso that at least one Ar' moiety bears at least one group Y' in which Z is not H; and

m' is 1 to 100.

2. A diesel fuel composition according to claim 1 wherein said compound is a compound of formula (II) wherein Y' is

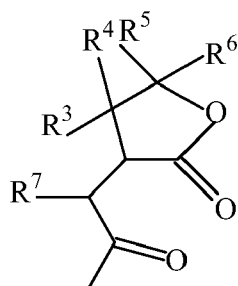
$Z(O(CR_2)_2)_yO-$, Z is an acyl group and y' is 1 to 6.

3. A diesel fuel composition according to claim 1 or claim 2 wherein Ar' is naphthalene, Y' is $ZOCH_2CH_2O-$, Z is an acyl group and L' is CH_2 .
4. A diesel fuel composition according to any preceding claim wherein Ar' is derived from 2-(2-naphthyloxy)-ethanol and m' is 2 to 25.
5. A diesel fuel composition according to any preceding claim wherein said Z is derived from either (i) a polyalkyl or polyalkenyl succinic acylating agent having $\overline{M}_n$ of from 100 to 5000 or (ii) from hydrocarbyl isocyanate.
6. A diesel fuel composition according to any preceding claim wherein said compound is a compound of Formula (III):

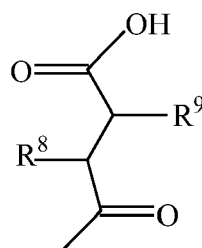


(III)

wherein one or more Y' are groups $Z(O(CR_2)_2)_yX-$ in which Z is derived from a lactone ester of formula IV, an acid ester of formula V, or a combination thereof;

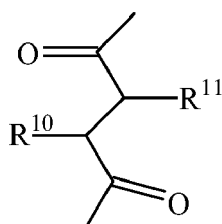


(IV)



(V)

wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 and R^9 are independently selected from H, alkyl and polyalkyl and polyalkenyl containing up to 200 C; and Z is bisacyl of formula VI;



(VI)

wherein R^{10} and R^{11} are independently selected from H, alkyl and polyalkyl and polyalkenyl containing up to 300 C; m' is 0 to 100; and p and s are each independently about 0 to about 25, with the proviso that $p \leq m'$; $s \leq m'$; and

$$p + s \geq 1.$$

7. A diesel fuel composition according to claim 6, wherein said compound is a compound of Formula (III) wherein from about 2% to about 98% of the Y' units are $Z(O(CR^2_2)_2)_yO-$, wherein Z is an acyl group and y' is 1 to 6, and from about 98% to 2% of Y' units are $-OR^{2''}$.
8. A diesel fuel composition according to claim 7, wherein said compound is a compound of Formula (III) wherein Ar' is naphthalene; from about 2% to about 98% of Y' units are $ZOCH_2CH_2O-$, from about 98% to 2% of Y' units are $-OCH_3$; and L' is CH_2 .
9. A diesel fuel composition according to claim 8, wherein said compound is a compound of Formula (III) wherein Ar' is naphthalene; from about 40% to about 60% of Y' units are $ZOCH_2CH_2O-$, and from about 60% to 40% of Y' units are $-OCH_3$; m' is from about 2 to about 25; p is from 1 to about 10; and s is from about 1 to about 10.
10. A diesel fuel composition according to any preceding claim wherein the detergent additive is present in an amount such that the fuel contains between 50 and 300 ppm by weight of a compound of formula (I) and/or a compound of formula (II), based on the weight of the fuel.
11. A method of substantially removing, or reducing the occurrence of, injector deposits in a diesel engine operated using a diesel fuel containing a minor amount of a metal-containing species, the method comprising adding to the diesel fuel a detergent additive comprising a compound of formula (I) and/or a compound of formula (II) as defined in any of claims 1 to 8, wherein the diesel engine is equipped with fuel injectors having a plurality of spray-holes, each spray-hole having an inlet and an outlet, and wherein the fuel injectors have one or more of the following characteristics:
 - (i) spray-holes which are tapered such that the inlet diameter of the spray-holes is greater than the outlet diameter;
 - (ii) spray-holes having an outlet diameter of 0.10 mm or less;
 - (iii) spray-holes where an inner edge of the inlet is rounded;
 - (iv) 6 or more spray-holes;
 - (v) an operating tip temperature in excess of 250°C.
12. The use of a detergent additive comprising a compound of formula (I) and/or a compound of formula (II) as defined in any of claims 1 to 8 to substantially remove, or reduce the occurrence of, injector deposits in a diesel engine operated using a diesel fuel containing a minor amount of a metallic species; wherein the diesel engine is equipped with fuel injectors having a plurality of spray-holes, each spray-hole having an inlet and an outlet, and wherein the fuel injectors have one or more of the following characteristics:
 - (i) spray-holes which are tapered such that the inlet diameter of the spray-holes is greater than the outlet diameter;
 - (ii) spray-holes having an outlet diameter of 0.10 mm or less;
 - (iii) spray-holes where an inner edge of the inlet is rounded;
 - (iv) 6 or more spray-holes;
 - (v) an operating tip temperature in excess of 250°C.
13. The method of claim 11 or the use of claim 12 wherein the fuel injectors have two, preferably three, more preferably four, most preferably all five of characteristics (i) to (v).

REFERENCES CITED IN THE DESCRIPTION

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